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QUANTUM-MECHANICAL STUDIES ON CHEMICAL REACTIVITY AND BALLISTIC CHEMISTRY. VII. SEMIEMPIRICAL MOLECULAR ORBITAL CALCULATIONS AND EXPERIMENTAL STUDIES ON RELATIVE CHEMICAL REACTIVITIES OF ISOMERIC TETRAZOLE DERIVATIVES, AND THEIR RELATIONSHIP TO THE EXPLOSIVE PROPERTIES OF SOME TETRAZOLE DERIVATIVES

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)* jmk

A number of observations in the literature indicate that the reactivity of side-chain substituents on tetrazoles (and other azoles as well) depends strikingly on whether the trivalent (pyrrole-type) nitrogen atom is located at the 1- or the 2- position of the tetrazole ring; this dependence has been observed in decarboxylation, hydrogen exchange, diazotization, nucleophilic substitution and other reactions. To understand these differences, physical measurements have been carried out on a number of tetrazole derivatives. ^{1}H, ^{19}F and ^{13}C NMR studies, as well as dissociation constant measurements, have been carried out on a

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variety of isomeric pairs of tetrazole derivatives. From the results of these studies the σ_I, σ_R, σ_m, and σ_p constants for isomeric pairs of 1- and 2-substituted-5-tetrazolyl and 5-tetrazoliumyl groups have been determined. The results indicate that 1-substituted-5-tetrazolyl groups are more electron-withdrawing by the field effect and by resonance than are the isomeric 2-substituted-5-tetrazolyl groups. Charge distributions and energies of reaction from CNDO/2 and INDO calculations are in accord with these observations. The relative reactivities of substituents at positions 1 and 2 of isomeric pairs of tetrazole derivatives are also considered but it is harder to distinguish any systematic trend for the N-substituents.

These results are used, together with information already in the literature, in an attempt at understanding certain trends in the explosive behavior of tetrazole derivatives in terms of the chemistry of related compounds, although it is pointed out that nonchemical factors such as hardness, thermal conductivity, etc. factors can also be important in determining properties of this type. The apparent greater explosiveness of 2,5- than 1,5-disubstituted tetrazoles, in the few cases that we are aware of in which isomeric compounds can be compared, could possibly be due to the relative rates of thermal decomposition. Another possible explanation might be that the tetrazole ring nitrogen atoms in the 2-isomers may be positioned in such a way as to cause more nitrogen gas to be given off at an earlier stage of the decomposition.

In view of the above, it is suggested that one factor responsible for the apparent tendency of 5-monosubstituted tetrazoles and tetrazolate salts to become more explosive with increasing electron-withdrawing ability of the 5-substituent may be an increase in the relative proportion of the more explosive or less stable 2-protonated or 2-associated forms relative to the 1-protonated or 1-associated forms. Such an increase could result from variations in intramolecular interactions, since an increase in electron-withdrawing ability of the 5-substituent should result in a more unfavorable interaction with the more electron-withdrawing 1-protonated or 1-associated form than with the less electron-withdrawing 2-associated form. However the situation is complicated and other chemical and nonchemical effects no doubt play a role also.

Some suggestions for future work are made.

4. Title (continued)

ISOMERIC TETRAZOLE DERIVATIVES, AND THEIR RELATIONSHIP TO THE EXPLOSIVE PROPERTIES OF SOME TETRAZOLE DERIVATIVES

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I. INTRODUCTION

The ultimate objective of the quantum chemistry program at BRL has been to relate the ballistic and explosive properties of high-energy compounds to their calculated and experimental molecular properties, and to understand the chemistry of the compounds[1]. The goal is a predictive model of the chemical aspects of ignition, combustion, deflagration and detonation.

Calculations of this type are potentially quite useful in the understanding and control of safety and shelf-life characteristics of high-energy materials; this is shown by our correlations of thermal stabilities and impact sensitivities of N-picrylazole derivatives with INDO oxidation energies for the corresponding N-unsubstituted azoles.[2]

However, if the calculations are to be used effectively in such applications, it will be necessary to have a clear understanding of their reliability, their limitations and the extent of their applicability. Thus, another very important aspect of our program must be the process of working out in some detail the relationship between the results of the calculations and the chemical reactivities of the molecules for which the calculations are being carried out. We have been attacking this aspect of the problem by carrying out semiempirical molecular orbital calculations on the relationship between molecular structure and chemical

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[1] *Previous report in this series: M. A. Schroeder, "Quantum Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. VI. Literature Review on the Relationship Between Structure and Reactivity in Isomeric Tetrazole Derivatives," BRL Report 1848, November 1975 (AD-A018652).*

[2] *(a) M. A. Schroeder, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. V. Correlation of Observed Thermal Stabilities and Impact Sensitivities for N-Picrylazole Derivatives with INDO Oxidation Energies," BRL Memorandum Report No. 2340, November 1973 (AD-771 118); (b) M. A. Schroeder and G. F. Adams, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry," E. Freedman and K. J. White, Eds. "1975 Annual Review of the ARMCOM Program, The Fundamentals of Ignition and Combustion," BRL Report No. 1883, May 1976 (AD B011 644L).*

reactivity of medium sized, ballistically interesting organic molecules.[3-6] The compounds under study include pyrrole and its aza derivatives, the diazoles, triazoles and tetrazoles.

The pertinence of these compounds to explosive and propellant chemistry is exemplified by the LASL work on picrylazoles as thermally

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[3] *M. A. Schroeder, R. C. Makino and W. M. Tolles, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. I. CNDO/2 Calculations on Pyrrole and on its Aza Derivatives," BRL Report No. 1557, November 1971 (AD-736-371).*

[4] *M. A. Schroeder, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. II. Substituent Effects of Azolyl Groups," BRL Report No. 1565, December 1971 (AD-736-843).*

[5] *M. A. Schroeder, R. C. Makino and W. M. Tolles, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. III. Effect of Assumed Molecular Geometry on CNDO/2 Electron Distribution for Some Tetrazole Derivatives," BRL Report No. 1592 (AD-746 614), May 1972; also Tetrahedron 29, 3463 (1973).*

[6] *M. A. Schroeder and R. C. Makino, "Quantum-Mechanical Studies on Chemical Reactivity and Ballistic Chemistry. IV. CNDO/2 Calculations on Azolium Cations and on the Zwitterions Resulting from their Deprotonation," BRL Report No. 1618, September 1972 (AD-755 521), 1999-9199; also Tetrahedron 29, 3469 (1973).*

stable explosives,[7] by polyvinyltetrazole rocket propellants,[8a-c] by the well-known sensitizer tetrazene (1-amino-1-(1H-tetrazol-5-yl)azo) guanidine hydrate),[8d] by the fact that preliminary results suggest that poly(2-methyl-5-vinyltetrazole) may show promise as an ingredient in wear-reducing additives for gun propellants,[8e] and by tetrazole-containing propellant plasticizers[8f,h,i].

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[7] *(a) M. D. Coburn, "Picrylamino-substituted Heterocylces. IV. Pyrazoles," J. Heterocycl. Chem. 7, 345 (1970); (b) M. D. Coburn and P. N. Neuman, "The Condensation of Amino- and Nitroimidazoles with Picryl Halides," Ibid. 7, 1391 (1970); (c) M. D. Coburn and T. E. Jackson, "Picrylamino-substituted Heterocycles. III. 1,2,4-Triazoles," Ibid. 5, 199 (1968); (d) P. N. Neuman, "Nitro Derivatives of Phenyl-1,2,4-triazole," Ibid. 8, 51 (1971).*

[8] *(a) W. G. Finnegan, R. A. Henry and S. Skolnick, "Substituted Tetrazoles, U.S. Patent 3,055,911, September 1962; (b) W. G. Finnegan and R. A. Henry, "Synthesis of Substituted Vinyltetrazoles," NAVORD Report 5405 (AD-314 300); (c) "Instructions for Preparation of Binder, Poly (2-methyl-5-vinyltetrazole) (PMVT)" (AD-848 260); (d) I. Dunstan, "Chemistry in the Technology of Explosives and Propellants," Chem. Brit. 7, 62 (1971); (e) M. A. Schroeder and M. Inatome, "The Relationship Between Chemical Composition and Wear-Reducing Effectiveness of Some Laminar Additives for Gun Propellants: Polyvinyltetrazole," BRL Memorandum Report No. 2512, August 1975; (f) H. S. Haiss, "5-(β-Hydroxyethyl) -1-methyltetrazole, an Energetic Plasticizer," U.S. Patent 3,564,005, February 1971 (Chem. Abstr., 74, 112805a (1971); (g) J. Cohen, R. A. Henry, W. G. Finnegan, and E. D. Besser, "Evaluation of Substituted 5-Aminotetrazoles and Related Compounds in Double-Base Propellant Formulations" NAVORD Report 5324, October 1956 (AD-117 889); (h) J. Cohen, W. G. Finnegan and R. A. Henry, U.S. Patent 3,073,731 "Plasticizing Agents for Nitrocellulose", January 1963; (i) R. R. Reed, C. W. Abernathy and R. A. Henry, "Addition Reactions of 1-Methyl-5-vinyltetrazole", NAVORD Report 6549, (AD 309 683); Presented at 24th Annual Northwest Regional American Chemical Society Meeting, Salt Lake City, Utah 12-13 June 1969.*

Tetrazoles and tetrazolate salts are of current interest as replacements for lead azide in detonators; this is exemplified by recent British work.[9] We feel that the results described in the present report may contribute to the understanding of some of the trends in explosive properties observed in this work; this point will be discussed in more detail later in the present report.

Furthermore, cast 2-methyl-5-nitrotetrazole appears in at least some respects to be a promising candidate primary explosive.[10]

Our effort to understand the relationship between calculated results and observed chemical reactivities has largely taken the form of use of the calculations, together with experimental work and literature searches, as tools in a study of the relationship between structure and reactivity among the five-membered heteroaromatic compounds already mentioned.

Many observations in the literature indicate that the reactivity of side-chain substituents attached to five-membered heteroaromatic rings depends markedly on the number and kind of hetero atoms and on their location relative to the reacting substituent. In general, two principal trends are observed: (1) Carbon atoms located α- to oxygen, sulfur or pyrrole-type nitrogen seem to be more electron-withdrawing with regard to their substituent groups than carbons located β- to such an atom; (2) Replacement of carbon by nitrogen increases the electron-withdrawing character of the azole ring, causing it to be less electron-donating or more electron-withdrawing relative to attached substituents. In a previous report in this series,[4] some of these structure-reactivity relationships were discussed and compared with the results of CNDO/2 calculations[3] in an effort to arrive at an understanding of the reasons for these trends. On the basis of this discussion, it was suggested[4] that trend (1) can be understood at least partially in terms of field (through-space electrostatic) effects; resonance (π-electron conjugative effects) also seems important

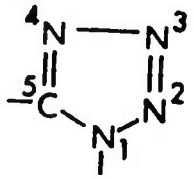
[9] *(a) G. W. C. Taylor and J. M. Jenkins, "Third Symposium on Chemical Problems Connected with the Stability of Explosives," Ystad, May 28-30, 1973, pp 43-6; (b) L. R. Bates and J. M. Jenkins, "Search for New Detonants," in "Proceedings of the International Conference on Research in Primary Explosives, 17, 18 and 19 March 1975," Volume 2, Presentation No. 14 (AD B013 628L); (c) P. J. Haskins, "Electronic Structure of Some Explosives and its Relationship to Sensitivity," in "Proceedings of the International Conference on Research in Primary Explosives, 17, 18 and 19 March 1975," Volume 1, Presentation No. 6 (AD B013 627L); (d) C. M. Tarver, T. C. Goodale, M. Cowperthwaite and M. E. Hill, "Structure-Property Correlations in Primary Explosives", SRI Final Technical Report 76-2, Project PYU-4770, Menlo Park, CA (February 1977), (AD A044 714). (e) See Also References 86-9.*

[10] *C. M. Tarver, T. C. Goodale and M. Cowperthwaite, "Structure-Property Correlations in Primary Explosives," SRI Interim Technical Report 76-1 (Semiannual) Project PYU-4770, Menlo Park, CA (June 1976), (AD A028 503).*

in the case of high-nitrogen compounds such as tetrazoles. In the case of low-nitrogen compounds such as pyrrole, resonance works against trend (1); thus most of the exceptions to this trend occur among derivatives of pyrrole, the diazoles and related compounds. Among isomers differing in the number of α-heteroatoms, inductive and hybridization effects may also be playing a role in establishing this trend. The exact reasons for trend (2) are less clear, but resonance seems important in many cases. Inductive effects may also be important, especially when carbon is replaced by nitrogen in an α-position relative to the reacting substituent. Hybridization effects may be important when carbon is replaced by nitrogen in an α-position, but they seem much less important when the added nitrogen is located in the β-position. When reactions carried out in protic solvents such as water are considered, it is also possible that trend (2) may be assisted by protonation or hydrogen-bonding of solvent molecules to the unshared electron pair of the added nitrogen; we have discussed this possibility for the proton-exchange reaction of azolium cations.[6]

Another possible contributor to trend (2) is a field effect due to the effect of the added nitrogen on the molecular dipole and to the atomic (lone pair) dipole of the added nitrogen. Some effect of the molecular-dipole field effect can possibly be seen in the results of our CNDO/2[6] calculations on H-D exchange of azolium cations. NDDO calculations,[11] which take explicit account of the atomic-dipole effect, suggest that this effect may be quite important in understanding the effect of added nitrogen on deprotonation of azabenzene derivatives. Possibly this provides at least a partial explanation of why CNDO/2 underestimates the effect of added pyridine-type nitrogen atoms on H-D exchange rates of azoles[12] and azolium cations.[6]

The relative chemical reactivities of substituents at position 5 of isomeric 1- and 2-substituted tetrazole derivatives are an example of trend (1); this subject was reviewed in the preceding report of this series.[1]



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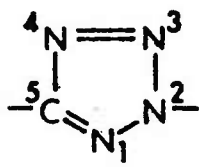

II

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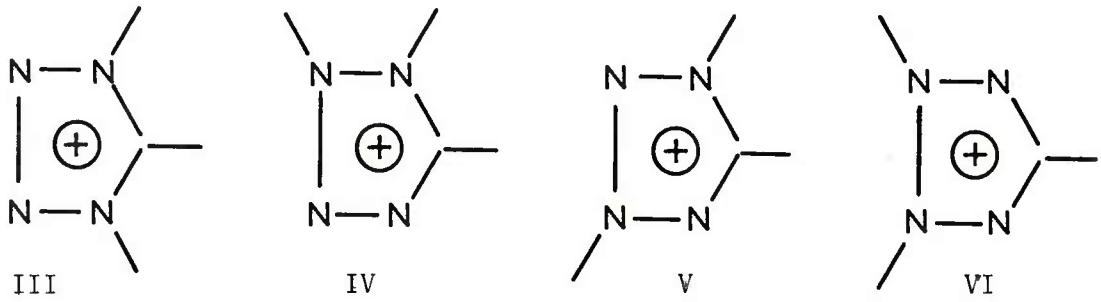
[11] *P. Birner, H. J. Kohler and C. Weiss, "C-H Acidity. Comparative CNDO/2 and NDDO Calculations on the Reactivity of Azabenzenes," Chem. Phys. Lett. 27, 347 (1974).*

[12] *M. A. Schroeder, unpublished work.*

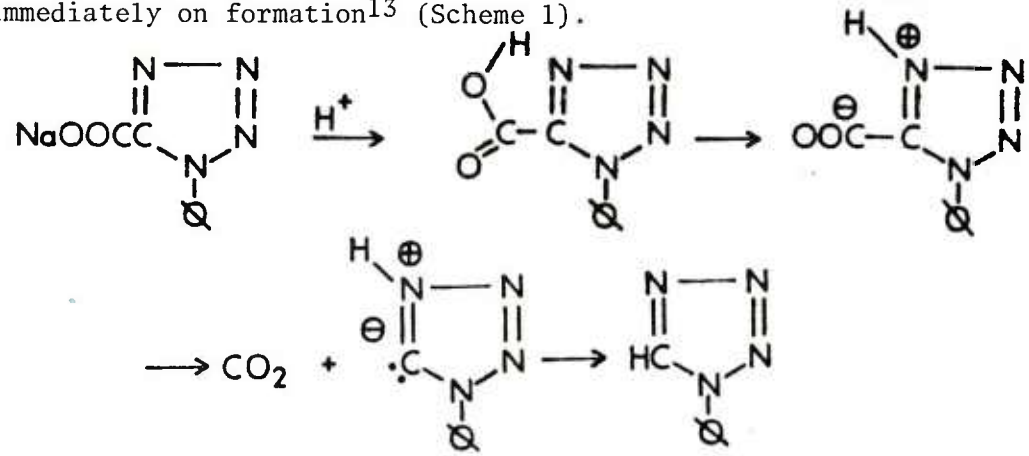
It is found that 1-substituted-5-tetrazolyl groups (as in I) appear to be considerably more electron-withdrawing than do 2-substituted-5-tetrazolyl groups (as in II), in agreement with trend (1). The relative electron-withdrawing abilities of 1,4-(III), 1,2-(IV), 1,3-(V) and 2,3-(VI) tetrazoliumyl groupings will also be considered. More tentatively but also in agreement with trend (1), it is suggested that their electron-withdrawing ability increases in the order 2,3 < 1,3- < 1,2- < 1,4-disubstitution.



III IV V VI

An understanding of the relative electron-withdrawing abilities of the groups III-VI would contribute to our understanding of such topics as the relative basicities of the isomeric dimethyl-5-iminotetrazoles; effect of 5-substituents on alkylation of 1,5- and 2,5-disubstituted tetrazoles; and effect of the 5-substituent on metal-tetrazole ring bonding in tetrazolate heavy-metal salts[9] being investigated as replacements for lead azide in detonators.

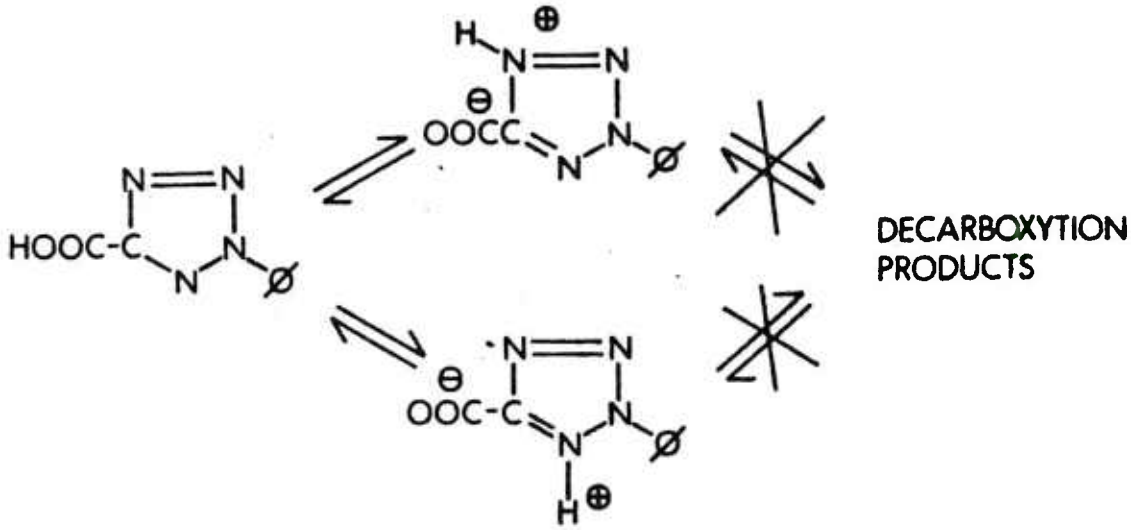
The literature contains many instances of large differences in reactivity between members of isomeric pairs of 1- and 2-substituted tetrazole derivatives. For example, 1-phenyl-5-tetrazolecarboxylic acid is so unstable that acidification of aqueous solutions of its salts yields only 1-phenyltetrazole and carbon dioxide, the acid having decarboxylated immediately on formation[13] (Scheme 1).



Scheme I

[13] *E. D. Amstutz, A. B. Kerr and C. R. Jacobsen, "Studies in Tetrazole Chemistry. III. Some Reactions of 1-Phenyl-5-chloromethyl-tetrazole," J. Org. Chem. 19, 1909 (1954).*

2-Phenyl-5-tetrazolecarboxylic acid, on the other hand, is stable, decarboxylating only on heating[14] (Scheme 2).



Scheme 2

In H-D exchange reactions at ring carbon atoms, tetrazole derivatives with a pyrrole-type nitrogen in the α-position relative to the exchanging proton are more reactive by a factor of ca 10^4-10^5 than the isomeric compounds with a pyrrole-type nitrogen in the β-position.[15-17]

The greater electron-withdrawing ability of 1-substituted-5-tetrazolyl groups apparently affects the relative diazotization behavior of isomeric 1- and 2-substituted-5-aminotetrazoles.[18] On diazotization of 5-aminotetrazole derivatives, the 1-substituted isomers yield the corre-

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[14] *F. R. Benson, "The Chemistry of the Tetrazoles," Chem. Rev. 41 1 (1947).*

[15] *R. A. Olofson, W. R. Thompson and J. S. Michelman, "Heterocyclic Nitrogen Ylides," J. Amer. Chem. Soc. 86, 1865 (1964).*

[16] *W. P. Norris and R. A. Henry, "The Action of Base on the 1,3-Dimethyltetrazolium Cation," Tetrahedron Lett., 1213 (1965).*

[17] *(a) R. A. Olofson, H. Kohn, R. V. Kendall and W. P. Piekelek, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, IL, September, 1970, Abstract ORGN 76; (b) H. L. Kohn, unpublished work included in R. V. Kendall, Thesis, Pennsylvania State University, 1970; (c) R. A. Olofson, Pennsylvania State University, Private communication, 1969.*

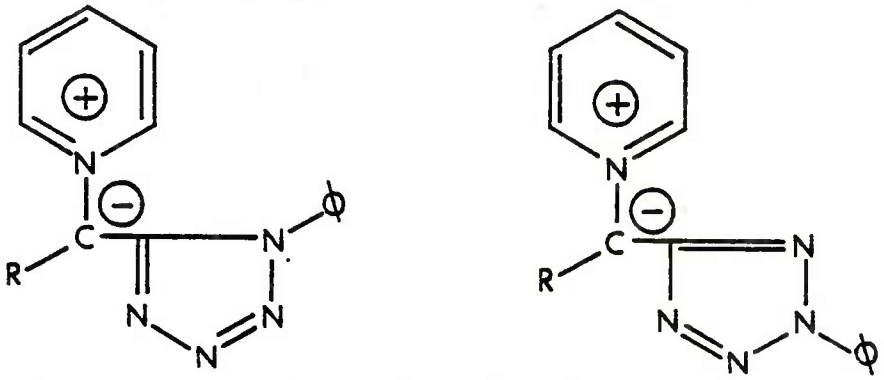
[18] *For a good leading reference, see R. N. Butler, "The Diazotization of Heterocyclic Primary Amines," Chem. Rev. 75, 241 (1975).*

sponding N-nitrosoamine; we know of no instance in which a diazonium cation has been isolated from diazotizatization of a 1-substituted-5-amino-tetrazole. Treatment of 2-substituted-5-aminotetrazoles with diazotization agents also yields N-nitrosoamines, but 1,3-di-(2-methyl-5-tetrazolyl triazene has been isolated from diazotization of 2-methyl-5-aminotetrazole; it was presumably formed via the 2-methyl-5-tetrazolediazonium cation.

The apparent greater electron-withdrawl by 1-than by 2-substituted-5-tetrazolyl groups also shows up in the behavior of isomeric 1- and 2-phenyl-5-chloromethyltetrazoles toward sodium iodide in acetone;[19a] 1-phenyl-5-chloromethyltetrazole gave the 5-iodomethyl compound after standing for one minute, but the corresponding 2-phenyl isomer required fifty minutes.

There is a similar effect on the chemistry of 5-tetrazole carbonyl compounds. The 1-isomers exhibit a marked tendency to form stable hydrates, hemiaminals, etc., and to split off the carbonyl substituent under alkaline conditions, but the 2-isomers exhibit a much lower tendency to form form hydrates, and a more normal behavior toward bases generally.[19b,c]

Consider the isomeric pyridinium tetrazol-5-ylmethylides shown below:



When R is H, the 1-isomer is alkylated by alkyl halides at the carbon to give C-alkylated pyridinium salt, while the 2-isomer under the same conditions underwent ion exchange to give pyridinium salts unsubstituted on the formerly ylidic carbon. When R is benzoyl, it is found that the benzoyl group of the 2-isomer (but not the 1-isomer) is sensitive to hydrolysis in protic solvents. This difference in reactivity was rationalized in terms of a weaker electron-withdrawing effect for the 2-substituted-5-tetrazolyl system.

[19] *(a) E. Lippmann, A. Konnecke and G. Beyer, "Nucleophile Substitutionen am 2-phenyl-5-chloromethyl-tetrazol," Z. Chem. 15, 102 (1975); (b) E. Lippmann, A. Konnecke and G. Beyer, "Synthese und Reactionen des 2-Phenyl-tetrazol-5-carbaldehydes," Monatsh. Chem. 106, 443 (1975); (c) D. Moderhack, "2-Substituierte 5-Tetrazolcarbaldehyde," Chem. Ber. 108, 887 (1975); (d) A. R. Katritzky and D. Moderhack, "Preparation and Reactions of Pyridinium Tetrazol-5-ylmethylides," J. Chem. Soc. Perkin Trans. 1, 909 (1976).*

It has been reported that the methyl protons of 1-phenyl-5-methyltetrazole are more acidic (by a factor of about 20) than the methyl protons of the isomeric 2-phenyl compound[19e].

Furthermore, when N-(4-dimethylaminophenyl) nitrones are reacted with hydrazoic acid, the product distributions are in agreement with the idea that 1-substituted-5-tetrazolyl groups are more electron-withdrawing than the isomeric 2-substituted-5-tetrazolyl groups[19f].

There are also a number of interesting reactivity differences among isomeric 1- and 2-substituted-5-vinyltetrazoles and their precursors[8f,8g,8h]. For example, although ethyl(2-methyl-5-tetrazolyl)-acetate is smoothly reduced to 2-methyl-5-(2-hydroxyethyl)tetrazole by lithium aluminum hydride in diethyl ether, the attempted reduction of the 1-methyl isomer under the same conditions leads to disruption of the tetrazole ring. Furthermore, when 2-methyl-5-(2-chlorethyl)tetrazole is dehydrochlorinated by methanolic potassium hydroxide, the corresponding 5-vinyl compound results; however, treatment of 1-methyl-5-(2-chloroethyl)tetrazole in the same manner yields 1-methyl-5-(2-methoxyethyl)tetrazole. The latter chloro compound is readily dehydrohalogenated by heating in aqueous sodium bicarbonate or in N-methylmorpholine; on the other hand, the 2-methyl-5-(2-chloroethyl)tetrazole is not converted to the vinyl compound by bicarbonate nor is it readily converted by boiling with the tertiary amine[8b,8f,8h].

This difference in activating effects of the isomerically substituted 5-tetrazolyl groups is also of practical interest. Thus, pure 5-(β-hydroxyethyl)-1-methyltetrazole, which is useful as an energetic plasticizer for high energy propellants, can be obtained by refluxing a mixture of 1- and 2-methyl-5-vinyltetrazoles with aqueous base; the two isomers apparently differ sufficiently in reactivity to allow the 1-methyl isomer to form the desired product, while the 2-methyl-5-vinyltetrazole apparently fails to react and can be distilled off when the reaction is over [8f].

It also seems worth mentioning that substituted 5-aminotetrazole plasticizers were used in propellant compositions together with nitrocellulose and nitroglycerine; the compositions containing the 1-isomers were less stable at 106° and 136° than those incorporating the 2-isomers (as measured by time to appearance of salmon color on methyl violet paper and by time to explosion or decomposition;[8g] possibly this was because the more electron-withdrawing 1-substituted-5-tetrazolyl group destabilized any 5-nitraminotetrazoles formed by reaction of the 5-amino group with nitrogen oxides.

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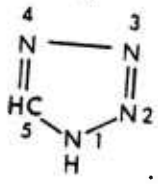
[19] *(e) N. N. Zatsepina, V. A. Zyranov, A. V. Kirova, V. L. Rusinov, I. Ya. Postovskii and I. F. Tupitsyn, "Isotopic Hydrogen Exchange in 1- and 2-aryl-5-methyltetrazoles", Chem. Heterocycl. Compounds, 104 (1977); (f) D. Moderhack, "Tetrazoles from N-(4-Dimethylaminophenyl) nitrones and Hydrogen Azide", J. Heterocycl. Chem., 14, 757 (1977).*

Further examples of reactivity differences between isomeric 1- and 2-substituted tetrazole derivatives were reviewed in the previous report of this series[1]. Since the appearance of that report, tetrazole chemistry generally has been thoroughly reviewed[20], and reactivity differences between isomeric tetrazoles have been discussed in the light of ^{1}H and ^{13}C NMR spectra of isomeric tetrazoles[19b, 21].

