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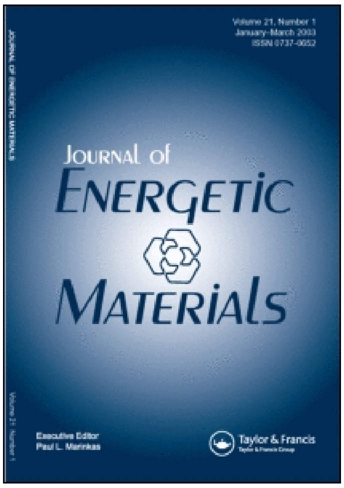

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MINDO/3, MNDO and AM1 calculations for nitro compounds

Larry P. Davis[a]; Donn Storch[a]; R. Martin Guidry[a]
[a] Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, Colorado

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MINDO/3, MNDO AND AM1 CALCULATIONS FOR NITRO COMPOUNDS

Larry P. Davis, Donn Storch, and R. Martin Guidry
Frank J. Seiler Research Laboratory
USAF Academy, Colorado Springs, Colorado 80840

ABSTRACT

Although the MINDO/3, MNDO and AM1 molecular orbital programs accurately predict physical properties for a wide variety of classes of chemical compounds, their ability to estimate the physcial properties of nitro-compounds has not been rigorously tested. This paper compares MINDO/3, MNDO and AM1 calculations to each other and to available experimental data for 105 nitro-compounds -- both aliphatic and aromatic. Properties evaluated include heats of formation, dipole moments, ionization potentials and molecular geometries. In general MINDO/3 predicts heats of formation, dipole moments and ionization potentials more accurately than MNDO and AM1. All three semi-empirical methods accurately predict molecular geometries.

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INTRODUCTION

Many investigators have used a variety of methods to perform molecular orbital calculations on nitro compounds, 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, MNDO and AM1 programs [8-10]. This paper compares the MINDO/3, MNDO and AM1 molecular orbital calculations to each other and to available experimental data for 105 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 to use calculational methods to aid in elucidating the kinetics and mechanisms of thermochemical decompositions of nitro-compounds.

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EXPERIMENTAL

The MINDO/3, MNDO and AM1 molecular orbital programs developed by M.J.S. Dewar, *et al*. [8-10] were used to calculate the geometries, heats of formation, ionization potentials and dipole moments for 105 aliphatic and aromatic nitro-compounds. We then compared calculated properties to available experimental data.

Molecular orbital calculations were done on a Digital Equipment Corporation VAX-11/780 minicomputer.

RESULTS AND DISCUSSIONS

Heats of Formation

Table 1 shows the observed heats of formation (ΔH_f at 25°C) and those calculated with MINDO/3, MNDO and AM1 for a series of normal nitroaliphatics. MINDO/3 predicts the enthalpies of formation much better than MNDO and AM1. Furthermore, MINDO/3 generally correctly predicts whether the heat of formation is exothermic or endothermic. MNDO and AM1, however, always predict heats of formation which are too endothermic. MNDO-calculated heats of formation are often several hundred per cent too endothermic.

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. AM1 yields an average absolute error of 20.9 kcal/mole and an average error of +20.9 kcal/mole.

As more nitro-groups are added to a molecule, MNDO and AM1 predict increasingly more endothermic heats of formation -- a 20-50 kcal/mole increase per nitro group added for MNDO and a 5-25 kcal/mole increase for AM1. 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

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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 as nitro group content approaches the maximum possible.

As carbon content increases, all three methods estimate a more exothermic enthalpy -- the same direction as actually observed. Each methylene group added increases the exothermicity by 5-10 kcal/mole. MINDO/3 consistently predicts the enthalpy change very near the experimentally measured value.

Table 2 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 and AM1 little change (1-3 kcal/mole) occurs.

Heats of formation for nitroaromatics are presented in Table 3. As with nitroaliphatics, MNDO and AM1 predict 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 and AM1.

With MNDO, adding an additional nitro group to the aromatic ring increases the endothermic heat by 20-30 kcal/mole while with AM1 the endothermic heat rises 10-20 kcal/mole for each

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nitro group added. With MINDO/3 the heats become more exothermic by 8-15 kcal/mole for each nitro group added to the ring. The position of the nitro groups on the ring affects the heats of formation very little (1-8 kcal/mole) with any of the calculational methods.

Replacing a ring hydrogen with a methyl group makes the heats more exothermic by 2-7 kcal/mole for all three methods. This effect decreases as the number of nitro substituents increases.

Heats of formation for several nitroamines and nitroalcohols are shown in Table 4. 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. MINDO/3, MNDO and AM1 heats become more exothermic when the hydroxyl function is present - by 40 kcal/mole in each case.

The amine and N-nitro substituents also cause exothermicity, but to a lesser degree - less than 10 kcal/mole. MINDO/3, MNDO and AM1 all predict more exothermic enthalpies for the nitroamines. As with other nitro-compounds MINDO/3 more accurately predicts heats of formation of nitroamines and nitro- alcohols.

Dipole Moments

Calculated and observed dipole moments for normal nitroaliphatics are compared in Table 5. MNDO overestimates the dipole

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moments while MINDO/3 generally predicts the dipole moments to within 0.2 D. Although AM1 values fall both below and above observed values, they are generally 0.5 D or more from the experimental value. With MINDO/3 the average absolute error is 0.17 D while the average error is - 0.02 D. AM1 yields error values of 0.57 D and +0.47 D respectively. For MNDO the average absolute error and average error are both 0.63 D.

All three methods tend to change in the same direction as the nitroaliphatic molecule is varied. They 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 5-8. 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 higher temperatures increase the dipole moment slightly.

Adding or repositioning nitro groups 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 beyond the propanes.

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Table 6 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 and AM1. 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 7. MNDO and AM1 nearly always predict dipole moments higher than MINDO/3. The major exceptions are when the dipole mements are near zero. Of the three 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. For AM1 they are 0.94 D and +0.92 D respectively. The high errors could be due, in part, to the sparsity 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 all three methods, the position of the nitro groups around the ring affects the calculated 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.

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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 8 contains dipole moment data for nitroamines and nitroalcohols. The same trends described above are evident here. MNDO- and AM1-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 9. Only ionization potentials measured using photoionization spectroscopy are reported. Electron impact values[11] are too inaccurate for comparing to calculated values. As with heats of formation and dipole moments, MINDO/3 predicts ionization potentials better than MNDO and AM1. 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 while for AM1 they are both 0.70 eV. Furthermore, MNDO and AM1 nearly always predict ionization potentials higher than those estimated by MINDO/3.

The same trends in ionization potential are predicted by MINDO/3, MNDO and AM1. Additional nitro groups 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

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ionization potential very little. Adding a methylene group decreases the ionization potential slightly. The effect disappears at higher carbon numbers (pentanes).

Branched nitroaliphatics again show the same tendencies as the normal nitroaliphatics. All three methods mirror these trends. Table 10 presents these results. Branching with a single methyl group generally slightly decreases the calculated ionization potential.

