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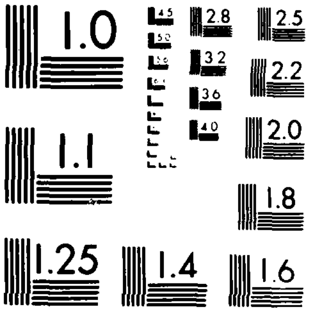

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MINDO/3 and MNDO Calculations for Nitro Compounds

R. M. GUIDRY

and

L. P. DAVIS

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

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Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840. Phone AC 303 472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Larry P Davis

Larry P. Davis
Project Scientist

Chester J Dymek

Chester J. Dymek, Jr, Lt Col
Director, Chemical Sciences

Kenneth E Siegenthaler

Kenneth E. Siegenthaler, Lt Colonel
Chief Scientist

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The semiempirical molecular orbital calculational methods MINDO/3 and MNDO were compared to each other and to available experimental data for a number of nitroaliphatic and nitroaromatic compounds. In general, MINDO/3 predicted heats of formation, dipole moments and ionization potentials better than MNDO. MNDO, however, predicted molecular geometries slightly better than MINDO/3 although both methods gave good estimates of the structural parameters.

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Maj R. Martin Guidry

Capt Larry P. Davis

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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command
U.S. Air Force Academy, Colorado 80840

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SUMMARY

The semiempirical molecular orbital calculational methods MINDO/3 and MNDO were compared to each other and to available experimental data for a number of nitroaliphatic and nitroaromatic compounds. In general, MINDO/3 predicted heats of formation, dipole moments and ionization potentials better than MNDO. MNDO, however, predicted molecular geometries slightly better than MINDO/3 although both methods gave good estimates of the structural parameters.

PREFACE

The research described was performed under Project 2303-F4-03 (Molecular Orbital Calculations of Excited Species). The overall research project encompassed a complete literature search for experimental data on physical and chemical properties of nitro-compounds. Approximately 450 literatures sources were identified, from which 247 literature articles were abstracted. Copies of the remaining sources are still being sought. Additionally, the properties of 93 nitro-compounds (nitroaliphatics, nitroaromatics, nitroalcohols and nitroamines) were calculated using the semi-empirical molecular orbital computer programs MINDO/3 and MNDO. The calculated data was analyzed to determine how well each calculational method predicted experimental data. Properties evaluated included heats of formation, dipole moments, ionization potentials and molecular geometries.

INTRODUCTION

Many investigators have used a variety of methods to perform molecular orbital calculations on nitrocompounds, including π-electron methods[1], semiempirical methods [2-6] and *ab initio* methods[7]. Few results, however, have appeared on nitro-compounds analyzed using the semiempirical MINDO/3 and MNDO programs [8-10]. This report compares the MINDO/3 and MNDO molecular orbital calculations to each other and to available experimental data for a number of nitro-compounds - both aliphatic and aromatic. The goal of this work is to determine which method better predicts particular physical and chemical properties of nitro-compounds. The ultimate goal of our research is using calculational methods to aid in elucidating the kinetics and mechanisms of thermochemical decompositions of nitro-compounds.

EXPERIMENTAL

The MINDO/3 and MNDO molecular orbital programs developed by M.J.S. Dewar, *et. al*. were used to calculate the geometries, heats of formation, ionization potentials and dipole moments for numerous aliphatic and aromatic nitro-compounds. We then compared calculated properties to available experimental data published in the scientific literature.

Molecular orbital calculations were done on a Digital Equipment Corporation VAX-780 minicomputer.

RESULTS AND DISCUSSIONS

Heats of Formation

Table I shows the observed heats of formation (ΔH_f at 25°C) and those calculated with MINDO/3 and MNDO for a series of normal nitroaliphatics. MINDO/3 predicts the enthalpies of formation much better than MNDO. Furthermore, MINDO/3 generally correctly predicts whether the heat of formation is exothermic or endothermic. MNDO, however, always predicts heats of formation which are too endothermic by several hundred per cent.

Enthalpies of formation calculated by MINDO/3 are always more exothermic than those calculated by MNDO and are generally near the experimental value. For MINDO/3 the average absolute error is 9.9 kcal/mole and the average error is -4.1 kcal/mole. With MNDO these values are 52.0 kcal/mole and +52.0 kcal/mole, respectively.

As more nitro-groups are added to a molecule, MNDO predicts increasingly more endothermic heats of formation - a 20-50 kcal/mole increase per nitro-group added. MINDO/3 does not show any trends with increasing nitro content. In fact, except for molecules with high nitro-content, MINDO/3 predicts values close to the experimental heats of formation. As nitro-content gets high, the observed heats of formation become more endothermic probably due in part to steric crowding. MINDO/3 may follow this trend, but does not compensate enough and, consequently, predicts too exothermic an enthalpy for nitroaliphatics containing near the limit of nitro groups.

As carbon content increases, MNDO estimates a less endothermic enthalpy. MINDO/3 predicts a more exothermic enthalpy - the same direction as actually observed. Each methylene group added increases the exothermicity by 5-10 kcal/mole.

Table II presents heat of formation data for several branched nitroaliphatics. Although no experimental data is available, the same trends seen with normal nitroaliphatics occur. Methyl branching affects the enthalpies very little. With MINDO/3 they become slightly less exothermic (5-10 kcal/mole) while with MNDO little change (1-3 kcal/mole) occurs.

Heats of formation for nitroaromatics are presented in Table III. As with nitroaliphatics, MNDO predicts considerably more endothermic heats of formation than MINDO/3. Although only a few experimental heats of formation are available for these nitroaromatics, MINDO/3 seems to estimate the enthalpies much better than MNDO.

With MNDO, adding an additional nitro group to the aromatic ring creases the endothermic heat by 20-30 kcal/mole. With MINDO/3 the heats be e more exothermic by 8-15 kcal/mole for each nitro group added to the rin The position of the nitro groups on the ring affect the heats of format very little (1-8 kcal/mole) with both calculational methods.

Replacing a ring hydrogen with a methyl group makes the heats more exothermic by 2-7 kcal/mole for both MINDO/3 and MNDO. This effect decreases as the number of nitro substituents increases.

Heats of formation for several nitroamines and nitroalcohols are shown in Table IV. The same trends observed for nitroaliphatics are evident here. The hydroxyl function definitely causes the heats of formation to be very exothermic - ∿50 kcal/mole more exothermic for experimental data. Both MINDO/3 and MNDO become more exothermic when the hydroxyl function is present - MINDO/3 by 30-40 kcal/mole and MNDO by 65-75 kcal/mole.

The amine and N-nitro substituents also cause exothermicity, but to a lesser degree - less than 10 kcal/mole. Both MINDO/3 and MNDO predict more exothermic enthalpies for the nitroamines.

As with other nitro-compounds MINDO/3 more accurately predicts heats of formation of nitroamines and nitroalcohols.

Dipole Moments

Calculated and observed dipole moments for normal nitroaliphatics are compared in Table V. MNDO overestimates the dipole moments while MINDO/3 generally predicts the dipole moments to within 0.2 D. With MINDO/3 the average absolute error is 0.17 D while the average error is - 0.02 D. For MNDO the average absolute error and average error are both 0.63 D indicating that MNDO, unlike MINDO/3, always overpredicts the dipole moment.