The present report describes CNDO/2 and INDO calculations and experimental results which are intended to (a) examine the ability of calculated charge distributions and energies of reaction to reproduce trends in chemical and physical properties of the tetrazoles, a series of compounds which are quite pertinent to explosive and propellant chemistry, as indicated above (p. 10 ff). Another object of this work is (b) to gain experience in using the calculations together with information already in the literature to understand the chemical and physical properties of high-energy materials. A third, and possibly the most important objective of the present work is that we hope (c) to contribute to the understanding of certain observed relationships between explosive behavior and chemical structure of tetrazole derivatives.

For the sake of clarity the structures of some of the compounds which will be mentioned frequently are given below, together with the numbers assigned to them for the purposes of the present report.

1.



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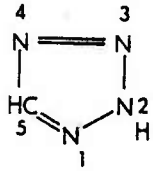

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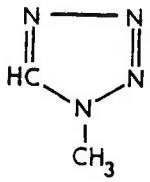

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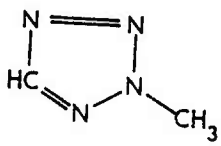

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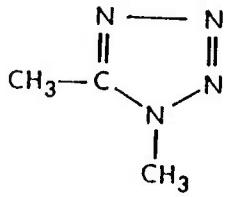

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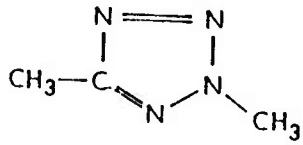
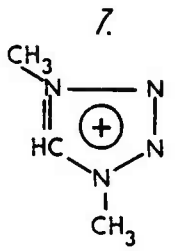
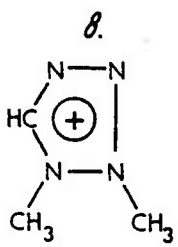
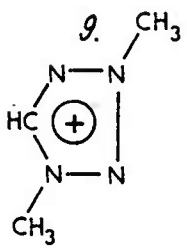


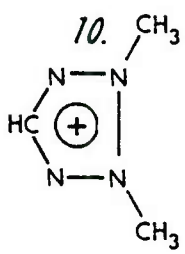
[20] *R. N. Butler, "Recent Advances in Tetrazole Chemistry," in A. R. Katritzky and A. J. Boulton, Eds., Advances in Heterocyclic Chemistry, Vol. 21, Academic Press, New York, 1977.*

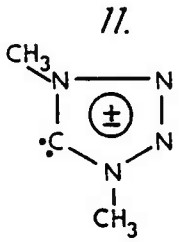
[21] *A. Konnecke, E. Lippmann and E. Kleinpeter, "Isomere N-Arltetrazole. II ^{1}H and ^{13}C NMR Spektren," Tetrahedron 32, 499 (1976).*

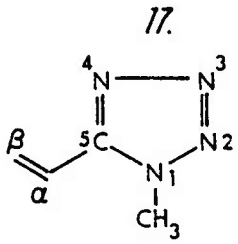


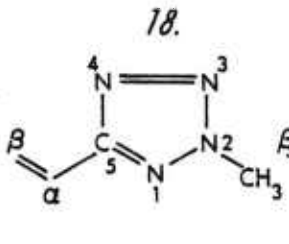


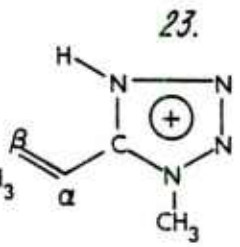


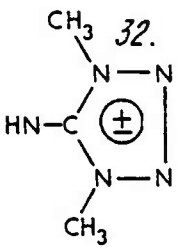


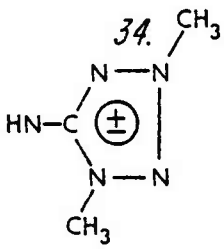


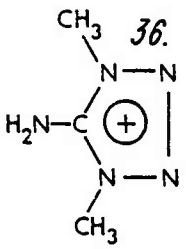


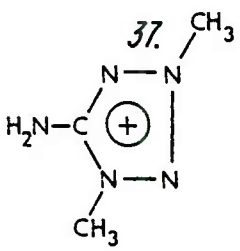












II. EXPERIMENTAL SECTION

General. Except as noted, experimental work was done at the Naval Weapons Center. A number of the compounds used were available as a result of previous investigations in these laboratories; these include 1- and

2-methyl-5-vinyltetrazoles,[22] 1- and 2-methyl-5-trifluoromethyltetrazoles,[23] 1- and 2-octyl-5-trifluoromethyltetrazoles,[24] 1- and 2-phenyltetrazoles, and 1- and 2-vinyltetrazoles.[25] Yields, melting points, and recrystallization solvents for all new compounds are given in Table XXIX.

Infrared Spectra. The infrared spectra of 1- and 2-methyl-5-tetrazolylacetate were recorded in chloroform (0.7% w/v) on a Perkin-Elmer Model 221 Spectrometer; others were recorded on a Perkin-Elmer Infracord 137 Spectrometer.

Nuclear Magnetic Resonance Spectra. Fluorine NMR spectra were measured on a Varian HR60 or HA60 Spectrometer at a concentration of 5% in methanol. 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane was used as an internal standard and the shifts relative to this compound were related to fluorobenzene measured under the same conditions. Each of the chemical shifts, tabulated in Table III, is the average of two or three scans on two or three different days.

Proton NMR Spectra were recorded on a Varian A60 Spectrometer.

Carbon-13 NMR Spectra were measured at California Institute of Technology using dioxane as solvent.[26] The chemical shifts are reported relative to TMS using internal dioxane as the secondary standard. The chemical shifts of carbons attached to hydrogen were obtained from proton-decoupled spectra and hence no J_{C-H} coupling constants were determined.

1-Methyl-5-(m- and p-fluorophenyl) tetrazoles. These compounds were synthesized from m- and p-fluorobenzamides,[27] phosphorous pentachloride, and hydrazoic acid following the procedure of Roberts, Fanta,

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[22] *R. A. Henry, U.S. Patent 3,351,627 (1967).*

[23] *W. P. Norris, "5-Trifluoromethyltetrazole and derivatives", J. Org. Chem. 27, 3248 (1962).*

[24] *W. R. Carpenter, "The formation of Tetrazoles by the Condensation or Organic Azides with Nitriles", J. Org. Chem. 27, 2085 (1962).*

[25] *R. A. Henry, U.S. Patent 3,055,911 (1967).*

[26] *We thank Dr. John B. Grutzner (California Institute of Technology) for carrying out these measurements.*

[27] *R. Campbell and C. J. Peterson, "N-Nitrobenzamides. I. Synthesis, Spectra and Structure", J. Org. Chem. 28, 2294 (1963).*

and Martin.[28] After crystallization from benzene, the compounds were purified further by chromatography on silica gel (eluant was chloroform followed by sublimation.

The infrared spectrum ($CHCl_3$) of 1-methyl-5-(m-fluorophenyl)tetrazole showed principal peaks at 1595, 1480, 1450 (shoulder), 1295, and 880 cm^{-1} and its NMR spectrum ($CDCl_3$) consisted of a singlet (3H) at τ 5.76 and a very broad, complex multiplet (4H) at τ 2.3-3.0.

The infrared spectrum ($CHCl_3$) of 1-methyl-5-(p-fluorophenyl)tetrazole showed principal peaks at 1615, 1485, and 847 cm^{-1}, and its NMR spectrum ($CDCl_3$) consisted of a singlet (3H) at τ 5.80 and two very broad, unsymmetrical multiplets (2H apiece), one centered at τ 2.2 and the other at τ 2.8.

5-Fluorophenyltetrazoles. These compounds were prepared by treating the appropriate substituted benzonitriles with trimethylammonium azide as described by Finnegan, Henry, and Lofquist[29].

2-Methyl-5-(m- and p-fluorophenyl)tetrazoles. The sodium salt of 5-(m- or p-fluorophenyl)tetrazole was methylated with dimethyl sulfate in water[30]. The resulting mixture of 1- and 2-methyl isomers was separated by chromatography on silica gel; the 2-isomers were eluted by benzene, and the 1-isomers by chloroform. The relative amounts of the isomers in both cases were one part 1-methyl isomer to abcut four parts of the 2-isomer; the total yield of the two isomers was 80-90% of theory.

The infrared spectrum of 2-methyl-5-(m-fluorophenyl)tetrazole showed principal peaks at 1580, 1510, 1470 (shoulder), 1450, and 880 cm^{-1}, and its NMR spectrum consisted of a singlet (3H) at τ 5.60 and a very broad, unsymmetrical multiplet (4H) at τ 2-3.

The infrared spectrum ($CHCl_3$) of 2-methyl-5-(p-fluorophenyl)tetrazole showed principal peaks at 1615 (shoulder), 1600, 1455, 1155, 1095, and 844 cm^{-1}, and its NMR spectrum consisted of a singlet (3H) at τ 5.60 and two unsymmetrical multiplets (2H apiece) centered at τ 1.9 and 2.8.

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[28] *C. W. Roberts, G. F. Fanta, and J. D. Martin, "Synthesis and Spectra of a Matched Series of 1-5-Disubstituted Tetrazoles", J. Org. Chem. 24, 654 (1959).*

[29] *W. G. Finnegan, R. A. Henry and R. Lofquist, "An Improved Synthesis of 5-Substituted Tetrazoles", J. Amer. Chem. Soc. 80, 3908 (1958).*

[30] *R. A. Henry and W. G. Finnegan, "Monoalkylation of Sodium 5-Aminotetrazole in Aqueous Medium", J. Amer. Chem. Soc. 76, 923 (1954).*

1,4-Dimethyl-5-(m-fluorophenyl)tetrazolium benzenesulfonate. 1-Methyl-5-(m-fluorophenyl)tetrazole (1.10 g, 6.17 mmoles) was heated with methyl benzenesulfonate (1.09 g, 6.33 mmoles) in an oil bath at 396°K (123°C) for 30 min. The mixture was cooled to room temperature, and recrystallized from 30 ml of ethylene dichloride to give 0.88 g (2.5 mmoles) (41%) of the desired compound. The NMR spectrum (D_2O) of this material showed a singlet (6H) at τ 5.57 and a complex multiplet (9H) in the region 1.7-2.5 τ.

1,3-Dimethyl-5-(m-fluorophenyl)tetrazolium benzenesulfonate. This compound was prepared in the same manner from 2-methyl-5-(m-fluorophenyl)-tetrazole. Its NMR spectrum ($CDCl_3$) showed singlets at τ 3.65 (3H) and τ 5.43 (3H), and a complex multiplet (9H) at τ 2-3. Its infrared spectrum ($CHCl_3$) showed principal peaks at 3000, 1475, 1175, 1125, 1035, and 1020 cm^{-1}.

This compound could also have been written as 1,2-dimethyl-5-(m-fluorophenyl)tetrazolium benzenesulfonate. However, we feel that the 1,2-dimethyl structure is very unlikely for the following reasons: (a) 2-methyltetrazole, on alkylation with methyl benzenesulfonate, yields 1,3-dimethyltetrazolium benzenesulfonate, whose structure has been proven by chemical means;[31] (b) 2-methyl-5-aminotetrazole, on alkylation with methyl benzenesulfonate, yields 1,3-dimethyl-5-iminotetrazoline, the structure of which has been proven by X-ray crystallograph;[32] and (c) as far as we are aware, all attempts[33] to prepare 1,2-disubstituted tetrazolines and tetrazolium salts by alkylation of 2-substituted tetrazoles have failed.

p-(5-Tetrazolyl)benzoic acid. A solution consisting of 15.5 g of 5-(p-tolyl)tetrazole, 7.8 g of sodium bicarbonate, and 200 ml of water was heated to boiling under reflux. Potassium permanganate solution (31 g in one liter of water) was added in 80 ml portions, allowing each portion to decolorize before adding the next (about 10 min). Refluxing was continued for one hr after the addition of oxidizer was completed; sulfur dioxide was then introduced to dissolve the precipitated manganese dioxide. The solution was filtered and treated with 24 ml of conc. hydrochloric acid. After the reaction mixture had been cooled to 278°K (5°C), the product was removed by filtration, washed with cold water, dried, and recrystallized from 95% ethanol. Analytical data are given in Table 29.

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[31] *W. P. Norris and R. A. Henry, "The Action of Base on the 1-3-Dimethyl-tetrazolium Cation", Tetrahedron Letters, 1213 (1965).*

[32] *J. H. Bryden, R. A. Henry, W. G. Finnegan, R. Boschan, W. S. McEwan, and R. W. VanDolah, "1,3-Dimethyl-5-iminotetrazole, a New Cyclic Mesoionic Compound", J. Amer. Chem. Soc. 75, 4863 (1953).*

[33] *(a) R. A. Henry, unpublished work; (b) W. G. Finnegan, unpublished work.*

The same procedure was used to prepare the meta isomer.

m- and p-(1- and 2-Methyl-5-tetrazolyl)benzoic Acids. These compounds were prepared by methylating the m- and p-(5-tetrazolyl)benzoic acids with dimethyl sulfate in aqueous base,[30] followed by basic hydrolysis to convert any carboxylate ester to salt, acidification and cooling to recover the substituted benzoic acids. The 2-methyl isomers could be isolated in a state of high purity by crystallization of the crude products since they were both the major component and the least soluble isomer. The more soluble 1-methyl isomers were only recovered from the mother liquors by tedious, fractional crystallization, as highly enriched mixtures. These mixtures contained about 85% 1-methyl isomers and 15% 2-methyl isomer. The pK_a values and σ-constants reported here for the 1-isomers result from measurements on these mixtures.

The structures of the 1- and 2-methyl-5-tetrazolylbenzoic acids were established by examining the NMR spectra of the isomers. Scott, Butler, and Feeney[34] have shown that NMR spectra can be used to locate methyl groups at the 1- or 2-positions of the tetrazole ring, since a methyl group at the 2-position absorbs downfield from a methyl group in the 1-position. The principal isomer from the methylation of m-(5-tetrazolyl) benzoic acid showed a methyl singlet at τ 5.40, while the minor isomer had a singlet at τ 5.68 (both in CD_3SOCD_3); the compound resonating at τ 5.68 was taken to be the 1-isomer. Similarly the methylation of p(5-tetrazolyl)benzoic acid gave an isomer with a resonance at τ 5.35 and one resonating at τ 5.60 (both in CD_3SOCD_3); the former was taken to be the 2-isomer. Similar results were obtained when the ^1H NMR spectra were determined in $D_2O \cdot LiOD$. The conclusions were confirmed by comparing the aromatic proton resonances with those in 1-methyl-5-phenyl-tetrazole and 2-methyl-5-phenyltetrazole.

Dissocation Constant Measurements. Apparent dissociation constants were measured in 50% ethanol-water. The general procedure of Dewar and Grisdale[35] was used; this involved measurement of the pH of a half-neutralized (with sodium hydroxide) solution of the acid. Either a Radiometer pH Meter 4, or a Beckmann Expandomatic pH meter was employed. In our hands benzoic acid was found to have a pK_a of 5.70 ± 0.03, which is in reasonable agreement with Dewar and Grisdale's value of 5.74 ± 0.02 using the same procedure. The σ_m and σ_p values estimated for the tetrazolyl groups are summarized in Table IV; they were obtained from the differences between pK_a values for substituted and unsubstituted benzoic acids as described in the footnotes to that table.

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[34] *F. L. Scott, R. N. Butler and J. Feeney "Proton Magnetic Resonance Spectra of Methylated 5-Aminotetrazole Derivatives", J. Chem. Soc. B, 919 (1967).*

[35] *M.J. S. Dewar and P. J. Grisdale, "Substituent Effects. III. Acid Dissociation Constants of Substituted 1-Naphthoic Acids and Carbonyl Stretching Frequencies of their Esters", J. Amer. Chem. Soc. 84, 3546 (1962).*

III. CALCULATIONS

Some of the CNDO/2 calculations[36] were carried out using a program which has been described previously.[3,5] The rest of the CNDO/2 calculations, and all of the INDO calculations, were carried out using quantum chemistry program Exchange Program No. 141, "CNINDO;" the program was modified to take bond lengths and angles as input, and to print bond indices and overlap populations as output. Two sets of calculations were carried out. In one set, the tetrazole rings were represented by regular pentagons 1.33 Å on a side, and in the other set the 1- and 2-substituted tetrazole rings were represented by the geometries found from crystallographic measurements (References in footnotes to Table I). The CH_3-N-C angle at position 1 of the 1-methyl isomers was taken as 132.3°, since this is the minimum energy angle found from experimental geometry CNDO/2 calculations on 1H-tetrazole.[3] Crystallographically-determined values were assigned to all other exterior ring angles. Except as noted, values for all remaining bond angles and bond lengths (including bond lengths for ring-methyl bonds) were as suggested by Pople and Gordon,[36a] with the following exceptions. (a) The C-NH_2 bonds in the experimental-geometry CNDO/2 calculations on the 1- and 2-Methyl-5-amino-tetrazoles are the CNDO/2 minimum-energy lengths of 1.380, 1.393 and 1.395 Å for the trigonal coplanar, trigonal perpendicular and tetrahedral forms of 1-methyl-5-aminotetrazole, respectively, and 1.384, 1.396 and 1.399 Å for the same forms of 2-methyl-5-aminotetrazole. (b) The C-NH_2 bonds in the 1.33 Å pentagon calculations on 1- and 2-methyl-5-aminotetrazoles were taken to be 1.37 Å long. (c) The N-vinyl C-N lengths in the N-vinyl-tetrazole derivatives were taken as 1.45 Å. (d) The C-NH_2 lengths in the dimethyl-5-aminotetrazolium cations were taken as 1.29 Å. Exceptions (b)-(d) are based on lengths for analogous bonds in the experimental-geometry references in the footnotes to Table I.

Orbital electron densities q_a and bond orders P_{ab} were defined by equation (1) and (2) respectively.

$$q_a = \sum_i^M n_i c_{ia}^2 \qquad (1)$$

$$P_{ab} = \sum_i^M n_i c_{ia} c_{ib} \qquad (2)$$

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[36] *(a) J. A. Pople and M. Gordon, "Molecular Orbital Theory of the Electronic Structure of Organic Compounds I. Substituent Effects and Dipole Moments", J. Amer. Chem. Soc. 89, 4253 (1967); (b) J. A. Pople and G. A. Segal, "Approximate Self Consistent Molecular Orbital Theory III. CNDO Results for AB_2 and AB_3 Systems", J. Chem. Phys. 44, 3289 (1966).*

where a and b are two different atomic orbitals, the i are the molecular orbitals, n_i is the occupation number of molecular orbital i, the c's are components of the CNDO eigenvector matrix, and M is the number of occupied molecular orbitals.

The bond index W_{ab} between orbitals a and b is defined[37] by

$$W_{ab} = P_{ab}^2 \tag{3}$$

CNDO/2 "overlap populations" q_{ab} may be defined by

$$q_{ab} = 2P_{ab}S_{ab} \tag{4}$$

where S_{ab} is the overlap integral between orbitals a and b. Due to neglect of overlap in normalizing the orbital wavefunctions, the q_{ab}'s are not true Mulliken overlap populations. However, from comparison[38] of INDO and minimum slater-type-orbital ab initio calculations on formaldehyde, it appears that the CNDO and INDO methods still yield values for $P_{ab}S_{ab}$ which are trying to mimic the ab initio values for $2P_{ab}S_{ab}$.[38a] Consequently, use of CNDO/2 and INDO $2P_{ab}S_{ab}$ values as a measure of trends in bond population seems justified.

The above comments refer only to bonded atoms, for example the 1- and 2-nitrogens of the tetrazole rings are bonded to each other. In the case of unbonded atoms (for example the 1- and 4-nitrogens of the tetrazole rings are not bonded to each other), it should be noted that ab initio SCF calculations[38b] using large Gaussian basis sets give large negative overlap populations; large negative overlap populations do not appear in the results of CNDO/2 and INDO calculations, although deorthogonalization of the CNDO/2 and INDO wavefunctions does give some degree of negative overlap population between nonbonded ring atoms. Bond Indices[37] are by definition incapable of giving negative values.

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[37] *K. B. Wiberg, "Application of the Pople-Santry-Segal CNDO Method to the Cyclopropylcarbinyl and Cyclobutyl Cation and to Bicyclobutane" Tetrahedron 24, 1083 (1968).*

[38] *(a) J. J. Kaufman, "Mulliken Population Analysis in CNDO and INDO LCAO-MO-SCF Methods", Int. J. Quantum Chem. Symposium No. 4, 205 (1971). (b) J. J. Kaufman, H. J. T. Preston, E. Kerman and L. C. Cusachs, "Comparison for Pyrrole and Pyrazole of Orbital Energies and Population Analyses from Ab-Initio SCF, CNDO/2, INDO, Extended Huckel and ARCANA Calculations", Int. J. Quantum Chem., Symposium No. 7, 249 (1973).*

IV. RESULTS

Tables 1 and 2 show respectively the CNDO/2 and INDO total energies and dipole moments for the compounds studied.

The fluorine chemical shift of some m- and p-(5-tetrazolyl) and (5-tetrazoliumyl)fluorobenzenes are given in Table 3 and the σ_I and σ_R values calculated from them by the usual equations[39a] are given in Table 4. The σ_I and σ_R values are in reasonable agreement with those estimated by ^{19}F NMR on 1- and 2-phenyl-5-fluorophenyltetrazoles.[39b] Also given in Table 4 are σ_m and σ_p values estimated from the dissociation constants of the appropriate m- and p-tetrazolylbenzoic acids. Values of pKa found for the tetrazolylbenzoic acids are as follows: m-(1-methyl-5-tetrazolyl)benzoic acid, 4.93 ± 0.02; p-(1-methyl-5-tetrazolyl)benzoic acid, 4.93 ± 0.04; m-(2-methyl-5-tetrazolyl)benzoic acid, 5.31 ± 0.03 and p-(2-methyl-5-tetrazolyl)benzoic acid, 5.19 ± 0.02. To reduce uncertainties due to day-to-day fluctuations in experimental conditions, the σ_m and σ_p values were calculated as described in footnote f, Table 4.

Table 5 shows the fluorine chemical shifts (relative to dichlorodifluoromethane in methanol) for 1- and 2-methyl and 1- and 2-(n-octyl)-5-trifluoromethyl tetrazoles. In each case, the 1-isomer is seen to resonate ca 2 ppm downfield from the 2-isomer.

The ^1H NMR spectra of 1- and 2-methyl-5-vinyltetrazoles were also measured; the first-order chemical shifts and splitting constants are given in Table 6. The τ values are believed accurate to within 0.02 ppm and the J values to within 0.3Hz. It can be seen that J_{AC} and J_{BC} are noticeably larger for the 1- than for the 2-isomer, while $\tau_B-\tau_A$ and $\tau_C-\tau_A$ are larger for the 2- than for the 1-isomer.

First order τ-values and coupling constants measured for 1- and 2-vinyl-tetrazoles are given in Table 7. The coupling constants are almost the same for the two isomers. The chemical shifts are somewhat lower for the 2- than for the 1-isomers; this is particularly true of the α-protons.

Tables 8, 9 and 10 show respectively CNDO/2 charge distributions, bond indices and ZDO "overlap populations" for 1- and 2-methyltetrazoles and 1,5- and 2,5-dimethyltetrazoles.

Tables 11, 12 and 13 show respectively INDO charge distribution, bond indices and ZDO "overlap populations" for 1- and 2-methyltetrazoles and for 1H- and 2H-tetrazoles.

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[39] *(a) W. A. Sheppard and R. W. Taft, "The Electronic Properties of Di-,Tri-Tetra-and Hexacorrdinate Sulfur Substituents", J. Amer. Chem. Soc. 94, 1919 (1972); (b) W. A. Sheppard, E. I. DuPont de Nemours and Co., private communication, 1968.*

TABLE 1. CNDO/2 AND INDO TOTAL ENERGIES FOR TETRAZOLE DERIVATIVES

	1.33 Å Pentagon		Experimental-Geometry	
	CNDO/2	INDO	CNDO/2	INDO
1H-Tetrazole (1)	-55.301	-53.039	-55.287[a,b]	-53.031[a]
2H-Tetrazole (2)	-55.294	-53.032	-55.290[a,b]	-53.030[a]
1-Methyltetrazole (3)	-63.994	-61.482	-63.989[c]	-61.478[c]
2-Methyltetrazole (4)	-63.991	-61.478	-64.002[d]	-61.489[d]
1,5-Dimethyltetrazole (5)	-72.700	-	-72.695[c]	-
2,5-Dimethyltetrazole (6)	-72.696	-	-72.705[d]	-
1,4-Dimethyltetrazolium (7)	-73.226	-70.497	-	-
1,2-Dimethyltetrazolium (8)	-73.206	-70.477	-	-
1,3-Dimethyltetrazolium (9)	-73.221	-70.491	-73.227[e]	-70.499[e]
2,3-Dimethyltetrazolium (10)	-73.200	-70.471	-73.204[f]	-70.476[f]
1,4-Dimethyltetrazoliumyl 5-Zwitterion (11)	-72.589	-69.819	-	-
1,2-Dimethyltetrazoliumyl 5-Zwitterion (12)	-72.543	-69.777	-	-
1,3-Dimethyltetrazoliumyl 5-Zwitterion (13)	-72.546	-69.780	-72.559	-69.795
2,3-Dimethyltetrazoliumyl 5-Zwitterion (14)	-72.503	-69.741	-72.500	-69.738
1-Methyl-3-tetrazoliumyl Methyl Zwitterion (15)	-72.534[g] -72.470[h]	-	-	-
3-Methyl-1-tetrazoliumyl Methyl Zwitterion (16)	-72.517[g] -72.463[h]	-	-	-

TABLE 1. CNDO/2 AND INDO TOTAL ENERGIES FOR TETRAZOLE DERIVATIVES

1-Methyl-5-Vinyltetrazole (17)	-	-76.645	-	-76.640[c]
2-Methyl-5-Vinyltetrazole (18)	-	-76.642	-	-76.650[d]
1-Vinyltetrazole (19)	-	-68.189	-	-68.185[c]
2-Vinyltetrazole (20)	-	-68.186	-	-68.196[d]
1-Methyl-2H-5-Vinyltetrazolium (21)	-	-77.200	-	-77.181[c]
1-Methyl-3H-5-Vinyltetrazolium (22)	-	-77.207	-	-77.195[c]
1-Methyl-4H-5-Vinyltetrazolium (23)	-	-77.222	-	-77.221[c]
2-Methyl-1H-5-Vinyltetrazolium (24)	-	-77.205	-	-77.203[d]
2-Methyl-3H-5-Vinyltetrazolium (25)	-	-77.186	-	-77.181[d]
2-Methyl-4H-5-Vinyltetrazolium (26)	-	-77.212	-	-77.221[d]
1-Vinyl-3-Methyltetrazolium (27)	-	-77.200	-	-77.209[e]
1-Methyl-3-Vinyltetrazolium (28)	-	-77.198	-	-77.210[e]
1-Vinyl-4-Methyltetrazolium (29)	-	-77.207	-	-77.206[c]
1-Methyl-5-aminotetrazole				
(30) Coplanar[i]	-76.459	-	-76.458[ℓ]	-
Tetrahedral[j]	-76.468	-	-76.467[ℓ]	-
Perpendicular[k]	-76.446	-	-76.443[ℓ]	-
2-Methyl-5-aminotetrazole				
(31) Coplanar[i]	-76.452	-	-76.465[ℓ]	-
Tetrahedral[j]	-76.462	-	-76.476[ℓ]	-
Perpendicular[k]	-76.439	-	-76.452[ℓ]	-

TABLE 1. CNDO/2 AND INDO TOTAL ENERGIES FOR TETRAZOLE DERIVATIVES

	1.33 Å Pentagon		Experimental-Geometry	
	CNDO/2	INDO	CNDO/2	INDO
1,4-Dimethyl-5-imino-tetrazoline (32)	-85.098	-	-	-
1,2-Dimethyl-5-iminotetrazoline (33)	-85.063[m]	-	-	-
1,3-Dimethyl-5-iminotetrazoline (34)	-85.048[m]	-	-85.074[c]	-
	-85.048[n]	-	-	-
2,3-Dimethyl-5-iminotetrazoline (35)	-84.990	-	-84.993[f]	-
1,4-Dimethyl-5-aminotetrazolium (36)	-85.693	-	-	-
1,2-Dimethyl-5-aminotetrazolium (37)	-85.676	-	-	-
1,3-Dimethyl-5-aminotetrazolium (38)	-85.680	-	-85.697[e]	-
2,3-Dimethyl-5-aminotetrazolium (39)	-85.652	-	-85.657[f]	-

TABLE 1. CNDO/2 AND INDO TOTAL ENERGIES FOR TETRAZOLE DERIVATIVES

[a]Using ring geometries estimated by M. Roche and L. Pujol, Bull. Soc. Chem. Fr., 1097 (1969).