Table 11 compares ionization potentials of nitroaromatics calculated by MINDO/3, MNDO amd AM1 to observed values. MINDO/3 consistently estimates a lower ionization potential than MNDO and AM1 by 0.4-1.7 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 and AM1. 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 any of the methods. Replacing a ring hydrogen with a methyl group reduces the ionization potential by 0.1-0.4 eV with all three methods.

In Table 12 are shown ionization potentials calculated for nitroamines and nitroalcohols. Again trends similar to those with nitroaliphatics are evident. MNDO and AM1 predict ioniza-

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tion 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 13-20 compare the observed data to calculated structural parameters using MINDO/3, MNDO and AM1 for nitroaliphatics and nitroaromatics. Molecular geometries were calculated using these methods for all 105 nitroaliphatics and nitroaromatics discussed; however, experimental data for comparison are not available for most. Comparing the calculated values, we find that generally MINDO/3 predicts shorter C-N distances and longer C-C and N-O distances. The differences are fairly small -- always less than 0.1 Å and usually less than 0.02 Å. All three methods calculate nearly 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 by 1-6° than that calculated by MNDO and AM1. To within 2° all three methods calculate the same HCC angles. For CCC bond angles no general trend occurs although the methods usually agree to within 6°.

Calculated values shown in Tables 13-20 are typical of those obtained for all molecules by the three calculational methods.

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All three methods predict reasonably accurate molecular geometries for nitroaliphatics and nitroaromatics. There are few general trends in how the methods predict parameters. For nitroaromatics all three methods estimate C-C bond distances to within 0.04 Å and C-H bond distances to within 0.02 Å. MNDO and AM1 generally predict C-N bond distances for nitroaromatics to better than 0.02 Å while MINDO/3 C-N bonds are usually too short by 0.04-0.05 Å. All methods calculate nitroaromatic bond angles to within ± 3° of each other and observed data.

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TABLE 1

Heats of Formation of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
NITROMETHANE	-12.2[b]	-10.5	+1.7	+3.4	+15.6	-9.9	+2.3
DINITROMETHANE	-14.3[c]	-15.9	-1.6	+28.5	+42.8	+4.0	+18.3
TRINITROMETHANE	-3.2[d]	-23.9	-20.7	+60.1	+63.3	+25.2	+28.4
TETRANITROMETHANE	+18.5[c]	-32.2	-50.7	+107.1	+88.6	+53.9	+35.4
NITROETHANE	-23.5[b]	-20.5	+3.0	-1.9	+21.6	-16.8	+6.7
1,1-DINITROETHANE	-24.1[c,e]	-21.6	+2.5	+25.6	+49.7	-0.2	+23.9
1,2-DINITROETHANE	-22.9[c,e]	-18.6	+4.3	+23.3	+46.2	-8.3	+14.6
1,1,1-TRINITROETHANE	-12.4[c,e]	-25.5	-13.1	+69.0	+81.4	+27.5	+39.9
1,1,2-TRINITROETHANE	--	-20.0	--	+59.3	--	+8.0	--
1,1,1,2-TETRANITROETHANE	--	-18.1	--	+94.2	--	+38.6	--
1,1,2,2-TETRANITROETHANE	--	-19.8	--	+86.1	--	+28.5	--
PENTANITROETHANE	--	-12.3	--	+131.3	--	+58.6	--
HEXANITROETHANE	+35.8[f]	-13.0	-48.8	+178.8	+143.0	+91.7	+55.9
1-NITROPROPANE	-29.7[b]	-26.7	+3.0	-6.9	+22.8	-23.6	+6.1
2-NITROPROPANE	-33.9[b]	-22.0	+11.9	-2.3	+31.6	-21.4	+12.5
1,1-DINITROPROPANE	-25.9[b]	-28.1	-2.2	+22.3	+48.2	-7.9	+18.0

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TABLE 1 (cont'd)

Heats of Formation of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
1,2-DINITROPROPANE	--	-16.1	--	+22.4	--	-10.6	--
1,3-DINITROPROPANE	-31.6[b,c]	-25.4	+6.2	+15.2	+46.8	-18.2	+13.4
2,2-DINITROPROPANE	-27.0[c,e]	-19.0	+8.0	+25.6	+52.6	-4.8	+22.2
1,1,1-TRINITROPROPANE	-18.4[c]	-25.8	-7.4	+59.2	+77.6	+17.3	+35.7
1,1,2-TRINITROPROPANE	--	-17.9	--	+55.0	--	+3.13	--
1,2,2-TRINITROPROPANE	--	-11.3	--	+57.9	--	+7.5	--
1,2,3-TRINITROPROPANE	--	-17.5	--	+46.9	--	-6.3	--
1,1,1,2-TETRANITROPROPANE	--	-10.6	--	+97.1	--	+30.9	--
1,1,1,3-TETRANITROPROPANE	--	-20.0	--	+84.2	--	+26.2	--
1,1,2,2-TETRANITROPROPANE	--	-9.2	--	+97.4	--	+30.9	--
1-NITROBUTANE	-34.4[b]	-32.6	+1.8	-11.4	+23.0	-30.4	+4.4
2-NITROBUTANE	-39.1[b]	-29.0	+10.1	-5.1	+34.0	-27.7	+11.4
1,1-DINITROBUTANE	-34.1[c]	-29.8	+4.3	+20.8	+54.9	-12.6	+21.5
1,2-DINITROBUTANE	--	-22.1	--	+19.2	--	-19.9	--
1,3-DINITROBUTANE	--	-19.5	--	+16.7	--	-21.8	--
1,4-DINITROBUTANE	-38.9[c,e]	-33.0	+5.9	+6.4	+45.3	-27.1	+11.8

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TABLE 1 (cont'd)

Heats of Formation of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
2,2-DINITROBUTANE	--	-20.7	--	+22.1	--	-11.0	--
2,3-DINITROBUTANE	--	-20.7	--	+18.5	--	-18.2	--
1,1,1-TRINITROBUTANE	--	-30.5	--	+17.4	--	+9.2	--
1,1,2-TRINITROBUTANE	--	-25.1	--	+46.1	--	-2.7	--
1,1,3-TRINITROBUTANE	--	-24.1	--	+40.9	--	-7.6	--
1,1,4-TRINITROBUTANE	--	-32.2	--	+36.3	--	-11.6	--
1,2,2-TRINITROBUTANE	--	-19.2	--	+52.1	--	+0.3	--
1,2,3-TRINITROBUTANE	--	-6.3	--	+43.6	--	-8.8	--
1,2,4-TRINITROBUTANE	--	-22.0	--	+37.1	--	-18.9	--
1,3,3-TRINITROBUTANE	--	-17.5	--	+45.7	--	-5.5	--
2,2,3-TRINITROBUTANE	--	-10.7	--	+54.5	--	+2.5	--
1,1,1,2-TETRANITROBUTANE	--	-20.9	--	+88.1	--	+24.4	--
1,1,1,3-TETRANITROBUTANE	--	-25.2	--	+80.2	--	+17.7	--
1,1,1,4-TETRANITROBUTANE	-24.9[c,e]	-27.8	-2.9	+73.9	+98.8	+14.3	+39.2
1,1,2,2-TETRANITROBUTANE	--	-10.5	--	+90.2	--	+21.2	--
1,1,2,3-TETRANITROBUTANE	--	-13.1	--	+79.6	--	+11.3	--

