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13. ABSTRACT (Maximum 200 words)
Energetic compounds restricted in composition to C, H, N, and O atoms were synthesized for utilization in formulations for explosives and propellants.

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**1. SUPERIOR ENERGETIC MATERIALS THAT CONTAIN COEXISTING
CARBOCATIONS AND ANIONS.**

**2. ENERGETIC MATERIALS RESTRICTED IN COMPOSITION TO C, H, N, AND O
ATOMS.**

FINAL REPORT

September 1, 1990–August 31, 1993

Peter Politzer and Joseph H. Boyer

October 30, 1993

U.S. ARMY RESEARCH OFFICE

DAAL-03-90-G-0205

University of New Orleans

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Synthesis Program

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Statement of the Problem Studied

Energetic compounds restricted in composition to C, H, N, and O atoms were sought for evaluation in formulations for explosives and propellants. Specific calculated properties required included density (d) above 2 g/cc, detonation velocity (D) above 9 mm/ μ sec and detonation pressure (P_{cv}) above 390 Kbar.

Summary of Results

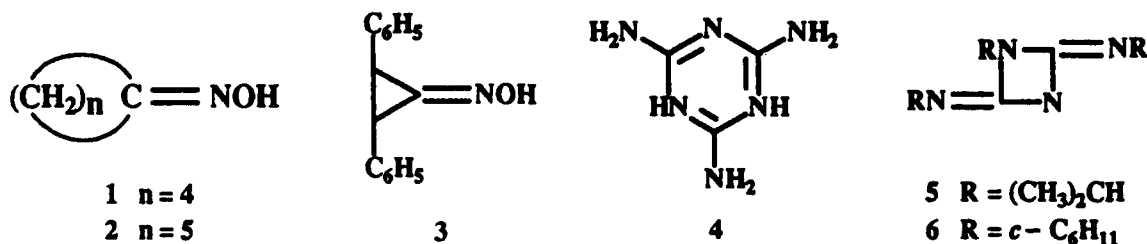
Syntheses were discovered and developed in each of the following five areas.

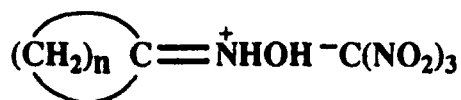
I. Trinitromethanide and tricyanomethanide Salts Restricted to C, H, N, and O Atoms:

A. Gunasekaran and Joseph H. Boyer, *Heteroatom Chem.*, 3, 1992, 611. Fifty copies have been submitted to ARO, Attn: AMXRO-IP-Library.

Summary

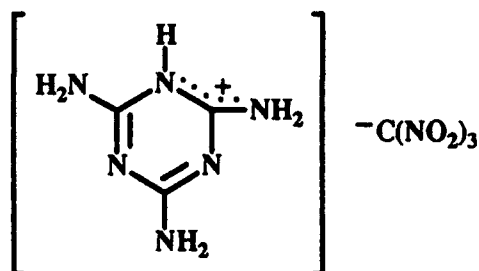
Trinitromethane combined with oximes 1-3 of cyclopentanone, cyclohexanone, and diphenylcyclopropanone and with melamine 4 and two 1,3-dialkyl-2,4-dialkylimino-1,3-diazetidines 5, 6 to give simple trinitromethanide salt adducts 7-9,11,12. Tricyanomethane added to diphenylcyclopropanone oxime to give hydroxylamino-2,3-diphenylcyclopropenylium tricyanomethanide 10.



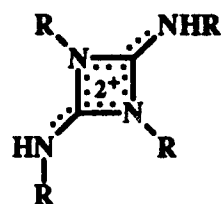


7 n = 4

8 n = 5

9 X = C(NO₂)₃10 X = C(CN)₃

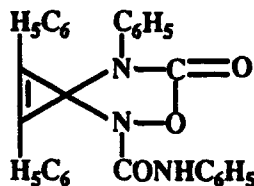
11 (six structures)

12a R = (CH₃)₂CH12b R = *c*-C₆H₁₁

The results led to a publication *An Adduct from Diphenylcyclopropenone Oxime and Phenyl Isocyanate*: A. Gunasekaran, N. Zhu, E. D. Stevens, and J. H. Boyer, *Chem. Lett.*, 1992, 1367. Fifty copies have been submitted to ARO, Attn: AMXRO-IP-Library.