[b]0.99 Å NH, bisecting ring angle.

[c]Assuming ring geometry found for 1H-5-aminotetrazole by K. Britts and I. L. Karle, Acta. Crystallogr. 22, 308 (1967).

[d]Assuming ring geometry found for 2-methyl-5-aminotetrazole by J. H. Bryden, Acta. Crystallogr. 9, 874 (1956).

[e]Assuming ring geometry found for 1,3-dimethyl-5-aminotetrazolium cation by J. H. Bryden, Acta Crystallogr. 8, 211 (1955).

[f]Assuming ring geometry found for anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide by Y. Kushi and Q. Fernando, J. Amer. Chem. Soc. 92, 1965 (1970).

[g]Trigonal CH_2 coplanar with ring.

[h]Trigonal CH_2 perpendicular to ring.

[i]Trigonal NH_2 coplanar with ring.

[j]Tetrahedral NH_2.

[k]Trigonal NH_2 perpendicular to ring.

[ℓ]Minimum-energy C-NH_2 length.

[m]NH anti. to Position 1.

[n]NH syn to Position 1.

TABLE 2. CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS (D) FOR TETRAZOLE DERIVATIVES

	1.33 Å Pentagon		Experimental-Geometry		Measured (D)
	CNDO/2	INDO	CNDO/2	INDO	
1H-Tetrazole (1)	5.51	5.38	5.26	5.15	5.30[a]
2H-Tetrazole (2)	2.40	2.37	2.14	2.10	2.19[a], 2.14[a]
1-Methyltetrazole (3)	5.61	5.41	6.06	5.06	5.46[b,c]
2-Methyltetrazole (4)	2.56	2.48	2.46	2.37	2.65[b,c]
1,5-Dimethyltetrazole (5)	5.75	-	5.46	-	5.30[b]
2,5-Dimethyltetrazole (6)	2.44	-	2.31	-	2.42[d]
1-Methyl-5-aminotetrazole (30)	6.00[e]	-	5.68[e]	-	~ 7[b]
2-Methyl-5-aminotetrazole (31)	2.93[e]	-	2.90[e]	-	~2.6[b]
1,4-Dimethyl-5-aminotetrazoline (32)	1.68	-	-	-	1.65[b]
1,3-Dimethyl-5-aminotetrazoline (34)	7.17[f]	-	5.78[g]	-	4.02[b]
	6.33[g]				

[a]Measured from microwave spectrum of tetrazole, C-deuteriotetrazole and N-deuteriotetrazole by W. D. Krugh and L. P. Gold, J. Mol. Spectroscop. 49, 423 (1974).

[b]M. H. Kaufman, F. M. Ernsberger and W. S. McEwen, J. Amer. Chem. Soc. 78, 4197 (1956).

[c]Value given for corresponding N-ethyltetrazole.

[d]J. H. Markgraf, W. T. Bachman and D. P. Hollis, J. Org. Chem. 30, 3472 (1965).

[e]Tetrahedral NH_2.

[f]NH oriented sym to position 1.

[g]NH oriented anti to Position 1.

TABLE 3. ^{19}F CHEMICAL SHIFTS (IN PPM) OF M- AND P-5-TETRAZOLYL_ AND M- AND P-5-TETRAZOLIUMYL-FLUOROBENZENES, F⟨O⟩X, IN VARIOUS SOLVENTS

X	Methanol[a]		Acetomitrile[b]		Benzene[b]		Chloroform	
	$\int^{X\text{-}C_6H_4F}_{TCTFCB}$[c]	$\int^{X\text{-}C_6H_4F}_{H\text{-}C_6H_4F}$	$\int^{X\text{-}C_6H_4F}_{TCTFCB}$[c]	$\int^{X\text{-}C_6H_4F}_{H\text{-}C_6H_4F}$	$\int^{X\text{-}C_6H_4F}_{TCTFCB}$[c]	$\int^{X\text{-}C_6H_4F}_{H\text{-}C_6H_4F}$	$\int^{X\text{-}C_6H_4F}_{TCTFCB}$[c]	$\int^{X\text{-}C_6H_4F}_{H\text{-}C_6H_4F}$
H	44.02	0.00	44.21	0.00	42.94	0.00	43.27[b]	0.00
m-(1-Methyl-5-tetrazolyl)	41.76	-2.26	42.11	-2.10	41.27	-1.67		
m-(2-Methyl-5-tetrazolyl)	42.84	-1.18	43.26	-0.95	42.21	-0.73		
p-(2-Methyl-5-tetrazolyl)	38.87	-5.15	39.90	-4.31	38.85	-4.09		
p-(2-Methyl-5-tetrazolyl)	40.85	-3.17	41.72	-2.49	40.55	-2.39		
m-(1,4-Dimethyl-5-tetrazoliumyl)[c]	38.70	-5.32	40.11	-4.10			38.02[d]	-5.25
m-(1,3-Dimethyl-5-tetrazoliumyl)[c]	40.36	-3.66	41.14	-3.07			39.73[a]	-3.54

[a] 5% Solution

[b] Extrapolated to infinite dilution from measurements at ca 20, 10 and 5% solute by weight.

[c] 1,1,2,2,-Tetrachloro-3,3,4,4-tetrafluorocyclobutane.

[d] Measurement on saturated solution (ca 1%).

TABLE 4. EXPERIMENTAL σ_R, σ_I, σ_m, and σ_p CONSTANTS OF METHYL-5-TETRAZOLYL AND DIMETHYL-5-TETRAZOLIUMYL GROUPS

GROUP	σ_I[a]	σ_m[f]	σ_p[f]	σ_R	σ_R^o
1-Methyl-5-tetrazolyl	0.40[b]	>0.55[g]	>0.54[g]	0.10[a,b]	>0.14[g,h]
	0.38[c]			0.08[a,c]	
	0.32[d]			0.08[a,d]	
2-Methyl-5-tetrazolyl	0.25[b]	0.27	0.35	0.07[a,b]	0.10[h]
	0.22[c]			0.05[a,c]	
	0.19[d]			0.06[a,d]	
1,4-Dimethyl-5-tetrazoliumyl	0.83[a]				
	0.66[b]				
	0.82[e]				
1,3-Dimethyl-5-tetrazoliumyl	0.60[a]				
	0.52[b]				
	0.58[e]				

[a]Calculated from the data in Table 3 as described by R. G. Pews, J. Amer. Chem. Soc. 89, 5605 (1967).

[b]In Methanol.

[c]In Acetonitrile.

[d]In Benzene.

[e]In Chloroform.

[f]Calculated from pK_a's of the appropriate tetrazolylbenzoic acids (p. 23), using $\rho = 1.423$ for the ionization of benzoic acids in 50% aqueous ethanol (H. H. Jaffe, Chem. Rev. 53, 191 (1953), and the pK_a of benzoic acid measured on the same day as the appropriate tetrazolylbenzoic acid (to correct for electrode behavior). At least 3 determinations on two different days were carried out.

[g]Minimum value; the (1-methyl-5-tetrazolyl) benzoic acid was contaminated with ca. 10-20% of the 2-methyl isomer.

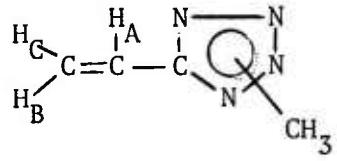
[h]$\sigma_p - \sigma_I$; see for example R. T. C. Brownlee, A. R. Katritzky and R. D. Topsom, J. Amer. Chem. Soc. 87, 3260 (1965).

TABLE 5. FLUORINE CHEMICAL SHIFTS (Ø) OF 5-TRIFLUOROMETHYLTETRAZOLES

	Fluorine chemical shift (Ø)[a]	
Substituent	5% (v/v)	20% (v/v)
1-Methyl	62.02	62.06
2--Methyl	63.94	63.95
1-(n-Octyl)	61.57	61.61
2-(n-Octyl)	63.86	64.10

[a]Relative to 2% CF_2Cl_2 (internal standard) at the indicated concentrations in methanol.

TABLE 6. FIRST-ORDER CHEMICAL SHIFTS (τ) AND SPLITTING CONSTANTS (HZ) FOR 1- AND 2-METHYL-5-VINYLTETRAZOLES

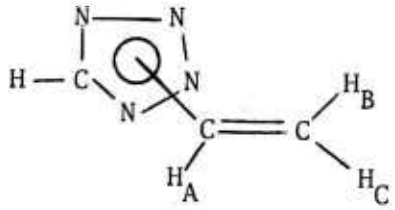


COMPOUND	τ_{CH_3}	τ_A	τ_B	τ_C	J_{AC}	J_{AB}	J_{BC}	$\tau_B-\tau_A$	$\tau_C-\tau_A$
1-Methyl-5-vinyltetrazole[a] (17)	5.80	3.21	3.58	4.09	9.3	17.0	3.5	0.37	0.88
2-Methyl-5-vinyltetrazole[b] (18)	5.60	3.15	3.66	4.32	10.4	17.5	2.3	0.51	1.17

[a]A small dilution effect was observed, so data for this compound are extrapolated to infinite dilution from scans on 2.5, 5, and 10% (v/v) solutions in $CDCl_3$.

[b]Five percent (v/v) in $CDCl_3$; no dilution effect was observed.

TABLE 7. FIRST-ORDER CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (HZ) FOR 1- AND 2- VINYLTETRAZOLES



COMPOUND	$\tau_{5\text{-H}}$	τ_A	τ_B	τ_C	J_{AB}	J_{AC}	J_{BC}	$\tau_B-\tau_A$	$\tau_C-\tau_A$
1-Vinyltetrazole (19)	0.295	2.20	3.76	4.42	9.0	16.0	1.6	1.56	2.22
2-Vinyltetrazole (20)	0.90	1.97	3.59	4.28	9.0	16.0	1.5	1.62	2.31

[a]Extrapolated to infinite dilution from scans at 50, 25 and 12.5% (v/v) in deuterioacetone.

TABLE 8. CNDO/2 ATOMIC CHARGES FOR METHYLATED TETRAZOLES

Compound	Position	Atomic Charges[a] 1.33Å Pentagon σ	π	Total	H	Experimental Geometry σ	π	Total	H
1-Methyltetrazole (3)	1	-474	+518	+ 44		-445	+432	- 13	
	2	+127	-212	- 85		+125	-180	- 55	
	3	+ 58	- 96	- 38		+ 28	- 45	- 17	
	4	+ 24	-170	-146		+ 55	-232	-177	
	5	+137	- 26	+111	+ 6	+117	+ 43	+160	+ 3
	CH_3	+ 55	+ 2	+ 57	+ 22[b] + 14[c]	+ 57	+ 8	+ 65	+ 20[b] + 8[c]
2-Methyltetrazole (4)	1	+ 56	-202	-146		+ 74	-231	-157	
	2	-424	+523	+ 99		-409	+523	+114	
	3	+ 97	-151	- 54		+ 66	- 97	- 31	
	4	+ 12	-140	-128		+ 38	-191	-153	
	5	+124	- 17	+107	+ 6	+117	+ 8	+125	+ 8
	CH_3	+ 55	- 2	+ 53	+ 24[d] + 21[c]	+ 46	- 2	+ 44	+ 22[d] + 20[c]

TABLE 8. CNDO/2 ATOMIC CHARGES FOR METHYLATED TETRAZOLES (continued)

Compound	Position	Atomic Charges[a] 1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
1,5-Dimethyltetrazole (5)	1	-472	+498	+ 26		-444	+414	- 30	
	2	+129	-221	- 92		+125	-187	- 62	
	3	+ 46	- 82	- 36		+ 17	- 35	- 18	
	4	+ 32	-200	-168		+ 65	-265	-200	
	5	+149	+ 4	+153		+128	+ 70	+198	
	CH_3(1)	+ 56	+ 3	+ 59	+ 21[b] + 11[c]	+ 55	+ 11	+ 66	+ 19[b] + 5[c]
	CH_3(5)	- 61	+ 15	- 46	+ 26[e] + 17[c]	- 63	+ 11	- 52	+ 26[e] + 22[c]
1,5-Dimethyltetrazole (5)	1	-472	+498	+ 26		-444	+415	- 29	
	2	+131	-223	- 92		+125	-188	- 63	
	3	+ 45	- 81	- 36		+ 17	- 34	- 17	
	4	+ 33	-202	-169		+ 66	-267	-201	
	5	+149	+ 5	+154		+128	+ 71	-199	
	CH_3(1)	+ 57	+ 2	+ 59	+ 12[f] + 13[g] + 20[h]	+ 58	+ 8	+ 66	+ 6[f] + 6[g] + 16[h]
	CH_3(5)	- 56	+ 10	- 46	+ 26[i] + 23[j] + 11[k]	- 59	+ 7	- 52	+ 28[i] + 28[j] + 14[k]

TABLE 8. CNDO/2 ATOMIC CHARGES FOR METHYLATED TETRAZOLES (continued)

Compound	Position	Atomic Charges[a] 1.33Å Pentagon σ	π	Total	H	Experimental Geometry σ	π	Total	H
2,5-Dimethyltetrazole (6)	1	+ 66	-236	-170		+ 86	-266	-180	
	2	-426	+524	+ 98		-413	+525	+112	
	3	+ 84	-136	- 52		+ 56	- 84	- 28	
	4	+ 18	-165	-147		+ 44	-215	-171	
	5	+139	+ 11	+150		+129	+ 36	+165	
	CH_3(2)	+ 55	- 1	+ 54	+ 23[d] + 19[c]	+ 45	- 1	+ 44	+ 20[d] + 19[c]
	CH_3(5)	- 53	+ 16	- 37	+ 14[e] + 15[c]	- 58	+ 16	- 42	+ 13[e] + 15[c]
2,5-Dimethyltetrazole (6)	1	+ 65	-234	-169		+ 85	-264	-179	
	2	-425	+523	- 98		-412	+524	+112	
	3	+ 85	-137	+ 52		+ 56	- 84	- 28	
	4	+ 17	-164	-147		+ 43	-214	-171	
	5	+139	+ 10	+149		+130	+ 34	+164	
	CH_3(2)	+ 55	- 1	+ 54	+ 23[l] + 17[g] + 22[m]	+ 44	0	+ 44	+ 13[l] + 16[g] + 19[m]
	CH_3(5)	- 52	+ 15	- 37	+ 15[i] + 17[j] + 12[k]	- 58	+ 16	+ 42	+ 14[e] + 18[j] + 12[k]

TABLE 8. CNDO/2 ATOMIC CHARGES FOR METHYLATED TETRAZOLES (continued)

[a]In units of 0.001 electronic charge.

[b]Single proton, in plane of ring and syn to Position 2.

[c]Charge on each of two equivalent protons.

[d]Single proton, in plane of ring and syn to position 3.

[e]Single proton, in plane of ring and syn to position 4.

[f]Below ring, syn to position 5.

[g]Above ring.

[h]Below ring, syn to position 2.

[i]Above ring syn to position 4.

[j]Below ring.

[k]Above ring, syn to position 1.

[ℓ]Below ring, syn to position 1.

[m]Below ring, syn to position 3.

TABLE 9. CNDO/2 BOND INDICES FOR METHYLATED TETRAZOLES

Compound		Bond Indices					
		1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1-Methyltetrazole (3)	1-2	0.940	0.247	1.187	0.922	0.171	1.093
	2-3	0.998	0.567	1.565	1.025	0.690	1.715
	3-4	0.975	0.323	1.298	0.953	0.228	1.181
	4-5	1.009	0.546	1.555	1.014	0.601	1.615
	5-1	0.951	0.340	1.291	0.960	0.219	1.279
	1-CH_3	0.9776	0.0289	1.0065	0.9823	0.0295	1.0118
2-Methyltetrazole (4)	1-2	0.951	0.260	1.211	0.938	0.224	1.162
	2-3	0.949	0.334	1.283	0.962	0.373	1.335
	3-4	0.994	0.478	1.472	0.985	0.465	1.450
	4-5	0.989	0.394	1.383	0.986	0.378	1.364
	5-1	0.995	0.535	1.530	0.998	0.561	1.559
	2-CH_3	0.9760	0.0316	1.0076	0.9750	0.0304	1.0054

TABLE 9. CNDO/2 BOND INDICES FOR METHYLATED TETRAZOLES (continued)

Compound		Bond Indices					
		1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1,5-Dimethyltetrazole (5)	1-2	0.942	0.231	1.173	0.924	0.159	1.083
	2-3	0.999	0.575	1.574	1.026	0.697	1.723
	3-4	0.978	0.320	1.298	0.956	0.224	1.180
	4-5	0.997	0.517	1.514	1.002	0.567	1.569
	5-1	0.938	0.328	1.266	0.947	0.305	1.252
	1-CH_3	0.9786	0.0300	1.0086	0.9831	0.0305	1.0136
	5-CH_3	0.9965	0.0473	1.0438	0.9937	0.0473	1.0410
2,5-Dimethyltetrazole (6)	1-2	0.951	0.247	1.198	0.937	0.213	1.150
	2-3	0.950	0.344	1.294	0.963	0.383	1.346
	3-4	0.996	0.473	1.469	0.988	0.458	1.446
	4-5	0.977	0.376	1.353	0.973	0.361	1.334
	5-1	0.984	0.512	1.496	0.987	0.535	1.522
	2-CH_3	0.9765	0.0320	1.0085	0.9755	0.0308	1.0063
	5-CH_3	0.9938	0.0442	1.0380	0.9913	0.0450	1.0363

TABLE 10. CNDO/2 "OVERLAP POPULATIONS" FOR METHYLTETRAZOLES

Compound	Bond	"Overlap Populations" 1.33Å Pentagon σ	π	Total	Experimental Geometry σ	π	Total
1-Methyltetrazole (3)	1-2	1.213	0.173	1.386	1.114	0.128	1.242
	2-3	1.233	0.262	1.495	1.375	0.337	1.712
	3-4	1.216	0.198	1.414	1.132	0.151	1.283
	4-5	1.448	0.323	1.771	1.463	0.344	1.807
	5-1	1.426	0.255	1.681	1.443	0.247	1.690
	1-CH_3	1.2478	0.0567	1.3045	1.2542	0.0573	1.3115
2-Methyltetrazole (4)	1-2	1.226	0.177	1.403	1.193	0.161	1.354
	2-3	1.218	0.201	1.419	1.304	0.235	1.539
	3-4	1.234	0.240	1.474	1.236	0.242	1.478
	4-5	1.433	0.274	1.707	1.401	0.259	1.660
	5-1	1.445	0.319	1.764	1.456	0.333	1.789
	2-CH_3	1.2572	0.0594	1.3166	1.2474	0.0582	1.3056

TABLE 10. CNDO/2 "OVERLAP POPULATIONS" FOR METHYLTETRAZOLES (continued)

Compound	Bond	"Overlap Populations" 1.33Å Pentagon σ	π	Total	Experimental Geometry σ	π	Total
1-Methyltetrazole (3)	1-2	1.213	0.173	1.386	1.114	0.128	1.242
	2-3	1.233	0.262	1.495	1.375	0.337	1.712
	3-4	1.216	0.198	1.414	1.132	0.151	1.283
	4-5	1.448	0.323	1.771	1.463	0.344	1.807
	5-1	1.426	0.255	1.681	1.443	0.247	1.690
	1-CH_3	1.2478	0.0567	1.3045	1.2542	0.0573	1.3115
2-Methyltetrazole (4)	1-2	1.226	0.177	1.403	1.193	0.161	1.354
	2-3	1.218	0.201	1.419	1.304	0.235	1.539
	3-4	1.234	0.240	1.474	1.236	0.242	1.478
	4-5	1.433	0.274	1.707	1.401	0.259	1.660
	5-1	1.445	0.319	1.764	1.456	0.333	1.789
	2-CH_3	1.2572	0.0594	1.3166	1.2474	0.0582	1.3056

TABLE 11. INDO ATOMIC CHARGES[a] FOR 1- AND 2-METHYL- AND 1H- and 2H-TETRAZOLES

Compound	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
1-Methyltetrazole (3)	1	-464	+532	+ 68	-	-452	+455	+ 3	-
	2	+ 98	-205	-107	-	+102	-174	- 72	-
	3	+ 79	-114	- 35	-	+ 55	-68	-13	-
	4	+ 1	-171	-170	-	+ 21	-227	-206	-
	5	+177	- 26	+151	- 13	+169	+ 35	+204	- 17
	CH_3	+ 92	+ 39	+131	- 2[b] - 11[c]	+ 97	+ 44	+141	- 5[b] - 18[c]
2-Methyltetrazole (4)	1	+ 10	-209	-199	-	+ 26	-231	-205	-
	2	-394	+543	+149	-	-383	+543	+160	-
	3	+ 78	-158	- 80	-	+ 62	-119	- 57	-
	4	- 2	-152	-154	-	+ 14	-189	-175	-
	5	+192	- 10	+182	- 15	+188	+ 10	+198	- 27
	CH_3	+ 91	+ 33	+124	+ 1[d] - 4[e]	+ 83	+ 32	+115	- 1[d] - 4[e]

TABLE 11. INDO ATOMIC CHARGES[a] FOR 1- AND 2-METHYL- and 1H- and 2H-TETRAZOLES (continued)

Compound	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
1-H-Tetrazole (1)	1	-461	+499	+ 38	+106	-452	+422	- 30	+108
	2	+100	-196	- 96	-	+106	-168	- 62	-
	3	+ 84	-114	- 30	-	+ 58	- 68	- 10	-
	4	+ 7	-176	-169	-	+ 26	-232	-206	-
	5	+176	- 13	+163	- 12	+169	+ 47	+216	- 17
2-H-Tetrazole (2)	1	+ 13	-197	-184	-	+ 30	-221	-191	-
	2	-391	+505	+114	+113	-377	+506	+132	+ 94
	3	+ 80	-144	- 64	-	+ 63	-105	- 42	-
	4	+ 3	-152	-149	-	+ 19	-188	-169	-
	5	+195	- 12	+183	- 12	+191	+ 8	+199	- 24

[a] In units of 10^{-3} electronic charge.

[b] Hydrogen in plane of ring syn to position 2.

[c] Two equivalent hydrogens out of plane of ring, syn to position 5.

[d] Hydrogen in plane of ring syn to position 3.

[e] Two equivalent hydrogens out of plane of ring, syn to position 1.

TABLE 12. INDO BOND INDICES FOR 1- and 2-METHYL-TETRAZOLES

Compound	Position	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1-Methyltetrazole (3)	1-2	0.935	0.256	1.191	0.908	0.182	1.090
	2-3	1.002	0.561	1.563	1.041	0.678	1.719
	3-4	0.977	0.323	1.300	0.949	0.233	1.182
	4-5	1.011	0.544	1.555	1.017	0.595	1.612
	5-1	0.941	0.344	1.285	0.949	0.327	1.276
	1-CH_3	0.971	0.032	1.003	1.975	0.033	1.008
2-Methyltetrazole (4)	1-2	0.952	0.265	1.217	0.938	0.233	1.171
	2-3	0.937	0.344	1.281	0.952	0.376	1.328
	3-4	1.006	0.466	1.472	0.996	0.456	1.452
	4-5	0.983	0.400	1.383	0.979	0.386	1.365
	5-1	0.990	0.529	1.519	0.996	0.553	1.549
	2-CH_3	0.968	0.035	1.003	0.967	0.034	1.001

TABLE 12. INDO BOND INDICES FOR 1- and 2-METHYL-TETRAZOLES (continued)

Compound	Position	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1H-Tetrazole (1)	1-2	0.943	0.255	1.198	0.917	0.182	1.099
	2-3	1.000	0.570	1.570	1.041	0.684	1.725
	3-4	0.975	0.319	1.294	0.946	0.231	1.177
	4-5	1.011	0.547	1.598	1.017	0.597	1.614
	5-1	0.950	0.348	1.298	0.956	0.330	1.286
2H-Tetrazole (2)	1-2	0.961	0.265	1.226	0.946	0.234	1.180
	2-3	0.944	0.315	1.289	0.960	0.377	1.337
	3-4	1.004	0.477	1.481	0.995	0.465	1.460
	4-5	0.981	0.394	1.375	0.976	0.381	1.357
	5-1	0.989	0.537	1.526	0.994	0.560	1.554

TABLE 13. INDO "OVERLAP POPULATIONS" FOR 1- AND 2-METHYLTETRAZOLES

Compound	Position	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1-Methyltetrazole (3)	1-2	1.196	0.176	1.372	1.093	0.133	1.226
	2-3	1.214	0.260	1.474	1.367	0.335	1.702
	3-4	1.202	0.198	1.400	1.118	0.153	1.271
	4-5	1.444	0.322	1.766	1.460	0.342	1.802
	5-1	1.419	0.256	1.675	1.435	0.250	1.685
	1-CH_3	1.243	0.060	1.303	1.248	0.061	1.309
2-Methyltetrazole (4)	1-2	1.220	0.179	1.399	1.185	0.164	1.349
	2-3	1.198	0.204	1.402	1.275	0.232	1.507
	3-4	1.223	0.237	1.460	1.226	0.240	1.466
	4-5	1.425	0.276	1.701	1.396	0.262	1.658
	5-1	1.441	0.317	1.758	1.452	0.331	1.785
	2-CH_3	1.253	0.062	1.315	1.245	0.061	1.306

TABLE 13. INDO "OVERLAP POPULATIONS" FOR 1- AND 2-METHYLTETRAZOLES (continued)

Compound	Position	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1H-Tetrazole (1)	1-2	1.205	0.175	1.380	1.101	0.133	1.234
	2-3	1.215	0.262	1.477	1.367	0.337	1.704
	3-4	1.201	0.196	1.397	1.116	0.152	1.268
	4-5	1.445	0.323	1.768	1.460	0.343	1.803
	5-1	1.430	0.257	1.687	1.442	0.251	1.693
2H-Tetrazole (2)	1-2	1.228	0.179	1.407	1.194	0.164	1.358
	2-3	1.205	0.204	1.409	1.293	0.223	1.516
	3-4	1.223	0.240	1.463	1.227	0.242	1.469
	4-5	1.423	0.274	1.697	1.393	0.261	1.654
	5-1	1.441	0.320	1.761	1.453	0.333	1.786

Tables 14, 15 and 16 show respectively INDO charge distributions, bond indices and ZDO "overlap populations" for 2,3-, 1,3-, 1,2- and 1,4-dimethyltetrazolium cations, while Tables 17, 18 and 19 give the same quantities for the corresponding 5-deprotonated zwitterions.

Tables 20, 21 and 22 show respectively CNDO/2 charge distributions, bond indices and ZDO "overlap populations" for 1- and 2-methyl-5-amino-tetrazoles, with the amino group in three configurations: trigonal and coplanar with the tetrazole ring; tetrahedral amino group; and trigonal coplanar amino group oriented perpendicular to the tetrazole ring.

Table 23 summarizes the available literature data on heats of formation for some isomeric 1,5- and 2,5-disubstituted tetrazoles.

Table 24 gives CNDO/2 π-atomic charges and bond indices for the exocyclic C-N bonds in 2,3-, 1,3-, 1,2- and 1,4-dimethyl-5-aminotetrazolines, in both protonated and unprotonated forms.

Tables 25 and 26 show INDO π-atomic charges, bond indices and ZDO "overlap populations" for vinyl groups of 1- and 2-methyl-5-vinyl-tetrazoles, 1- and 2-vinyltetrazoles, and some of their N-protonated and N-methylated cations, for both experimental (Table 25) and 1.33 Å-pentagon (Table 26) geometries.

Tables 27 and 28 show respectively CNDO/2 atomic charges and π-bond indices for tetrazoliumylmethyl zwitterions, and π-bond indices for 1,3-dimethyltetrazolium cation. The CNDO/2 atomic charges for 1,3-dimethyltetrazolium cation have already been reported.[6]

Table 29 shows yields, recrystallization solvents, melting points and analytical data for all new compounds prepared in the course of this work.

Figure I shows ^{13}C NMR chemical shifts for several isomeric pairs of 1,5- and 2,5-disubstituted tetrazole derivatives.

Figure II shows a plot of INDO π-electron excess charge density[40] for a series of substituted ethylenes against σ_R for the respective substituents.