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TABLE 1 (cont'd)

Heats of Formation of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
1,1,2,4-TETRANITROBUTANE	--	-21.6	--	+69.8	--	+3.6	--
1,1,3,3-TETRANITROBUTANE	--	-18.1	--	+79.8	--	+14.1	--
1,1,3,4-TETRANITROBUTANE	--	-23.1	--	+69.2	--	+3.7	--
1,1,4,4-TETRANITROBUTANE	--	-32.2	--	+66.3	--	+5.2	--
1,2,2,3-TETRANITROBUTANE	--	-5.2	--	+85.8	--	+13.5	--
1,2,2,4-TETRANITROBUTANE	--	-13.6	--	+76.7	--	+5.1	--
1,2,3,3-TETRANITROBUTANE	--	-6.0	--	+82.4	--	+10.6	--
1,2,3,4-TETRANITROBUTANE	--	-11.9	--	+71.7	--	-1.2	--
2,2,3,3-TETRANITROBUTANE	--	+2.4	--	+98.4	--	+26.5	--
1-NITROPENTANE	--	-38.4	--	-14.6	--	-36.9	--
2-NITROPENTANE	--	-33.4	--	-12.8	--	-34.1	--
3-NITROPENTANE	--	-31.7	--	-8.3	--	-30.7	--
1,1-DINITROPENTANE	-38.2[c,e]	-40.2	-2.0	+12.9	+51.1	-21.4	+16.8
Ave. Absolute Error	--	--	9.9	--	52.0	--	20.9
Ave. Error	--	--	-4.1	--	+52.0	--	+20.9

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TABLE 1 (Cont'd)
Heats of Formation of Normal Nitroaliphatics

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

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TABLE 2

Heats of Formation of Branched Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
2-METHYL-1-NITROPROPANE	--	-24.3	--	-8.0	--	-28.5	--
2-METHYL-2-NITROPROPANE	--	-16.6	--	-3.4	--	-23.9	--
2-METHYL-1,1-DINITROPROPANE	--	-21.5	--	+21.9	--	-12.9	--
2-METHYL-1,2-DINITROPROPANE	--	-10.3	--	+23.2	--	--	--
2-METHYL-1,3-DINITROPROPANE	--	-19.1	--	+17.4	--	-23.1	--
2,2-DIMETHYL-1,3-DINITROPROPANE	--	-5.8	--	+21.0	--	-25.3	--

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

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TABLE 3

Heats of Formation of Nitroaromatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
NITROBENZENE	+15.4[b,c]	+12.7	-2.7	+38.2	+22.8	+25.4	+10.0
1,2-DINITROBENZENE	--	-2.5	--	+61.4	--	+39.2	--
1,3-DINITROBENZENE	--	-2.4	--	+58.7	--	+33.4	--
1,4-DINITROBENZENE	--	-0.2	--	+58.5	--	+33.4	--
1,2,3-TRINITROBENZENE	--	-19.0	--	+91.0	--	+55.8	--
1,2,4-TRINITROBENZENE	--	-20.0	--	+81.9	--	+50.1	--
1,3,5-TRINITROBENZENE	--	-9.6	--	+84.2	--	+44.9	--
1,2,3,4-TETRANITROBENZENE	--	-30.9	--	+112.5	--	+72.1	--
1,2,3,5-TETRANITROBENZENE	--	-31.6	--	+110.1	--	+68.5	--
1,2,4,5-TETRANITROBENZENE	--	-32.0	--	+109.9	--	+77.3	--
PENTANITROBENZENE	--	-39.9	--	+143.8	--	+92.9	--
HEXANITROBENZENE	--	-36.4	--	+179.5	--	+117.4	--
2-NITROTOLUENE	+9.3[d,e]	+6.9	-2.4	+32.1	+22.8	+19.0	+9.7
3-NITROTOLUENE	+5.9[d,e]	+6.7	+0.8	+30.1	+24.2	+17.6	+11.7
4-NITROTOLUENE	--	+6.3	--	+29.9	--	+17.3	--
2,3-DINITROTOLUENE	--	-9.7	--	+54.8	--	+32.0	--
2,4-DINITROTOLUENE	--	-10.3	--	+52.5	--	+26.5	--

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TABLE 3 (cont'd)

Heats of Formation of Nitroaromatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
2,5-DINITROTOLUENE	--	-3.8	--	+56.2	--	+27.1	--
2,6-DINITROTOLUENE	--	-1.6	--	+59.8	--	+30.3	--
3,4-DINITROTOLUENE	--	-12.8	--	+51.0	--	+30.6	--
3,5-DINITROTOLUENE	--	-5.7	--	+51.3	--	+25.4	--
2,3,4-TRINITROTOLUENE	--	-22.3	--	+78.5	--	+46.9	--
2,3,5-TRINITROTOLUENE	--	-20.7	--	+75.6	--	--	--
2,3,6-TRINITROTOLUENE	--	-17.8	--	+78.5	--	--	--
2,4,5-TRINITROTOLUENE	--	-22.2	--	+75.2	--	--	--
2,4,6-TRINITROTOLUENE	+12.9	-16.9	-29.8	+75.4	+62.5	+44.7	+31.8
3,4,5-TRINITROTOLUENE	--	-25.9	--	+76.5	--	+45.8	--
2,3,4,5-TETRANITROTOLUENE	--	-34.0	--	+107.0	--	+65.0	--
2,3,4,6-TETRANITROTOLUENE	--	-30.8	--	+107.4	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	-30.0	--	+107.7	--	--	--
PENTANITROTOLUENE	--	-37.8	--	+141.6	--	--	--
Ave. Absolute Error	--	--	8.9	--	33.1	--	15.8
Ave Error	--	--	-8.5	--	+33.1	--	+15.8

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TABLE 3 (cont'd)

Heats of Formation of Nitroaromatics[a]

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

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

[c] Y. Y. Maksimov, Russ J. Phys. Chem., 42, 1550 (1968).

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

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

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

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TABLE 4

Heats of Formation for Nitroamines and Nitroalcohols[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	ΔH_f	ΔH_f	Error	ΔH_f	Error	ΔH_f	Error
NITROAMINE	--	-30.2	--	+23.1	--	+12.9	--
N-NITROETHYLAMINE	--	-32.2	--	+13.3	--	+9.4	--
N-NITROBUTYLAMINE	--	-47.8	--	+4.3	--	-4.2	--
N-NITRODIMETHYLAMINE	-3.2[b,c]	-4.0	-0.8	+23.1	+26.3	+21.7	+24.9
N-NITRODIETHYLAMINE	-13.8[c]	-21.5	-7.7	+16.0	+29.8	+12.5	+26.3
NITROETHANOL	-75.1[d,e]	-64.5	+10.6	-45.2	+29.9	-60.1	+15.0
3-NITRO-2-BUTANOL	--	-64.6	--	-42.2	--	-69.5	--
Ave. Absolute Error	--	--	6.4	--	28.7	--	22.1
Ave. Error	--	--	+0.7	--	+28.7	--	+22.1

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

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

[c] R. C. Cass, S. E. Fletcher, C. T. Mortimer, P. G. Quincey and H. D. Springall, J. Chem. Soc., 1958, 958 (1958).