Summary

Diphenylcyclopropenone oxime combined with phenyl isocyanate to give 1,2,7-triphenyl-4-[(phenylamino)carbonyl]-5-oxa-4,7-diazaspiro-[2,4]hept-1-en-6-one 13.



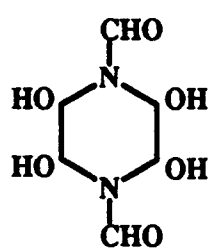
13

II. *2,6-Dithiodecahydro-1H,5H-diimidazo[4,5-b:4',5'-e]pyrazine and Related Dioxo- and Diiminodecahydrodiimidazopyrazines*: M. Vedachalam and J. H. Boyer, *Heteroatom Chem.*, 4, 1993, 85. Fifty copies have been submitted to ARO, Attn: AMXRO-IP-Library.

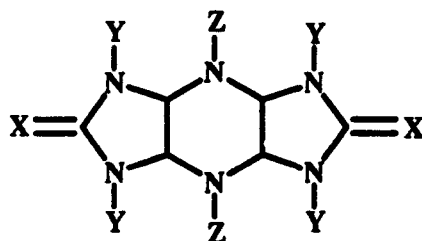
Summary

Thiourea condensed with 1,4-diformyl-2,3,5,6-tetrahydropiperazine 14 in the presence of

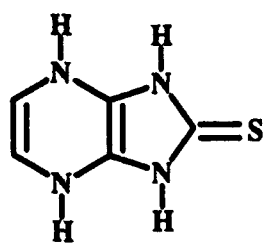
hydrochloric acid to give 2,6-dithiododecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **15** isolated as the dihydrochloride salt. The salt **15** • 2HCl was converted to the free base **15** by lithium hydroxide, to the dinitrate salt **15** • 2HNO₃ by silver nitrate, degraded to 2-thio-2,3,4,7-tetrahydro-1*H*-imidazo[4,5-*b*]pyrazine **16** in a reaction with *tert*-butyl amine, and converted to 4,8-dihydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic acid **17** by nitric acid (100%) at -40 °C. Denitration of the dinitramine **17** to give 4,8-dihydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **18** was brought about by methanolic hydrogen chloride in ether. In one run nitration without oxidation converted the salt **15** • 2HCl to the dinitrate salt of the 4,8-dinitro derivative **19**; treatment with triethyl amine liberated the free base **19** from the salt. Degradation of 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **20** to 2-oxo-2,3-dihydro-1,3-dinitro-1*H*-imidazo[4,5-*b*]pyrazine **21** was brought about by hydrochloric acid. Treatment with lithium hydroxide also liberated 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **22** from its dihydrochloride salt. Attempts to liberate 2,6-diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **23** from its tetrahydrochloride salt led instead to intractable mixtures. The tetrahydrochloride salt **23** • 4HCl was converted to the dihydrochloride salt **23** • 2HCl in a reaction with *tert*-butyl amine.



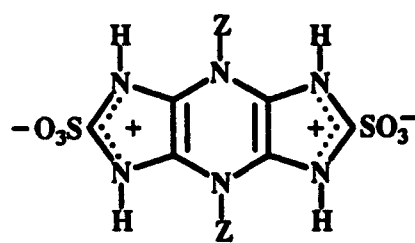
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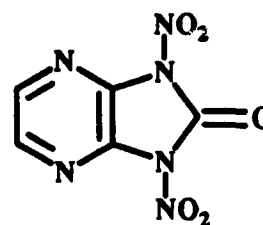
- 15** X = S Y = Z = H
19 X = S Y = H Z = NO₂
20 X = O Y = Z = NO₂
22 X = O Y = Z = H
23 X = NH Y = Z = H