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[40] *R. T. C. Brownlee and R. W. Taft "A CNDO/2 Theoretical Study of Substituent Effects on Electronic Distribution in Fluorine Molecular Orbitals. Comparison with Meta-and Para-Substituent Fluorine Nuclear Magnetic Resonance Shifts", J. Amer. Chem. Soc. 92, 7007 (1970).*

TABLE 14. INDO ATOMIC CHARGES[a] FOR DIMETHYLTETRAZOLIUM CATIONS

Cation	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
2,3-Dimethyltetrazolium (10)	1(4)	+ 38	-101	- 63	-	+ 37	- 88	- 51	-
	2(3)	-410	+588	+178	-	-405	+584	+179	-
	5	+186	+ 23	+209	+ 73	+183	+ 7	+190	+ 67
	CH_3	+114	- 6	+108	+ 58[b]	+115	- 7	+108	+ 58[b]
					+ 39[c]				+ 39[c]
1,3-Dimethyltetrazolium (9)	1	-492	+632	+140	-	-482	+593	+111	-
	2	+140	-158	- 18	-	+141	-154	- 13	-
	3	-428	+664	+236	-	-434	+701	+267	-
	4	+ 60	-164	-104	-	+ 76	-180	-104	-
	5	+170	+ 22	+192	+ 70	+157	+ 39	+196	+ 80
	$CH_3(1)$	+125	- 7	+118	+ 40[d]	+124	- 3	+121	+ 38[d]
					+ 38[e]				+ 34[e]
	$CH_3(3)$	+121	- 12	+109	+ 50[b]	+110	- 14	+ 96	+ 50[b]
					+ 45[c]				+ 46[c]

TABLE 14. INDO ATOMIC CHARGES[a] FOR DIMETHYLTETRAZOLIUM CATIONS (continued)

Cation	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
1,2-Dimethyltetrazolium (8)	1	-466	+555	+ 89	-				
	2	-397	+553	+156	-				
	3	+101	- 37	+ 64	-				
	4	+ 62	-133	- 71	-				
	5	+154	+ 68	+222	+ 70				
	CH_3(1)	+123	- 6	+117	+ 43[f]				
					+ 34[g]				
	CH_3(2)	+116	- 5	+111	+ 56[h]				
					+ 37[i]				
1,4-Dimethyltetrazolium (7)	1(4)	-491	+620	+129	-				
	2(3)	+143	-129	+ 14	-				
	5	+157	+ 25	+182	+ 70				
	CH_3	+122	- 4	+118	+ 44[d]				
					+ 34[e]				

[a]In units of 0.001 electronic charge. [b]Single H atom coplanar with ring, oriented syn to position 4.
[c]Two equivalent H atoms out of plane of ring anti to position 4. [d]Single H atom coplanar with ring, syn to position
[e]Two equivalent H atoms out of plane of ring, syn to position 5. [f]Single H atom, coplanar with ring, syn to position
[g]Two equivalent H atoms, out of plane of ring, syn to position 2.
[h]Single H atom, coplanar with ring, syn to position 3.
[i]Two equivalent H atoms, out of plane of ring and syn to position 1.

TABLE 15. INDO BOND INDICES FOR TETRAZOLIUM CATIONS

Cation	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
2,3-Dimethyltetrazolium (10)	5-1(4)	0.981	0.470	1.451	0.977	0.469	1.446
	1(4)-2(3)	0.962	0.358	1.320	0.967	0.365	1.332
	2-3	0.928	0.262	1.190	0.922	0.253	1.175
	2(3)-CH_3	0.935	0.033	0.968	0.934	0.033	0.967
1,3-Dimethyltetrazolium (9)	5-1	0.941	0.356	1.297	0.938	0.303	1.301
	1-2	0.967	0.349	1.316	0.963	0.313	1.276
	2-3	0.970	0.445	1.415	0.978	0.479	1.457
	3-4	0.950	0.283	1.233	0.951	0.287	1.238
	4-5	1.009	0.558	1.567	1.003	0.546	1.549
	1-CH_3	0.936	0.029	0.965	0.942	0.030	0.972
	3-CH_3	0.933	0.033	0.966	0.933	0.031	0.964

TABLE 15. INDO BOND INDICES FOR TETRAZOLIUM CATIONS (continued)

Cation	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1,2-Dimethyltetrazolium (8)	5-1	0.941	0.420	1.361			
	1-2	0.940	0.187	1.127			
	2-3	0.948	0.426	1.374			
	3-4	0.997	0.421	1.418			
	4-5	1.003	0.468	1.471			
	1-CH_3	0.939	0.029	0.968			
	2-CH_3	0.935	0.032	0.967			
1,4-Dimethyltetrazolium (7)	5-1(4)	0.970	0.439	1.409			
	1(4)-2(3)	0.941	0.265	1.206			
	2-3	1.019	0.605	1.624			
	1(4)-CH_3	0.937	0.028	0.965			

TABLE 16. INDO "OVERLAP POPULATIONS" FOR TETRAZOLIUM CATIONS

Cation	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
2,3-Dimethyltetrazolium (10)	5-1(4)	1.433	0.299	1.734	1.384	0.282	1.666
	1(4)-2(3)	1.225	0.208	1.433	1.239	0.216	1.455
	2-3	1.227	0.178	1.405	1.207	0.168	1.375
	2(3)-CH_3	1.231	0.061	1.292	1.229	0.060	1.289
1,3-Dimethyltetrazolium (9)	5-1	1.415	0.260	1.675	1.355	0.239	1.594
	1-2	1.225	0.205	1.430	1.181	0.186	1.367
	2-3	1.227	0.232	1.459	1.299	0.264	1.563
	3-4	1.214	0.185	1.399	1.246	0.194	1.440
	4-5	1.452	0.326	1.778	1.395	0.305	1.700
	1-CH_3	1.223	0.057	1.280	1.228	0.057	1.285
	3-CH_3	1.233	0.060	1.293	1.221	0.059	1.280

TABLE 16. INDO "OVERLAP PAOPULATIONS" FOR TETRAZOLIUM CATIONS (continued)

Cation	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1,2-Dimethyltetrazolium (8)	5-1	1.425	0.283	1.708			
	1-2	1.237	0.150	1.387			
	2-3	1.208	0.227	1.435			
	3-4	1.219	0.225	1.444			
	4-5	1.438	0.299	1.737			
	1-CH_3	1.223	0.057	1.280			
	2-CH_3	1.231	0.060	1.291			
1,4-Dimethyltetrazolium (7)	5-1	1.441	0.289	1.730			
	1(4)-2(3)	1.199	0.179	1.378			
	2-3	1.230	0.270	1.500			
	1(4)-CH_3	1.224	0.056	1.280			

TABLE 17. INDO ATOMIC CHARGES[a] FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS

Zwitterion	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
2,3-Dimethyltetrazoliumyl (14)	1(4)	- 1	- 91	- 92	-	- 5	- 92	- 97	-
	2(3)	-409	+513	+104	-	-398	+513	+115	-
	5	-432	+186	-246	-	-445	+190	-255	-
	CH_3	+ 82	+ 37	+119	+ 11[b]	+ 80	+ 37	+117	+ 13[b]
					- 9[c]				- 10[c]
1,3-Dimethyltetrazoliumyl (13)	1	-445	+605	+160	-	-439	+551	+112	-
	2	+ 90	-227	-137	-	+ 85	-223	-138	-
	3	-446	+632	+186	-	-435	+676	+241	-
	4	+ 38	-208	-170	-	+ 49	-234	-185	-
	5	-481	+220	-261	-	-485	+253	-232	-
	CH_3(1)	+ 94	+ 35	+129	- 14[d]	+ 92	+ 40	+132	- 14[d]
					- 5[e]				- 12[e]
	CH_3(3)	+ 84	+ 32	+116	+ 8[b]	+ 69	+ 29	+ 98	+ 8[b]
					- 3[c]				0[c]

TABLE 17. INDO ATOMIC CHARGES[a] FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS (continued)

Zwitterion	Position	1.33Å Pentagon				Experimental Geometry			
		σ	π	Total	H	σ	π	Total	H
1,2-Dimethyltetrazoliumyl (12)	1	-414	+502	+ 88	-				
	2	-385	+452	+ 67	-				
	3	+ 19	- 43	- 24	-				
	4	+ 38	-154	-116	-				
	5	-500	+281	-219	-				
	$CH_3(1)$	+ 86	+ 45	+131	+ 6[f]				
					- 19[g]				
	$CH_3(2)$	+ 86	+ 39	+125	+ 3[h]				
					- 11[i]				
1,4-Dimethyltetrazoliumyl (11)	1(4)	-428	+546	+118	-				
	2(3)	+ 73	-160	- 87	-				
	5	-516	+263	-253	-				
	CH_3	+ 93	+ 41	+134	- 13[d]				
					- 12[e]				

[a]Atomic charges in units of 0.001 electronic charge; for other footnotes refer to Table XIV.

TABLE 18. INDO BOND INDICES FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS

Zwitterion	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
2,3-Dimethyltetrazoliumyl (14)	5-1(4)	0.986	0.463	1.449	0.971	0.462	1.433
	1(4)-2(3)	0.899	0.325	1.224	0.914	0.326	1.240
	2-3	0.921	0.204	1.125	0.913	0.203	1.116
	2(3)-CH_3	0.963	0.037	1.000	0.962	0.037	0.999
1,3-Dimethyltetrazoliumyl (13)	5-1	0.904	0.363	1.267	0.898	0.362	1.260
	1-2	0.951	0.310	1.261	0.945	0.269	1.214
	2-3	0.969	0.416	1.385	0.977	0.455	1.432
	3-4	0.887	0.269	1.156	0.901	0.276	1.177
	4-5	1.031	0.526	1.557	0.013	0.508	1.521
	1-CH_3	0.972	0.033	1.005	0.977	0.034	1.011
	3-CH_3	0.964	0.036	1.000	0.962	0.033	0.995

TABLE 18. INDO BOND INDICES FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS

Zwitterion	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1,2-Dimethyltetrazoliumyl (12)	5-1	0.924	0.437	1.361			
	1-2	0.899	0.127	1.026			
	2-3	0.944	0.360	1.304			
	3-4	0.965	0.476	1.441			
	4-5	1.004	0.395	1.399			
	1-CH_3	0.972	0.035	1.007			
	2-CH_3	0.964	0.037	1.001			
1,4-Dimethyltetrazoliumyl (11)	5-1(4)	0.949	0.427	1.376			
	1(4)-2(3)	0.931	0.217	1.148			
	2-3	1.024	0.633	1.657			
	1(4)-CH_3	0.973	0.032	1.005			

TABLE 19. INDO "OVERLAP POPULATIONS" FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS

Zwitterion	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
2,3-Dimethyltetrazoliumyl(14)	5-1(4)	1.396	0.297	1.693	1.342	0.280	1.622
	1(4)-2(3)	1.170	0.198	1.368	1.191	0.203	1.394
	2-3	1.230	0.157	1.387	1.208	0.151	1.359
	2(3)-CH_3	1.245	0.064	1.309	1.241	0.064	1.305
1,3-Dimethyltetrazoliumyl(13)	5-1	1.355	0.263	1.618	1.289	0.239	1.528
	1-2	1.212	0.193	1.405	1.166	0.173	1.339
	2-3	1.230	0.224	1.454	1.302	0.258	1.560
	3-4	1.157	0.180	1.337	1.199	0.190	1.389
	4-5	1.425	0.316	1.741	1.364	0.294	1.658
	1-CH_3	1.248	0.060	1.308	1.249	0.062	1.311
	3-CH_3	1.248	0.063	1.311	1.234	0.061	1.295

TABLE 19. INDO "OVERLAP POPULATIONS" FOR DIMETHYLTETRAZOLIUMYL ZWITTERIONS

Zwitterion	Bond	1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1,2-Dimethyltetrazoliumyl(12)	5-1	1.368	0.288	1.656			
	1-2	1.199	0.124	1.323			
	2-3	1.210	0.208	1.418			
	3-4	1.187	0.240	1.427			
	4-5	1.409	0.274	1.683			
	1-CH_3	1.244	0.062	1.306			
	2-CH_3	1.245	0.064	1.309			
1,4-Dimethyltetrazoliumyl(11)	5-1(4)	1.390	0.285	1.675			
	1(4)-2(3)	1.188	0.162	1.350			
	2-3	1.235	0.277	1.512			
	1(4)-CH_3	1.249	0.060	1.309			

TABLE 20. CNDO/2 ATOMIC CHARGES FOR 5-AMINOTETRAZOLES

Compound	Position	Atomic Charges: 1.33Å Pentagon σ	π	Total	H	Experimental Geometry σ	π	Total	H
1-Methyl-5-aminotetrazole(30) (trigonal NH_2)	1	-451	+441	-10	-	-431	+372	-59	-
	2	+156	-266	-110	-	+144	-218	-74	-
	3	+25	-45	-20	-	+3	-8	-5	-
	4	+74	-297	-223	-	+108	-361	-253	-
	5	+202	+74	+276	-	+190	+122	+312	-
	CH_3	+52	+11	+63	+20[a]	+55	+15	+70	+18[a]
					+5				0
	NH_2	-369	+112	-257	+133[b]	-374	+114	-260	+134[b]
					+117				+118
1-Methyl-5-aminotetrazole(30) (tetrahedral NH_2)	1	-461	+460	-1	-	-440	+389	-51	-
	2	+148	-251	-103	-	+138	-206	-68	-
	3	+32	-57	-25	-	+10	-18	-8	-
	4	+59	-266	-207	-	+90	-325	-235	-
	5	+199	+52	+251	-	+183	+103	+286	-
	CH_3	+53	+9	+62	+21[a]	+56	+13	+69	+19[a]
					+9				+4
					+6[c]				+1[c]
	NH_2	-642	+429	-213	+108[b]	-643	+424	-219	+109[b]
					+92				+94
1-Methyl-5-aminotetrazole(30) (trigonal NH_2 ⊥ ring)	1	-491	+494	+3	-	-461	+412	-49	-
	2	+133	-227	-94	-	+177	-192	-15	-
	3	+45	-80	-35	-	-30	-33	-63	-
	4	+23	-213	-190	-	+57	-277	-220	-
	5	+238	+15	+253	-	+215	+79	+294	-
	CH_3	+56	+7	+63	+19[a]	+57	+12	+69	+17[a]
					+10				+4
	NH_2	-256	-29	-285	+123	-262	-32	-294	+127

TABLE 20. CNDO/2 ATOMIC CHARGES FOR 5-AMINOTETRAZOLES

Compound	Position	Atomic Charges: 1.33Å Pentagon σ	π	Total	H	Experimental Geometry σ	π	Total	H
2-Methyl-5-aminotetrazole[31] (trigonal NH_2)	1	+110	-336	-226	-	+125	-357	-232	-
	2	-416	+511	+95	-	-404	+509	+105	-
	3	+65	-102	-37	-	+43	-59	-16	-
	4	+44	-234	-190	-	+65	-272	-207	-
	5	+194	+73	+267	-	+188	+90	+278	-
	CH_3	+55	0	+55	+20[a]	+47	0	+47	+18[9]
					+17				+17
	NH_2	-356	+102	-254	+119[b]	-362	+102	-260	+118[b]
					+117				+115
2-Methyl-5-aminotetrazole[31] (tetrahedral NH_2)	1	+92	-302	-210	-	+106	-319	-213	-
	2	-419	+515	+96	-	-407	+513	+106	-
	3	+72	-113	-41	-	+50	-70	-20	-
	4	+32	-211	-179	-	+53	-247	-194	-
	5	+191	+53	+244	-	+183	+69	+252	-
	CH_3	+55	0	+55	21[a]	+48	-1	+47	+19[a]
					19				+19
					18[c]				+18[c]
	NH_2	-637	+427	-210	94[b]	-640	+423	-217	+93[b]
					93				+90

TABLE 20. CNDO/2 ATOMIC CHARGES FOR 5-AMINOTETRAZOLES

Compound	Position	Atomic Charges: 1.33Å Pentagon σ	π	Total	H	Experimental Geometry σ	π	Total	H
2-Methyl-5-aminotetrazole(31) (trigonal NH_2 ⊥ ring)	1	+51	-243	-192	-	+71	-268	-197	-
	2	-422	+519	+97	-	-408	+515	+107	-
	3	+85	-136	-51	-	+60	-88	-28	-
	4	0	-169	-169	-	+25	-210	-185	-
	5	+230	+18	+248	-	+218	+40	+258	-
	CH_3	+55	-1	+54	22[a]	+48	-1	+47	+20[a]
					19				+18
	NH_2	-256	-23	-279	+116	-266	-22	-288	+115

[a]In plane of ring and syn to position 2 or 3; [b]Syn to position 4; [c]On same side of ring as NH_2 protons.

TABLE 21. CNDO/2 BOND INDICES FOR 5-AMINOTETRAZOLES

Compound	Bond	Bond Indices: 1.33Å Pentagon			Bond Indices: Experimental Geometry		
		σ	π	Total	σ	π	Total
1-Methyl-5-aminotetrazole(30) (trigonal NH_2)	1-2	0.940	0.178	1.118	0.923	0.126	1.049
	2-3	0.998	0.603	1.601	1.025	0.714	1.739
	3-4	0.979	0.299	1.278	0.957	0.211	1.168
	4-5	0.994	0.472	1.466	0.999	0.509	1.508
	5-1	0.943	0.317	1.260	0.950	0.291	1.241
	1-CH_3	0.979	0.0298	1.009	0.9836	0.0301	1.0137
	5-NH_2	0.983	0.120	1.103	0.979	0.127	1.106
1-Methyl-5-aminotetrazole(30) (tetrahedral NH_2)	1-2	0.941	0.195	1.136	0.923	0.138	1.061
	2-3	0.998	0.594	1.592	1.025	0.708	1.733
	3-4	0.979	0.306	1.285	0.957	0.216	1.173
	4-5	0.995	0.488	1.483	1.001	0.533	1.534
	5-1	0.940	0.322	1.263	0.949	0.299	1.248
	1-CH_3	0.979	0.0298	1.009	0.9829	0.0301	1.0130
	5-NH_2	0.988	0.090	1.078	0.983	0.088	1.071
1-Methyl-5-aminotetrazole(30) (trigonal $NH_2 \perp$ ring)	1-2	0.943	0.225	1.168	0.925	0.156	1.081
	2-3	0.996	0.577	1.573	1.024	0.697	1.721
	3-4	0.979	0.318	1.297	0.957	0.224	1.181
	4-5	0.993	0.511	1.504	1.000	0.561	1.561
	5-1	0.923	0.329	1.252	0.936	0.307	1.243
	1-CH_3	0.978	0.0297	1.008	0.9826	0.0301	1.0127
	5-NH_2	1.004	0.054	1.058	0.9935	0.0503	1.0438

TABLE 21. CNDO/2 BOND INDICES FOR 5-AMINOTETRAZOLES (continued)

Compound	Bond	Bond Indices: 1.33Å Pentagon σ	π	Total	Experimental Geometry σ	π	Total
2-Methyl-5-aminotetrazole(31) (trigonal NH_2)	1-2	0.952	0.199	1.151	0.939	0.172	1.111
	2-3	0.951	0.371	1.322	0.962	0.400	1.362
	3-4	0.996	0.453	1.449	0.987	0.444	1.431
	4-5	0.975	0.350	1.325	0.973	0.334	1.307
	5-1	0.985	0.483	1.468	0.990	0.502	1.492
	2-CH_3	0.977	0.0326	1.010	0.9767	0.0314	1.0081
	5-NH_2	0.981	0.109	1.090	0.9732	0.111	1.0842
2-Methyl-5-aminotetrazole(31) (tetrahedral NH_2)	1-2	0.953	0.214	1.167	0.941	0.187	1.128
	2-3	0.950	0.362	1.312	0.961	0.392	1.353
	3-4	0.997	0.460	1.457	0.988	0.451	1.439
	4-5	0.975	0.359	1.334	0.974	0.345	1.319
	5-1	0.984	0.494	1.478	0.988	0.519	1.507
	2-CH_3	0.977	0.0324	1.009	0.9757	0.0313	1.007
	5-NH_2	0.986	0.082	1.068	0.978	0.077	1.055
2-Methyl-5-aminotetrazole(31) (trigonal NH_2 $\perp$ ring)	1-2	0.955	0.241	1.196	0.942	0.209	1.151
	2-3	0.947	0.343	1.290	0.959	0.375	1.334
	3-4	0.997	0.474	1.471	0.989	0.464	1.453
	4-5	0.969	0.372	1.341	0.969	0.357	1.326
	5-1	0.974	0.510	1.484	0.980	0.536	1.516
	2-CH_3	0.977	0.0321	1.009	0.976	0.0309	1.0070
	5-NH_2	0.997	0.0513	1.048	0.986	0.047	1.033

TABLE 22. CNDO/2 "OVERLAP POPULATIONS" FOR 5-AMINOTETRAZOLES

Compound	Bond	"Overlap Populations" 1.33Å Pentagon			Experimental Geometry		
		σ	π	Total	σ	π	Total
1-Methyl-5-aminotetrazole (30) (trigonal NH_2)	1-2	1.215	0.146	1.361	1.114	0.111	1.225
	2-3	1.232	0.270	1.502	1.378	0.344	1.722
	3-4	1.219	0.190	1.409	1.137	0.146	1.283
	4-5	1.434	0.300	1.734	1.450	0.317	1.767
	5-1	1.419	0.246	1.665	1.435	0.236	1.671
	1-CH_3	1.249	0.0576	1.307	1.2551	0.0579	1.3130
	5-NH_2	1.423	0.140	1.563	1.403	0.142	1.545
1-Methyl-5-aminotetrazole (30) (tetrahedral NH_2)	1-2	1.215	0.153	1.368	1.115	0.116	1.231
	2-3	1.232	0.268	1.500	1.378	0.343	1.721
	3-4	1.219	0.192	1.411	1.137	0.147	1.284
	4-5	1.435	0.305	1.740	1.452	0.324	1.776
	5-1	1.417	0.248	1.665	1.434	0.239	1.673
	1-CH_3	1.249	0.0576	1.307	1.2545	0.0579	1.3124
	5-NH_2	1.394	0.121	1.515	1.352	0.114	1.466
1-Methyl-5-aminotetrazole (30) (trigonal NH_2 ⊥ (ring)	1-2	1.215	0.165	1.380	1.116	0.123	1.239
	2-3	1.231	0.264	1.495	1.377	0.340	1.717
	3-4	1.219	0.196	1.415	1.136	0.150	1.286
	4-5	1.438	0.312	1.750	1.455	0.332	1.787
	5-1	1.407	0.250	1.657	1.426	0.242	1.668
	1-CH_3	1.247	0.0575	1.305	1.2536	0.0579	1.3115
	5-NH_2	1.443	0.094	1.537	1.400	0.087	1.487

TABLE 22. CNDO/2 "OVERLAP POPULATIONS" FOR 5-AMINOTETRAZOLES (continued)

Compound	Bond	"Overlap Populations" 1.33Å Pentagon σ	π	Total	Experimental Geometry σ	π	Total
2-Methyl-5-aminotetrazole (31) (trigonal NH_2)	1-2	1.228	0.155	1.383	1.195	0.141	1.337
	2-3	1.218	0.212	1.430	1.293	0.240	1.533
	3-4	1.234	0.234	1.468	1.239	0.236	1.475
	4-5	1.421	0.258	1.679	1.394	0.244	1.638
	5-1	1.435	0.303	1.738	1.448	0.315	1.763
	2-CH_3	1.259	0.0603	1.319	1.2498	0.0592	1.3090
	5-NH_2	1.424	0.133	1.557	1.394	0.131	1.525
2-Methyl-5-aminotetrazole (31) (tetrahedral NH_2)	1-2	1.228	0.161	1.389	1.196	0.147	1.343
	2-3	1.219	0.209	1.428	1.293	0.237	1.530
	3-4	1.234	0.236	1.470	1.239	0.238	1.477
	4-5	1.421	0.261	1.682	1.394	0.248	1.642
	5-1	1.434	0.307	1.741	1.448	0.320	1.768
	2-CH_3	1.258	0.0600	1.318	1.2495	0.0589	1.3084
	5-NH_2	1.394	0.116	1.510	1.343	0.106	1.449
2-Methyl-5-aminotetrazole (31) (trigonal NH_2, $\perp$ ring)	1-2	1.229	0.171	1.400	1.197	0.155	1.352
	2-3	1.217	0.203	1.420	1.291	0.232	1.523
	3-4	1.236	0.239	1.475	1.239	0.242	1.481
	4-5	1.421	0.266	1.687	1.394	0.252	1.646
	5-1	1.430	0.312	1.742	1.446	0.325	1.771
	2-CH_3	1.258	0.0597	1.318	1.249	0.0587	1.308
	5-NH_2	1.439	0.092	1.531	1.390	0.084	1.474

TABLE 23. HEATS OF FORMATION FOR 1,5- and 2,5- DISUBSTITUTED TETRAZOLE DERIVATIVES

	Heat of Formation[a]		
	1-Isomer	2-Isomer	$\Delta\Delta H_f$
N-Methyl-5-aminotetrazole	46.2[b]	50.40[b]	-4.2
N-Allyl-5-aminotetrazole	63.43[b]	67.61[b]	-4.18
N-Phenyl-5-methyltetrazole	70.57[c]	65.62[c]	4.95
N,5-Diphenyltetrazole	99.32[c]	94.40[c]	4.92
N-N'Dimethyl-5,5'-azotetrazole	189.33[b,d] 188.62[b,e]	180.35[b]	8.98

[a]In kcal/mole at 25°. [b]M.M. Williams, W.S. McEwen and R.A. Henry, J. Phys. Chem, 61, 261 (1957). [c]W.S. McEwen and M.W. Rigg, J. Amer. Chem. Soc. 73, 4725 (1951). [d]Trans isomer. [e]Cis isomer.

TABLE 24. CNDO/2 π-ELECTRON CHARGE DISTRIBUTIONS FOR N,N'-DIMENTHYL-5-IMINOTETRAZOLINE DERIVATIVES

Compound			π-Electron Atomic Charges Carbon	Nitrogen	π-Electron Bond Index
2,3-Dimethyl-5-iminotetrazoline	(Neutral)	(35)	+136	-620	0.432
			+124*	-556*	0.499*
	(Protonated)	(39)	+112	+173	0.192
			+106*	+185*	0.204*
1,3-Dimethyl-5-iminotetrazoline	(Neutral)	(37)	+143	-560	0.498
			+139*	-483*	0.584*
	(Protonated)	(38)	+132	+193	0.218
			+157*	+217*	0.251*
1,3-Dimethyl-5-iminotetrazoline	(Neutral)	(33)	+146	-471	0.575
	(Protonated)	(37)	+176	+221	0.257
1,4-Dimethyl-5-iminotetrazoline	(Neutral)	(32)	+138	-508	0.558
	(Protonated)	(36)	+147	+216	0.248

** Experimental ring geometry from references in Table 1; all other numbers in this table are from 1.33Å pentagon calculations.*

TABLE 25. INDO π-ELECTRON CHARGE DISTRIBUTION OF VINYL GROUPS IN VINYLTETRAZOLE DERIVATIVES (EXPERIMENTAL GEOMETRIES)

MOLECULE OR CATION	π-Atomic Charges					Total Charges			π-Bond Indices		"Overlap Populations (π)	
	R^a	α	β	β-α	α+β ($\Sigma\Delta q_{(\pi)}^{C}$)	R^a	α	β	R^a-α	α-β	R^a-α	α-β
2-Methyl-5-Vinyltetrazole (18)	+ 19	+ 5	- 4	- 9	+ 1	+218	- 2	+ 4	0.086	0.912	0.130	0.516
1-Methyl-5-Vinyltetrazole (17)	+ 47	- 12	+ 23	+ 35	+ 11	+225	- 12	+ 23	0.088	0.910	0.131	0.515
1H-2-Methyl-5-Vinyltetrazolium (24)	+142	- 72	+139	+211	+ 67	+303	- 38	+ 97	0.108	0.878	0.145	0.506
3H-2-Methyl-5-Vinyltetrazolium (25)	+ 65	- 53	+ 93	+146	+ 40	+264	- 18	+ 65	0.091	0.901	0.133	0.513
4H-2-Methyl-5-Vinyltetrazolium (26)	+ 91	- 50	+ 97	+147	+ 47	+278	- 27	+ 70	0.097	0.895	0.137	0.511
2H-1-Methyl-5-Vinyltetrazolium (21)	+147	- 75	+141	+216	+ 66	+305	- 33	+ 98	0.104	0.881	0.142	0.507
3H-1-Methyl-5-Vinyltetrazolium (22)	+111	- 71	+126	+197	+ 55	+283	- 29	+ 88	0.098	0.890	0.138	0.509
4H-1-Methyl-5-Vinyltetrazolium (23)	+146	- 72	+139	+211	+ 67	+308	- 43	+ 98	0.106	0.880	0.144	0.506
1-Vinyltetrazole (19)	+473	- 2	- 46	- 44	- 48	+ 15	+106	- 45	0.064	0.934	0.088	0.522
2-Vinyltetrazole (20)	+556	- 8	- 30	- 22	- 38	+170	+ 84	- 32	0.064	0.934	0.088	0.522
1-Vinyl-3-Methyltetrazolium (27)	+620	- 68	+ 59	+127	- 9	+128	+ 81	+ 22	0.054	0.939	0.081	0.523
1-Methyl-3-Vinyltetrazolium (28)	+709	- 82	+ 84	+166	+ 2	+271	+ 60	+ 40	0.056	0.933	0.082	0.522
1-Vinyl-4-Methyltetrazolium (29)	+571	- 69	+ 55	+124	- 14	+ 87	+ 86	+ 18	0.051	0.943	0.078	0.524
1-Vinylpyrazole (40)[b]	+479	- 1	- 49	- 48	- 50	+ 73	+ 96	- 45	0.065	0.933	0.088	0.521
[c]	+478	+ 9	- 61	70	- 52	+ 73	+100	- 56	0.066	0.931	0.089	0.521

[a] Ring atom to which vinyl is attached

[b] Vinyl syn to Position 2

[c] Vinyl syn to Position 5

TABLE 26. INDO π-ELECTRON CHARGE DISTRIBUTIONS OF VINYL GROUPS IN VINYLTETRAZOLE DERIVATIVES (1.33 Å PENTAGON)

Molecule or Cation	π-Atomic Charges					Total Charges			π-Bond Indices		"Overlap Populations (π)	
	R^a	α	β	β-α	α+β ($\Sigma\Delta q_{(\pi)}{}^{C}$)	R^a	α	β	R^a-α	α-β	R^a-α	α-β
2-Methyl-5-Vinyltetrazole (18)	0	+ 5	- 8	- 13	- 3	+206	+ 4	+ 1	0.086	0.912	0.130	0.516
1-Methyl-5-Vinyltetrazole (17)	- 11	- 7	+ 8	+ 15	+ 1	+176	- 4	+ 14	0.091	0.906	0.133	0.514
1H-2-Methyl-5-Vinyltetrazolium (24)	+130	- 72	+136	+208	+ 64	+293	- 33	+ 95	0.105	0.880	0.143	0.506
3H-2-Methyl-5-Vinyltetrazolium (25)	+ 52	- 54	+ 91	+145	+ 37	+258	- 14	+ 64	0.090	0.903	0.132	0.513
4H-2-Methyl-5-Vinyltetrazolium (26)	+ 80	- 50	+ 95	+145	+ 45	+264	- 20	+ 67	0.096	0.896	0.137	0.511
2H-1-Methyl-5-Vinyltetrazolium (21)	+116	- 73	+137	+210	+ 64	+279	- 31	+ 96	0.105	0.880	0.143	0.506
3H-1-Methyl-5-Vinyltetrazolium (22)	+ 58	- 68	+114	+182	+ 46	+243	- 24	+ 80	0.096	0.892	0.137	0.510
4H-1-Methyl-5-Vinyltetrazolium (23)	+ 91	- 67	+126	+193	+ 59	+258	- 34	+ 90	0.105	0.882	0.143	0.507
1-Vinyltetrazole (19)	+549	- 11	- 29	- 18	- 40	+ 78	+ 95	- 33	0.060	0.937	0.085	0.523
2-Vinyltetrazole (20)	+556	- 8	- 30	- 22	- 38	+160	+ 93	- 32	0.066	0.933	0.089	0.521
1-Vinyl-3-Methyltetrazolium (27)	+651	- 76	+ 69	+145	- 7	+152	+ 77	+ 28	0.053	0.939	0.080	0.523
1-Vinyl-4-Methyltetrazolium (29)	+637	- 79	+ 69	+148	- 10	+140	+ 76	+ 28	0.051	0.942	0.078	0.524
1-Methyl-3-Vinyltetrazolium (28)	+681	- 73	+ 75	+148	+ 2	+248	+ 74	+ 33	0.059	0.931	0.085	0.521

[a]Ring atom to which vinyl is attached.