[d] L. Medard and M. Thomas, Mem. Poudres, 35, 155 (1953).

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

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TABLE 5

Dipole Moments of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
NITROMETHANE	3.46[b,c]	3.53	+0.07	4.18	+0.72	4.17	+0.71
DINITROMETHANE	--	3.37	--	4.17	--	3.71	--
TRINITROMETHANE	2.63[d,e]	1.93	-0.70	2.79	+0.16	2.26	-0.37
TETRANITROMETHANE	0.19[f,g]	0.12	-0.07	0.55	+0.36	0.10	-0.09
NITROETHANE	3.58[h,i]	3.62	+0.04	4.29	+0.71	4.39	+0.81
1,1-DINITROETHANE	3.50[d,e]	3.94	+0.44	4.79	+1.29	3.96	+0.46
1,2-DINITROETHANE	--	5.62	--	6.77	--	0.01	--
1,1,1-TRINITROETHANE	3.20[d,e]	3.14	-0.06	3.57	+0.37	3.37	+0.17
1,1,2-TRINITROETHANE	--	4.81	--	5.86	--	5.83	--
1,1,1,2-TETRANITROETHANE	--	2.69	--	3.15	--	2.54	--
1,1,2,2-TETRANITROETHANE	--	0.07	--	0.02	--	0.02	--
PENTANITROETHANE	--	1.63	--	1.98	--	1.83	--
HEXANITROETHANE	--	0.14	--	0.02	--	0.03	--
1-NITROPROPANE	3.72[j,k]	3.70	-0.02	4.35	+0.63	4.51	+0.79
2-NITROPROPANE	3.73[j,k]	3.72	-0.01	4.37	+0.64	4.53	+0.80
1,1-DINITROPROPANE	--	3.95	--	4.72	--	4.16	--

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TABLE 5 (cont'd)

Dipole Moments of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
1,2-DINITROPROPANE	--	3.60	--	4.49	--	4.06	--
1,3-DINITROPROPANE	--	6.12	--	7.48	--	3.94	--
2,2-DINITROPROPANE	--	4.29	--	5.24	--	4.80	--
1,1,1-TRINITROPROPANE	--	3.54	--	4.41	--	3.91	--
1,1,2-TRINITROPROPANE	--	3.85	--	4.56	--	3.94	--
1,2,2-TRINITROPROPANE	--	5.43	--	6.79	--	6.43	--
1,2,3-TRINITROPROPANE	--	4.92	--	6.10	--	6.03	--
1,1,1,2-TETRANITROPROPANE	--	3.46	--	4.04	--	3.82	--
1,1,1,3-TETRANITROPROPANE	--	0.77	--	0.76	--	0.78	--
1,1,2,2-TETRANITROPROPANE	--	4.32	--	5.47	--	4.92	--
1-NITROBUTANE	3.61[e,j]	3.72	+0.11	4.36	+0.75	4.56	+0.95
2-NITROBUTANE	--	3.79	--	4.46	--	4.46	--
1,1-DINITROBUTANE	--	4.04	--	4.79	--	4.49	--
1,2-DINITROBUTANE	--	1.50	--	1.61	--	1.06	--
1,3-DINITROBUTANE	--	3.32	--	3.64	--	3.57	--
1,4-DINITROBUTANE	--	0.02	--	0.00	--	0.01	--

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TABLE 5 (cont'd)

Dipole Moments of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
2,2-DINITROBUTANE	--	4.54	--	5.34	--	5.00	--
2,3-DINITROBUTANE	--	5.01	--	6.47	--	6.56	--
1,1,1-TRINITROBUTANE	--	3.67	--	4.67	--	4.04	--
1,1,2-TRINITROBUTANE	--	4.37	--	4.76	--	4.46	--
1,1,3-TRINITROBUTANE	--	3.75	--	4.21	--	4.13	--
1,1,4-TRINITROBUTANE	--	3.38	--	3.80	--	3.57	--
1,2,2-TRINITROBUTANE	--	5.92	--	7.02	--	6.86	--
1,2,3-TRINITROBUTANE	--	3.78	--	3.86	--	3.34	--
1,2,4-TRINITROBUTANE	--	5.69	--	4.97	--	6.20	--
1,3,3-TRINITROBUTANE	--	2.53	--	3.71	--	4.07	--
2,2,3-TRINITROBUTANE	--	3.27	--	3.37	--	3.04	--
1,1,1,2-TETRANITROBUTANE	--	3.82	--	4.42	--	3.92	--
1,1,1,3-TETRANITROBUTANE	--	4.18	--	5.30	--	4.76	--
1,1,1,4-TETRANITROBUTANE	--	2.46	--	3.69	--	3.44	--
1,1,2,2-TETRANITROBUTANE	--	4.86	--	5.50	--	4.99	--
1,1,2,3-TETRANITROBUTANE	--	3.70	--	4.40	--	4.00	--

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TABLE 5 (cont'd)

Dipole Moments of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
1,1,2,4-TETRANITROBUTANE	--	0.79	--	0.65	--	0.55	--
1,1,3,3-TETRANITROBUTANE	--	4.30	--	5.34	--	5.23	--
1,1,3,4-TETRANITROBUTANE	--	4.84	--	5.89	--	5.65	--
1,1,4,4-TETRANITROBUTANE	--	0.30	--	0.10	--	0.03	--
1,2,2,3-TETRANITROBUTANE	--	4.07	--	5.32	--	5.57	--
1,2,2,4-TETRANITROBUTANE	--	2.68	--	3.27	--	3.55	--
1,2,3,3-TETRANITROBUTANE	--	3.59	--	3.36	--	3.91	--
1,2,3,4-TETRANITROBUTANE	--	0.12	--	0.06	--	0.02	--
2,2,3,3-TETRANITROBUTANE	--	0.76	--	0.60	--	0.32	--
1-NITROPENTANE	--	3.71	--	4.34	--	4.38	--
2-NITROPENTANE	--	3.87	--	4.48	--	4.51	--
3-NITROPENTANE	--	3.82	--	4.46	--	4.53	--
1,1-DINITROPENTANE	--	4.14	--	4.84	--	4.39	--
Ave. Absolute Error	--	--	0.17	--	0.63	--	0.57
Ave. Error	--	--	-0.02	--	+0.63	--	+0.47

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TABLE 5 (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] E. Tannenbaum, R. J. Myers and W. D. Gwinn, *J. Chem Phys.*, *25*, 42 (1956).

[d] Benzene solution at 25°C.

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

[f] Carbon tetrachloride solution at 25°C.

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

[h] Gas at 25°C.

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

[j] Gas at ~100°C.