Both MINDO/3 and MNDO tend to change in the same direction as the nitroaliphatic molecule is varied. Both generally also mirror changes in the observed dipole moments. The variances may be in the observed values and not the calculated values. Measured dipole moments are quite susceptible to solvent and temperature. Where possible, gas-phase values at 25°C are reported in Tables V-VIII. Where not available, measured values at higher temperatures or in an "inert" solvent (e.g., benzene) at 25°C are given. In general "reactive" solvents tend to reduce the dipole moment while increasing temperature increases the dipole moment slightly.

Adding or repositioning nitrogroups on the nitroaliphatic molecule tends to change the observed and calculated dipole moments according to polarity changes. Adding a methylene group to the nitroaliphatic initially slightly increases the dipole moment, but this effect disappears as carbon number increases. Additional methylene groups have little effect after the propanes.

Table VI contains calculated and observed dipole moments for branched nitroaliphatics. The same observations are evident for branched as for normal nitroaliphatics. Here, also, MNDO/3 predicts dipole moments better than MNDO. As expected, branching with a single methyl group tends to increase the dipole moment of the molecule because of the polarity increase.

Nitroaromatic dipole moments are compared in Table VII. MNDO nearly always predicts dipole moments higher than MINDO/3. The major exceptions are when the dipole mements are near zero. Of the two calculational methods, MINDO/3 better estimates the observed dipole moment. For MINDO/3 the average absolute error and average error are both 0.62 D while for MNDO these values are 0.99 D and +0.95 D. The high errors could be due, in part, to the sparcity of good experimental data. Few gas-phase data at 25°C are available; therefore, "inert" solvent data were used. This would tend to yield lower experimental values than gas phase data. The high, positive errors tend to confirm this.

For both methods, the position of the nitro groups around the ring affects the value of the dipole moment more than the number of nitro groups on the aromatic ring. As the polarity of the aromatic molecule increases, the dipole moment increases. Both methods react to changes on the ring in the same way.

Substituting a methyl group for a hydrogen atom on the ring affects the dipole moment according to how the polarity changes. The effect is generally less than 1 D.

Table VIII contains dipole moment data for nitroamines and nitroalcohols. The same trends described above are evident here. MNDO-calculated values are generally slightly higher than values predicted by MINDO/3.

Ionization Potentials

The calculated and observed ionization potentials for normal nitroaliphatics are presented in Table IX. Only ionization potentials measured using photoionization spectroscopy are reported. Electron impact values[11] are too inaccurate for comparing to calculated values here. As with heats of formation and dipole moments, MINDO/3 is a better predictor of ionization potentials than MNDO. For normal nitroaliphatics the average absolute error with MINDO/3 is 0.08 eV while the average error is -0.06 eV. For MNDO both of these values are 0.65 eV. Furthermore, MNDO always predicts an ionization potential about 8-10% higher than that estimated by MINDO/3.

The same trends in ionization potential are predicted by MINDO/3 and MNDO. Additional nitrogroups tend to increase the ionization potential by 0.3-0.5 eV per nitro group. The position of the nitro group on the aliphatic backbone affects ionization potential very little. Adding a methylene group decreases the ionization potential slightly. The effect disappears at higher carbon numbers (pentanes). Both MINDO/3 and MNDO mirror these changes with MINDO/3 giving a better estimate of the observed ionization potential.

Branched nitroaliphatics again show the same tendencies as the normal nitroaliphatics. Both MINDO/3 and MNDO mirror the trends. Table X presents these results.

Branching with a single methyl group generally slightly decreases the calculated ionization potential.

Table XI compares ionization potentials of nitroaromatics calculated by MINDO/3 and MNDO to observed values. MINDO/3 consistently estimates a lower ionization potential than MNDO by 0.4-1.5 eV. It appears from the few observed ionization potentials available that MINDO/3 more nearly predicts the correct ionization potential.

Increasing the nitro groups around the ring increases the ionization potential by 0.1-0.6 eV for MINDO/3 and 0.3-0.8 eV for MNDO. The position of the nitro groups around the ring has a rather minor effect (0.1-0.2 eV) on the ionization potential calculated by either method.

Replacing a ring hydrogen with a methyl group reduces the ionization potential by 0.1-0.4 eV with both MINDO/3 and MNDO.

In Table XII are shown ionization potentials calculated for nitroamines and nitroalcohols. Again trends similar to those with nitroaliphatics are evident. MNDO predicts ionization potentials about 4-16% higher than those calculated by MINDO/3.

Molecular Geometries

There is a scarcity of experimental structural data available on nitro-compounds. Tables XIII-XX compare the observed data to calculated structural parameters using both MINDO/3 and MNDO for nitroaliphatics and nitroaromatics. Molecular geometries were calculated with MINDO/3 and MNDO for many other nitroaliphatics and nitroaromatics. Comparing the calculated values, we find that generally MINDO/3 predicts shorter C-C and C-N distances and longer N-O distances. The differences are fairly small - always less than 0.1 Å and usually less than 0.02 Å. Both methods calculate almost the same C-H distances - to within 0.01 Å.

In predicting bond angles MINDO/3 predicts a slightly smaller ONC angle by 3-6°. The CCN angle predicted by MINDO/3 is slightly larger than that calculated by MNDO by 1-6°. To within 2° both methods calculate the same HCC angles. For CCC bond angles no general trend occurs. Both methods usually agree to within 6°, but either may predict the larger angle.

Calculated values shown in Tables XIII-XX are typical of those obtained for all molecules by the two calculational methods.

Both MINDO/3 and MNDO predict reasonably accurate molecular geometries for nitroaliphatics and nitroaromatics. MNDO, in general, calculates slightly more accurate structural parameters; however, the differences are not great. There are few general trends in how the methods predict parameters. For nitroaromatics both methods overestimate the C-C bond distance by 0.03-0.04 Å and C-H bond distances by ~0.02 Å. MNDO generally predicts C-N bond distances for nitroaromatics to better than 0.02 Å while MINDO/3 C-N bonds are too short by 0.04-0.05 Å.

Both methods do well in calculating nitroaromatic bond angles with MNDO having a slight edge in reproducting observed data. Generally, both programs calculate bond angles to within ± 3° of each other and observed data.

REFERENCES

1. Howe, G. R., J. Chem. Soc. B, 1971, 981.
2. Bloor, J. E. and Breen, D. L., J. Phys. Chem., 1968, 72, 716.
3. Tinland, B., Theor. Chim. Acta, 1969, 13, 171
4. Sieiro, C. and Fernandez-Alonso, J. I., Chem. Phys. Lett., 1973, 18, 557.
5. Brownlee, R. T. C., and Taft, R. W., J. Amer. Chem. Soc., 1970, 92, 7007.
6. Gropen, O. and Skanche, P. N., Acta Chem. Scandinavica, 1969, 23, 2685.
7. Hehre, W. J.; Radom, L. and Pople, J. A., J. Amer. Chem. Soc., 1972, 94, 1496.
8. Bingham, R. C.; Dewar, M. J. S. and Lo, D. H., J. Amer. Chem. Soc., 1975, 97, 1285.
9. Dewar, M. J. S. and Thiel, W., J. Amer. Chem. Soc., 1977, 99, 4899, 4907.
10. Dewar, M. J. S.; Shanshal, M. and Worley, S. D., J. Amer. Chem. Soc., 1969, 91, 3590.
11. Dewar, M. J. S. and Worley, S. D., J. Phys. Chem., 1969, 50, 654.