TABLE 27. CNDO/2 ATOMIC CHARGES[a] FOR TETRAZOLIUMYLMETHYL ZWITTERIONS (1.33 Å PENTAGON)

COMPOUND	POSITION	CH_2 COPLANAR WITH RING				CH_2 PERPENDICULAR TO RING			
		σ	π	Total	H	σ	π	Total	H
3-Methyl-1-Tetrazoliumylmethyl (16)	1	-635	+891	+256	-	-532	+782	+250	-
	2	+320	-499	-179	-	+104	-155	- 51	-
	3	-366	+441	+ 75	-	-435	+555	+120	-
	4	- 5	- 65	- 70	-	+ 61	-179	-118	-
	5	+198	-178	+ 20	+ 40	+108	- 19	+ 89	+ 58
	CH_2(1)	+280	-573	-293	+ 8[b] + 14[c]	-603	+ 97	-506	- 2[e]
	CH_3(3)	+ 67	- 4	+ 63	+ 23[b,d] + 20[c,e]	+ 71	- 16	+ 55	+ 38[b,d] + 35[c,e]
1-Methyl-3-Tetrazoliumylmethyl (15)	1	-443	+469	+ 26	-	-486	+546	+ 60	-
	2	+363	-579	-216	-	+136	-208	- 72	-
	3	-600	+917	+317	-	-493	+822	+329	-
	4	+153	-366	-213	-	+ 40	-179	-139	-
	5	+ 93	+ 84	+177	+ 20	+126	- 5	+121	+ 34
	CH_2(3)	+246	-508	-262	+ 21[b] + 21[c]	-590	+ 92	-498	+ 7[e]
	CH_3(1)	+ 60	+ 5	+ 65	+ 11[b,e]	+ 69	- 10	+ 59	+ 37[b,d]

[a] In units of .001 electronic charge

[b] Syn to Position 5

[c] Two equivalent H atoms

[c] Syn to Position 2

[d] Single H atom coplanar with ring

TABLE 28. CNDO/2 π-ELECTRON BOND INDICES FOR 1,3-DIMETHYLTETRAZOLIUM CATION AND RELATED METHYLTETRAZOLIUMYLMETHYL ZWITTERIONS (133 Å PENTAGON)

COMPOUND		5-1	1-2	2-3	3-4	4-5	N-CH_3	N-CH_2
1,3-Dimethyl-tetrazolium cation (9)		0.353	0.350	0.446	0.280	0.561	0.027 (1) 0.031 (2)	
3-Methyl-1-Tetrazoliumyl-methyl zwitterion (16)	(CH_2 Coplanar)	0.256	0.307	0.145	0.302	0.561	0.033	0.362
	(CH_2 Perpendicular)	0.363	0.428	0.359	0.267	0.549	0.031	0.049
1-Methyl-3-Tetrazoliumyl methyl zwitterion (15)	(CH_2 Coplanar)	0.409	0.096	0.307	0.193	0.495	0.030	0.446
	(CH_2 Perpendicular)	0.348	0.269	0.509	0.295	0.550	0.028	0.056

TABLE 29. NEW TETRAZOLE DERIVATIVES PREPARED IN THE COURSE OF THIS WORK

Substituent and Position	Empirical Formula	Yield, %	Recryst. Solvent	mp, °C	Analyses Calcd. C	H	N	EQ WT	F	Found C	H	N	EQ WT	F
5-(m-Fluorophenyl)	$C_7H_5FN_4$	100	...	143-144	51.22	3.07	34.14	.....	11.58	51.05	3.27	34.13	.....	11.32
1-Methyl-5-(m-fluorophenyl)	$C_8H_7FN_4$	34	Benzene[a]	81.5-83.5	53.92	3.97	31.45	.....	10.66	53.84	3.97	31.66	.....	10.87
2-Methyl-5-(m-fluorophenyl)	$C_8H_7FN_4$	55	a	55-7	53.92	3.97	31.45	.....	10.66	54.28	4.04	31.05	.....	10.42
5-(p-Fluorophenyl)	$C_7H_5FN_4$	100	95% Ethanol	208-209	51.22	3.07	34.14	.....	11.58	51.16	3.04	34.15	.....	11.61
1-Methyl-5-(p-fluorophenyl)	$C_8H_7FN_4$	31	Benzene[a]	105.5-107	53.92	3.97	31.45	.....	10.66	54.07	4.01	31.36	.....	10.86
2-Methyl-5-(p-fluorophenyl)	$C_8H_7FN_4$	64	a	82-3	53.92	3.97	31.45	.....	10.66	54.74 54.28	4.22 4.12	31.61	.....	10.40
1,4-Dimethyl-5-(m-fluorophenyl)tetrazolium benzenesulfonate	$C_{15}H_{15}FN_4O_3S$	41	$C_2H_4Cl_2$	160.5-162.5	.....	.....	15.99	.....	5.42	.....	.....	16.01	.....	5.57
1,3-Dimethyl-5-(m-fluorophenyl)tetrazolium benzenesulfonate	$C_{15}H_{15}FN_4O_3S$	22	$C_2H_4Cl_2$	93.2-94.5	.....	.....	15.99	.....	.....	.....	.....	16.08	.....	.....
5-(m-Carboxyphenyl)	$C_8H_6N_4O_2$	72	95% Ethanol	273-274	50.53	3.18	29.46	95.1	.....	50.59	3.10	29.40	97.6	.....
1-Methyl-5-(m-carboxyphenyl)	$C_9H_8N_4O_2$	78	H_2O	213-214	53.04	3.95	27.44	204	.....	52.75	3.89	27.50	210	.....
2-Methyl-5-(m-carboxyphenyl)	$C_9H_8N_4O_2$		95% Ethanol	241-242	53.04	3.95	27.44	204	.....	53.18	3.85	27.50	208	.....
5-(p-Carboxyphenyl)	$C_8H_6N_4O_2$	100	95% Ethanol	>300	50.53	3.18	29.46	.....	.....	50.47	3.16	29.37	.....	.....
1-Methyl-5-(pcarboxyphenyl)	$C_9H_8N_4O_2$	86	H_2O	260-262	53.04	3.95	27.44	204	.....	52.75	4.12	27.16	205	.....
2-Methyl-5-(p-carboxyphenyl)	$C_9H_8N_4O_2$		H_2O	269-271	53.04	3.95	27.44	.....	.....	52.79	3.84	27.36	.....	.....

[a]Also purified by chromatography on silica sal, followed by sublimation .

[b]There was also isolated 10% of the methyl ester, mp 77-80, of the 2-methyl isomer.

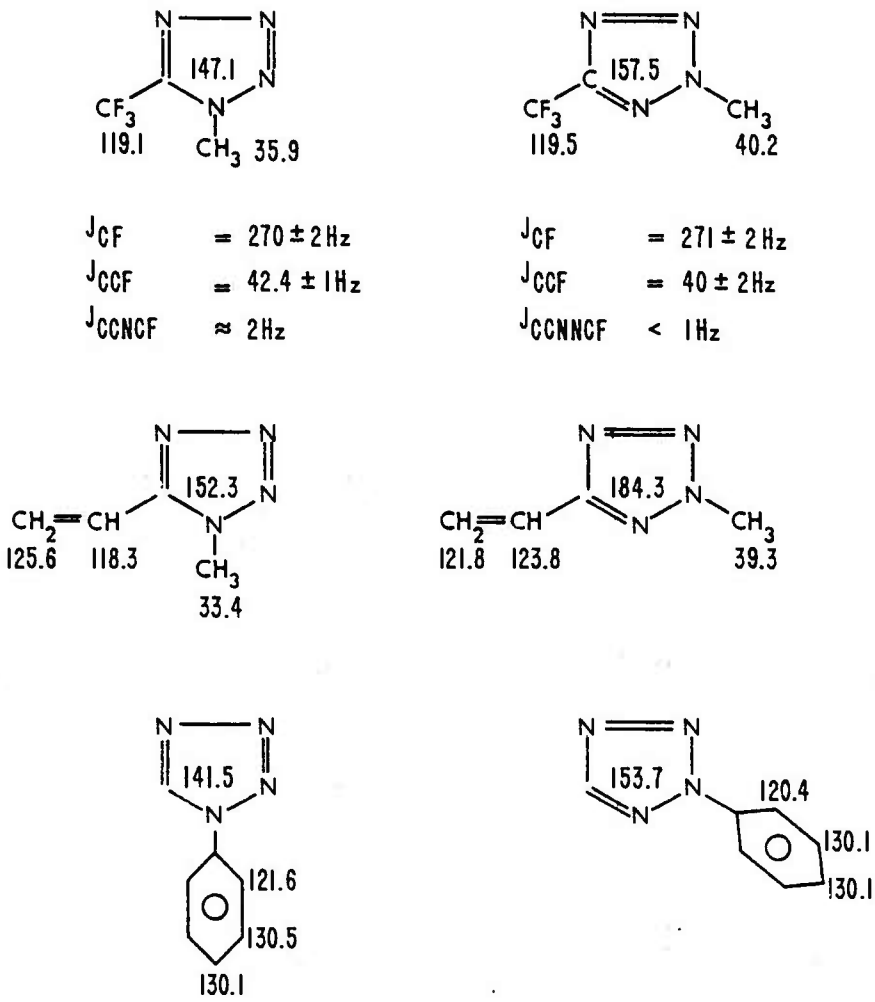

Figure 1. ^{13}C NMR Results for Isomeric Tetrazole Derivatives

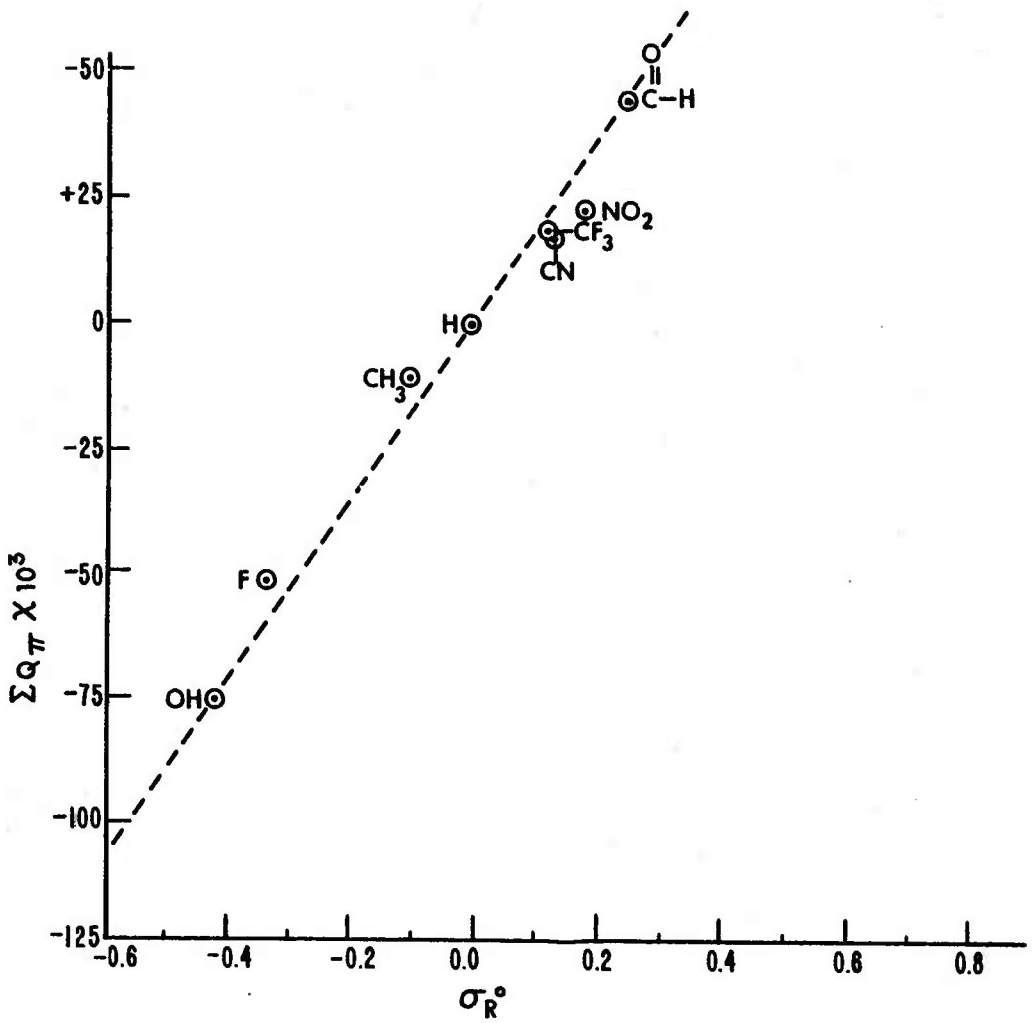

Figure 2. INDO π-Electron Excess Charge Densities in Vinyl Group of Substituted Ethylenes vs σ_R

V. DISCUSSION

The Discussion section of this report is divided into two parts. The first part presents experimental and theoretical evidence in support of our previous conclusions (based on observed chemical reactions) that 1-substituted-5-tetrazole groups (I) are considerably more electron-withdrawing than 2-substituted-5-tetrazolyl groups (II); relative electron-withdrawing power of 1- and 2- tetrazolyl groups will also be considered.

In the second part of the discussion we will consider the properties of tetrazole derivatives in the light of the electronic character of the isomeric tetrazolyl groups. The information available to us on explosive properties of isomeric tetrazole derivatives will be summarized. An attempt will be made to compare the thermal stabilities and gas-generation capabilities of the isomeric tetrazole groups. In the light of these considerations, an attempt will be made to relate the electronic character of the isomeric 5-tetrazolyl groups to the recently-described[9] general tendency for 5-substituted tetrazoles and their salts to become more explosive with increasing electron-withdrawing power of the 5-substituent, and a possible explanation for this trend will be suggested.

A. Electronic Character of Isomeric Tetrazolyl Groups

1. Semiempirical Molecular Orbital Calculations trends in energies of reactions calculated from the CNDO/2 and INDO total energies (Table 1) are generally in agreement with experimental trends, and with the conclusions given in our previous report regarding the relative electron-withdrawing powers of isomeric N-substituted-5-tetrazolyl groups. For example, the CNDO/2 and INDO total energies of the dimethyltetrazolium cations (7-10) increase in the order 1,4->1,3≥1,2>2,3-dimethyl for both regular-Pentagon and experimental-geometry calculations; a similar ordering is observed for the 1,3-dimethyl-5-amino-tetrazolium cations. These orderings are in agreement with, for example the following facts: (a) 1,3-Dimethyltetrazolium Benzenesulfonate (9) can be prepared in quantitative yield from 2-methyltetrazole(4) and methylbenzenesulfonate in refluxing toluene[16]; (b) Quaternization of 1,5-disubstituted tetrazoles by, for example, methyl iodide, gives 1,4-disubstituted tetrazolium salts;[41] (c) 1,3,5-trisubstituted tetrazole salts have been isolated from alkylation of 1,5-disubstituted tetrazoles, although the more stable

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[41] *G. F. Duffin, "The Quaternization of Heterocyclic Compounds," in A. R. Katritzky, ed., Advances in Heterocyclic Chemistry, Vol. 3, Academic Press, New York, 1964.*

1,4,5-isomers[42,43,44], are the main products; (d) On the basis of ^{1}H and ^{13}C NMR studies, it has been suggested that 1- and 2-phenyltetrazoles protonate on position 4 in sulfuric acid; the assignments were based on comparison of observed spectra with those of the authentic N-ethyl analogs of the protonated species[44b,c]. (e) Furthermore, it has been found that alkylation of 1-phenyltetrazoles gives mixtures of 1-aryl-3-alkyl and 1-aryl-4-alkyl-tetrazolium salts, while alkylation of 2-phenyltetrazoles gives exclusively 2-aryl-5-alkyltetrazolium salts. Similar conclusions have been reached on the basis of acidity and basicity measurements and substituent constant correlations on tetrazole and substituted tetrazoles[44d,e]. (f) As far as we are aware, No. 1,2,5- or 2,3,5-trisubstituted tetrazolium salt has been isolated from alkylation of the corresponding 1,5- or 2,5-disubstituted tetrazole.

The differences between total energies of isomeric 1,5- and 2,5-disubstituted tetrazoles are smaller than between the trisubstituted derivatives and the ordering of stabilities of the isomers is dependent on the assumed molecular geometries used for the calculations; this suggests that the energies for these isomers are very close together. In agreement with this, alkylations of tetrazoles and N-unsubstituted 5-alkyl tetrazoles yields mixtures of 1- and 2-substituted isomers, [45] and a variety of experimental and theoretical work suggests that the 1H- and 2H- forms of tetrazole are very close in energy[46a] although NDDO/I calculations [46b] suggest that the 1- isomers are more stable than the 2-isomers by about 12 kcal/Mole.

[42] *T. Isida, S. Kozima, S. I. Fujimora and K. Sisido, "Preparation and Thermal Decomposition of 1,4,5- and 1,3,5-Trimethyl-tetrazolium Iodides," Bull. Chem. Soc. Jap. 45, 1471 (1972).*

[43] *T. Isida, S. Kozima, K. Nabika and K. Sisido, "Formation of 2-Alkyl-5-Phenyltetrazoles from 1-Alkyl-5-Phenyltetrazoles," J. Org. Chem. 36, 3807-11 (1971), and references cited therein.*

[44] *(a) R. A. Henry, W. G. Finnegan and E. Lieber, "1,2- and 1,4-Dialkyl-5-aminotetrazoles," J. Amer. Chem. Soc. 76, 2894 (1954). (b) A. Koennecke, E. Lippmann and E. Kleinpeter, "Isomere N-Aryltetrazole-IV. ^{1}H and ^{13}C NMR-Untersuchungen zur Struktur von Tetrazoliumkationen", Tetrahedron, 33, 1399 (1977); (c) A. Koennecke and E. Lippmann, "Quaternierung einiger 5-Substituiertier N-Phenyltetrazole" Z. Chem., 17, 261-2 (1977). (d) V. A. Ostrovskii, G. I. Koldobskii, B. V. Gidaspov and E. N. Osokina, "Basicity of Tetrazoles", J. Org. Chem. USSR, 14, 2251 (1977); (e) M. M. Sokolova, V. A. Ostrovskii, G. I. Koldobskii, V. V. Mel'nikov and B. V. Gidaspov, "Protonation of Tetrazole", J. Org. Chem. USSR, 10, 1097 (1975)*

[45] *F. R. Benson, "The Tetrazoles," in Heterocyclic Compounds, ed. by R. C. Elderfield, New York, Wiley and Sons, Inc., 1967, Vol. 8, pp 1-104.*

[46] *(a) W. D. Krugh and L. P. Gold, "The Microwave Spectrum of Tetrazole," J. Mol. Spectrosc. 49, 423 (1974); (b) M. J. S. Dewar, "MO Studies of some Nonbenzenoid Aromatic Systems" Pure Appl. Chem, 44, 767 (1975).*

Energy differences calculated from the total energies in Table 1 are also in agreement with the trends noted in the previous report[1] in this series; for example (a) the protonation energies of 32 and 34 are respectively -0.595 and -0.632 a.u, in agreement with the greater basicity of 34; (b) Deprotonation energies for the tetrazolium cations 7-10 are in agreement with the reactivity order (1,4>1,3>2,3-dimethyl) toward proton exchange of the 5-protons (literature references summarized in references 1 and 6), and the 1-methyl-3-tetrazolylmethyl) zwitterion 15 is found to be more stable than the isomeric 3-methyl-1-tetrazolylmethyl zwitterion, in agreement with the greater acidity of the 3- than the 1-methyl proton of the 1,3-dimethyltetrazolium cations (literature references summarized in Reference 1).

These correspondences between theory and experiment could be taken to constitute additional justification to that cited previously[2,6] for predictive use of CNDO/2 and INDO energies of reaction. However it should be remembered that as mentioned before these methods incorporate many approximations; these are detailed in the original references[36]. In view of developments since the previous reports, it seems appropriate to consider one problem in particular at this point, namely the neglect of interatomic lone-pair interactions arising from the necessity to preserve rotational invariance at the ZDO level of approximation [11].

These interactions can be important in determining the relative acidities of azabenzenes and azatoluenes; thus the NDDO and IRDO methods are considerably superior to the CNDO/2 method at correlating the CH-acidities of azabenzenes and azatoluenes.[11,47] Furthermore, we have found that the CNDO/2 method gives a poorer account[12] of the C-H acidity[48] of neutral N-methyl azoles than is the case for azolium cations;[6] in the case of the neutral azole-carbanion transformations CNDO/2 predicts incorrectly that addition of nitrogen to the ring will decrease rather than increase CH acidity in certain cases.[12]

However, this problem should not have too much effect on the conclusion reached in the present report since the examples mentioned in the preceding paragraph involve replacement of pyridine type nitrogen by a CH group, while the isomeric tetrazole rings differ only in the positioning of these groups. In accordance with this, predicted reactivity orderings for tetrazole derivatives based on the CNDO/2 and INDO results given in Table 1 seem to be generally in accord with experiment (pp. 80-82).

[47] *P. Birner, H. J. Kohler and C. Weiss, "Wechselwirkungen gerichteter Ladungsverteilungen. I. IRDO (Intermediate Retention of Differential Overlap)-Berechnungen zum Einfluss..des einsamen Elektronenpaars am Stickstoff auf die Relative Aciditat des β-Picolins," Int. J. Quantum Chem. 9, 917 (1975).*

[48] *(a) R. A. Olofson, H. Kohn, R. V. Kendall and W. P. Piekielek, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, IL, September, 1970, Abstract ORGN 76; (b) H. L. Kohn, unpublished work included in R. V. Kendall, Thesis, Pennsylvania State University, 1970; (c) R. A. Olofson, Pennsylvania State University, private communication, 1969.*

The above examples[11,12,47] concern transformations between neutral and negatively-charged species. There may be reason to believe that this effect may be less important for transformations involving only neutral and positively-charged species. For example, in the case of the azolium cation-ylid deprotonation the CNDO/2 method correctly predicts in every case studied[6] that the effect of adding nitrogen to the azole ring will be to increase the rate of proton exchange, although the calculated effect of added nitrogen was unexpectedly small relative to the effect of interchanging α- and β pyrrole - type nitrogen atoms. Another paper[49a] reports only a limited correlation between CNDO/2 proton affinities and relative base strengths of diazoles and triazoles; however the reported total energy for pyrazolium cation was incorrect due to an error in assumed molecular geometry[49b]. When a correct value[12] of 0.529 au for the protonation energy of pyrazole is used, a reasonable correlation is obtained. It has also been pointed out[50] that due caution should be exercised in interpreting CNDO/2 results on neutral systems containing lone-pairs although the lone-pair problem is expected to be particularly emphasized in carbanions.* Thus it would appear that, in addition to the possible reasons discussed earlier, the increase in rate of proton exchange with increasing nitrogen content in the azole ring may well be due at least in part to the effect of the atomic dipoles of the added nitrogen.

2. Relative Electron-Withdrawing Abilities of Isomeric 1- and 2-Substituted-5-tetrazolyl Groups. The substituent effects of tetrazolyl groups will be taken as the sum of the following factors: (1) Steric effects; (2) Inductive effects (electron withdrawl through the bonds); (3) Hybridization (the amount of s character in the bond between the tetrazole ring and the substituent); (4) Resonance between the tetrazole ring and the

*There appears to be an error in the CNDO/2 deprotonation energy for toluene given in reference 50. The calculations were repeated by one of us (M.A.S.) for deprotonation of toluene, m-fluorotoluence and p-methyltoluene using a coplanar trigonal configuration for the carbanionic CH_2; the deprotonation energies obtained were 25.095, 24.771 and 25.049 eV respectively; the last two numbers seem in reasonable agreement with the values in Table II of reference 50, but the value for toluene itself is considerably lower than the value of 25.897 eV given in reference 50. Use of this value in Table 1 and 2 and Figures 4 and 8 of reference 50 appears to reduce some of the discrepancies between CNDO/2 and experimental results.

[49] *(a) J. D. Vaughan and M. O'Donnell, "Relative Base Strengths from CNDO/2 Calculations," Tetrahedron Letters, 3727 (1968); (b) J. D. Vaughan, private communication, 1975.*

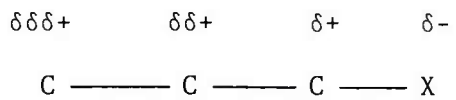
[50] *A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens and D. M. E. Reuben, in Quantum Aspects of Heterocyclic Compounds in Chemistry and Biochemistry, E. D. Bergmann and B. Pullman, eds., The Israel Academy of Sciences and Humanities, Jerusalem, 1970, pp 160-78.*

reacting substituent; (5) Field effects (through-space electrostatic interaction between the reacting substituent and the tetrazole ring to which it is attached); and (6) solvent effects. The importance of each of these factors to the observed reactivity differences between isomeric 1- and 2-substituted-5-tetrazolyl dericatives will now be considered in turn.

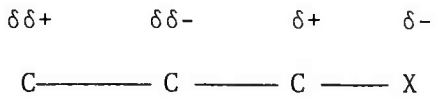
Steric Effects. We feel that the experimental facts suggest that steric effects are probably not of overriding importance. This follows from the reactivity differences summarized in the previous report of the series[1] and in the introduction to the present report; the principal trend seems to be that the reactions which proceed slower in the case of 1- than the 2-isomers are those expected to be hindered by electron-withdrawl, rather than those expected to be hindered by steric interference by the 1-substituent of the 1-substituted-5-tetrazolyl group.

Inductive Effects. Inductive effects can operate through either the σ- or the π-electron systems.

The σ-inductive effect is a shift of electrons away from the less electronegative atoms and toward the more electronegative atoms in the molecule; it results in the most electronegative atoms assuming net negative σ-charges. The σ-inductive effect is traditionally considered to withdraw electrons from all atoms in a chain attached to an electronegative atom, X.