16



- 17** Z = NO₂
18 Z = H

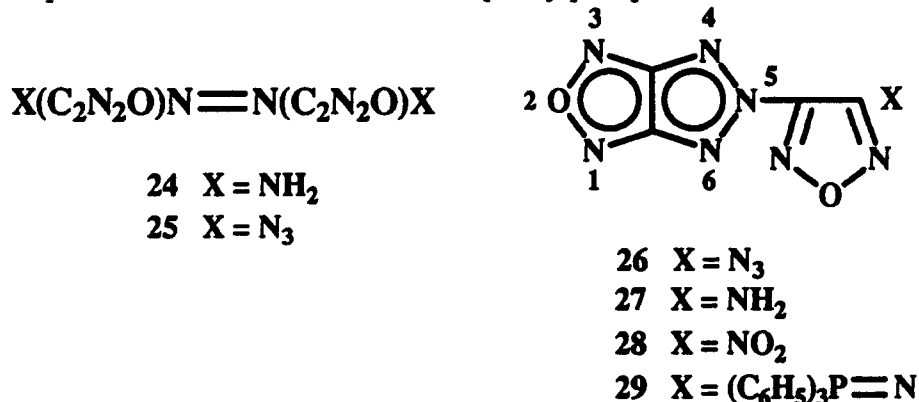


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III. *Dense Energetic Compounds of C, H, N, and O Atoms. III. 5-[4-Nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole*: A. Gunasekaran and J. H. Boyer, *Heteroatom Chem.*, 4, 1993, 521. Fifty copies have been submitted to ARO, Attn: AMXRO-IP-Library.

Summary

Diazidoazofurazan **25** was obtained from the bis-diazonium salt of diaminoazofurazan **24** by treatment with sodium azide and underwent thermolysis to 5-[4-azido-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole **26**. The corresponding amine **27** was obtained from the azide **25** by reduction with stannous chloride and was oxidized by ammonium persulfate to 5-[4-nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole **28**. The azide **25** was converted to a phosphinimine **29** in a reaction with triphenylphosphine.

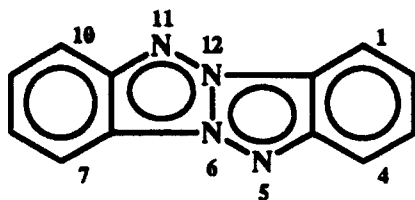


IV. *Dense Energetic Compounds of Carbon, Hydrogen, Nitrogen, and Oxygen Atoms.*

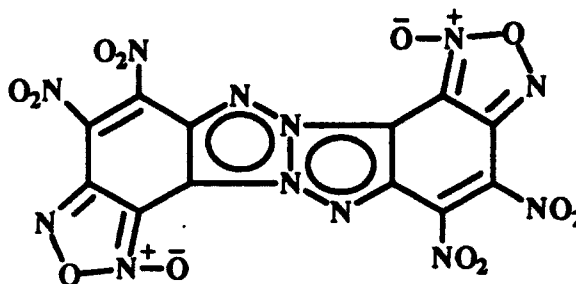
IV. *Thermally Insensitive Polynitro Derivatives of Bisfuroxano-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazoles*: G. Subramanian and J. H. Boyer, *Heteroatom Chem.*, submitted. A copy of the manuscript will be submitted to ARO, Attn: AMXRO-IP-Library.

Summary

5,11-Dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole **30** was converted to the high energy, high density ($d > 1.9$), and heat resistant ($\text{dec} > 300\text{ }^\circ\text{C}$) 1,2,7,8-bisfuroxano-3,4,9,10-tetranitro derivative **31** (a tentative assignment). Investigations are continuing.



30 W = X = Y = Z = H



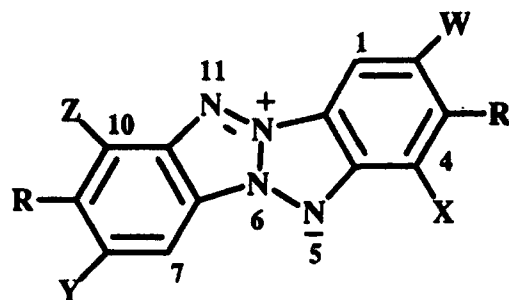
31

V. *Luminescent Nitro Derivatives of Benzotriazolo[2,1-a]benzotriazole*: Q. Lu and J. H. Boyer, *Heteroatom Chem.*, 4, 1993, 91. Fifty copies were submitted to ARO, Attn: AMXRO-IP-Library.