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

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TABLE 6

Dipole Moments of Branched Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
2-METHYL-1-NITROPROPANE	3.71[b,c]	3.81	+0.10	4.45	+0.74	4.52	+0.81
2-METHYL-2-NITROPROPANE	3.74[b,c]	3.91	+0.17	4.63	+0.89	4.66	+0.92
2-METHYL-1,1-DINITROPROPANE	--	4.43	--	5.29	--	4.77	--
2-METHYL-1,2-DINITROPROPANE	--	5.38	--	6.39	--	--	--
2-METHYL-1,3-DINITROPROPANE	--	2.61	--	3.49	--	3.81	--
2,2-DIMETHYL-1,3-DINITROPROPANE	--	1.72	--	2.63	--	3.10	--
Ave. Absolute Error	--	--	0.14	--	0.82	--	+0.87
Ave. Error	--	--	+0.14	--	+0.82	--	+0.87

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

[b] Gas at ~100°C.

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

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TABLE 7

Dipole Moments of Nitroaromatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
NITROBENZENE	$4.23^{b,c}$	5.11	+0.88	5.37	+1.14	5.24	+1.01
1,2-DINITROBENZENE	$6.05^{d,e}$	7.22	+1.17	8.03	+1.98	7.77	+1.72
1,3-DINITROBENZENE	$4.10^{f,g}$	4.60	+0.50	5.00	+0.90	4.84	+0.74
1,4-DINITROBENZENE	$0.0^{d,h}$	0.04	+0.04	0.05	+0.05	0.02	+0.02
1,2,3-TRINITROBENZENE	--	7.34	--	8.31	--	7.86	--
1,2,4-TRINITROBENZENE	--	3.77	--	4.26	--	4.03	--
1,3,5-TRINITROBENZENE	$0.0^{d,h}$	0.09	+0.09	0.07	+0.07	0.02	+0.02
1,2,3,4-TETRANITROBENZENE	--	5.71	--	6.67	--	6.29	--
1,2,3,5-TETRANITROBENZENE	--	3.08	--	3.63	--	3.26	--
1,2,4,5-TETRANITROBENZENE	--	0.02	--	0.01	--	0.03	--
PENTANITROBENZENE	--	2.90	--	3.44	--	3.12	--
HEXANITROBENZENE	--	0.07	--	0.01	--	0.10	--
2-NITROTOLUENE	$3.97^{i,g}$	4.69	+0.72	5.15	+1.18	5.03	+1.06
3-NITROTOLUENE	$4.41^{i,g}$	5.15	+0.74	5.42	+1.01	5.44	+1.03
4-NITROTOLUENE	$4.72^{i,g}$	5.35	+0.63	5.50	0.78	5.72	+1.00
2,3-DINITROTOLUENE	$5.81^{d,g}$	7.21	+1.40	8.23	2.42	7.96	+2.15

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TABLE 7 (cont'd)

Dipole Moments of Nitroaromatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
2,4-DINITROTOLUENE	4.33[d,h]	4.90	+0.57	5.37	1.04	5.45	+1.12
2,5-DINITROTOLUENE	0.58[d,h]	0.74	+0.16	0.67	0.09	0.83	+0.25
2,6-DINITROTOLUENE	2.81[d,h]	3.51	+0.70	4.13	1.32	3.69	+0.88
3,4-DINITROTOLUENE	6.38[d,g]	7.40	+1.02	8.24	1.86	8.34	+1.96
3,5-DINITROTOLUENE	4.33[d,h]	4.88	+0.55	5.19	0.86	5.34	+1.01
2,3,4-TRINITROTOLUENE	--	8.02	--	8.74	--	8.71	--
2,3,5-NITROTROTOLUENE	--	4.12	--	4.59	--	--	--
2,3,6-TRINITROTOLUENE	--	3.34	--	3.78	--	--	--
2,4,5-TRINITROTOLUENE	--	4.54	--	4.83	--	--	--
2,4,6-TRINITROTOLUENE	1.37[d,j]	1.47	+0.10	0.94	-0.41	1.25	-0.12
3,4,5-TRINITROTOLUENE	--	7.78	--	8.71	--	8.82	--
2,3,4,5-TETRANITROTOLUENE	--	6.55	--	7.34	--	7.30	--
2,3,4,6-TETRANITROTOLUENE	--	3.85	--	4.22	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	1.23	--	0.98	--	--	--
PENTANITROTOLUENE	--	4.24	--	4.51	--	--	--
Ave Absolute Error	--	--	0.62	--	0.99	--	0.94
Ave. Error	--	--	+0.62	--	+0.95	--	+0.92

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TABLE 7 (cont'd)
Dipole Moments of Nitroaromatics

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

[b] Gas at 25°C.

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

[d] Benzene solution at 25°C.

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

[f] Hexane solution at 25°C.

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

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

[i] Hexane solution at 30°C.

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

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TABLE 8

Dipole Moments for Nitroamines and Nitroalcohols[a]

NITRO-COMPOUND	OBSERVED	MINDO/3		MNDO		AM1	
	μ	μ	Error	μ	Error	μ	Error
NITROAMINE	3.78[b,c]	3.94	0.16	4.01	0.23	4.20	+0.42
N-NITROETHYLAMINE	--	4.18	--	4.28	--	4.78	--
N-NITROBUTYLAMINE	--	4.52	--	4.40	--	4.93	--
N-NITRODIMETHYLAMINE	4.61[b,d]	3.02	-1.59	3.91	-0.70	4.67	+0.06
N-NITRODIETHYLAMINE	--	3.13	--	3.81	--	4.60	--
NITROETHANOL	--	3.51	--	3.88	--	3.78	--
3-NITRO-2-BUTANOL	--	3.55	--	3.95	--	3.42	--
Ave. Absolute Error	--	--	0.88	--	0.46	--	0.24
Ave Error	--	--	-0.72	--	0.24	--	+0.24

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

[b] Dioxane solution at 20°C.

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

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

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TABLE 9

Ionization Potentials of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
NITROMETHANE	11.08[b,c]	11.14	+0.06	11.54	+0.46	11.97	+0.89
DINITROMETHANE	--	11.44	--	12.37	--	12.61	--
TRINITROMETHANE	--	11.80	--	12.98	--	13.05	--
TETRANITROMETHANE	--	12.13	--	13.25	--	13.22	--
NITROETHANE	10.88[b,c]	10.83	-0.05	11.49	+0.61	11.71	+0.83
1,1-DINITROETHANE	--	11.20	--	12.25	--	12.23	--
1,2-DINITROETHANE	--	11.18	--	11.94	--	12.29	--
1,1,1-TRINITROETHANE	--	11.63	--	12.65	--	12.46	--
1,1,2-TRINITROETHANE	--	11.55	--	12.10	--	12.67	--
1,1,1,2-TETRANITROETHANE	--	11.61	--	12.51	--	12.75	--
1,1,2,2-TETRANITROETHANE	--	11.62	--	13.10	--	13.09	--
PENTANITROETHANE	--	11.82	--	13.22	--	13.20	--
HEXANITROETHANE	--	12.04	--	13.47	--	13.15	--
1-NITROPROPANE	10.81[b,c]	10.73	-0.08	11.46	+0.65	11.71	+0.90
2-NITROPROPANE	10.71[b,c]	10.61	-0.10	11.44	+0.73	11.53	+0.82
1,1-DINITROPROPANE	--	11.09	--	12.23	--	12.07	--