However, it has been suggested,[36a] on the basis of CNDO/2 calculations on aliphatic compounds, that the effect may alternate:



The π-inductive effect arises when a substituent induces a charge on a conjugated atom to which it is attached; this charge polarizes the attached π-system, which then affects the reaction center by a field effect or by secondary polarization of intervening σ-bonds[51,55] This effect alternates with distance similarly to the resonance effect.

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[51] *M. J. S. Dewar and P. J. Grisdale, "Substituent Effects. I. Introduction," J. Amer. Chem. Soc. 84, 3539-41 (1962).*

It would be surprising if isomeric 1- and 2-substituted-5-tetrazolyl groups (as in I and II) differed greatly in their σ-inductive effects since the electronegativities of the atoms involved are the same in both cases; the 5-substituent is attached to the carbon atom of the tetrazole ring, which in turn is attached to two ring nitrogens. Support for this point of view is provided by the fact that the interproton coupling constants for the vinyl protons in 1- and 2-methyl-5-vinyl-tetrazoles are very similar to each other (Table 4); in view of existing correlations[52] between substituent electronegativities and coupling constants in substituted ethylenes, this would suggest that the 1- and 2-methyl-5-tetrazolyl groups are very similar in electronegativity and hence in their ability to withdraw electrons by the σ-inductive effect. In any case, σ-inductive effects are probably not chemically significant more than one bond away from the tetrazole ring; this follows from the extensive literature on substituent effects in the benzene and naphthalene series[53].

To the extent that π-inductive effects depend on polarization via the σ-inductive effect, they are thus probably similar for the isomeric 1- and 2-substituted 5-tetrazolyl groups; but there is also the possibility of polarization via the field effect. However, this should be small relative to direct action of the field effect on the reaction center. Therefore it seems likely that π-inductive effects may safely be regarded as being negligible or similar for the isomeric 1- and 2-substituted 5-tetrazolyl groups.

Hybridization Effects. Other things being equal, the acidity of a compound X-H increases with increasing s character in the X-H bond; thus acetylene is a stronger acid than ethane. It thus seems appropriate to consider the probability that differences in hybridization could be responsible for some of the observed differences in reactivity among substituents attached to tetrazolyl and other heterocyclic rings.

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[52] *See for example S. Sternhell, "Correlation of Interproton Spin-Spin Coupling Constants with Structure," Quarterly Reviews 23, 236 (1969).*

[53] *See for example (a) W. Adcock, M. J. S. Dewar, R. Golden and M. A. Zeb, "Substituent Effects XII. Substituent Effects by ^{19}F NMR", J. Amer. Chem. Soc. 97, 2198 (1975), and other papers in the series; (b) K. Bowden and R. C. Young, "Transmission of Polar Effects. Part XI. Polar and Steric Effects in the Reactions of Arylaliphatic Carboxylic Acids," Can. J. Chem. 47, 2775 (1969), and preceding papers in the series. (c) C. F. Wilcox and C. Leung, "Transmission of Substituent Effects. Dominance of Field Effects," J. Amer. Chem. Soc. 90, 3360 (1968). (c) F. W. Baker, R. C. Parish and L. M. Stock, "Dissociation Constants of Bicyclo (2.2.2oct-octa-2,5diene-2-carboxylic Acids, Dibenzobicyclo (2.2.2)octa-2,5-diene-1-carboxylic Acids, and Cubanecarboxylic Acids," J. Amer. Chem. Soc., 89, 5677 (1967).*

We[4,6] have discussed this point in terms of CNDO/2 bond indices and CH coupling constants for proton exchange and other reactions of substituents attached to azole rings; we concluded that, while hybridization could be important when an electronegative atom such as nitrogen is added in a position α- to, e.g., a proton undergoing H-D exchange it is probably not very important (the difference not greater than a factor of ea 10) when nitrogen is added in a β-position or when (as in the case of isomeric 1- and 2-substituted-5-tetrazolyl groups), α- and β-pyridine and pyrrole type nitrogen are interchanged. This conclusion is not materially affected by since-published[54] values for carbon-hydrogen coupling constants for isomeric 1- and 2-substituted tetrazoles.

We conclude that hybridization effects, if they are at all significant, are probably not the determining factor in the relative reactivities of isomeric 1- and 2-substituted tetrazoles, since they apparently cannot account for the factors of ca 10^3 - 10^5 by which some isomeric pairs differ in reactivity.[1]

Field Effects. Field effects are through-space electrostatic interactions between the tetrazole ring and the attached substituent. It appears that field effects may be fairly important in determining the relative reactivities of isomeric 1- and 2-substituted 5-tetrazolyl groups. 1-substituted-5-tetrazolyl groups seem to be significantly more electron withdrawing by the field effect than the 2-isomers. This follows primarily from the σ_I constants given in Table 4, since the polar effect measured by σ_I is believed to be due primarily to electrostatic field effects rather than to through-bond inductive effects,[53,55,56] and since according to the values in Table 4 σ_I is significantly larger for the 1-methyl than for the 2-methyl-5-tetrazolyl group, and also larger for the 1,4- than for the 1,3-Dimethyltetrazolyl group.

A very rough, "zeroth order" notion of the importance of field effects in tetrazole reactivities is given by the following treatment. 1-Methyl-5-acetylaminotetrazole is about 100 times as strong an acid as

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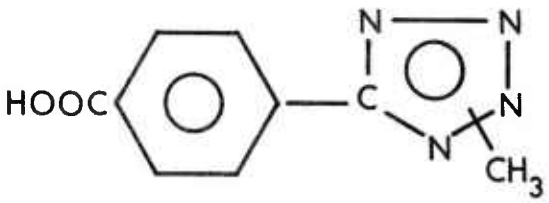
[54] *(a) M. Begtrup, "^{13}C-H Coupling Constants as a Tool in Tautomerism Studies of 1,2,3-Triazole, 1,2,4 Triazole and Tetrazole," J. Chem. Soc. Perkin Trans. 2, 736 (1976); (b) A. Konnecke, E. Lippman and E. Kleinpeter, "Isomere N-Aryltetrazole II. ^{1}H and ^{13}C-NMR-Spectren," Tetrahedron 32, 499 (1970); (c) See reference[21].*

[55] *A. R. Katritzky and R. D. Topsom, "The σ- and π-Inductive Effects," J. Chem. Educ. 48, 427 (1971).*

[56] *L. M. Stock, "The Origin of the Inductive Effect," J. Chem. Educ. 49, 400 (1972).*

2-methyl-5-acetylaminotetrazole.[57] Furthermore, σ_I for the 1-methyl-5-tetrazolyl group is 0.15 σ units higher than σ_I for the 2-methyl-5-tetrazolyl group (Table IV). Thus, the field effect alone will cause p-(1-methyl-5-tetrazolyl)benzoic acid to have a pK_a 0.15 pK units higher than that of p-(2-methyl-5-tetrazolyl)benzoic acid. This is due to the interaction of the negative charges on the respective anions with the sum of the atomic charges (group dipole moments) of the tetrazolyl groups.

Consider the following diagrams of the molecules concerned. It can be seen that the negative charge in the anion will be ca. 2-3 times



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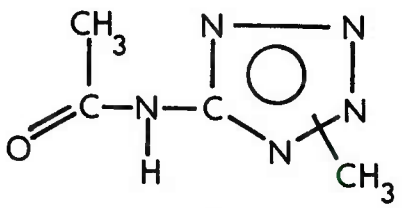

41

farther from the center of the tetrazole group dipole moment in 40 anion than in 41 anion. The change in pK_a (ΔpK_a) due to the field effect can be considered to vary with distance in two ways: inversely with the distance (as in the F-M treatment of Dewar[53a]) or inversely as the square of the distance (as in the Kirkwood-Westheimer treatment.[58]). We will use σ_I as a measure of the field effect contribution to ΔpK_a in the tetrazolyl benzoic acids, and take $\Delta\sigma_I$ (the difference between the σ_I values for 1- and 2-methyl-tetrazolyl groups) to be 0.15 (Table 4). The field effect contribution to ΔpK_a (the difference between the pK_a values of the 1- and 2-methyl isomers of 41) is then predicted to be ca. 0.4 (if the field effect on pK_a varies inversely with distance) or ca. 1 (if the field effect on pK_a varies inversely with the square of the distance). These are respectively ca. 20% and 50% of the experimental value of 2.1.[57]

Application of a similar treatment (using 0.23 for $\Delta\sigma_I$ between the 1,3- and 1,4-dimethyltetrazoliumyl groups) to the difference[1] (pK_b = 2.8) between the pK_b's of 1,3- and 1,4-dimethyl-5-iminotetrazole suggests that the field effect contributions are ca. 0.7 (25%) or 2.1 (75%) depending on whether the field effect contribution is considered to vary inversely with the distance or the square of the distance.

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[57] *V. P. Schipanov, "The Tatomerism of 5-Aminotetrazole III. Methylation of Acetyl Derivatives of 5-Aminotetrazoles," J. Org. Chem. USSR 2, 347 (1900).*

[58] *K. B. Wiberg, Physical Organic Chemistry, John Wiley & Sons, New York, N.Y., pp. 282-5 (1964).*

The principal point to be made from the above estimate is that the field effect is quite capable of making a respectable contribution to the reactivity differences between isomeric 1- and 2-substituted tetrazole derivatives. The estimated contributions of the field effect do not equal 100% but it should be remembered that the nature of the reaction is such that resonance (see below) is also expected to play a role in determining the relative reactivities of these compounds.

The CNDO/2 and INDO charge distributions (Tables 8, 11, 14, 17, and 20) are in agreement with this greater electron-withdrawing field effect of 1- than of the isomeric 2-substituted-5-tetrazolyl groups, since the pyridine-type nitrogen atoms are calculated to have negative total charges, while the pyrrole-type nitrogens and associated substituents have positive net charges; the results of, for example, nonempirical[59], CNDO/2 and other simplified semiempirical[34,60] calculations are in agreement with this. Thus the 1-substituted ring I, with the center of positive charge in the tetrazole ring located closer, and the center of negative charge farther away from the 5-substituent than in the case of the isomeric 2-substituted ring II, should exert a stronger electron-withdrawing field effect.

A variant on the field effect is the adjacent charge or Coulombic effect,[2] due to creation and destruction of favorable or unfavorable charge distributions among the atoms of the azole ring in going from reactants to products or transition states. As we use the terms, the Coulombic effect differs somewhat from the field effect: the field effect refers to the effect an undisturbed azole ring on a reaction center external to the ring, while the adjacent-charge or Coulombic effect has meaning only for reactions such as decarboxylation (as in Scheme 1) or deprotonation, in which one of the atoms involved in the reaction is actually part of the azole ring.

We[6] have considered the adjacent-charge ("Coulombic") effect in the case of proton exchange of azolium cations. Partitioning of energy differences from CNDO/2 calculations suggests that this effect may be important in determining relative proton exchange reactivities of the isomeric dimethyltetrazolium cations; quite possibly it is also important in other proton exchange and decarboxylation reactions of these and related compounds.

We conclude that field and adjacent-charge ("Coulombic") effects are probably important contributors to the apparent greater electron-

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[59] *M. H. Palmer, R. H. Findlay and A. J. Gaskell, "Electronic Charge Distribution and Dipole Moments of Five- and Six-Membered Heterocycles", J. Chem. Soc. Perkin Trans. II, 420 (1974).*

[60] *M. Roche and L. Pujol, "Etudes Theoriques dans la Serie des Azoles: Introduction des Electrons σ: Bull. Soc. Chim. Fr., 273 (1970).*

withdrawing ability of 1- than of 2-substituted-5-tetrazolyl groups; they operate in the right direction and seem to be of sufficient magnitude to make a significant contribution to the observed reactivity differences.

Resonance Effects. The available evidence seems to indicate that the apparent greater electron-withdrawing ability of 1- than of 2-substituted-5-tetrazolyl groups involves a significant contribution from resonance effects.

This follows first from the σ_R and σ_R^o values given in Table 4, which are larger by ca 0.03 for the 1- than for the 2-methyl-5-tetrazolyl group. Furthermore, application of the correlation of Maciel and Natterstad[61] to the ^{13}C NMR chemical shifts given by Begtrup[62] for 1- and 2-methyl-5-phenyltetrazoles yields values of 0.10 and 0.07 for σ_R^o for the 1- and 2-methyl-5-tetrazolyl groups in approximate agreement with the values in Table 4.

However, the possibility of steric inhibition of resonance should be kept in mind, since the 1-methyl group in the 1-methyl-5-aryltetrazoles would be expected to force the 1-methyl-5-tetrazolyl group out of the plane of the phenyl ring, with the result that the apparent σ_R and σ_R^o values given in Table 4 for the 1-isomers are probably not as large, relative to the 2-isomers, as would be the case if the two isomers were considered on a truly equivalent basis. The results of ^1H and ^{13}C NMR studies on tetrazoles and related compounds are in agreement with the idea that the 1-substituent in 1-substituted-5-phenyltetrazoles inhibits the coplamarity of the phenyl and tetrazole rings to a considerable degree[62,63,64].

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[61] *G. E. Maciel and J. J. Natterstad, "Study of ^{13}C Chemical Shifts of Substituted Benzenes," J. Chem. Phys. 42, 2427 (1965).*

[62] *M. Begtrup, "^{13}C-NMR of Phenyl-Substituted Azoles: "A Conformational Study," Acta Chem. Scand. 27, 3101 (1973).*

[63] *R. R. Fraser and K. E. Haque, "Nuclear Magnetic Resonance and Mass Spectral Properties of 5-Aryltetrazoles," Can. J. Chem. 46, 2855 (1968).*

[64] *L. A. Lee and J. W. Wheeler, "Proton Magnetic Resonance Spectra of Some Tetrazoles, Triazoles and Tetrazolium and Triazolium Salts," J. Org. Chem. 37, 348 (1972).*

Based on an examination of available data for these and related compounds,[64,65,66] it seems reasonable to suppose that the aromatic rings in the 2-methyl isomers are almost coplamar, but that those in the 1-methyl isomers are approximately 40° out of plane. If the σ_R (or σ_R^o) for the twisted and planar forms are related by the equation*

$$\sigma_{R(twisted)} = \sigma_{R(planar)} \cos^2\theta$$

where θ is the angle of twist between the phenyl and tetrazole rings, then if θ is taken to be 40°, $\cos^2\theta$ is 0.587, and the numbers given for the 1-methyl-5-tetrazolyl group in the last two columns of Table 4 are raised to 0.15 (for σ_R (planar)) and 0.24 (for σ_R^o (planar)). This correction could be important in some cases, since for example 5-amino-tetrazole or 5-vinyltetrazoles should be less sterically hindered than 5-phenyltetrazole derivitives; thus differences in resonance between these compounds and their 2-isomers may well be more pronounced than expected on the basis of the hindered 1-methyl-5-phenyltetrazoles.

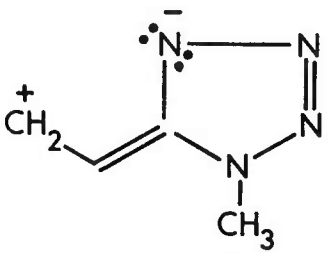
The ^{13}C NMR data (Figure I) on the isomeric vinyltetrazoles is consistent with a stronger electron-withdrawing resonance effect by 1- than by 2-substituted-5-tetrazolyl groups, since the chemical shifts of the vinyl carbons are similar for 2-methyl-5-vinyltetrazole, whereas for 1-methyl-5-vinyltetrazole the β-atom of the vinyl group has an appreciably higher shift than the α-carbon, suggesting lower electron density as would be expected if the 1-substituted-5-tetrazole ring were more electron-withdrawing by resonance than the isomeric 2-substituted ring. Application of a similar argument to the proton NMR data on 1- and 2-methyl-5-vinyltetrazoles (Table 6) also shows that they are consistent with a greater electron-withdrawing resonance effect for the 1- than for the isomeric 2-substituted tetrazolyl groups.

*Derived by analogy with equation 11.15 of reference 66d, assuming σ_R, δ_X^C and charge density are linearly related.

[65] *R. N. Butler, "A Study of the Proton Nuclear Magnetic Resonance Spectra of Aryl and Mono- and Disubstituted N-Methylazoles," Can. J. Chem. 51, 2315 (1973).*

[66] *See for example (a) References 62 and 63, (b) S. Tabak, I. I. Grandberg and A. N. Kost, "Steric Effects in 1-Phenyl-5-Substituted Pyrazoles," Tetrahedron 22, 2703 (1966); (c) F. Bergmann, I. Tamir, Z. Neiman and D. Lichtenberg, "A Nuclear Magnetic Resonance Study of Hindered Rotation in 8-Phenylpurines," Tetrahedron 30, 3045 (1974); (d) J. B. Stothers, Carbon-12 NMR Spectroscopy, Academic Press, New York, 1972, pp. 427 ff.*

CNDO/2 and INDO charge distributions (Tables 8-22 and 24-28) are also in agreement with the idea of stronger electron-withdrawl by resonance in the case of the 1- than 2-substituted-5-tetrazolyl groups; examination of the tables reveals that, for example, π charges, the "overlap populations", and bond indices, are in agreement with the greater importance of valence-bond resonance structures such as 42 and 43 in the 1-isomer than of 44 and 45 for the 2-isomer of 5-vinyl and 5-amino tetrazoles respectively. Possibly this is due to the fact that for the 1-isomer two forms (e.g. 42 and 46) can be written involving delocalization



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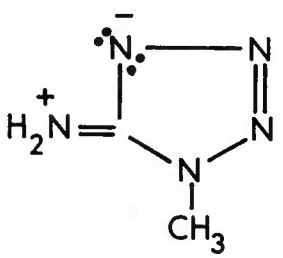

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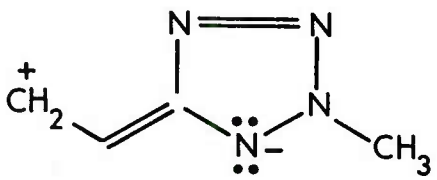

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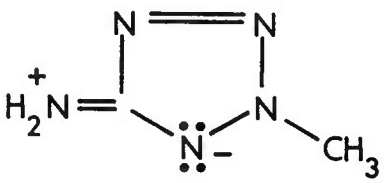

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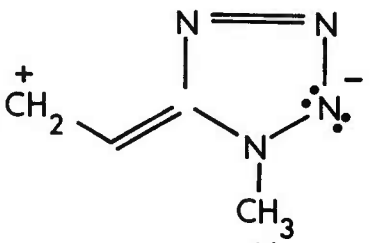

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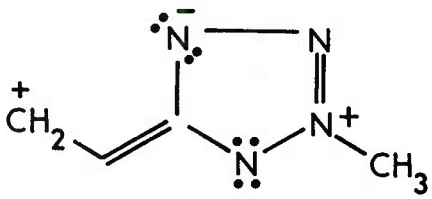


47

of electrons from the substituent into the tetrazole ring, but for the 2-isomer the second form (compare forms 44 and 47) corresponds to higher energy as it involves double separation of charge.

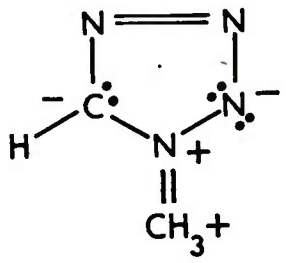
Another index of the relative electron-withdrawing resonance effect of isomeric 1- and 2-substituted tetrazolyl groups might be the π-electron density on the 5-carbon of the tetrazole ring; this follows from the fact that for every resonance form which puts a π-charge on this carbon another can be written putting the same charge on the substituent attached to it, as in forms 42-7.

As experimental indices of π-charge at position 5 of the tetrazole ring we will consider (a) the proton shifts of the 5-proton of 5-unsubstituted tetrazoles and (b) the carbon-13 shifts of the 5-carbon of the tetrazole ring. The 5-protons of 1-monosubstituted tetrazoles generally resonate at lower τ (higher δ) relative to the corresponding

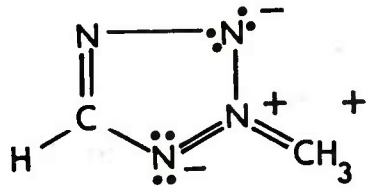
2-isomers;[67] this downfield shift is consistent with lower π-electron-density at the 5-positions of the 1- than the 2-isomers, and hence a stronger electron-withdrawing resonance effect of the 1-isomer.

The carbon-13 shifts of the 5-carbon atoms of 1,5-disubstituted tetrazoles, however, are consistent with the opposite order of electron densities; the 1-isomers have chemical shifts ca 10 ppm lower than the 2-isomers (Figure I). This is in agreement with other studies on the ^{13}C NMR of tetrazole derivatives.[68]

Our calculated CNDO/2 and INDO π-electron charges (Tables 8, 11, 14, 17, 20) are in agreement with more positive (or less negative) π-electron charge at the 5-carbon of 1-substituted than the isomeric 2-substituted tetrazoles, provided that the calculations are based on experimentally-determined molecular geometries. When a regular-pentagon geometry is assumed for the tetrazole rings, the CNDO/2 calculations (Tables 8, 20) still agree provided that some allowance is made for the possibility of hyperconjugation involving the methyl groups, via forms such as 48a and 49b. The regular-pentagon INDO calculations (Tables 11, 14, 17), however, suggest that the opposite ordering is



48a



48b

[67] *(a) G. B. Barlin and T. J. Batterham, "The Proton Magnetic Resonance Spectra of some Diazoles, Triazoles and Tetrazoles," J. Chem. Soc. B, 516 (1967); (b) D. W. Moore and A. G. Whittaker, "Substitution Effect in Nuclear Magnetic Resonance Spectra of Tetrazole and its Derivatives," J. Amer. Chem. Soc. 82, 5007 (1960); (c) See reference 21.*

[68] *(a) J. Elguero, C. Marzin and J. D. Roberts, "Carbon-13 Magnetic Resonance Studies of Azoles. Tautomerism, Shift Reagent Effects, and Solvent Effects," J. Org. Chem. 39, 357 (1974); (b) M. S. Poonian, E. F. Nowoswiat, J. F. Blount and M. J. Kramer, "Synthesis of Tetrazole Ribonucleosides and their Evaluation as Antiviral Agents. 2. 5-Amino-1-(-D-ribofuranosyl)-1H-tetrazole and 5-Amino-2-(-D-ribofuranosyl)-2H-tetrazole," J. Med. Chem. 19, 1017 (1976); (c) See reference 21.*

followed. However the differences between isomers in all of these regular-pentagon cases are small, and other trends are generally similar for the two types of geometry.

Existing molecular orbital calculations on isomeric pairs of N-substituted tetrazole derivatives[3,59,60,69] are generally in agreement with the notion of more π-electron withdrawal from the 5-carbons of the 1- than the 2-isomers, but there are some exceptions.[69c,69f]

On the basis of the available PMR, CMR and theoretical results, we conclude that π-electron densities on the 5-carbon of the tetrazole ring are probably lower for the 1- than for the 2-isomers, although a completely final conclusion does not seem possible at this time. This conclusion is based largely on the following considerations:

(a) Existing molecular orbital calculations on isomeric pairs of tetrazole derivatives[3,59,60,69] together with those described in the present report, lead to the impression that the results are generally in agreement with the idea of lower π-electron density at the 5-carbon of the 1- than of the 2-isomers. The exceptions (references 69c and 69f, and Tables 11, 14 and 17) appear to involve π-electron-only (as opposed to all-electron or all-valence-electron) calculations, and/or regular-pentagon (as apposed to experimentally determined) molecular geometries.

(b) The proton chemical shifts of isomeric tetrazole derivatives are in agreement with the idea of lower π-electron density at the 5-carbon of the 1- than of the 2-isomers, but the carbon-NMR chemical shifts suggest the opposite prediction. However, both carbon-13 and proton chemical shifts are influenced by a number of factors other than charge densities[70] such as bond order terms, magnetic anisotropy affects, average excitation energies, etc., and it apparently does not even seem certain that carbon-13 NMR shifts are in all cases a more reliable criterion of charge densities than proton shifts. Also, it has been noted previously[68a] that the carbons giving the worst correlation with calculated charge densities were those located between two pyridine-type nitrogen atoms, such as the 5-carbon of the 2-substituted tetrazole ring.

In any case, the theoretical and experimental studies on 5-substituents

[69] *(a) A. J. Owen, "The Electronic Structure of some Heteroatom Conjugated Compounds," Tetrahedron 14, 237 (1961); (b) W. Woznicki and B. Zurawski, "On the Ground State Properties of Five-membered Heterocycles Containing Nitrogen," Acta Phys. Polonica 31, 95 (1967); (c) J. B. Lounsbury, "On the Origin of the Dipole Moment of Tetrazoles," J. Phys. Chem. 67, 721 (1963); (d) M. Roche and L. Pujol, "Etudes Theorique dans la Serie des Azoles: Introduction des Electrons σ" Bull. Soc. Chim. Fr., 273 (1970); (e) M. Roche and L. Pujol, "Traitement LCAO-SCF Approche des Azoles," J. Chim. Phys. Physico-chim. Biol. 68, 465 (1971); (f) See reference 21.*

[70] *D. G. Farnum, Advances in Physical Organic Chemistry, Vol. II, V. Gold and D. Bethel, Eds., Academic Press, New York, 1975, pp. 123-75.*

of isomeric 1,5- and 2,5-disubstituted tetrazoles would seem to resolve the situation more conclusively in favor of greater electron withdrawal by resonance involving the 1-substituted-5-tetrazole group than the isomeric 2-substituted-5-tetrazole group. There have also been suggestions[63,65] of electron-donation in the 2-isomers that does not operate in the 1-isomers.

We now consider the relative resonance effects of isomeric N, N' disubstituted tetrazolyl groups (III-VI). We begin with an attempt to estimate approximate values of σ_R^o constants for the isomeric 1, 2-, 2, 3-, 1, 3- and 1, 4-disubstituted tetrazoliumyl groups. A correlation has been reported[71] between σ_R and σ_R^o constants and calculated (CNDO/2) indices for π-electron resonance effects; the best index is apparently the summation, $\Sigma\Delta q_{(\pi)}^c$, of π-electron effects over the entire π-electron system of the molecule in question.

Figure II shows a plot of INDO values for $\Sigma\Delta q_{(\pi)}^c$ vs σ_R^o for some common substituents attached to the vinyl group. A reasonably good plot is obtained. Comparisons of the $\Sigma\Delta q_{(\pi)}^c$ value calculated for 5-vinyl-tetrazolylvinyl compounds and summarized in column 6 of Table XXV suggests the following approximate values for σ_R^o of the indicated 5-tetrazole and 5-tetrazolyl groups:

1H-2-Methyl	0.38
3H-2-Methyl	0.23
4H-2-Methyl	0.27
2H-1-Methyl	0.38
3H-1-Methyl	0.31
4H-1-Methyl	0.38

Similar trends and approximate magnitudes emerge when the results calculated using a regular-pentagon geometry for the tetrazole ring are used (Table 26, Col. 6).

However, the same procedure suggests that σ_R^o is 0.06 for the 1- and 0.01 for the 2-methyl-5-tetrazolyl group, as opposed to experimental values (Table 4) of ca 0.1-0.2 for the 1-isomer and 0.1 or less for the 2-isomer. Thus it does not seem advisable to say more than the following: This particular application of the INDO method suggests that σ_R^o values for N,N' disubstituted tetrazolvinyl groups should be appreciably higher than those for the uncharged tetrazolyl groups, and should increase in the order 2,3- < 1,3 < 1,2 ≤ 1,4-disubstituted, with differences between isomers being quite possibly of approximately the same order of magnitude as the ca 0.1 difference in σ_R^o between uncharged 1- and 2-methyl-5-tetrazolyl groups.

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[71] *R. T. C. Brownlee and R. W. Taft, "A CNDO/2 Theoretical Study of Substituent Effects on Electronic Distributions in Fluorine Molecular Orbitals. Comparison with Meta- and Para-Substituent Fluorine Nuclear Magnetic Resonance Shifts," J. Amer. Chem. Soc. 92, 7007 (1970).*

Examination of the calculated 5-substituent π-charge distributions for 1- and 2-methyl-5-amino tetrazoles (Tables 20 - 22), N,N' dimethyl-5-amino tetrazole derivitives (Table 24), 5-vinyltetrazoles and 5-vinyltetrazolium cations (Tables 25, 26) also suggest the ordering to be 2,3- < 1,3 < 1,2 ≤ 1,4, since substituent π charges become more positive and ring-substituent bond indices and approximate overlap populations increase in that order. Comparison of the magnitudes of the charges for the nonosubstituted 5-amino tetrazoles (Tables 20 - 22) and 5-vinyltetrazoles with those for the N,N' disubstituted 5-imino and 5-vinyltetrazole derivatives suggests that the differences between isomers maybe at least as large, and possibly larger, for the disubstituted tetrazolium compounds as for the monosubstituted tetrazole derivatives.