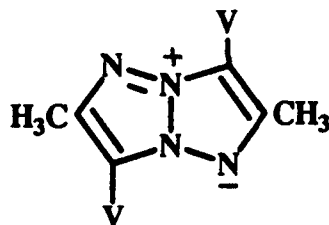
Summary

Fluorescence was enhanced and laser activity introduced by substitution in 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole 32 to give 2-nitro, 2,8-dinitro, 2,4,8-trinitro, and 2,4,8,10-tetranitro derivatives 33a-d. Luminescence for compounds 32 and 33a-d and the 2,8-dinitro-3,9-dimethyl and 2,3,8,9-tetramethyl-4,10-dinitro derivatives 34a,b was erratically solvent dependent when examined in ethyl acetate, acetonitrile, and acetone and was most efficient in the 2,8-dinitro derivative 33b [λ_f 479 nm (ethyl acetate) Φ 0.98, λ_f 501 nm (acetonitrile) Φ 0.58, and λ_f 494 nm (acetone) Φ 0.61] and in the tetranitro derivative 33d [λ_f 509 nm (acetonitrile) Φ 0.81 and λ_f 511 nm (acetone) Φ 0.66]. With laser activity at 560-590 nm (acetonitrile) the dye 33b was 30% as efficient as rhodamine 6G (ethanol) in power output. Luminescence was quenched by the reduction of nitro groups to give 2-amino and 2,8-diamino derivatives 33e,f and by the conversion of the tetranitro compound 33d to an unassigned diazido dinitro derivative 33g. Luminescence was not detected in 2,5-dimethyl-3,6-dinitro-1,3*a*-4,6*a*-tetraazapentalene 35 and ethyl 2,5-dimethyl-1,3*a*,4,6*a*-tetraazapentalene-3,6-dicarboxylate 36. Azidoazobenzenes were obtained from 4-methyl- and 4,5-dimethyl-1,2-phenylene diamines via oxidation with lead dioxide to aminoazobenzene derivatives followed by treatment of the diazotized amines with sodium azide and thermolysis of azido intermediates to give 3,9-dimethyl and 2,3,8,9-tetramethyl derivatives 37a,b of the triazolotriazole 32. Nitration also converted the

triazole 32 to the 2,4,8-trinitro derivative 33c and the alkyltriazoles to their dinitro derivatives 34a,b.



- | | | | |
|-----|---------------------------------------|-----|---|
| 32 | W = X = Y = Z = R = H | 33f | W = Y = NH ₂ X = Z = R = H |
| 33a | W = NO ₂ X = Y = Z = R = H | 33g | unassigned diazodinitro derivative |
| 33b | W = Y = NO ₂ X = Z = R = H | 34a | W = Y = NO ₂ X = Z = H R = CH ₃ |
| 33c | W = X = Y = NO ₂ Z = R = H | 34b | W = Y = R = CH ₃ X = Z = NO ₂ |
| 33d | W = X = Y = Z = NO ₂ R = H | 37a | W = X = Y = Z = H R = CH ₃ |
| 33e | W = NH ₂ X = Y = Z = R = H | 37b | W = R = Y = CH ₃ X = Z = H |



- | | |
|----|---|
| 35 | V = NO ₂ |
| 36 | V = CO ₂ CH ₂ CH ₃ |

Participating scientific personnel: J. H. Boyer, PI and post-doctoral research associates:

A. Gunasekaran, Q. Lu, M. Vedachalam, and G. Subramanian.

There were no publications of technical reports.

The work did not produce reportable inventions.