Table I

Heats of Formation of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	ΔH_f [a]	ΔH_f [a]	Error[2]	ΔH_f [a]	Error[a]
NITROMETHANE	-12.2[b]	-10.5	+1.7	+3.4	+15.6
DINITROMETHANE	-14.3[c]	-15.9	-1.6	+28.5	+42.8
TRINITROMETHANE	-3.2[d]	-23.9	-20.7	+60.1	+63.3
TETRANITROMETHANE	+18.5[c]	-32.2	-50.7	+107.1	+88.6
NITROETHANE	-23.5[b]	-20.5	+3.0	-1.9	+21.6
1,1-DINITROETHANE	-24.1[c,e]	-21.6	+2.5	+25.6	+49.7
1,2-DINITROETHANE	-22.9[c,e]	-18.6	+4.3	+23.3	+46.2
1,1,1-TRINITROETHANE	-12.4[c,e]	-25.5	-13.1	+69.0	+81.4
1,1,2-TRINITROETHANE	--	-20.0	--	+59.3	--
1,1,1,2-TETRANITROETHANE	--	-18.1	--	+94.2	--
1,1,2,2-TETRANITROETHANE	--	-19.8	--	+86.1	--
PENTANITROETHANE	--	-12.3	--	+131.3	--
HEXANITROETHANE	+35.8[f]	-13.0	-48.8	+178.8	+143.0
1-NITROPROPANE	-29.7[b]	-26.7	+3.0	-6.9	+22.8
2-NITROPROPANE	-33.9[b]	-22.0	+11.9	-2.3	+31.6
1,1-DINITROPROPANE	-25.9[b]	-28.1	-2.2	+22.3	+48.2
1,2-DINITROPROPANE	--	-16.1	--	+22.4	--
1,3-DINITROPROPANE	-31.6[b,c]	-25.4	+6.2	+15.2	+46.8
2,2-DINITROPROPANE	-27.0[c,e]	-19.0	+8.0	+25.6	+52.6
1,1,1-TRINITROPROPANE	-18.4[c]	-25.8	-7.4	+59.2	+77.6
1,1,2-TRINITROPROPANE	--	-17.9	--	+55.0	--
1,2,2-TRINITROPROPANE	--	-11.3	--	+57.9	--
1,2,3-TRINITROPROPANE	--	-17.5	--	+46.9	--
1,1,1,2-TETRANITROPROPANE	--	-10.6	--	+97.1	--
1,1,1,3-TETRANITROPROPANE	--	-20.0	--	+84.2	--
1,1,2,2-TETRANITROPROPANE	--	-9.2	--	+97.4	--

Table I (cont'd)

Heats of Formation of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	ΔH_f [a]	ΔH_f [a]	Error[a]	ΔH_f [a]	Error[a]
1-NITROBUTANE	-34.4[b]	-32.6	+1.8	-11.4	+23.0
2-NITROBUTANE	-39.1[b]	-29.0	+10.1	-5.1	+34.0
1,1-DINITROBUTANE	-34.1[c]	-29.8	+4.3	+20.8	+54.9
1,2-DINITROBUTANE	--	-22.1	--	+19.2	--
1,3-DINITROBUTANE	--	-19.5	--	+16.7	--
1,4-DINITROBUTANE	-38.9[c,e]	-33.0	+5.9	+6.4	+45.3
2,2-DINITROBUTANE	--	-20.7	--	+22.1	--
2,3-DINITROBUTANE	--	-20.7	--	+18.5	--
1,1,1-TRINITROBUTANE	--	-30.5	--	--	--
1,1,2-TRINITROBUTANE	--	-25.1	--	--	--
1,1,3-TRINITROBUTANE	--	-24.1	--	--	--
1,1,4-TRINITROBUTANE	--	-32.2	--	--	--
1,2,2-TRINITROBUTANE	--	-19.2	--	--	--
1,2,3-TRINITROBUTANE	--	-6.3	--	--	--
1,2,4-TRINITROBUTANE	--	-22.0	--	--	--
1,3,3-TRINITROBUTANE	--	-17.5	--	--	--
2,3,3-TRINITROBUTANE	--	-10.7	--	--	--
1,1,1,4-TETRANITROBUTANE	-24.9[c,e]	-27.8	-2.9	--	--
1,1,2,2-TETRANITROBUTANE	--	-10.5	--	--	--
1-NITROPENTANE	--	-38.4	--	-14.6	--
2-NITROPENTANE	--	-33.4	--	-12.8	--
3-NITROPENTANE	--	-31.7	--	-8.3	--
1,1-DINITROPENTANE	-38.2[c,e]	-40.2	-2.0	+12.9	+51.1
Ave. Absolute Error	--	--	9.9	--	52.0
Ave. Error	--	--	-4.1	--	+52.0

Table I (Cont'd)

Heats of Formation of Normal Nitroaliphatics

[a] Units are kcal/mole at 25°C for gas.

[b] Holcomb, D. E. and Dorsey, C. L., Jr., Indust and Eng. Chem., 1949, 41, 2788.

[c] Istomin, B.I. and Palm, V., Reakts. Sposobnosi Org. Soedin., 1973, 10, 583.

[d] Carpenter, G. A.; Zimmer, M. F., Baroody, E. E. and Robb, R. A., J. Chem. Eng. Data, 1970, 15, 553

[e] Liebedera, N. D. and Ryadnenko, V. L., Russ J. Phys. Chem., 1968, 42, 1225.

[f] Noble, P., Jr.; Reed, W. L.; Gallaghan, J. A. and Borgardt, F.G., Amer. Inst. Aeron. Astron. (AIAA) J., 1963, 1, 395.

Table II

Heats of Formation of Branched Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	ΔH_f^a	ΔH_f^a	Error[a]	ΔH_f^a	Error[a]
2-METHYL-1-NITROPROPANE	--	-24.3	--	-8.0	--
2-METHYL-2-NITROPROPANE	--	-16.6	--	-3.4	--
2-METHYL-1,1-DINITROPROPANE	--	-21.5	--	+21.9	--
2-METHYL-1,2-DINITROPROPANE	--	-10.3	--	+23.2	--
2-METHYL-1,3-DINITROPROPANE	--	-19.1	--	+17.4	--
2,2-DIMETHYL-1,1-DINITROPROPANE	--	-5.8	--	+21.0	--

[a] Units are kcal/mole at 25°C for gas

Table III

Heats of Formation of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	ΔH_f [a]	ΔH_f [a]	Error[a]	ΔH_f [a]	Error[a]
NITROBENZENE	+15.4[b,c]	+12.7	-2.7	+38.2	+22.8
1,2-DINITROBENZENE	--	-2.5	--	+61.4	--
1,3-DINITROBENZENE	--	-2.4	--	+58.7	--
1,4-DINITROBENZENE	--	-0.2	--	+58.5	--
1,2,3-TRINITROBENZENE	--	-19.0	--	+91.0	--
1,2,4-TRINITROBENZENE	--	-20.0	--	+81.9	--
1,3,5-TRINITROBENZENE	--	-9.6	--	+84.2	--
1,2,3,4-TETRANITROBENZENE	--	-30.9	--	+112.5	--
1,2,3,5-TETRANITROBENZENE	--	-31.6	--	+110.1	--
1,2,4,5-TETRANITROBENZENE	--	-32.0	--	+109.9	--
PENTANITROBENZENE	--	-39.9	--	+143.8	--
HEXANITROBENZENE	--	-36.4	--	+179.5	--