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TABLE 9 (cont'd)

Ionization Potentials of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
1,2-DINITROPROPANE	--	10.99	--	11.97	--	12.14	--
1,3-DINITROPROPANE	--	10.99	--	11.70	--	12.11	--
2,2-DINITROPROPANE	--	11.01	--	12.15	--	12.05	--
1,1,1-TRINITROPROPANE	--	11.54	--	12.77	--	12.48	--
1,1,2-TRINITROPROPANE	--	11.20	--	12.41	--	12.54	--
1,2,2-TRINITROPROPANE	--	11.37	--	12.01	--	12.42	--
1,2,3-TRINITROPROPANE	--	11.22	--	12.17	--	12.48	--
1,1,1,2-TETRANITROPROPANE	--	11.51	--	12.63	--	12.71	--
1,1,1,3-TETRANITROPROPANE	--	11.44	--	12.18	--	12.42	--
1,1,2,2-TETRANITROPROPANE	--	11.46	--	12.60	--	12.72	--
1-NITROBUTANE	10.71[d]	10.73	+0.02	11.46	+0.75	11.67	+0.04
2-NITROBUTANE	10.71[d]	10.53	-0.18	11.41	+0.70	11.44	+0.73
1,1-DINITROBUTANE	--	11.01	--	12.15	--	12.13	--
1,2-DINITROBUTANE	--	10.79	--	12.03	--	12.00	--
1,3-DINITROBUTANE	--	10.94	--	11.76	--	11.90	--
1,4-DINITROBUTANE	--	10.83	--	11.78	--	11.98	--

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TABLE 9 (cont'd)

Ionization Potentials of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
2,2-DINITROBUTANE	--	10.97	--	12.10	--	12.04	--
2,3-DINITROBUTANE	--	10.94	--	11.80	--	11.97	--
1,1,1-TRINITROBUTANE	--	11.48	--	12.76	--	12.36	--
1,1,2-TRINITROBUTANE	--	11.16	--	12.36	--	12.39	--
1,1,3-TRINITROBUTANE	--	11.21	--	12.17	--	12.26	--
1,1,4-TRINITROBUTANE	--	11.23	--	11.99	--	12.24	--
1,2,2-TRINITROBUTANE	--	11.31	--	12.17	--	12.41	--
1,2,3-TRINITROBUTANE	--	11.14	--	12.18	--	12.43	--
1,2,4-TRINITROBUTANE	--	11.22	--	12.09	--	12.27	--
1,3,3-TRINITROBUTANE	--	11.16	--	11.96	--	12.22	--
2,2,3-TRINITROBUTANE	--	11.15	--	12.36	--	12.37	--
1,1,1,2-TETRANITROBUTANE	--	11.38	--	12.52	--	12.49	--
1,1,1,3-TETRANITROBUTANE	--	11.21	--	12.13	--	12.29	--
1,1,1,4-TETRANITROBUTANE	--	11.23	--	11.98	--	12.30	--
1,1,2,2,-TETRANITROBUTANE	--	11.38	--	12.77	--	12.60	--
1,1,2,3-TETRANITROBUTANE	--	11.19	--	12.56	--	12.63	--

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TABLE 9 (cont'd)

Ionization Potentials of Normal Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
1,1,2,4-TETRANITROBUTANE	--	11.35	--	12.19	--	12.49	--
1,1,3,3-TETRANITROBUTANE	--	11.41	--	12.49	--	12.64	--
1,1,3,4-TETRANITROBUTANE	--	11.43	--	12.35	--	12.62	--
1,1,4,4-TETRANITROBUTANE	--	11.42	--	12.68	--	12.62	--
1,2,2,3-TETRANITROBUTANE	--	11.42	--	12.42	--	12.65	--
1,2,2,4-TETRANITROBUTANE	--	11.39	--	12.22	--	12.59	--
1,2,3,3-TETRANITROBUTANE	--	11.46	--	12.31	--	12.62	--
1,2,3,4-TETRANITROBUTANE	--	11.36	--	12.44	--	12.69	--
2,2,3,3-TETRANITROBUTANE	--	11.32	--	12.78	--	12.60	--
1-NITROPENTANE	--	10.69	--	11.46	--	11.52	--
2-NITROPENTANE	--	10.53	--	11.39	--	11.43	--
3-NITROPENTANE	--	10.44	--	11.38	--	11.35	--
1,1-DINITROPENTANE	--	11.04	--	12.20	--	11.75	--
Ave. Absolute Error	--	--	0.08	--	0.65	--	0.70
Ave. Error	--	--	-0.06	--	-0.65	--	+0.70

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TABLE 9 (cont'd)

Ionization Potentials of Normal Nitroaliphatics

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

[b] By photoionization spectroscopy.

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

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

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TABLE 10

Ionization Potentials of Branched Nitroaliphatics[a]

NITROALIPHATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
2-METHYL-1-NITROPROPANE	--	10.66	--	11.44	--	11.64	--
2-METHYL-2-NITROPROPANE	--	10.46	--	11.35	--	11.36	--
2-METHYL-1,1-DINITROPROPANE	--	11.04	--	12.18	--	12.18	--
2-METHYL-1,2-DINITROPROPANE	--	10.96	--	11.72	--	--	--
2-METHYL-1,3-DINITROPROPANE	--	10.83	--	11.88	--	12.03	--
2,2-DIMETHYL-1,3-DINITROPROPANE	--	10.74	--	11.87	--	11.96	--

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

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TABLE 11

Ionization Potentials of Nitroaromatics[a]

NITROAROMATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
NITROBENZENE	9.92[b,c]	9.97	+0.05	10.33	+0.41	10.56	+0.64
1,2-DINITROBENZENE	--	10.55	--	11.15	--	11.31	--
1,3-DINITROBENZENE	--	10.61	--	11.21	--	11.43	--
1,4-DINITROBENZENE	--	10.61	--	11.10	--	11.34	--
1,2,3-TRINITROBENZENE	--	10.94	--	11.92	--	12.06	--
1,2,4-TRINITROBENZENE	--	10.84	--	11.91	--	12.05	--
1,3,5-TRINITROBENZENE	--	11.09	--	12.10	--	12.24	--
1,2,3,4-TETRANITROBENZENE	--	11.11	--	12.55	--	12.61	--
1,2,3,5-TETRANITROBENZENE	--	11.15	--	12.61	--	12.69	--
1,2,4,5-TETRANITROBENZENE	--	11.05	--	12.57	--	12.67	--
PENTANITROBENZENE	--	11.38	--	13.00	--	13.14	--
HEXANITROBENZENE	--	11.66	--	13.31	--	13.51	--
2-NITROTOLUENE	--	9.66	--	10.15	--	10.17	--
3-NITROTOLUENE	--	9.69	--	10.18	--	10.20	--
4-NITROTOLUENE	9.82[d,e]	9.77	-0.05	10.29	+0.47	10.30	+0.48
2,3-DINITROTOLUENE	--	10.26	--	10.93	--	10.88	--

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TABLE 11 (cont'd)