COMPUTATIONAL STUDIES

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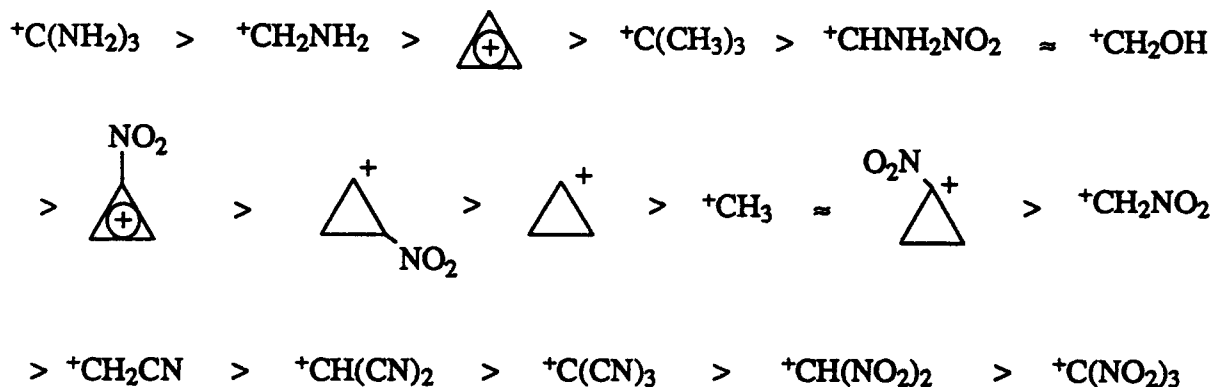
Statement of Problem Studied

We have investigated a new class of energetic materials, compounds containing coexisting carbocations and anions (C^+C^- systems), that have been predicted to show superior performance as explosives and/or propellants. The carbocations of interest have been primarily derivatives of cyclopropene and diaziridine, while the anions include the trinitromethanide, $-C(NO_2)_3$, the nitraminate $-NHNO_2$, and the dinitramide, $-N(NO_2)_2$. Predicted detonation and propellant properties have been estimated by means of well-established empirical procedures, and indicate performance levels superior to HMX.

Our efforts have been computational, and have been complementary to synthetic work. The structures, stabilities and reactive behavior of the target molecules, key precursors and related systems have been the focus of our work.¹⁻⁶

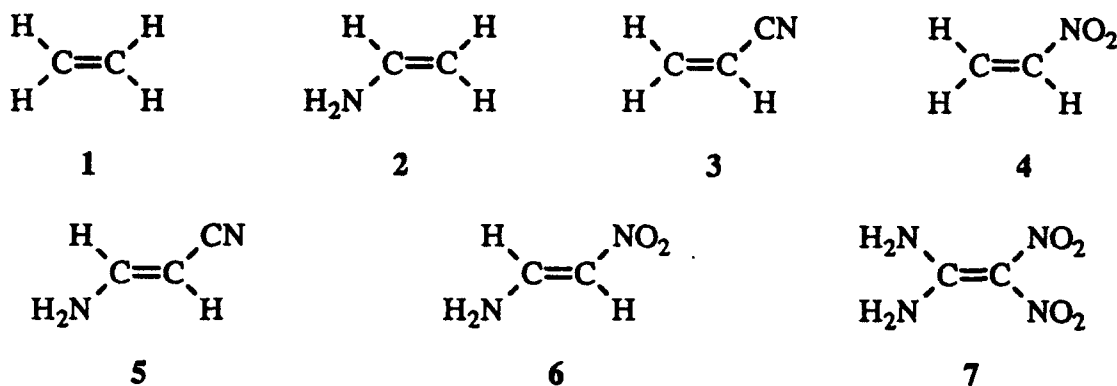
Summary of Results

We have carried out a computational investigation of carbocation relative stabilities.¹ The results, in order of decreasing stability are:



As might be anticipated, α -nitro groups generally destabilize carbocations relative to the parent cations. However the effect is often weaker than would be expected from the strongly electron-withdrawing nature of NO_2 , due to the formation of an intramolecular ring involving the nitro group that can occur when a neighboring or ipso carbon is sufficiently positive.¹

We have carried out calculations on the $C^{+\delta}=C^{-\delta}$ systems 1 - 7, emphasizing primarily the "push-pull" ethylenes 5 - 7. An important feature of 3 - 7 is the diminished rotational barrier of



the $C^{+\delta}=C^{-\delta}$ bond compared to ethylene (1) and vinylamine (2), for which the barriers are roughly 60-65 kcal/mole.² Apparently the presence of the strongly electron-withdrawing cyano and nitro groups, even in the presence of the electron-donating amine group, effectively reduces the electron density in the C=C double bond region, resulting in diminished rotational barriers. The presence of NH_2 alone has little effect on the barrier, despite the availability of the amine lone pair, perhaps due to a lack of electronic demand in the double bond region.