Table III (cont'd)

Heats of Formation of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	ΔH_f[a]	ΔH_f[a]	Error[a]	ΔH_f[a]	Error[a]
2-NITROTOLUENE	+9.3[d,e]	+6.9	-2.4	+32.1	+22.8
3-NITROTOLUENE	+5.9[d,e]	+6.7	+0.8	+30.1	+24.2
4-NITROTOLUENE	--	+6.3	--	+29.9	--
2,3-DINITROTOLUENE	--	-9.7	--	+54.8	--
2,4-DINITROTOLUENE	--	-10.3	--	+52.5	--
2,5-DINITROTOLUENE	--	-3.8	--	+56.2	--
2,6-DINITROTOLUENE	--	-1.6	--	+59.8	--
3,4-DINITROTOLUENE	--	-12.8	--	+51.0	--
3,5-DINITROTOLUENE	--	-5.7	--	+51.3	--
2,3,4-TRINITROTOLUENE	--	-22.3	--	--	--
2,3,5-TRINITROTOLUENE	--	-20.7	--	--	--
2,3,6-TRINITROTOLUENE	--	-17.8	--	--	--
2,4,5-TRINITROTOLUENE	--	-22.2	--	--	--
2,4,6-TRINITROTOLUENE	+12.9	-16.9	-29.8	74.9	+62.0
3,4,5-TRINITROTOLUENE	--	-25.9	--	--	--
2,3,4,5-TETRANITROTOLUENE	--	-34.0	--	--	--
2,3,4,6-TETRANITROTOLUENE	--	-30.8	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	-30.0	--	--	--
PENTANITROTOLUENE	--	-37.8	--	--	--
Ave. Absolute Error	--	--	8.9	--	33.0
Ave Error	--	--	-8.5	--	+33.0

Table III
Heats of Formation of Nitroaromatics

a Units are kcal/mole at 25°C for gas.

b Stull, D. R.: Westrum, E. F., Jr. and Sinke, G. C., The Chemical Thermodynamics of Organic Compounds (John Wiley and Sons, Inc., New York), 1969.

c Maksimov, Y. Y., Russ J. Phys. Chem., 1968, 42, 1550.

d Garner, W. E. and Abernathy, C. L., Proc. - Royal Soc. London, Series A, 1921, 99A, 213.

e Berliner, J. F. T. and May, O. E., J. Amer. Chem. Soc., 1926, 48, 2630.

f Marantz, S. and Armstrong, G. T., J. Chem. Eng Data, 1968, 13, 118, 455.

Table IV

Heats of Formation for Nitroamines and Nitroalcohols

NITRO-COMPOUND	OBSERVED	MINDO/3		MNDO	
	$\Delta_f H$[a]	$\Delta_f H$[a]	Error[a]	$\Delta_f H$[a]	Error[a]
NITROAMINE	--	-30.2	--	+23.1	--
N-NITROETHYLAMINE	--	-32.2	--	+13.3	--
N-NITROBUTYLAMINE	--	-47.8	--	+4.3	--
N-NITRODIMETHYLAMINE	-3.2[b,c]	-4.0	-0.8	+23.1	+26.3
N-NITRODIETHYLAMINE	-13.8[c]	-21.5	-7.7	+16.0	+29.8
NITROETHANOL	-75.1[d,e]	-64.5	+10.6	-45.2	+29.9
3-NITRO-2-BUTANOL	--	-64.6	--	-42.2	--
Ave. Absolute Error	--	--	6.4	--	28.7
Ave. Error	--	--	+0.7	--	+28.7

[a] Units are kcal/mole at 25°C for gas

[b] Stull, D. R.; Westrum, E. F. Jr. and Sinke, G. C., <u>The Chemical Thermodynamics of Organic Compounds</u> (John Wiley & Sons, Inc., New York), 969

[c] Cass, R. C.; Fletcher, S. E.; Mortimer, C. T.; Quincey, P. G. and Springall, H. D., <u>J. Chem. Soc.</u>, <u>1958</u>, 958.

[d] Medard, L. and Thomas, M., <u>Mem. Poudres</u>, 1953, <u>35</u>, 155.

[e] Istomin, B. I. and Palm, V., <u>Reakts. Sposobnosi Org. Soedin.</u>, 1973, <u>10</u>, 583.

Table V

Dipole Moments of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
NITROMETHANE	3.46[b,c]	3.53	+0.07	4.18	+0.72
DINITROMETHANE	--	3.37	--	4.17	--
TRINITROMETHANE	2.63[d,e]	1.93	-0.70	2.79	+0.16
TETRANITROMETHANE	0.19[f,g]	0.12	-0.07	0.55	+0.36
NITROETHANE	3.58[h,i]	3.62	+0.04	4.29	+0.71
1,1-DINITROETHANE	3.50[d,e]	3.94	+0.44	4.79	+1.29
1,2-DINITROETHANE	--	5.62	--	6.77	--
1,1,1-TRINITROETHANE	3.20[d,e]	3.14	-0.06	3.57	+0.37
1,1,2-TRINITROETHANE	--	4.81	--	5.86	--
1,1,1,2-TETRANITROETHANE	--	2.69	--	3.15	--
1,1,2,2-TETRANITROETHANE	--	0.07	--	0.02	--
PENTANITROETHANE	--	1.63	--	1.98	--
HEXANITROETHANE	--	0.14	--	0.02	--
1-*NITROPROPANE*	3.72[j,k]	3.70	-0.02	4.35	+0.63
2-NITROPROPANE	3.73[j,k]	3.72	-0.01	4.37	+0.64
1,1-DINITROPROPANE	--	3.95	--	4.72	--
1,2-DINITROPROPANE	--	3.60	--	4.49	--
1,3-DINITROPROPANE	--	6.12	--	7.48	--
2,2-DINITROPROPANE	--	4.29	--	5.24	--
1,1,1-TRINITROPROPANE	--	3.54	--	4.41	--
1,1,2-TRINITROPROPANE	--	3.85	--	4.56	--
1,2,2-TRINITROPROPANE	--	5.43	--	6.79	--
1,2,3-TRINITROPROPANE	--	4.92	--	6.10	--
1,1,1,2-TETRANITROPROPANE	--	3.46	--	4.04	--
1,1,1,3-TETRANITROPROPANE	--	0.77	--	0.76	--
1,1,2,2-TETRANITROPROPANE	--	4.32	--	5.47	--

Table V (cont'd)