Ionization Potentials of Nitroaromatics[a]

NITROAROMATIC	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
2,4-DINITROTOLUENE	--	10.34	--	11.06	--	11.03	--
2,5-DINITROTOLUENE	--	10.25	--	10.95	--	10.90	--
2,6-DINITROTOLUENE	--	10.25	--	10.92	--	10.94	--
3,4-DINITROTOLUENE	--	10.26	--	11.02	--	10.95	--
3,5-DINITROTOLUENE	--	10.34	--	11.01	--	10.97	--
2,3,4-TRINITROTOLUENE	--	10.77	--	11.70	--	11.57	--
2,3,5-TRINITROTOLUENE	--	10.76	--	11.66	--	--	--
2,3,6-TRINITROTOLUENE	--	10.70	--	11.66	--	--	--
2,4,5-TRINITROTOLUENE	--	10.72	--	11.71	--	--	--
2,4,6-TRINITROTOLUENE	--	10.84	--	11.83	--	11.73	--
3,4,5-TRINITROTOLUENE	--	10.76	--	11.68	--	11.58	--
2,3,4,5-TETRANITROTOLUENE	--	11.02	--	12.28	--	12.12	--
2,3,4,6-TETRANITROTOLUENE	--	11.05	--	12.35	--	--	--
2,3,5,6-TETRANITROTOLUENE	--	10.93	--	12.27	--	--	--
PENTANITROTOLUENE	--	11.26	--	12.83	--	--	--
Ave. Absolute Error	--	--	0.05	--	0.44	--	0.56
Ave. Error	--	--	0.00	--	+0.44	--	+0.56

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TABLE 11 (cont'd)
Ionization Potentials of Nitroaromatics[a]

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

[b] By photoionization spectroscopy.

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

[d] By mass spectroscopy

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

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TABLE 12

Ionization Potentials for Nitro-Compounds[a]

NITRO-COMPOUND	OBSERVED	MINDO/3		MNDO		AM1	
	IP	IP	Error	IP	Error	IP	Error
NITROAMINE	--	11.44	--	11.85	--	12.03	--
N-NITROETHYLAMINE	--	10.42	--	11.69	--	11.14	--
N-NITROBUTYLAMINE	--	10.50	--	11.67	--	11.12	--
N-NITRODIMETHYLAMINE	--	9.72	--	11.24	--	10.78	--
N-NITRODIETHYLAMINE	--	9.58	--	11.16	--	10.65	--
NITROETHANOL	--	10.99	--	11.56	--	11.84	--
3-NITRO-2-BUTANOL	--	10.58	--	11.46	--	11.52	--

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

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TABLE 13

Molecular Geometry of Nitromethane

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C-N	1.46	1.453	1.546	1.500
N-O	1.208	1.225	1.210	1.201
C-H	--	1.115	1.109	1.119
Bond Angle (°)				
ONO	127	131.4	121.4	122.4
ONC	116.5	114.3	119.3	118.8
HCN	--	113.6	108.8	108.2

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

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TABLE 14

Molecular Geometry of Tetranitromethane

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C-N	1.47	1.532	1.578	1.599
N-O	1.22	1.212	1.201	1.184
Bond Angle (°)				
ONC	116.5	113.8	118.4	116.2
NCN	109.5	112.39	110.2	110.6

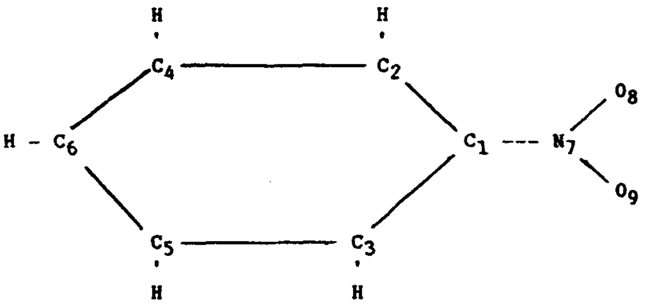
[a] A. J. Stosick, *J. Amer. Chem. Soc.*, 61, 1127 (1939).

TABLE 15

Molecular Geometry of Nitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C1-C2	1.367	1.431	1.422	1.405
C2-C4	1.426	1.405	1.403	1.393
C4-C6	1.363	1.403	1.415	1.395
C1-N7	1.486	1.437	1.495	1.485
N7-O8	1.208	1.229	1.213	1.202
Ave. C-H	--	1.104	1.091	1.102
Bond Angle (°)				
C1C2C4	116	120.0	119.4	119.1
C2C4C6	121	120.7	120.3	120.2
C4C6C5	121	120.0	120.8	120.5
C3C1C2	125	118.8	119.8	120.7
N7C1C2	117	120.6	120.1	119.7
O8N7C1	118	115.2	119.8	118.9
Ave. HCC	--	120.9	120.2	119.9

[a]



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

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TABLE 16

Molecular Geometry of m-Dinitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C1-C2	1.384	1.428	1.415	1.403
C2-C4	1.384	1.427	1.416	1.397
C4-C6	1.386	1.427	1.416	1.406
C5-C3	1.386	1.405	1.404	1.391
C1-C3	1.381	1.422	1.416	1.403
C1-N7	1.491	1.442	1.498	1.488
C4-N10	1.494	1.441	1.498	1.489
N7-O8	1.276	1.226	1.211	1.200
N7-O9	1.220	1.227	1.211	1.201
N10-O11	1.266	1.227	1.211	1.201
N10-O12	1.230	1.226	1.211	1.200
C2-H13	1.12	1.106	1.095	1.110
C3-H14	0.90	1.106	1.093	1.106
C5-H15	0.90	1.104	1.091	1.101
C6-H16	0.87	1.106	1.093	1.105
Bond Angle (°)				
C1C2C4	115.7	121.4	119.9	119.7
C2C4C6	124.0	118.4	120.1	120.3
C1C3C5	119.1	120.7	119.8	119.7
C3C1C2	123.1	130.3	120.7	120.0
C1N7O8	118.3	115.1	119.8	118.8
C1N7O9	118.3	114.6	119.5	118.5

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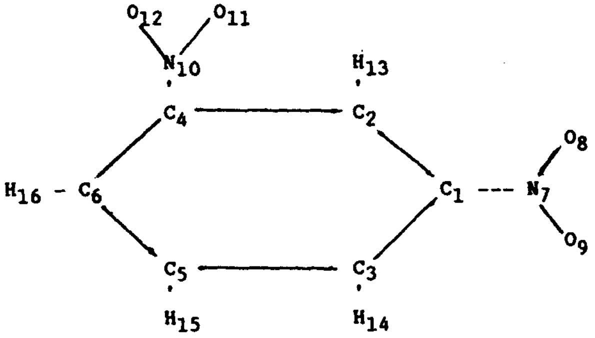
TABLE 16 (cont'd)