We have computed the average local ionization energy $\bar{I}(r)$ on the molecular surfaces of over fifty carbon, oxygen and nitrogen anions, including $-C(NO_2)_3$, $-C(CN)(NO_2)_2$, $-N(NO_2)_2$ and $-\Delta$.^{3,4} We have found an excellent relationship between the pK_a of each conjugate acid and the lowest calculated $\bar{I}(r)$ on the molecular surface ($\bar{I}_{S,min}$) of the anion. Extending our investigation to second and third row anions, we have shown that the gas phase protonation enthalpies of a group of nine hydrides and their anions can be expressed in a dual-parameter relationship that includes the electrostatic potential minimum, $V_{S,min}$, as well as $\bar{I}_{S,min}$.⁵

In the spirit of our interest in $X^{+\delta} - Y^{-\delta}$ systems, we have carried out calculations on the Lewis acid-base complexes $F_3B \cdot NH_3$ and $Cl_3B \cdot NH_3$ at the MP2 level.⁶ The formation of $Cl_3B \cdot NH_3$ is found to be favored by 4.27 kcal/mole over $F_3B \cdot NH_3$, in agreement with the experimental observation that the Lewis acidities of the boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3$. We suggest that this trend reflects the importance of Lewis base $\rightarrow BX_3$ charge transfer in these complexes, and the fact that the ability to accept charge, as indicated by the charge capacities, increases in the order $BF_3 < BCl_3 < BBr_3$.

References

1. P. C. Redfern, J. S. Murray and P. Politzer, *Can. J. Chem.*, **70**, 636 (1992).
2. D. Habibollahzadeh, Ph. D. dissertation, University of New Orleans, 1993.
3. T. Brinck, J. S. Murray and P. Politzer, *J. Org. Chem.*, **56**, 5012 (1991).
4. J. S. Murray, T. Brinck and P. Politzer, *Int. J. of Quantum Chem., Quantum Biol. Symp.*, **18**, 91 (1991).
5. T. Brinck, J. S. Murray and P. Politzer, *Int. J. Quant. Chem.*, **48**, 73 (1993).
6. T. Brinck, J. S. Murray and P. Politzer, *Inorg. Chem.*, **32**, 2622 (1993).

Personnel Associated With Computational Studies

Dr. Tore Brinck

Ms. Anita Buckel

Dr. M. Edward Grice

Dr. Dariush Habibollahzadeh

Dr. Jane S. Murray

Dr. Shoba Ranganathan

Dr. Paul Redfern

Advanced Degrees Obtained in Connection With This Project

Dr. Tore Brinck

Dr. Dariush Habibollahzadeh

Inventions and Patents

No inventions or patents were applied for or received.

Research Publications Resulting from Computational Studies

Articles in print:

- (1) "Surface Local Ionization Energies and Electrostatic Potentials of the Conjugate Bases of a Series of Cyclic Hydrocarbons in Relation to Their Aqueous Acidities"
J. S. Murray, T. Brinck, and P. Politzer, *Int. J. Quant. Chem., Quantum Biology. Symp.* 18, 91 (1991).
- (2) "Relationships Between the Aqueous Acidities of Some Carbon, Oxygen and Nitrogen Acids and the Calculated Surface Local Ionization Energies of Their Conjugate Bases"
T. Brinck, J. S. Murray and P. Politzer, *J. Org. Chem.*, **56**, 5012 (1991).
- (3) "Radial Behavior of the Average Local Ionization Energies of Atoms"
P. Politzer, J. S. Murray, M. E. Grice, T. Brinck and S. Ranganathan, *J. Chem. Phys.*, **95**, 6699 (1991).
- (4) "Computational Determination of the Relative Stabilities of Some Nitro Carbocations"
P. C. Redfern, J. S. Murray and P. Politzer, *Can. J. Chem.*, **70**, 636 (1992).