Dipole Moments of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
1-NITROBUTANE	3.61[e,j]	3.72	+0.11	4.36	+0.75
2-NITROBUTANE	--	3.79	--	4.46	--
1,1-DINITROBUTANE	--	4.04	--	4.79	--
1,2-DINITROBUTANE	--	1.50	--	1.61	--
1,3-DINITROBUTANE	--	3.32	--	3.64	--
1,4-DINITROBUTANE	--	0.02	--	0.00	--
2,2-DINITROBUTANE	--	4.54	--	5.34	--
2,3-DINITROBUTANE	--	5.01	--	6.47	--
1,1,1-TRINITROBUTANE	--	3.67	--	--	--
1,1,2-TRINITROBUTANE	--	4.37	--	--	--
1,1,3-TRINITROBUTANE	--	3.75	--	--	--
1,1,4-TRINITROBUTANE	--	3.38	--	--	--
1,2,2-TRINITROBUTANE	--	5.92	--	--	--
1,2,3-TRINITROBUTANE	--	3.78	--	--	--
1,2,4-TRINITROBUTANE	--	5.69	--	--	--
1,3,3-TRINITROBUTANE	--	2.53	--	--	--
2,3,3-TRINITROBUTANE	--	3.27	--	--	--
1,1,1,4-TETRANITROBUTANE	--	2.46	--	--	--
1,1,2,2-TETRANITROBUTANE	--	4.86	--	--	--
1-NITROPENTANE	--	3.71	--	4.34	--
2-NITROPENTANE	--	3.87	--	4.48	--
3-NITROPENTANE	--	3.82	--	4.46	--
1,1-DINITROPENTANE	--	4.14	--	4.84	--
Ave. Absolute Error	--	--	0.17	--	0.63
Ave. Error	--	--	-0.02	--	+0.63

Table V (cont'd)
Dipole Moments of Normal Nitroaliphatics

[a] Units are Debye. Calculated values are for gas at 25°C.

[b] By microwave spectroscopy on gas at 25°.

[c] Tannenbaum, E.; Myers, R. J. and Gwinn, W. D., *J. Chem Phys.*, 1956, 25, 42.

[d] Benzene solution at 25°C.

[e] McClellan, A. L., *Tables of Experimental Dipole Moments* (W. H. Freeman an Co.; San Francisco), 1963.

[f] Carbon tetrachloride solution at 25°C.

[g] Weissberger, A. and Sängewald, R., *Berichte*, 1932, 65, 701.

[h] Gas at 25°C.

[i] Dewar. M. J. S.; Shanshal, M. and Worley, S. D., *J. Amer. Chem. Soc.*, 1969, 91, 3590.

[j] Gas at ∿100°C.

[k] Smyth, C. P. *J. Amer. Chem. Soc.*, 1941, 63, 57.

Table VI

Dipole Moments of Branched Nitroaliphatics

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
2-METHYL-1-NITROPROPANE	3.71[b,c]	3.81	+0.10	4.45	+0.74
2-METHYL-2-NITROPROPANE	3.74[b,c]	3.91	+0.17	4.63	+0.89
2-METHYL-1,1-DINITROPROPANE	--	4.43	--	5.29	--
2-METHYL-1,2-DINITROPROPANE	--	5.38	--	6.39	--
2-METHYL-1,3-DINITROPROPANE	--	2.61	--	3.49	--
2,2-DIMETHYL-1,1-DINITROPROPANE	--	1.72	--	2.63	--
Ave. Absolute Error	--	--	0.14	--	0.82
Ave. Error	--	--	+0.14	--	+0.82

[a] Units are Debye. Calculated values are for gas at 25°C.

[b] Gas at ∿100°C.

[c] McClellan, A.L., Tables of Experimental Dipole Moments, (W. H. Freeman and Co.; San Francisco), 1963.

Table VII

Dipole Moments of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
NITROBENZENE	4.23[b,c]	5.11	+0.88	5.37	+1.14
1,2-DINITROBENZENE	6.05[d,e]	7.22	+1.17	8.03	+1.98
1,3-DINITROBENZENE	4.10[f,g]	4.60	+0.50	5.00	+0.90
1,4-DINITROBENZENE	0.0[d,h]	0.04	+0.04	0.05	+0.05
1,2,3-TRINITROBENZENE	--	7.34	--	8.31	--
1,2,4-TRINITROBENZENE	--	3.77	--	4.26	--
1,3,5-TRINITROBENZENE	0.0[d,h]	0.09	+0.09	0.07	+0.07
1,2,3,4-TETRANITROBENZENE	--	5.71	--	6.67	--
1,2,3,5-TETRANITROBENZENE	--	3.08	--	3.63	--
1,2,4,5-TETRANITROBENZENE	--	0.02	--	0.01	--
PENTANITROBENZENE	--	2.90	--	3.44	--
HEXANITROBENZENE	--	0.07	--	0.01	--

Table VII (cont'd)

Dipole Moments of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
2-NITROTOLUENE	3.97[i,g]	4.69	+0.72	5.15	+1.18
3-NITROTOLUENE	4.41[i,g]	5.15	+0.74	5.42	+1.01
4-NITROTOLUENE	4.72[i,g]	5.35	+0.63	5.50	0.78
2,3-DINITROTOLUENE	5.81[d,g]	7.21	+1.40	8.23	2.42
2,4-DINITROTOLUENE	4.33[d,h]	4.90	+0.57	5.37	1.04
2,5-DINITROTOLUENE	0.58[d,h]	0.74	+0.16	0.67	0.09
2,6-DINITROTOLUENE	2.81[d,h]	3.51	+0.70	4.13	1.32
3,4-DINITROTOLUENE	6.38[d,g]	7.40	+1.02	8.24	1.86
3,5-DINITROTOLUENE	4.33[d,h]	4.88	+0.55	5.19	0.86
2,3,4-TRINITROTOLUENE	--	8.02	--	--	--
2,3,5-TRINITROTOLUENE	--	4.12	--	--	--
2,3,6-TRINITROTOLUENE	--	3.34	--	--	--
2,4,5-TRINITROTOLUENE	--	4.54	--	--	--
2,4,6-TRINITROTOLUENE	1.37[d,j]	1.47	+0.10	0.96	-0.41
3,4,5-TRINITROTOLUENE	--	7.78	--	--	--
2,3,4,5-TETRANITROTOLUENE	--	6.55	--	--	--
2,3,4,6-TETRANITROTOLUENE	--	3.85	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	1.23	--	--	--
PENTANITROTOLUENE	--	4.24	--	--	--
Ave Absolute Error	--	--	0.62	--	0.99
Ave. Error	--	--	+0.62	--	+0.95

Table VII

Dipole Moments of Nitroaromatics

[a] Units are Debye. Calculated values are for gas at 25°C.

[b] Gas at 25°C.

[c] LeFevre, J. W. and Russell, P., *J. Chem. Soc.*, *1936*, 491.

[d] Benzene solution at 25°C.

[e] Williams, J. W. and Schwingel, C. H., *J. Amer. Chem. Soc.*, 1928, *50*, 362.

[f] Hexane solution at 25°C.

[g] McClellan, A. L., *Tables of Experimental Dipole Moments* (W. H. Freeman and Co., San Francisco), 1963.

[h] Cass, R. C.; Spedding, H. and Springall, H. D., *J. Chem. Soc.*, *1957*, 3451.

[i] Hexane solution at 30°C.

[j] LeFevre, C. G. and LeFevre, R. J., *J. Chem. Soc.*, *1950*, 1829.