Examination of the ultraviolet and 1R spectra of 1,3- and 2,3-diphenyl-5-oxotetrazoles suggested that the C=0 grouping was more polar in the 2,3- than in the 1,3-isomers.[72] The comparisons can be extended to the 1,4-isomers by considering the C=0 frequencies of the 2,3- and 1,3-diphenyl isomers (1665 and 1695 cm^{-1} respectively)[72] together with those reported for a number of 1-vinyl-4-substituted-tetrazolin-5- ones[73] (1720-1770 cm^{-1}). These data suggest that contributions from valence-bond resonance forms involving charge separation in the carbonyl group decrease in the order of 2,3- < 1,3 < 1,4 substitution, which is equivalent to saying that electron-withdrawal by resonance increases in the same order.

We now attempt a rough estimate of the possible magnitude of the effect of resonance on the relative reactivities of isomeric 1- and 2-substituted 5-tetrazolyl derivatives. First a comparison of σ_R^o and σ_R values for 5-tetrazole groups with common substituent groups[74] can be made; the 1-methyl-5-tetrazolyl group (σ_R^o ca 0.2 to 0.25 when corrected for steric inhibition of resonance in the 5-phenylderivatives, pp12-13 seems somewhat more electron-withdrawing by resonance than a nitro or carbonyl group ($\sigma_R \simeq 0.15$-0.2),[74] while the 2-methyl-5-tetrazolyl group ($\sigma_R^o = 0.10$, Table 4) is about half as electron-withdrawing by resonance as the 1-isomer.

Thermochemical studies on several isomeric pairs of tetrazole

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[72] *P. B. Talukbar, S. K. Sengupta, A. K. Datta and A. Chakrovorty, "Comparative Studies on Two Tetrazolium Mesoionic Systems," J. Indian Chem. Soc. 11, 611 (1973).*

[73] *G. Denecker, G. Smets and G. L'Abbe', "Synthesis and Spectral Characteristics of Vinyltetrazolinones," Tetrahedron 31, 765 (1975).*

[74] *J. Hine, Structural Effects on Equilibria in Organic Chemistry, John Wiley and Sons, Inc., New York, N.Y., 1975, p. 80.*

derivatives are recorded in the literature;[75] the results of these investigations are summarized in Table 23. The 1-alkyl-5-aminotetrazoles are found to be more stable than the isomeric 2-alkyl-5-aminotetrazoles, but the opposite conclusion is reached for compounds with methyl, phenyl and azotetrazolyl groups in position 5. The differences in energy (last column) are such as to suggest that replacement of methyl, phenyl or azotetrazolyl by amino at position 5 causes relative heat of formation to change in a direction favoring greater stability for the 1-isomer, as expected in view of the π-electron donating nature of the amino group and the greater π-electron-withdrawing nature of the 1- than the 2-substituted-5-tetrazolyl group. The magnitude of the change is ca 9 kcal/Mole. This suggests that in a reaction resulting in replacement of a weakly resonating group by the π-donor-NH_2 group, an energy change corresponding to a change in relative rate or equilibrium constant between the 1- and 2-isomers of as much as 10^6 or 10^7 could take place. It seems most likely that this difference is due mainly to resonance effects since (a) Differences in intermolecular interaction should at least partially cancel due to the fact that differences between isomers are considered throughout the series; and (b) the 5-substituents considered in Table 23 include methyl, phenyl, and amino. The most important interaction among these is probably donation of electrons by the amino group to the tetrazole ring. Since comparisons of σ_R^o and σ_I values for methyl, phenyl and amino groups[74,76] show that σ_I and σ_R^o values are ca 0 ± 0.1 with the exception that σ_R^o for the amino group, is considerably more negative (-0.48). However, it should be remembered that the substituent constants were determined on reaction series and compounds, such as substituted phenyl derivatives, in which the substituents are much farther from the reaction centers than a tetrazole ring is from its attached 5-substituent. Furthermore, effects due to factors such as hydrogen bonding and imino-amino tautomerism cannot be ruled out. However, it would appear, on the basis of the above discussions, that differences in the ability of isomeric 1- and 2-substituted-5-tetrazolyl groups to withdraw electrons from the 5-substituent by resonance seem quite capable of accounting for a very significant amount of the observed differences in chemical reactivity between 1- and 2-substituted-5-tetrazolyl groups.

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[75] *(a) W. S. McEwan and M. W. Rigg, "The Heats of Combustion of Compounds Containing the Tetrazole Ring," J. Amer. Chem. Soc. 73, 4725 (1951); (b) M. M. Williams, W. S. McEwan and R. A. Henry, "The Heats of Combustion of Substituted Triazoles, Tetrazoles, and Related High Nitrogen Compounds," J. Phys. Chem. 61, 261 (1957).*

[76] *A. J. Gordon and R. A. Ford, The Chemist's Companion. A Handbook of Practical Data, Techniques and References, Wiley-Interscience, New York, N.Y., 1972, pp. 152-3.*

3. Relative Reactivities of 1- and 2-Substituents in Isomeric Pairs of Tetrazole Deriviatives. In the previous report of the series,[1] we summarized literature information on relative reactivities of isomeric 1- and 2-substituted tetrazole derivative;however itwas difficult to discern any systematic trend since at least in the case of the dealkylation reaction the reactivity order seemed dependent on the nature of the substituent in position 5. Furthermore, consideration[1] of the substituent constants of isomeric 1- and 2-tetrazolyl groups suggested that the electron-withdrawing tendency of isomeric 1- and 2-tetrazolyl groups is large and about the same (σ_I ca 0.6) for the field effect, but nearly zero for the resonance effect. Thus the electron-withdrawing effects of 1- and 2-tetrazolyl groups apparently differ only slightly; this is in agreement with the observed similarity in pKa's of 5-amino-1-, 5-amino-2- and 5-trifluoromethyl-1-tetrazoleactic acids[77].

The results described in the present report are in agreement with this. First ^{13}C chemical shifts for 1- and 2-phenyltetrazoles are given in Figure 1; these shifts are in reasonable agreement with those already recorded in the literature[62,78]. Application of the correlation of Maciel and Natterstad[61] to these ^{13}C chemical shifts (Figure 1) for the m- and p- carbons of 1- and 2-phenyltetrazoles suggests that σ_R^o for the 2-tetrazolyl group is 0.00, while that for the 1-tetrazolyl group is -0.02. This is in agreement with values of 0.00 and -0.03 estimated by ^{19}F NMR[36b] of 1- and 2-fluorophenyl-5-phenyltetrazoles respectively. Thus it would appear that at least for reactions not involving strong resonance interaction between the tetrazole ring and the reaction center, the resonance effects of 1- and 2-tetrazolyl groups should be almost identical and nearly zero; hence in such cases resonance probably would not contribute appreciably to any observed reactivity differences between isomeric 1- and 2-tetrazolyl derivatives.

Further evidence for the similarity in resonance effects of 1- and 2-tetrazolyl groups is furnished by the ^1H NMR spectra of the isomeric 1- and 2-vinyltetrazoles (Table 7). The numbers in columns are the differences between chemical shifts of the protons in the α- and β-positions; these differences could be used as indices of electron donation or withdrawl by π-electron resonance between the tetrazole ring and the vinyl group. The $\tau_A - \tau_B$ and $\tau_A - \tau_C$ values given for the vinyl group of the 1- and 2-vinyltetrazoles (19 and 20) are quite similar for the two isomers; in particular they are much more similar than for the vinyl groups of the isomeric 1- and 2-methyl-5-vinyltetrazoles (17 and 18) (Table 6). In the case of the 5-vinylisomers 17 and 18, the σ_R values for the 1- and 2-methyl-5-tetrazolyl groups differ by ca. 0.1; hence this approach suggests that the difference between σ_R values for the 1- and 2-tetrazolyl groups should be appreciably less than 0.1, in agreement

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[77] *F. Einberg, "Alkylation of 5-Substituted Tetrazoles with Chlorocarbonyl Compounds," J. Org. Chem. 35, 3978 (1970).*

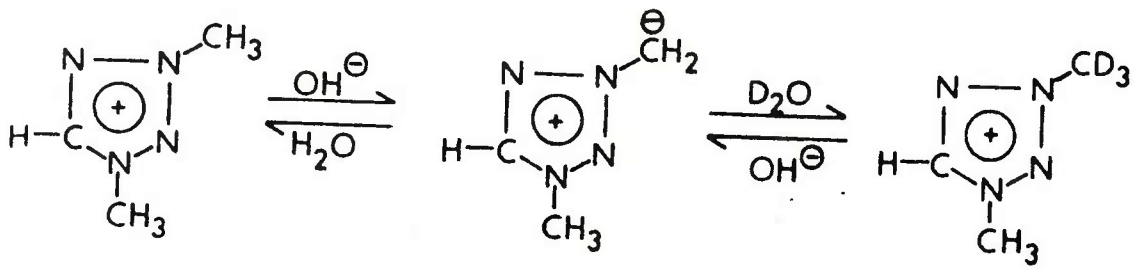
[78] *See Reference 21.*

with the discussion in the preceding paragraph.

Another quantitative evaluation of the resonance effect of 1- and 2-tetrazolyl groups can be attempted, using the INDO charge distributions for 1- and 2-vinyltetrazoles and for tetrazolium cations given in Table 25. Using the $\Sigma\Delta q_{\pi}^{c}$ values in column 6 of Table 25 together with the plot of σ_R^o vs $\Sigma\Delta q_{\pi}^{c}{}^{o}$ (Figure II), we obtain the following theoretical values of σ_R^o for the indicated group: 1-tetrazolyl, - 0.26; 2-tetrazolyl, - 0.22; 1-methyl-3-tetrazoliumyl, + 0.02; 3-methyl-1-tetrazoliumyl, - 0.05; 4-methyl-1-tetrazoliumyl, - 0.08. These values may be compared with the following experimental estimates 1-tetrazolyl, - 0.02; 2-tetrazolyl, 0.00; 1-ethyl-3-tetrazoliumyl, 0.20.* The σ_R^o values estimated from the INDO calculations apparently are too negative by ca 0.20. However, the ordering is correct in that the 1- and 2-tetrazolyl groups are predicted to have almost equal σ_R^o values, with the value for the 1-ethyl-3-tetrazoliumyl group shifted ca 0.2 in the positive direction.

The π-electron charge distribution in the tables of this report are generally consistent with the ideas expressed in the preceding paragraphs. Many of these π-electron charge distributions are also consistent with the idea that the resonance effects of 1-substituted-3- and 3-substituted-1-tetrazoliumyl groups differ from each other more than for the corresponding uncharged 1- and 2-tetrazolyl groups.

It seems instructive to consider the relative proton exchange rates of the methyl groups attached to tetrazolium cations. For example, 1,3-dimethyltetrazolium chloride, in basic solution, exchanges deuterium for hydrogen at the 3-methyl group but not at the 1-methyl group.[31]



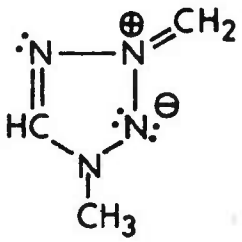
*The values for the 1- and 2-tetrazolyl groups are those given in the preceding two paragraphs. The value for the 1-methyl-3-tetrazolyliumyl group was obtained as follows: ^{13}C chemical shifts for the meta and para positions of 1-ethyl-3-phenyltetrazolium tetrafluoroborate are reported to be 130.3 and 133.1 respectively.[79] The difference between them is 2.8; application of the correlation of Maciel and Natterstad[61] then leads to a σ_R^o value of 0.20.

[79] *E. Lippman and A. Konnecke, "2-Aryltetrazole-Synthese and Eigenschaften," Z. Chem. 16, 90 (1976).*

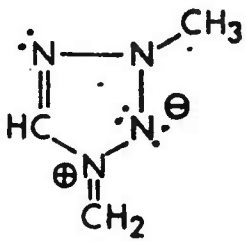
Similarly, the 3-methyl protons of 1,3,5-trimethyl-tetrazolium iodide (but not the 1-methyl protons) undergo exchange in very basic (pD 13.50) solution.[80] The N-methyl protons of 1,4,5-trimethyltetrazolium iodide apparently do not undergo exchange.[80]

It is difficult to see how solvent or steric effects could account for this difference. Inductive and hybridization effects seem insufficient, as both types of groups have the same environment until the third atom away from the exchanging hydrogen. As discussed on page 97, the field effects are apparently quite similar for 1- and 2- tetrazolyl groups and it is not easy to see offhand how addition of an extra methyl group could affect the situation enough to produce the observed differences in reactivity, although such a possibility should be considered.

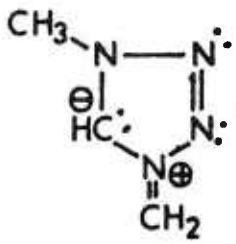
One possible explanation is furnished by π-electron resonance involving the carbanionoid lone pairs of the zwitterion. The greater acidity of the 3- than the 1-methyl protons of 1,3-dimethyltetrazolium cations seems explainable in terms of delocalization of carbanionic charge via classical resonance structures 49-51:



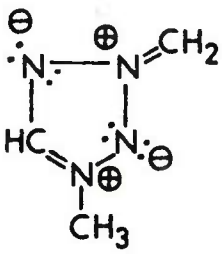
49a



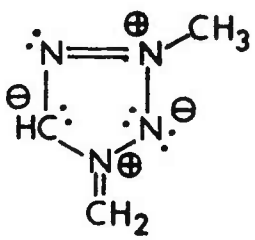
50a



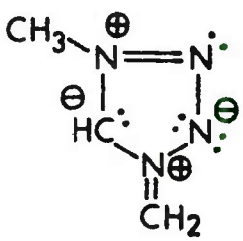
51a



49b



50b



51b

Forms 50 and 51 should correspond to higher energy than 49, since they each have one formal negative charge on carbon, whereas structures 49 have both negative charges on the more electronegative nitrogen atoms. Thus, a 3-tetrazoliumyl group could be more electron-withdrawing by resonance toward a strong electron donor (such as a carbanionoid lone pair) than a 1-tetrazoliumyl group would be.

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[80] *T. Isida, S. Fujimori, K. Nabika, K. Sisido and S. Kozima, "Hydrogen Deuterium Exchange in 1,4,5- and 1,3,5-Trimethyltetrazolium Iodides," Bull. Chem. Soc. Japan 45, 1246 (1972).*

Comparison of the π-electron distribution for the tetrazoliumylmethyl zwitterions (Table 27 column 4) with that for the parent dimethyl-tetrazolium cation (Reference 6, Table 6, Column 4) is in agreement with this; it can be seen that, for both the 1- and 3- deprotonated zwitterions, most of the CNDO/2 π-charge entering the ring goes to the ring atoms adjacent to the one bearing the deprotonated methyl group. Also, the CNDO/2 π-electron bond index between the ring and the carbanion-CH_2 group is 0.446 for the 3-deprotonated zwitterion, but only 0.362 for the 1-deprotonated isomer (Table 28 , last column).

Furthermore, when the trigonal CH_2 is rotated from the configuration coplamar with the ring to the perpendicular position one would expect the resonance interaction to disappear. According to CNDO/2, this is what happens; the CNDO/2 π-electron distribution for the zwitterion with -CH_2 groups perpendicular to the ring resembles those for the parent 1,3-dimethyl-tetrazolium cation (reference 6, Table 6, last 4 columns) much more than those for the zwitterion with CH_2 groupings coplanar with the tetrazole ring.

The calculated total energies (Table 1) are in agreement with the above discussion. The 3-deprotonated zwitterion (15) is calculated (CNDO/2) to be more stable (by 0.017 a.u. (11 Kcal/mole)) than the 1-deprotonated isomer in agreement with the fact (p.) that the 3-methyl group has been found to deprotonate while the 1-methyl group does not.[37,80] When resonance between the CH_2 and the ring is eliminated by making the deprotanated CH_2 perpendicular to the ring, the 3-deprotonated isomer is still predicted by CNDO/2 to be the more stable, but the difference is now reduced to 0.007 a.u (4.4 Kcal/mole). Note that the coplanar isomers are calculated to be more stable than the ones with the CH_2 perpendicular to the ring, in agreement with the expected stabilizing effect of the resonance in this type of reaction. CNDO/2 thus agrees with the observed greater CH acidity of the 3-methylprotons, and suggests that over half of the difference is due to resonance. However we did not optimize the molecular geometries; in particular it should be remembered that the carbanionic CH_2 group may well be tetrahedral rather than coplamar trigonal; and that the differences in bond indices to the carbanionic center (Table 28) are large enough to raise the possibility that the equilibrium N-CH_2 bond length for the 1- and 3-deprotonated isomer ring be significantly different, with that in the 3-deprotonated isomer probably being the shorter of the two.

4. Summary of Tetrazolyl Group Substituent Effects. We will now summarize our conclusions on the nature and origins of variations in apparent electron-withdrawing ability of isomeric 1- and 2-substituted tetrazolyl groups.

Isomeric 1- and 2-Substituted-5-Tetrazolyl Groups. The apparent greater electron-withdrawing abilities of 1- than 2-substituted-5-tetrazolyl groups are apparently due primarily to resonance and field or coulombic effect.

and hybridization effects do not seem to be very important in determining the relative reactivities of substituents attached to position 5 of isomeric 1- and 2-substituted tetrazolyl groupings. Attempts to estimate the approximate magnitudes of field and resonance effects on tetrazole reactivities yield results which suggest that these effects are indeed capable of making a significant contribution to the observed reactivity differences.

A tendency has been noted[4] for azolic carbon atoms located α- to oxygen, sulfur or pyrrole type nitrogen atoms to appear more electron-withdrawing relative to their attached substituents than carbon atoms in isomeric compounds located β- to such an atom. It was suggested that this trend could be understood at least partially in terms of field effects; resonance also seemed important in the case of high-nitrogen compounds such as the tetrazoles. The results described in the present report are in agreement with this.

Isomeric 1- and 2-Tetrazolyl Groups. Although there are a number of instances of significant differences in relative reactivity of 1- and 2-substituents attached to tetrazole rings, it is harder to distinguish any particular trends. In at least one case (dealkylation)[1] the reactivity ordering is dependent on the nature of the substituent at position 5. Furthermore, substituent constants are generally quite similar for the 1- and 2-tetrazolyl groups.

Although more work is needed in this area, possibly the following tentative summary would express the current situation: Isomeric 1- and 2-tetrazolyl and tetrazoliumyl groups generally have quite similar field and resonance effects. However, in certain cases, for example resonance delocalization from a carbanionic lone pair into the tetrazole ring, the resonance interaction can become strong enough to cause a significant reactivity difference among isomeric N-tetrazolyl groups, as discussed on pages 98 ff. This difference has been observed in the case of the deprotonation of the methyl groups in 1,3-dimethyltetrazolium cation (pages 98 ff) but there seems to be no obvious reason why a similar effect should not also operate in, for example, reactions including deprotonation of the methyl groups of 1- and 2-methyl tetrazoles, or reactions involving the amino groups of 1- and 2-amino tetrazole derivatives.

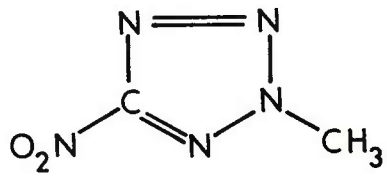
B. Possible Relationship of Tetrazole Isomerism to the Explosive Properties of Tetrazole Derivatives.

In this section of the report, we will use the results described above in an attempt to contribute to the understanding of the explosive and ballistic properties of tetrazole derivatives. We will begin with a brief discussion of the dependance of explosive and ballistic properties of tetrazole derivatives, on their chemical structure. We will then attempt to understand these variations in terms of the thermal stabilities, gas evaluation and electron-withdrawing abilities of 1,5- and 2,5-

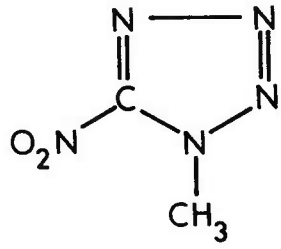
disubstituted tetrazole derivatives. Finally, some suggestions as to future work will be made.

1. Structure-Explosive Property Relationships among Tetrazole Derivatives: 1,5 - vs 2,5-Disubstituted Tetrazoles. There seem to be only a very few instances in which explosive properties of isomeric tetrazole derivaties can be compared; the few that we are aware of are summarized in the following paragraphs.

Cast 2-Methyl-5-nitrotetrazole (52a) is apparently more explosive than cast 1-methyl-5-nitrotetrazole (52b). This can be seen from the fact[81] that the 2-isomer 52a is much more sensitive to hot bridge wire initiation, requiring a threshold voltage of only 110 volts on the apparatus employed, as opposed to a threshold voltage of 375 volts for the 1-isomer 52b.

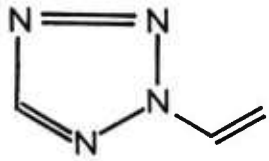


52a

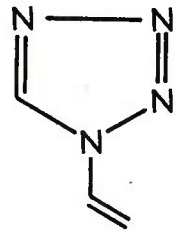


52b

2-Vinyltetrazole (53a) is much more sensitive to impact than is than is the 2-isomer 53b[82]



53a



53b

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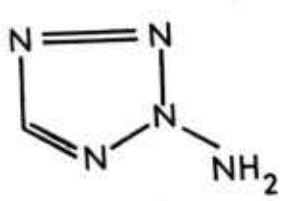
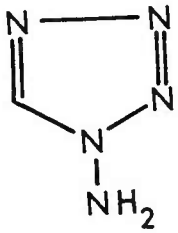
[81] *(a) See reference 10; (b) J. M. Guimont, M. E. Hill, R. Shaw and C. M. Tarver, "Structure-Property Correlations in Primary Explosives," SRI Technical Progress Report 75-2 (Annual) Project PYU-3692, Menlo Park, CA (September 1975), AD-A027 090.*

[82] *(a) W. G. Finnegan and R. A. Henry, "Synthesis of Substituted Vinyltetrazoles" NAVORD Report 5405, 22 October 1959, Page 22; (b) W. G. Finnegan, Naval Weapons Center, China Lake, California, Private Communication.*

It has also been noted[83] that 2-aminotetrazole (54a) and its 5-substituted derivatives appear to be distinctly more explosive than the corresponding-1-amino (e.g. 54b) isomer



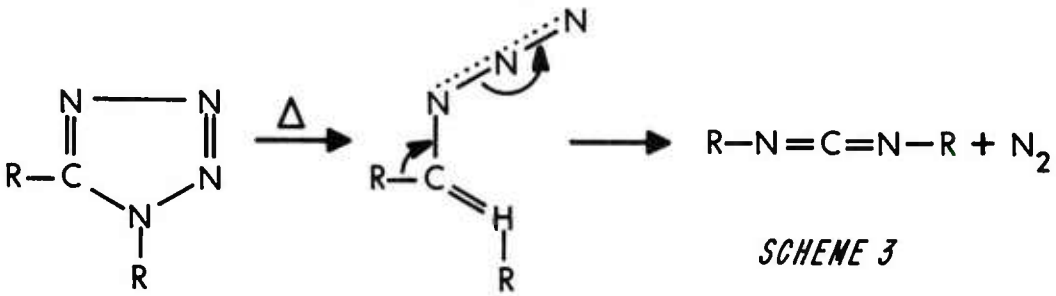
54a



54b

Judging from these few examples, it might seem that 2-substituted tetrazole rings tend to be more plosophoric than those containing 1-substituted tetrazole rings. However, it should be remembered that the nitro, vinyl and amino groups prevalent in these molecules are capable of exerting fairly strong resonance and field effects, and hence they may interact with either the tetrazole rings or their decomposition intermediates in such a way that the above explosivity orderings may not represent the true patterns that might be expected on the basis of the intrinsic behavior of the isomeric tetrazole rings themselves.

In addition to the intrinsic decomposition kinetics of the isomeric tetrazole rings it seems worth suggesting that a factor contributing to greater explosivity of 2-substituted tetrazole rings might be more copious gas evolution on decomposition of 2-substituted than the isomeric 1-substituted tetrazole rings. An idea of how this could come about can be gained by comparing the thermal decomposition pathways for 1,5-(Scheme 3)[14,84] and 2,5-disubstituted tetrazoles[14,85] (Scheme 4):



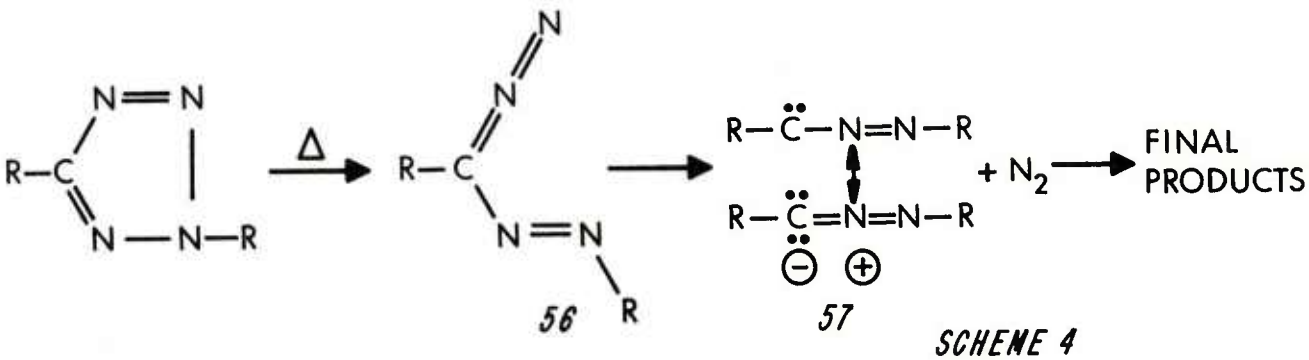
55

SCHEME 3

[83] *R. Raap, "Amination of Tetrazoles with Hydroxylamine-O-sulfonic Acid: 1- and 2-Aminotetrazoles," Can. J. Chem. 47, 3677 (1969).*

[84] *R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland and G. Wallbillich, "The Formation of Nitrile Imines in the Thermal Breakdown of 2,5-Disubstituted Tetrazoles," J. Org. Chem. 24, 892 (1959).*

[85] *(a) J. Vaughan and P. A. S. Smith, "The Effect of some Substituents on the Thermal Breakdown of Diaryltetrazoles," J. Org. Chem. 23, 1909 (1958); (b) P. A. S. Smith and E. Leon, "The Thermal Breakdown of Diaryltetrazoles," J. Amer. Chem. Soc., 80, 4647 (1958).*



56 57

SCHEME 4

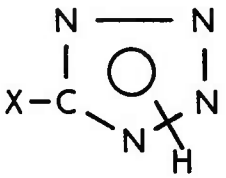
Both isomers can also give products characteristic of decomposition to organic azide and nitrile[14] Note that in the carbodiimides formed from decomposition of the 1-substituted isomers, the nitrogens are separated, while in the intermediates 56 and 57 from the 2-isomers, they are still bonded to each other and hence could easily be eliminated as N_2. In solution at ca 200°C, the intermediate 57 generally undergoes condensation or coupling reactions,[84] but 56 and 57 have azo-compound character; consequently it seems conceivable that at the more extreme conditions characteristics of explosions the second molecule of N_2 could be eliminated forthwith. Thus rapid evolution of a larger quantity (up to twice as much) of gas for the 2- than for the 1-isomers could account for the apparent greater explosivity of the 2- than of the 1-substituted tetrazoles. If this is what is happening, it could also be important in connection with the explosive behavior of the heavy metal tetrazole salts (See below).

However, it should be remembered that chemical decomposition rates are not the only factor affecting explosive behavior of materials; a variety of physical and mechanical factors such as hardness, specific heats, thermal conductivity, crystal structure and form, etc. can play a role and in some cases may well override chemical effects as a determinant of explosive behavior. One effect that seems particularly worth mentioning in the present case is crystal forces. 1,5-Disubstituted tetrazoles generally have dipole moments of ca 5, and the isomeric 2,5-disubstituted have dipole moments of about 2.5. The difference seems large enough to raise a distinct possibility that the 1- isomer may be stabilized relative to the 2-isomer by intermolecular interaction, with the possible exception of tetrazoles substituted at position 5 with very polar substituents, such as a nitro group.*

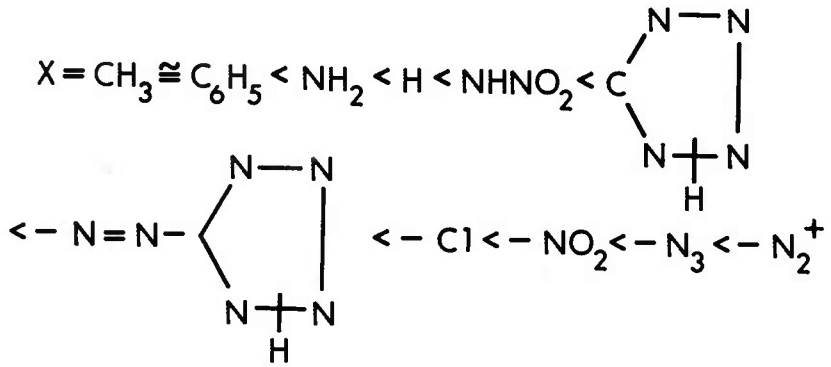
*Note that 1-methyl-5-nitrotetrazole has a lower melting point (52°C) than does the isomeric 2-methyl-5-nitrotetrazole (85°C)[9d]. This would seem to suggest that intermolecular dipole interactions are less important in the 1- than in the 2-isomer, since the trend is opposite to that observed in the tetrazoles generally, for the 1-isomer to have higher melting points and boiling points than the corresponding 2-isomers. If this is so, it would suggest that intermolecular electrostatic interactions alone cannot explain the greater explosivity of 2- than of 1-methyl-5-nitrotetrazole.