- (5) "Polarizability and Volume"
T. Brinck, J. S. Murray and P. Politzer,
J. Chem. Phys., 98, 4305 (1993).
- (6) "A Computational Analysis of the Bonding in Boron Trifluoride and Boron Trichloride and Their Complexes with Ammonia"
T. Brinck, J. S. Murray and P. Politzer, Inorg. Chem., 32, 2622 (1993).
- (7) "Molecular Surface Electrostatic Potentials and Local Ionization Energies of Group V - VII Hydrides and Their Anions. Relationships for Aqueous and Gas-Phase Acidities."
T. Brinck, J. S. Murray and P. Politzer, Int. J. Quant. Chem., 48, 73 (1993).

Article in preparation:

- (8) "A Computational Study of Push-Pull Ethylenes"
D. Habibollahzadeh and P. Politzer, in preparation.

ABSTRACTS OF JOURNAL ARTICLES RESULTING FROM COMPUTATIONAL STUDIES

- (1) "Surface Local Ionization Energies and Electrostatic Potentials of the Conjugate Bases of a Series of Cyclic Hydrocarbons in Relation to Their Aqueous Acidities" J. S. Murray, T. Brinck, and P. Politzer, Int. J. Quant. Chem., Quantum Biology. Symp. 18, 91 (1991).

We have computed surface local ionization energies $[\bar{I}_S(r)]$ and electrostatic potential minima (V_{\min}) for the conjugate bases of a series of cyclic hydrocarbons, using an *ab initio* self-consistent-field molecular orbital approach. Our $\bar{I}_S(r)$ and V_{\min} results are discussed in relation to the acidities of the parent hydrocarbons. A good correlation exists between experimentally-determined pK_a values and the lowest surface $\bar{I}(r)$ values $[\bar{I}_{S,\min}]$, providing a predictive capability for estimating unknown pK_a 's. The electrostatic potential minima, V_{\min} , do not relate as well to pK_a as does $\bar{I}_{S,\min}$. Using our $\bar{I}_{S,\min}$ versus pK_a correlation, we predict the pK_a 's of the strained cage polyhedranes cubane, triprismane and tetrahedrane to be 36, 32 and 26, respectively.

- (2) "Relationships Between the Aqueous Acidities of Some Carbon, Oxygen and Nitrogen Acids and the Calculated Surface Local Ionization Energies of Their Conjugate Bases"
T. Brinck, J. S. Murray and P. Politzer, J. Org. Chem., 56, 5012 (1991).

Average local ionization energies $[\bar{I}(r)]$ have been computed on the molecular surfaces of the conjugate bases for four different groups of carbon and oxygen acids, using an *ab initio* self-consistent-field molecular orbital approach. The lowest surface $\bar{I}(r)$ $[\bar{I}_{S,\min}]$ are generally found on the atom from which the proton has been abstracted. Good linear relationships between aqueous acidities and $\bar{I}_{S,\min}$ are found for the different groups. A single linear relationship between pK_a and $\bar{I}_{S,\min}$ that includes the four groups and three additional nitrogen acids also exists; the correlation coefficient is 0.97. This provides a means for predicting the pK_a 's of a large variety of carbon, oxygen and nitrogen acids.

- (3) "Radial Behavior of the Average Local Ionization Energies of Atoms" P. Politzer, J. S. Murray, M. E. Grice, T. Brinck and S. Ranganathan, *J. Chem. Phys.*, **95**, 6699 (1991).

The radial behavior of the average local ionization energy, $\bar{I}(r)$, has been investigated for the atoms He - Kr, using *ab initio* Hartree-Fock atomic wave functions. $\bar{I}(r)$ is found to decrease in a stepwise manner, with the inflection points serving effectively to define boundaries between electronic shells. There is a good inverse correlation between polarizability and the ionization energy in the outermost region of the atom, suggesting that $\bar{I}(r)$ may be a meaningful measure of local polarizabilities in atoms and molecules.