Table VIII

Dipole Moments for Nitroamines and Nitroalcohols

NITRO-COMPOUND	OBSERVED	MINDO/3		MNDO	
	μ[a]	μ[a]	Error[a]	μ[a]	Error[a]
NITROAMINE	3.78[b,c]	3.94	0.16	4.01	0.23
N-NITROETHYLAMINE	--	4.18	--	4.28	--
N-NITROBUTYLAMINE	--	4.52	--	4.40	--
N-NITRODIMETHYLAMINE	4.61[b,d]	3.02	-1.59	3.91	-0.70
N-NITRODIETHYLAMINE	--	3.13		3.81	--
NITROETHANOL	--	3.51	--	3.88	--
3-NITRO-2-BUTANOL	--	3.55	--	3.95	--
Ave. Absolute Error	--	--	0.88	--	0.46
Ave Error	--	--	-0.72	--	0.24

[a] Units are Debye. Calculated values are for gas at 25°C.

[b] Dioxane solution at 20°C.

[c] McClellan, A. L., Tables of Experimental Dipole Moments, (W. H. Freeman and Co., San Francisco), 1963.

[d] George, M. V. and Wright, G. F., J. Amer. Chem. Soc., 1958, 80, 1200.

Table IX

Ionization Potentials of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED IP[a]	MINDO/3 IP[a]	MINDO/3 Error[a]	MNDO IP[a]	MNDO Error[a]
NITROMETHANE	11.08[b,c]	11.14	+0.06	11.54	+0.46
DINITROMETHANE	--	11.44	--	12.37	--
TRINITROMETHANE	--	11.80	--	12.98	--
TETRANITROMETHANE	--	12.13	--	13.25	--
NITROETHANE	10.88[b,c]	10.83	-0.05	11.49	+0.61
1,1-DINITROETHANE	--	11.20	--	12.25	--
1,2-DINITROETHANE	--	11.18	--	11.94	--
1,1,1-TRINITROETHANE	--	11.63	--	12.65	--
1,1,2-TRINITROETHANE	--	11.55	--	12.10	--
1,1,1,2-TETRANITROETHANE	--	11.61	--	12.51	--
1,1,2,2-TETRANITROETHANE	--	11.62	--	13.10	--
PENTANITROETHANE	--	11.82	--	13.22	--
HEXANITROETHANE	--	12.04	--	13.47	--
1-NITROPROPANE	10.81[b,c]	10.73	-0.08	11.46	+0.65
2-NITROPROPANE	10.71[b,c]	10.61	-0.10	11.44	+0.73
1,1-DINITROPROPANE	--	11.09	--	12.23	--
1,2-DINITROPROPANE	--	10.99	--	11.97	--
1,3-DINITROPROPANE	--	10.99	--	11.70	--
2,2-DINITROPROPANE	--	11.01	--	12.15	--
1,1,1-TRINITROPROPANE	--	11.54	--	12.77	--
1,1,2-TRINITROPROPANE	--	11.20	--	12.41	--
1,2,2-TRINITROPROPANE	--	11.37	--	12.01	--
1,2,3-TRINITROPROPANE	--	11.22	--	12.17	--
1,1,1,2-TETRANITROPROPANE	--	11.51	--	12.63	--
1,1,1,3-TETRANITROPROPANE	--	11.44	--	12.18	--
1,1,2,2-TETRANITROPROPANE	--	11.46	--	12.60	--

Table IX (cont'd)

Ionization Potentials of Normal Nitroaliphatics

NITROALIPHATIC	OBSERVED IP[a]	MINDO/3 IP[a]	MINDO/3 Error[a]	MNDO IP[a]	MNDO Error[a]
1-NITROBUTANE	10.71[d]	10.73	+0.02	11.46	+0.75
2-NITROBUTANE	10.71[d]	10.53	-0.18	11.41	+0.70
1,1-DINITROBUTANE	--	11.01	--	12.15	--
1,2-DINITROBUTANE	--	10.79	--	12.03	--
1,3-DINITROBUTANE	--	10.94	--	11.76	--
1,4-DINITROBUTANE	--	10.83	--	11.78	--
2,2-DINITROBUTANE	--	10.97	--	12.10	--
2,3-DINITROBUTANE	--	10.94	--	11.80	--
1,1,1-TRINITROBUTANE	--	11.48	--	--	--
1,1,2-TRINITROBUTANE	--	11.16	--	--	--
1,1,3-TRINITROBUTANE	--	11.21	--	--	--
1,1,4-TRINITROBUTANE	--	11.23	--	--	--
1,2,2-TRINITROBUTANE	--	11.31	--	--	--
1,2,3-TRINITROBUTANE	--	11.14	--	--	--
1,2,4-TRINITROBUTANE	--	11.22	--	--	--
1,3,3-TRINITROBUTANE	--	11.16	--	--	--
2,3,3-TRINITROBUTANE	--	11.15	--	--	--
1,1,1,4-TETRANITROBUTANE	--	11.23	--	--	--
1,1,2,2,-TETRANITROBUTANE	--	11.38	--	--	--
1-NITROPENTANE	--	10.69	--	11.46	--
2-NITROPENTANE	--	10.53	--	11.39	--
3-NITROPENTANE	--	10.44	--	11.38	--
1,1-DINITROPENTANE	--	11.04	--	12.20	--
Ave. Absolute Error	--	--	0.08	--	0.65
Ave. Error	--	--	-0.06	--	-0.65

Table IX (cont'd)

Ionization Potentials of Normal Nitroaliphatics

[a] Units are electron-volts (eV).

[b] By photoionization spectroscopy.

[c] Watanabe, K.; Nakayama, T. and Motte, J., *J. Quant. Spec.-Rad. Transfer.*, 1962, 2, 369.

[d] Dewar, M. J. S.; Shanshal, M. and Worley, S. D., *J. Amer. Chem. Soc.*, 1969, 91, 3590.

Table X

Ionization Potentials of Branched Nitroaliphatics

NITROALIPHATIC	OBSERVED IP[a]	MINDO/3 IP[a]	MINDO/3 Error[a]	MNDO IP[a]	MNDO Error[a]
2-METHYL-1-NITROPROPANE	--	10.66	--	11.44	--
2-METHYL-2-NITROPROPANE	--	10.46	--	11.35	--
2-METHYL-1,1-DINITROPROPANE	--	11.04	--	12.18	--
2-METHYL-1,2-DINITROPROPANE	--	10.96	--	11.72	--
2-METHYL-1,3-DINITROPROPANE	--	10.83	--	11.88	--
2,2-DIMETHYL-1,1-DINITROPROPANE	--	10.74	--	11.87	--

[a] Units are electron-volts (eV).