Molecular Geometry of m-Dinitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Angle (°)				
C4N10O11	116.1	114.3	119.4	118.5
C4N10O12	116.8	114.7	119.8	118.8
C2C1N7	118.3	120.9	120.1	120.0
C3C1N7	118.6	121.0	120.0	120.0
C2C4N10	117.5	121.0	120.0	119.8
C6C4N10	118.4	120.6	119.9	119.9
H13C2C1	--	119.7	120.2	120.0
H14C3C1	--	122.4	120.1	119.7
H15C5C3	--	119.5	119.7	119.5
H16C6C4	--	122.3	121.7	120.2

a



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

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TABLE 17

Molecular Geometry of p-Dinitrobenzene[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C1-C2	1.385	1.425	1.417	1.403
C2-C3	1.385	1.405	1.408	1.393
C1-C3	1.385	1.425	1.415	1.401
C1-N4	1.41	1.445	1.503	1.492
N4-O5	1.23	1.227	1.211	1.200
N4-O6	1.23	1.228	1.211	1.200
Ave. C-H	--	1.104	1.092	1.105
Bond Angle (°)				
C1C2C3	--	120.6	119.9	119.3
C2C3C1	--	120.8	120.0	119.6
C3C1C2	--	118.5	119.8	120.8
O5N4C1	118.5	114.8	119.6	118.7
O6N4C1	117.5	114.8	119.6	118.7
N4C1C2	--	120.8	120.1	119.4
N4C1C3	--	120.7	120.1	119.6
C1C2H	--	123.1	122.2	120.5
C2C3H	--	116.2	117.6	120.2

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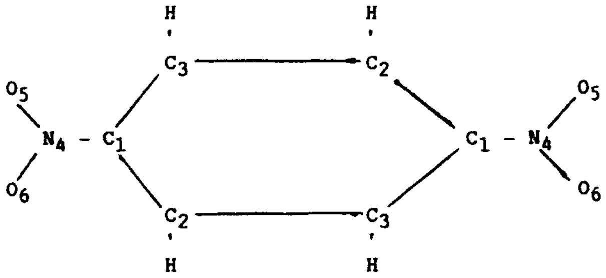
TABLE 17 (cont'd)

Molecular Geometry of p-Dinitrobenzene[a]

a



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

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TABLE 18

Molecular Geometry of 1,3,5-Trinitrobenzene

STRUCTURAL PARAMETER	OBSERVED[a] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
C-C	1.380	1.426	1.415	1.403
C-N	1.480	1.448	1.502	1.493
N-O	1.208	1.225	1.209	1.199
C-H	1.071	1.106	1.096	1.111
Bond Angle (°)				
CCC	120.1	120.1	119.9	120.0
NCC	118.4	120.6	119.8	119.3
ONC	117.1	114.8	119.5	118.4
HCC	122.5	119.1	120.0	120.7

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

TABLE 19

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

STRUCTURAL PARAMETER	OBSERVED[b] VALUE		MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
	Form A	Form B			
Bond Distance (Å)					
C1-C2	1.408	1.379	1.444	1.422	1.409
C2-C3	1.373	1.387	1.422	1.410	1.397
C3-C4	1.375	1.373	1.422	1.408	1.403
C4-C5	1.415	1.344	1.421	1.407	1.402
C5-C6	1.364	1.383	1.420	1.413	1.404
C1-C7	1.505	1.507	1.500	1.513	1.482
C2-N11	1.449	1.494	1.447	1.510	1.504
N11-O12	--	--	1.224	1.2008	1.199
N11-O13	--	--	1.224	1.208	1.197
C4-N14	1.443	1.482	1.447	1.505	1.498
N14-O15	--	--	1.225	1.209	1.198
N14-O16	--	--	1.225	1.208	1.200
C6-N17	1.496	1.459	1.445	1.510	1.504
N17-O18	--	--	1.223	1.209	1.198
N17-O19	--	--	1.224	1.209	1.198
Ave Methyl C-H	--	--	1.110	1.109	1.121
Ave Arom. C-H	--	--	1.108	1.094	1.109

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TABLE 19 (cont'd)

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

STRUCTURAL PARAMETER	OBSERVED[b] VALUE Form A	OBSERVED[b] VALUE Form B	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Angle (°)					
C1C2C3	--	--	122.1	123.7	122.2
C2C3C4	--	--	121.2	118.0	118.4
C3C4C5	--	--	117.8	121.6	121.5
C4C5C6	--	--	121.5	118.0	118.4
C7C1C2	--	--	122.0	123.7	123.0
N11C2C3	--	--	115.7	115.7	118.2
O12N11C2	--	--	113.6	118.8	118.4
Bond Angle (°)					
O13N11C2	--	--	113.7	118.7	118.4
N14C4C5	--	--	121.2	119.2	119.2
O15N14C4	--	--	114.6	118.6	118.5
O16N14C4	--	--	114.6	118.7	118.4
N17C6C1	--	--	121.4	121.0	120.3
O18N17C6	--	--	114.2	118.7	118.5
O19N17C6	--	--	113.4	118.7	118.2
Ave. Methyl HCC	--	--	113.6	111.7	111.0
Ave. Arom. HCC	--	--	119.4	121.0	120.7

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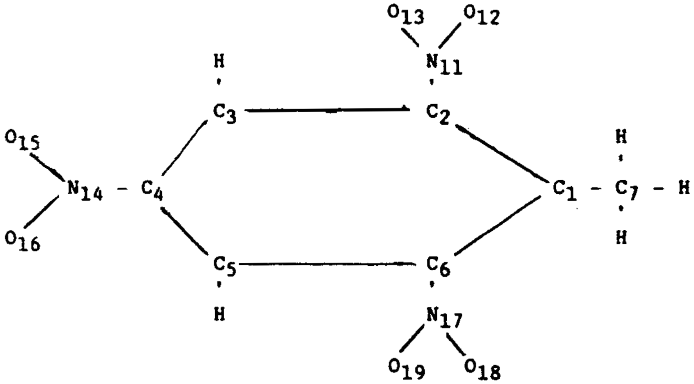
TABLE 19 (cont'd)

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

a



b W. R. Carper, L. P. Davis and M. W. Extine, *J. Phys. Chem.*, 86, 459 (1982).

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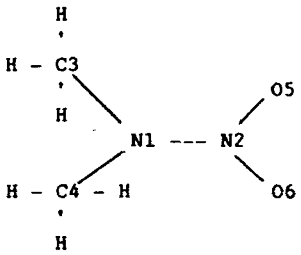
TABLE 20

Molecular Geometry of N-Nitrodimethylamine[a]

STRUCTURAL PARAMETER	OBSERVED[b] VALUE	MINDO/3 VALUE	MNDO VALUE	AM1 VALUE
Bond Distance (Å)				
N1-C3	1.41	1.429	1.482	1.457
N1-C4	1.41	1.430	1.485	1.458
N1-N2	1.33	1.345	1.423	1.413
N2-O5	1.21	1.223	1.204	1.204
N2-O6	1.21	1.223	1.210	1.204
Ave C-H	--	1.120	1.113	1.122
Bond Angle (°)				
C3N1C4	--	117.8	115.8	113.3
C3N1N2	123	120.7	115.4	116.8
O5N2N1	118	113.3	116.4	118.5
O6N2N1	118	115.3	120.1	118.5
Ave. HCN	--	113.7	110.6	109.7

[a]



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