- (4) "Computational Determination of the Relative Stabilities of Some Nitro Carbocations" P. C. Redfern, J. S. Murray and P. Politzer, *Can. J. Chem.*, **70**, 636 (1992).

The relative stabilities of a group of nitro carbocations (derivatives of the methyl, cyclopropyl and cyclopropenyl cations) are determined by means of *ab initio* SCF/3-21G calculations, and compared to the corresponding results for other substituent groups, both electron-donating and -withdrawing. The α -nitro carbocations are generally destabilized relative to the parent cation, but often to a lesser extent than anticipated from the strongly electron-withdrawing nature of NO_2 . The optimized structures indicate that this is due to the stabilizing formation of an intramolecular ring involving the nitro group; however this requires the proximity of a sufficiently positive carbon.

- (5) "Polarizability and Volume" T. Brinck, J. S. Murray and P. Politzer, *J. Chem. Phys.*, **98**, 4305 (1993).

We have computed *ab initio* HF/6-31G*//HF/6-31G* volumes corresponding to the 0.01, 0.005, 0.002 and 0.001 au contours of the electronic density for twenty-five molecules of a variety of sizes, shapes and degrees of polarity. Our results confirm that there is certainly a general relationship between polarizability and volume. To obtain a really good correlation, however, it seems to be necessary to go beyond volume alone. We have shown that one effective approach is to include a measure of the tightness of binding of the electrons on the molecular surface, \bar{I}_{ave} .

- (6) "A Computational Analysis of the Bonding in Boron Trifluoride and Boron Trichloride and Their Complexes with Ammonia" T. Brinck, J. S. Murray and P. Politzer, *Inorg. Chem.*, **32**, 2622 (1993).

Complexation energies for the interactions of BF_3 and BCl_3 with NH_3 have been calculated at the *ab initio* Hartree-Fock and MP2 levels of theory, using large polarized basis sets. The formation of $\text{H}_3\text{N} \cdot \text{BCl}_3$ is found to be favored by 4.27 kcal/mole over $\text{H}_3\text{N} \cdot \text{BF}_3$ at the MP2 level. This is in agreement with the experimental observation that the Lewis acidities of the boron trihalides increase in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$. Calculated atomic charges and molecular electrostatic potentials show the boron to be much more positive in BF_3 than in BCl_3 , as would be expected from the respective electronegativities of fluorine and chlorine. These results and the relevant $\pi\text{-}\pi$ overlap integrals do not support using the concept of back-bonding and consequent stabilization to explain the trend in Lewis acidities. As an alternative explanation, it is suggested that this trend reflects the importance of Lewis base $\rightarrow \text{BX}_3$ charge transfer in these complexes, and the fact that the ability to accept the charge, as indicated by charge capacities, increases in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.

- (7) "Molecular Surface Electrostatic Potentials and Local Ionization Energies of Group V - VII Hydrides and Their Anions. Relationships for Aqueous and Gas-Phase Acidities." T. Brinck, J. S. Murray and P. Politzer, *Int. J. Quant. Chem.*, **48**, 73 (1993).

We have computed *ab initio* HF/6-31+G* electrostatic potentials and average local ionization energies on the molecular surfaces of the Group V - VII hydrides and corresponding anions of the first three rows of the periodic table. The surfaces were defined to be specified contours (0.002 or 0.001 au) of the molecular electronic density. The most negative potentials, $V_{S,\min}$, and lowest ionization energies, $\bar{I}_{S,\min}$, were located and determined. Their magnitudes separately satisfy limited correlations with gas phase protonation enthalpies and aqueous pK_a values. Our results indicate that $V_{S,\min}$ and $\bar{I}_{S,\min}$ are complementary, the former reflecting electrostatic factors and the latter being related to charge transfer/polarization. More general relationships for protonation enthalpies are obtained when both $V_{S,\min}$ and $\bar{I}_{S,\min}$ are explicitly included. Solution phase and gas phase acidities are shown to correlate very well if electrostatic effects are explicitly taken into account.