Table XI

Ionization Potentials of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	IP[a]	IP[a]	Error[a]	IP[a]	Error[a]
NITROBENZENE	9.92[b,c]	9.97	+0.05	10.33	+0.41
1,2-DINITROBENZENE	--	10.55	--	11.15	--
1,3-DINITROBENZENE	--	10.61	--	11.21	--
1,4-DINITROBENZENE	--	10.61	--	11.10	--
1,2,3-TRINITROBENZENE	--	10.94	--	11.92	--
1,2,4-TRINITROBENZENE	--	10.84	--	11.91	--
1,3,5-TRINITROBENZENE	--	11.09	--	12.10	--
1,2,3,4-TETRANITROBENZENE	--	11.11		12.55	--
1,2,3,5-TETRANITROBENZENE	--	11.15	--	12.61	--
1,2,4,5-TETRANITROBENZENE	--	11.05	--	12.57	--
PENTANITROBENZENE	--	11.38	--	13.00	--
HEXANITROBENZENE	--	11.66	--	13.31	--

Table XI (cont'd)

Ionization Potentials of Nitroaromatics

NITROAROMATIC	OBSERVED	MINDO/3		MNDO	
	IP[a]	IP[a]	Error[a]	IP[a]	Error[a]
2-NITROTOLUENE	--	9.66	--	10.15	--
3-NITROTOLUENE	--	9.69	--	10.18	--
4-NITROTOLUENE	9.82[d,e]	9.77	-0.05	10.29	+0.47
2,3-DINITROTOLUENE	--	10.26	--	10.93	--
2,4-DINITROTOLUENE	--	10.34	--	11.06	--
2,5-DINITROTOLUENE	--	10.25	--	10.95	--
2,6-DINITROTOLUENE	--	10.25	--	10.92	--
3,4-DINITROTOLUENE	--	10.26	--	11.02	--
3,5-DINITROTOLUENE	--	10.34	--	11.01	--
2,3,4-TRINITROTOLUENE	--	10.77	--	--	--
2,3,5-TRINITROTOLUENE	--	10.76	--	--	--
2,3,6-TRINITROTOLUENE	--	10.70	--	--	--
2,4,5-TRINITROTOLUENE	--	10.72	--	--	--
2,4,6-TRINITROTOLUENE	--	10.84	--	--	--
3,4,5-TRINITROTOLUENE	--	10.76	--	--	--
2,3,4,5-TETRANITROTOLUENE	--	11.02	--	--	--
2,3,4,6-TETRANITROTOLUENE	--	11.05	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	10.93	--	--	--
PENTANITROTOLUENE	--	11.26	--	--	--

[a] Units are electron-volts (eV).

[b] By photoionization spectroscopy.

[c] Watanabe, K.; Nakayama, T. and Motte, J., J. Quant. Spectr.-Rad. Transfer, 1962, 2, 369.

[d] By mass spectroscopy

[e] Crable, G. F. and Kearns, G. L., J. Phys. Chem., 1962, 66, 436.

Table XII

Ionization Potentials for Nitro-Compounds

NITRO-COMPOUND	OBSERVED	MINDO/3		MNDO	
	IP[a]	IP[a]	Error[a]	IP[a]	Error[a]
NITROAMINE	--	11.44	--	11.85	--
N-NITROETHYLAMINE	--	10.42	--	11.69	--
N-NITROBUTYLAMINE	--	10.50	--	11.67	--
N-NITRODIMETHYLAMINE	--	9.72	--	11.24	--
N-NITRODIETHYLAMINE	--	9.58	--	11.16	--
NITROETHANOL	--	10.99	--	11.56	--
3-NITRO-2-BUTANOL	--	10.58	--	11.46	--

[a] Units are electron-volts (eV).

Table XIII

Molecular Geometry of Nitromethane

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C-N	1.46	1.453	1.546
N-O	1.208	1.225	1.210
C-H	--	1.115	1.109
Bond Angle (°)			
ONO	127	131.4	121.4
ONC	116.5	114.3	119.3
HCN	--	113.6	108.8

[a] Brockway, L. O.; Beach, J. Y. and Pauling, L., J. Amer. Chem. Soc., 1935, 57, 2693. See also Rogowski, F., Berichte, 1942, 75, 244; Naturwiss., 1940, 28, 517.

Table XIV

Molecular Geometry of Tetranitromethane

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C-N	1.47	1.532	1.578
N-O	1.22	1.212	1.201
Bond Angle (°)			
ONC	116.5	113.8	118.4
NCN	109.5	112.39	110.2

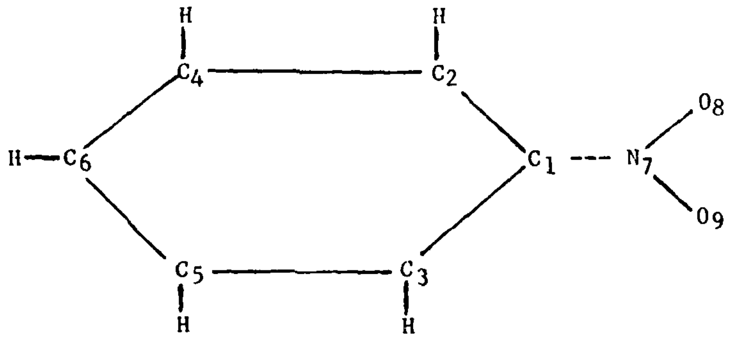
[a] Stosick, A. J., J. Amer. Chem. Soc., 1939, 61, 1127.

Table XV

Molecular Geometry of Nitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C1-C2	1.367	1.431	1.422
C2-C4	1.426	1.405	1.403
C4-C6	1.363	1.403	1.415
C1-N7	1.486	1.437	1.495
N7-O8	1.208	1.229	1.213
Ave. C-H	--	1.104	1.091
Bond Angle (°)			
C1C2C4	116	120.0	119.4
C2C4C6	121	120.7	120.3
C4C6C5	121	120.0	120.8
C3C1C2	125	118.8	119.8
N7C1C2	117	120.6	120.1
O8N7C1	118	115.2	119.8
Ave. HCC	--	120.9	120.2

[a]



[b] Trotter, J., Tetrahedron, 1960, 8, 13.

Table XVI

Molecular Geometry of m-Dinitrobenzene[a]

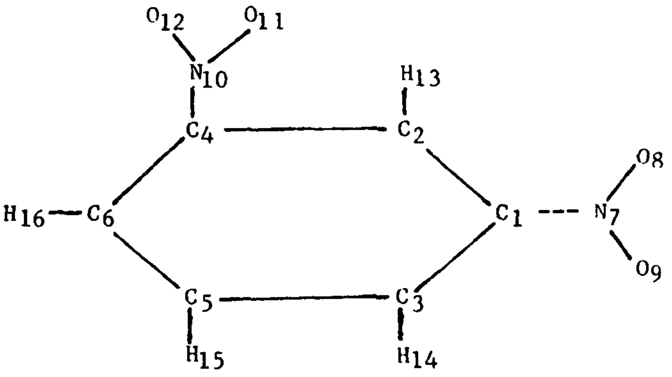
STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C1-C2	1.384	1.428	1.415
C2-C4	1.384	1.427	1.416
C4-C6	1.386	1.427	1.416
C5-C3	1.386	1.405	1.404
C1-C3	1.381	1.422	1.416
C1-N7	1.491	1.442	1.498
C4-N10	1.494	1.441	1.498
N7-O8	1.276	1.226	1.211
N7-O9	1.220	1.227	1.211
N10-O11	1.266	1.227	1.211
N10-O12	1.230	1.226	1.211
C2-H13	1.12	1.106	1.095
C3-H14	0.90	1.106	1.093
C5-H15	0.90	1.104	1.091
C6-H16	0.87	1.106	1.093
Bond Angle (°)			
C1C2C4	115.7	121.4	119.9
C2C4C6	124.0	118.4	120.1
C1C3C5	119.1	120.7	119.8
C3C1C2	123.1	130.3	120.7
C1N7O8	118.3	115.1	119.8
C1N7O9	118.3	114.6	119.5

Table XVI (cont'd)