2. Effect of 5-Substituent on Explosive Behavior of Tetrazole Metal Salts. 5-Monosubstituted tetrazoles and their metallic salts have been of considerable interest as primary explosives in detonators. In particular, considerable work on this subject has been done in Great Britain,[9,86-89] in an effort to find a replacement for lead azide.

The British workers studied a large number of 5-substituted tetrazoles[4]



and their metal salts. Of special interest were tetrazolate salts with heavy metals such as lead, silver, copper, etc. In general terms they ranked the compounds approximately as follows in order of increasing explosive behavior[9b,9c].



Scheme 5

It was suggested[9b,9c] that the ordering may be related to the electron-withdrawing power of the 5-substituent, which varies in approximately the

[86] *J. M. Jenkins and J. R. White, "The Salts of 5-Substituted Tetrazoles: Part 1: 5,5'-Hydrazotetrazole and the Salts of 5-Nitrotetrazole and 5-Chlorotetrazole," ERDE Technical Note No. 21, June 1970 (AD-886-419).*

[87] *L. R. Bates and J. M. Jenkins, "The Salts of 5-Substituted Tetrazoles: Part 2: Some Metallic Salts and Complexes of Tetrazole, 5-Aminotetrazole, 5-Phenyltetrazole and 5-Methyltetrazole," ERDE Technical Note No. 25, August 1970 (AD-727-350).*

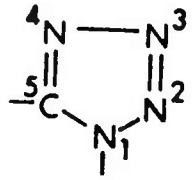
[88] *A. J. Barratt, L. R. Bates, J. M. Jenkins and J. R. White, "Some Reactions of the Azotetrazole Anion with Dilute Mineral Acids", ERDE Technical Note No. 44, November 1971 (AD-752-370).*

[89] *N. J. Blay, D. G. Davies, D. C. Mullenger and R. J. Rapley, "Silver Nitrotetrazole: its Stability and Compatibility with other Materials", ERDE Technical Report No. 163, January 1974 (AD-B001-158).*

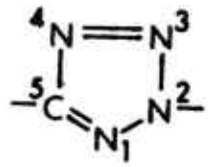
same order. This is consistent with the report[9c] that extended Huckel calculations of electron-withdrawal by the substituents from tetrazole rings yields approximately the ordering given.

The work described earlier in the present report (pp. 9-100) may be useful in understanding the ordering of Scheme 5. Note however that the systems involved here are undoubtedly quite complex, and the following suggestions, if operative, may well represent only part of a much more complex picture.

Two isomeric forms of the 5-substituted tetrazoles are possible (I and II):



I



II

When the N-substituent is hydrogen, its position is indeterminate[90]; it can be on either the 1- or the 2-nitrogen and the two forms may well be in rapid equilibrium under the extreme conditions characteristic of explosive phenomena. The position of equilibrium (relative amounts of the two isomers present) could conceivably be important in determining sensitivity and other explosive properties of the 5-monosubstituted tetrazoles, since there is no obvious reason to assume that the thermal stabilities, susceptibility to electronic excitation events etc. of the two forms are the same. The results of the resent work indicates that the 1-substituted-5-tetrazolyl groups (as in I) are more electron-withdrawing with regard to X than the isomeric 2-substituted-5-tetrazolyl groups (as in II); hence an increase in electron-withdrawing ability of the 5-substituent should displace the equilibrium in favor of the 2-substituted form II.

Thus the observed tendency for more electron-withdrawing substituents to lead to more explosive behavior could be due to the presence, under explosion conditions, of a greater proportion of the 2-isomer II, if this form is considered to be more susceptible to some form of initiation, or to be more plosophoric than the 1-isomer due to the placement of the nitrogens, as suggested in the previous section (pp. 103-104).

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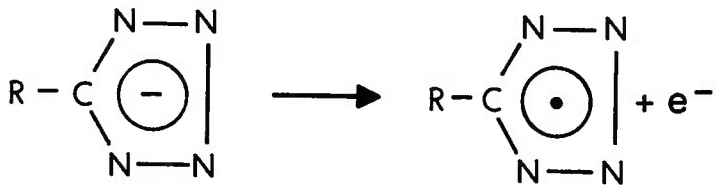
[90] *Reference 20, pp 332-4.*

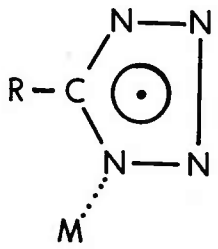
In the case of the heavy-metal tetrazolate salts, it can be suggested, by analogy with the heavy-metal azide salts[91], that the first step in the explosive decomposition may be loss of an electron by the tetrazolate ion, to give a 5-monosubstituted tetrazolyl radical (Scheme 6) although the possibility that the tetrazolate ion may decompose by some other path should be kept in mind.



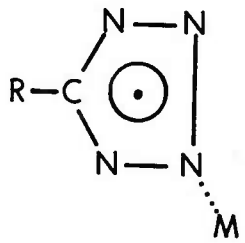
Scheme 6

However, this process would be retarded by increasing electron-withdrawal into the 5-substituent rather than accelerated as required to explain the observed ordering (Scheme 5)

The observed ordering (Scheme 5) can be rationalized if the tetrazolyl radical or anion is associated with a metal atom or ion, as in Ia and IIa



Ia



IIa

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[91] *(a) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids", Butterworths, London, 1958, pp. 45-56. (b) J. N. Bradley, "Flame and Combustion Phenomena", Chapman and Hall, London, 1969, p. 128; (c) P. G. Fox and R. W. Hutchinson, "Slow Thermal Decomposition", Chapter 6 in H. D. Fair and R. F. Walker, eds., "Energetic Materials. 1. Physics and Chemistry of the Inorganic Azides" (Plenum Pres, New York, 1977). (d) M. M. Chaudri and J. E. Field, Ibid., Chapter 8, "Fast Decomposition in the Inorganic Azides"; (e) J. Alster, D. S. Downs, T. Gora, Z. Iqbal, P. G. Fox and P. Mark, Ibid., Chapter 9, "Stability and the Initiation and Propagation of Reaction in the Azides".*

Association to IIa rather than to Ia should be favored by a more electron-withdrawing 5-substituent R; this follows by analogy with the lesser electron-withdrawing character (discussed earlier in the present report) of the 2-substituted-5-tetrazolyl grouping II relative to the isomeric 1-substituted grouping I. Thus the observed tendency for more electron-withdrawing substituents to lead to more explosive behavior could be due to the presence under explosion conditions of a greater contribution or proportion of the 2-isomer II or IIa, if this form is considered to be less stable thermally, or more susceptible to initiation via some other type of process, or to be more strongly phosophoric than the 1-isomer due to the placement of the nitrogens, as suggested in the previous section (pp. 103-104).

Two points worth considering in this connection are (a) the effect of the 5-substituent on the relative proportions of I(Ia) and II(IIa); and (b) the relative thermal stabilities of isomeric 1- and 2-substituted tetrazoles. These points will now be considered separately.

(a) The following are in agreement with the notion that presence of an electron-withdrawing substituent on position 5 should lead to a greater proportion of the 2-substituent form II (or IIa): (1) In the alkylation of 5-monosubstituted tetrazoles and tetrazolate anions with alkylating agents such as alkyl halides, dialicyl sulfates and diazomethane, mixtures of 1- and 2-substituted derivatives are generally obtained. Electronegative 5-substituents tend to direct substitution to the 2-nitrogen[92-94]; however, the trends are precarious and it is difficult to make predictions for individual compounds[94]. (2) In a study[95] of isomerization energetics and mechanism for palladium phosphine complexes containing 5-methyl and 5-trifluoromethyltetrazoles, it is found that the 5-methyl compound exhibited a greater tendency for 1-substitution than did the compound with the more electron-withdrawing 5-trifluoromethyl grouping. (3) On the basis of estimated macroscopic ionization constants for 1H- and 2H- tetrazoles, it was suggested that

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[92] *F. R. Benson, "The Tetrazoles", in R. C. Elderfield, Ed., Heterocyclic Compounds, Volume 8, Wiley, New York, 1967, pp. 53-5.*

[93] *R. N. Butler, "The Alkylation Reactions of Tetrazoles", Leicester Chem. Rev., 12, (1969).*

[94] *See Reference 20, pp. 361-5.*

[95] *D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore and H. B. Jonassen, "Isomerism Energetics and Mechanisms for Palladium (II) Phosphine Complexes Containing 5-Methyl- and 5-trifluoromethyltetrazoles", J. Amer. Chem. Soc. 96, 6298 (1974). (b) M. Charton, "Annular Tautomerism in Nitrogen Heterocycles. Part I. Tetrazoles", J. Chem. Soc., B, 1240 (1969); (c) See reference 20, p. 334.*

the relative proportion of 2H-tautomer in 5-monosubstituted tetrazoles would increase with increasing electron-withdrawing ability of the substituent[95b]. The prediction of the position of the equilibrium is in contradiction to ^{13}C NMR data for aqueous solutions of tetrazole[95c] itself; but the predicted trend seems of interest (see also note added in proof, p. 116).

(b) It is hard to tell whether 1- or 2-substituted tetrazoles are less stable thermally, since there seem to be few cases in which isomeric pairs of appropriately substituted compounds have been studied. At first glance it might appear that the 2-isomers are less stable since 2,5-diphenyltetrazole decomposes thermally at 150°[84] while 5-substituted-1-aryltetrazoles including the 1,5-diphenyl and 1-phenyl-5-methyl derivatives are more stable; they lose nitrogen when heated at ca 200-250°C[85]. However, the presence of the phenyl groups on the 2-nitrogen apparently makes a difference, since 2-phenyl-5-methyl tetrazole decomposes at 160°, while 2-methyl-5-phenyltetrazole decomposes at 220°[96]. The effect of interchanging the methyl and phenyl groups in this isomeric pair of 2-substituted derivatives suggests that some factor, possibly a resonance effect of the phenyl group on the 2-nitrogen with the tetrazole ring or its counterpart in one of the decomposition intermediates or products, exerts an effect potentially strong enough to reverse the thermal-stability ordering of the isomers.

The following seems worth mentioning although the compounds in question are not actually isomeric: 1-Trimethylsilyltetrazole decomposed on heating in an oil bath at 135-40° to give di(trimethylsilyl) carbodiimide, nitrogen and cyanamide polymer, while 1-trimethylsilyl 5-trimethylsilylamino tetrazole decomposes at 150-60° in an oil bath to give trimethylsilyl azide and carbodiimide[97]. On the other hand 2-trimethylsilyl-5-phenyltetrazole is more stable, requiring a higher temperature for decomposition; it decomposes in an oil bath at about 200°[97], giving 1-(bi-trimethylsilylamino)-3,5-diphenyl-1,2,4 triazole. Thus, in the case of the N-trimethylsilyl tetrazoles the 1-isomers seem to be less stable than the 2-isomer, which appears to be opposite to the situation with the N-phenyl derivatives. Possible reasons for this discrepancy include substituent effects, perhaps involving π-electron resonance of the phenyl groups in the N-phenyltetrazoles or some type of effect including the d-orbital of silicon. It should also be remembered that intermolecular interactions or entropy factors could conceivably be playing a role, as the compounds differ appreciably in molecular size, shape and dipole moment.

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[96] *R. Huisgen, J. Sauer and M. Seidel, "Ringoffnungen der Azole, VI. Die Thermolyse 2,5-disubstitutierter Tetrazole zu Nitrilimine", Chem. Ber. 94, 2503 (1961).*

[97] *L. Birkofer, A. Ritter, and P. Richter, "Thermolyse Silylierter Tetrazole", Chem. Ber. 96, 2750 (1963).*

NDDO/1 calculations suggest that 1H-tetrazole is more stable by about 12 Kcal/mole than the 2H-isomer[46b] although a variety of other theoretical and experimental evidence[46b] suggests that the two isomers are about equal in energy. See also the discussion on page 81 of the present report.

The following argument suggests the possibility that the 2-isomers may intrinsically decompose faster, at least when the 5-substituent is phenyl. N-unsubstituted 5-aryltetrazoles decompose at about 180-90°C to give products characteristic of the 2H- rather than the 1H-isomers[98a]. A similar trend is observed in the gas phase[98b]. Now tetrazole itself, like other azoles, shows signal-averaging behavior in its proton NMR spectra in several solvents[99]; hence rapid exchange between the 1H- and the 2H- forms is apparently taking place. Similar rapid exchange might be expected in the case of 5-aryltetrazoles and it seems as though there should be some of the 1H-isomer present even if the 2-isomer predominates. If this is true and the 1H and 2H isomers are rapidly equilibrating, then slow thermal decomposition of a 5-monosubstituted tetrazole might be expected to yield products characteristic of the least stable isomer since this isomer should decompose first, and the supply of it be replenished via equilibrium with the more stable isomers. Since products characteristic of 2-substitution are isolated[98] it can be tentatively concluded that, at least for 5-phenyltetrazoles, the 2-isomers seem to be generally less stable thermally than the 1-isomer. See Note added in Proof, p. 116).

Since we are considering the effects of substituents (Scheme 5) on explosive properties, we should also consider the effects of substituents on rates of thermal decomposition of tetrazoles. In the case of 2,5-disubstituted tetrazoles, thermal decomposition (Scheme 4) is speeded by electron withdrawing substituents at the 2-nitrogen (ρ = 1.16) but is slightly retarded (ρ = - 0.23) by electron-withdrawing substituents at position 5[100]. In the case of 1-5-disubstituted tetrazoles,

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[98] *(a) J. H. Markgraf, S. H. Brown, M. W. Kaplinsky and R. G. Peterson, "The Thermolysis of 5-Aryltetrazoles", J. Org. Chem. 29, 2629 (1964): (b) C. Wentrup, "(1,2,3) triazoloazine/(Diazomethyl)azine Valence Tautomers from 5-Azinyltetrazoles", Heluetica Chimica Acta, 61, 1975 (1978), and references cited therein.*

[99] *M. L. Roumestant, P. Viallefont, J. Elguero, R. Jacquier, and E. Arnal, "Recherches dans la Serie des Azoles. XLIII. Etude par RMN de la Tautomerie des Azoles", Tetrahedron Lett. 495 (1969).*

[100] *S. Y. Hung and J. E. Baldwin, "Cycloadditions. XIX. Kinetics of the Thermal Decomposition of 2,5-diaryltetrazoles". Tetrahedron 24, 3787 (1969).*

the first step of Scheme 3 could be modeled by the well-known tetrazole-Azidoazomethine equilibrium, in which electron-withdrawing substituents generally favor the ring-opened form;[101] in other words, the ring opening reaction would appear to be accelerated by electron-withdrawing substituents, unless the trend is offset somehow at a later stage of its decomposition. Thus, it should be remembered that, since changing the electron-withdrawing ability of 5-substituents may well have opposite effects on the thermal decomposition of the 1- and 2- isomers, it may be that for tetrazoles with electron-donating 5-substituents the 2-isomers will decompose faster while for more electron-withdrawing 5-substituents the 1- isomers might decompose faster. However, if differences in initial thermochemical decomposition rates are responsible for observed variations in explosive properties of these compounds, it would appear that for most if not all the 5-substituents listed in Scheme 5 the 2-substituted configuration II might be associated with a more rapid thermal decomposition rate than the 1-substituted configuration I. This follows from the observed greater explosivity of 2-methyl than 1-methyl-5-nitrotetrazole,[81] since if lower thermal stability leads to greater explosiveness, the greater explosiveness of the 2-methyl-5-nitro isomer would seem to suggest that it decomposes faster than the 1-methyl isomer. The above discussions suggest that the difference should be accentuated by 5-substituents less electron-withdrawing than nitro, since these might be expected to lead to less rapid decomposition for the 1- isomers, but more rapid decomposition for the 2- isomers.

However, apart from thermal decomposition rates, there is at least one other possible way for the 2-substituted configuration to become associated with greater explosivity; this includes the possibility that the nitrogen atoms in the 2-isomer might be positioned in such a way as to allow earlier and easier release of nitrogen (N_2) gas than the nitrogen atom in the 1-isomer, as discussed on pp. 103-104. If this is the case, the greater explosiveness of the 2- than of the 1-isomer would not be due necessarily to faster decomposition, but to the fact that the nitrogen atoms in the 2-isomers are positioned in such a way as to be able to come free as molecular nitrogen at an earlier stage of the reactions (Scheme 4 and accompanying discussion) than in the case of the 1-isomer (Scheme 3).

If this nitrogen-arrangement explanation is responsible for the greater explosiveness of the 2- than of the 1-isomers studied to date, then the effect of substituents on explosiveness of tetrazole salts (Scheme 5 and accompanying discussion) could possibly be explained without necessarily having to postulate a more rapid thermal decomposition rate for the 2-isomer, or equating a faster rate of decomposition for the

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[101] *(a) R. N. Butler, "Azidoazomethine-Tetrazole Isomerism - Fused Tetrazoloheterocycles", Chem. Ind. (London), 371 (1973); (b) See Reference 20, P. 402ff.*

2-isomer with a faster decomposition rate for a tetrazolate anion or radical engaged in a possibly relatively small degree of covolent interaction with a metal ion at position 7. All that would be necessary would be that the covalent association with the metal at position 2 be sufficient to induce the tetrazole ring to decompose as a 2-isomer (Scheme 4) rather than as a 1-isomer (Scheme 3). As discussed above (pp 107-109) a more electron-withdrawing substituent at position 5 should lead to stronger association at position 2 relative to position 1. This should lead to a greater tendency to decompose as a 2-isomer (Scheme 4) than as a 1-isomer (Scheme 3), hence to faster evolution of gas at an earlier stage of the decomposition, and hence to greater explosiveness for tetrazole or tetrazolate salts with more electron-withdrawing 5-substituents.

However, the situation is complicated by a number of factors, among them the following: (a) the 1,5-disubstituted tetrazole ring (as in I) has a much higher dipole moment (ca 5 D) than does the 2,5-disubstituted form (as in II) (ca 2-3 D); this could lead to stabilization and desensitization of 1,5-relative to 2,5-isomers due to intermolecular dipole interactions, unless the large moment of the 1-substituted ring is offset by a large group moment in the substituent X. (b) Some of the substituents considered in Scheme 5, for example $-NO_2$ and $-N_3$ are themselves plosophoric or are capable of altering the oxygen balance. (c) As discussed earlier in the present report, electron donation and withdrawal by a substituent can take place by several mechanisms, and some substituents are electron-withdrawing by some mechanisms and electron-donating by others; for example the amino group ($-NH_2$) is electron-donating by the resonance effect and electron-withdrawing by the field and inductive effects. (d) The substituents considered differ widely in such properties as size, shape, oxygen balance, presence of acidic protons and ability to participate in hydrogen bonding. (e) Explosive properties such as impact sensitivity, DDT time etc. can depend not only on chemical properties, but also on physical properties such as hardness, thermal conductivity, etc.

VI. CONCLUSION

The evidence summarized in the introduction and in part A of the discussion indicates that 1-substituted-5-tetrazolyl groups are apparently considerably more electron-withdrawing than the isomeric 2-substituted-5-tetrazolyl groups by both resonance and field effects; other effects are apparently not too important in determining the observed, often large differences in reactivity of 5-substituents attached to isomeric 1- and 2-substituted-5-tetrazolyl groups.

There seem to be very few cases in the literature in which relative explosiveness of isomeric 1- and 2-substituted tetrazole derivatives can be compared. On the basis of the few examples we are aware of, it would appear that the 2-isomers are generally more explosive than the 1-isomers. Information in the literature does not seem inconsistent

with the idea that these differences could be due to relative rates of thermal decomposition of the 1- and 2-isomers; another possible explanation might be that the tetrazole ring in the 2-isomers is structured in such a way as to give off a greater volume of nitrogen gas at an earlier stage of the decomposition (see discussion on pp 103-104). However, it should be remembered that other chemical and nonchemical factors can also be important in determining explosive properties.

In view of the above, it is suggested that one factor responsible for the apparent tendency of 5-monosubstituted tetrazoles and tetrazolate salts to become more explosive with increasing electron-withdrawing ability of the 5-substituent may be an increase in the relative proportion of more explosive or less stable 2-protonated or 2-associated relative to the 1-protonated or associated forms. Such an increase could result from variations in the intramolecular interactions, since an increase in electron-withdrawing ability of the 5-substituent should result in a more unfavorable interaction with the more electron-withdrawing 1-protonated or associated than with the less electron-withdrawing 2-protonated or associated form. This behavior would be analogous to that observed in alkylation[92-4] of 5-monosubstituted tetrazoles and tetrazolate ions, and in complexation behavior of tetrazole derivatives[95]; it could be operative in the solid state (by analogy with heavy metal azide salts[91] or in the melt.

It is of course quite conceivable that the above explanation for the explosivity ordering of 5-substituted tetrazolate salts may not prove correct. If this happens, it should still be remembered that a more electron-withdrawing 5-substitutent might be expected to bring about more covalent bonding at the 2-relative to the 1-position of the tetrazole ring. This might very well have an effect on the intermolecular interactions and hence on the properties of the material. Thus an understanding of tetrazole isomerism and of its effects on the substituent effect exerted by the tetrazole ring might prove crucial to the understanding of the mechanical and explosive properties of tetrazoles and of heavy-metal tetrazolate salts.

We repeat that the foregoing discussion of tetrazole isomerism as applied to substituent effects on explosivity of tetrazoles and and tetrazolate salts is not intended to give a complete picture of the effects that may be operating in these complicated systems. Rather, we are attempting merely to call attention to the possibility that tetrazole isomerism may be one factor influencing the substituent effects on the explosivity ordering of tetrazoles and tetrazolate salts (Scheme 5).

It should be remembered that very little is known about these systems, and it is possible to suggest other explanations for the ordering. One explanation in particular that seems worth mentioning is the following: Crystal or other condensed-phase forces may cause association to favor the more polar 1-associated forms, I or Ia preventing

any meaningful contribution from the 2-isomers II or IIa. If this is the case, the first step in the decomposition might well be ring-opening to give the imide azide.

By analogy with known examples of the tetrazole-azidomethine equilibrium[101], this ring opening should be favored by electron-withdrawing substituents; this could also explain the explosivity ordering of Scheme 5. This explanation could operate either alone or together with the isomerism-based rationalization presented previously (pp 103-104).

Another possibility might be that cation-anion interionic (covalent plus electrostatic) forces might decrease as electron-withdrawing ability of the 5-substituent increases, in a manner similar to the ring-proton forces that determine acidity. If this were the case, and if explosiveness were determined by interionic forces, explosiveness might be expected to parallel electron-withdrawal by the 5-substituent.

VII. SUGGESTIONS FOR FUTURE WORK

The above discussion suggests a number of areas in which further research could lead to improved understanding of the relationship between molecular structure and explosive properties, both for tetrazole derivatives and for explosives generally. For example, there is a need for crystallographic and other studies that might elucidate the nature and extent of covalent bonding in the tetrazolate heavy metal salts, both at room temperature and under explosion conditions. There is also a need for further studies on the relative thermal stabilities of isomeric 1,5- and 2,5-disubstituted tetrazoles.

Studies on explosive properties such as impact sensitivity, DDT time etc. of isomeric pairs of tetrazole derivatives would also be extremely useful, as would studies of the effect of systematic variations in 1-, 2-, and 5-substituents individually. Possibly control of operational characteristics such as shelf life, safety hazards and ability to withstand temperature extremes will be best attained by studying a series of chemically related compounds of similar molecular size, shape, oxygen balance etc., and which might reasonably be expected to decompose by similar mechanisms, at least prior to the highest point on the potential surface. In this way, many differences in the frequency factor A in the Arrhenius equation

$$k = Ae^{-Ea/RT}$$

should hopefully cancel, and differences in the rate constant k for decomposition might depend primarily on differences in activation energy E_a; these variations can then be estimated by theoretical or empirical means, provided of course that the mechanism or decomposition is known or can be guessed at closely enough. In addition to series of 5-substituted tetrazoles and tetrazolate salts, and of 1,5- and 2,5-

disubstituted tetrazoles, other good series for such studies might include (a) the series of N-picrylazoles prepared and studied experimentally at LASL,[7] and theoretically by ourselves[2,102]; and (b) the series of α - CH picryl compounds studied experimentally at NOL[103] and theoretically by ourselves[2,102].

An interesting example of this type of approach has been described recently[10,81]; in this work some of the physical variables such as density and crystal structure are eliminated by using cast materials for study. The most important variable, chemical structure, was retained by studying two isomers, 1-methyl-5-nitrotetrazole and 2-methyl-5-nitrotetrazole. As mentioned above (p. 102), the 2-methyl isomer was found to have much stronger explosive properties than the 1-isomer.

There is also a need for further development of quantum-chemical computational methods, at both the semiempirical and nonempirical levels. It may well be that for some time to come the best compromise between accuracy and economy will involve semiempirical calculations at the NDDO level[11,43,104]; these would include the lone-pair effects (pp 81-83) without the expense of full ab initio calculations.

The most important point has been saved for last; there is also a tremendous need for studies on the actual chemical mechanisms involved in combustion and explosive behavior. This applies not only to the tetrazoles and tetrazolate salts, but also to other classes of propellant and explosive compounds such as nitrate esters, nitramines, polynitroaromatic compounds etc. The need for further elucidation of the chemical processes involved in the combustion and explosive behavior of these compounds cannot be overemphasized; it will not be really possible to understand or reliably predict the operational characteristics of ballistic materials until the chemical processes involved are understood.

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[102] *M. A. Schroeder and M. Inatome, in I. W. May and A. W. Barrows, Eds., "Army Materiel Command Program, The Fundamentals of Ignition and Combustion. Volume I: Ignition", BRL Report 1707, April 1974, AD 919 315L.*

[103] *(a) J. M. Rosen and J. C. Dacons, Explosivestoffe 16, 250 (1968); (b) M. J. Kamlet and D. V. Sickman, "The Relationship of Sensitivity with Structure of Organic High Explosives. II. Polynitroaromatic Compounds", NOLTR 62-73 (AD 331 340L).*

[104] *(a) M. J. S. Dewar and W. Thiel, "Ground States of Molecules 38. The MNDO Method. Approximations and Parameters", J. Amer. Chem. Soc., 99, 4899 (1977); (b) R. G. Jesaitis and A. Streitwieser, Jr., "Semiempirical and All-Valence-Electron Calculations of Acidities of Cycloalkanes", Theoret. Chim Acta, 17, 165 (1970).*

Note Added in Proof: The effect of the 5-substituent on annular tautomerism of 5-monosubstituted tetrazoles has been studied by carbon-13 NMR[105]. Although no quantitative correlation was found, the results do not contradict the idea that a more electron-withdrawing 5-substituent should lead to a greater proportion of the 2-isomer; in fact they generally seem to agree with it in a crude manner. It is interesting to note that 5-aryltetrazoles seem to exist mainly as the 1H-tautomer, although they are often represented in the literature as being the 2H-isomer.

A similar conclusion has been reached[106] on the basis of substituent effect correlations on the acidity of 5-phenyltetrazoles; this seems especially significant in view of the decomposition of 5-Aryltetrazoles, to give products characteristic of the 2-isomers, suggesting that the 2-isomers may undergo thermal decomposition more easily than the 1-isomers (see discussion on page 110). However it should be remembered that solvent effects may be important.

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[105] *(a) R. N. Butler and T. M. McEvoy, "A Carbon-13 NMR Study of Annular Tautomerism in some 5-Substituted Tetrazoles", Proc. R. Ir. Acad., Sect. B, 77B(19-47), 359 (1977)(Chem. Abstr., 89, 128843g); (b) R. N. Butler and T. M. McEvoy, "A Carbon-13 and Proton Nuclear Magnetic Resonance Study of Annular Tautomerism and Interannular Conjugation in some Substituted 5-Aryltetrazoles", J. Chem. Soc., Perkin Trans., Part 2, 1087 (1978).*

[106] *V. A. Ostrovskii, G. I. Koldobski, N. P. Shirokova, I. Yu. Shirobokov, and B. V. Gidospov, "Tetrazoles. I. Acidity of Tetrazole and 5-Phenyltetrazoles", J. Org. Chem. USSR, 14, 1582 (1978).*

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