Molecular Geometry of m-Dinitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE
C4N10O11	116.1	114.3	119.4
C4N10O11	116.8	114.7	119.8
C2C1N7	118.3	120.9	120.1
C3C1N7	118.6	121.0	120.0
C2C4N10	117.5	121.0	120.0
C6C4N10	118.4	120.6	119.9
H13C2C1	--	119.7	120.2
H14C3C1	--	122.4	120.1
H15C5C3	--	119.5	119.7
H16C6C4	--	122.3	121.7

[a]



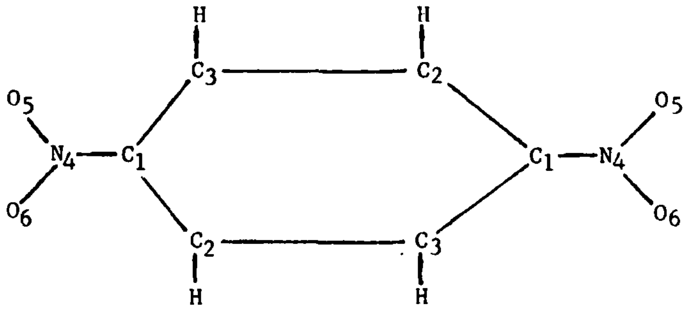
[b] Trotter, J. and Williston, C. S., Acta Cryst., 1966, 21, 285. See also Gregory, N. W. and Lassettre, E. N., J. Amer. Chem. Soc., 1947, 69, 102; Archer, E. M., Proc., Royal Soc. (London), 1946, 188A, 51.

Table XVII

Molecular Geometry of p-Dinitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C1-C2	1.385	1.425	1.417
C2-C3	1.385	1.405	1.408
C1-C3	1.385	1.425	1.415
C1-C4	1.41	1.445	1.503
N4-O5	1.23	1.227	1.211
N4-O6	1.23	1.228	1.211
Ave. C-H	--	1.104	1.092
Bond Angle (°)			
C1C2C3	--	120.6	119.9
C2C3C1	--	120.8	120.0
C3C1C2	--	118.5	119.8
O5N4C1	118.5	114.8	119.6
O6N4C1	117.5	114.8	119.6
N4C1C2	--	120.8	120.1
N4C1C3	--	120.7	120.1
C1C2H	--	123.1	122.2
C2C3H	--	116.2	117.6

[a]



[b] Llewellyn, F. J., J. Chem. Soc., 1947, 884. See also Banerjee, K., Philosoph. Mag. and J. Sci., 1934, 18, 1004; James, R. W.; King, G. and Horrocks, H. Proc., Royal Soc. (London), 1935, 153A, 225.

Table XVIII

Molecular Geometry of 1,3,5-Trinitrobenzene

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
C-C	1.380	1.426	1.415
C-N	1.480	1.448	1.502
N-O	1.208	1.225	1.209
C-H	1.071	1.106	1.096
Bond Angle (°)			
CCC	120.1	120.1	119.9
NCC	118.4	120.6	119.8
ONC	117.1	114.8	119.5
HCC	122.5	119.1	120.0

[a] Choi, C. S. and Abel, J. E., Acta Cryst., 1972, B28, 193.

Table XIX

Molecular Geometry of 2,4,6-Trinitrotoluene[a]

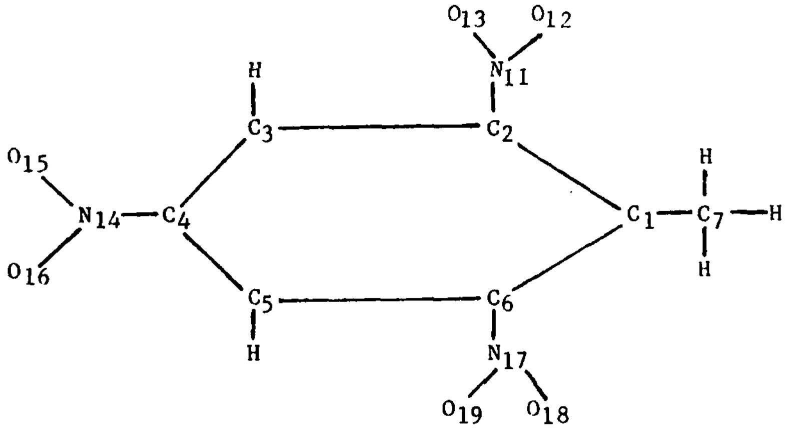
STRUCTURAL PARAMETER	OBSERVED[b] VALUE Form A	Form B	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)				
C1-C2	1.408	1.379	1.444	--
C2-C3	1.373	1.387	1.422	--
C3-C4	1.375	1.373	1.422	--
C4-C5	1.415	1.344	1.421	--
C5-C6	1.364	1.383	1.420	--
C1-C7	1.505	1.507	1.500	--
C2-N11	1.449	1.494	1.447	--
N11-O12	--	--	1.224	--
N11-O13	--	--	1.224	--
C4-N14	1.443	1.482	1.447	--
N14-O15	--	--	1.225	--
N14-O16	--	--	1.225	--
C6-N17	1.496	1.459	1.445	--
N17-O18	--	--	1.223	--
N17-O19	--	--	1.224	--
Ave Methyl C-H	--	--	1.110	--
Ave Arom. C-H	--	--	1.108	--
Bond Angle (°)				
C1C2C3	--	--	122.1	--
C2C3C4	--	--	121.2	--
C3C4C5	--	--	117.8	--
C4C5C6	--	--	121.5	--
C7C1C2	--	--	122.0	--
N11C2C3	--	--	115.7	--
O12N11C2	--	--	113.6	--

Table XIX (cont'd)

Molecular Geometry of 2,4,6-Trinitrotoluene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE Form A	Form B	MINDO/3 VALUE	MNDO VALUE
O13N11C2	--	--	113.7	--
N14C4C5	--	--	121.2	--
O15N14C4	--	--	114.6	--
O16N14C4	--	--	114.6	--
N17C6C1	--	--	121.4	--
O18N17C6	--	--	114.2	--
O19N17C6	--	--	113.4	--
Ave. Methyl HCC	--	--	113.6	--
Ave. Arom. HCC	--	--	119.4	--

a



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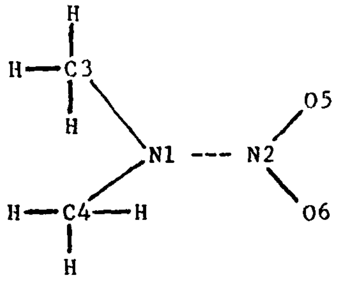
[b] Carper, W. R.; Davis, L. P. and Extine, M. W., J. Phys. Chem., 1982, 86, 459.

Table XX

Molecular Geometry of N-Nitrodimethylamine[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE
Bond Distance (Å)			
N1-C3	1.41	1.429	1.482
N1-C4	1.41	1.430	1.485
N1-N2	1.33	1.345	1.423
N2-O5	1.21	1.223	1.204
N2-O6	1.21	1.223	1.210
Ave C-H	--	1.120	1.113
Bond Angle (°)			
C3N1C4	--	117.8	115.8
C3N1N2	123	120.7	115.4
O5N2N1	118	113.3	116.4
O6N2N1	118	115.3	120.1
Ave. HCN	--	113.7	110.6

[a]



[b] Urbanski, T., Chemistry and Technology of Explosives (The Macmillan Co.; New York), 1964. See also Costain, W. and Cox, E. G., Nature, 1947, 160, 826.