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MOLECULAR MODELS FOR EXPLOSIVES

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Any fundamental understanding of detonations and explosives' behavior requires as a starting point a knowledge of molecular properties. Indeed, there is a sizable literature concerning observed decomposition kinetics, X-ray crystal structures, heats of formation, etc. for explosives.[1] As a result of this extensive experimental work, a large and ever increasing number of observed properties of explosives are available. Given sufficient data, models for the prediction of molecular properties can be developed and calibrated. Nevertheless, many desirable molecular properties can be obtained only with considerable effort and, in many cases, experimental measurements are not possible for practical reasons; e.g., bond dissociation energies are very difficult to obtain for explosives. Consequently, theoretical methods for obtaining these properties are quite desirable. In addition, it is oftentimes desired to estimate the properties of unknown molecules.

Among the properties of interest are crystal densities, molecular geometries, and bond dissociation energies; an accurate description of the electronic structure of an explosive is also desirable, as this is among the most fundamental of molecular properties. Although the relationship between these fundamental molecular properties and explosives' behavior is not always understood, it is our hope that the extension and development of means by which these properties may be calculated (perhaps even a priori) will provide a rational basis for the design and development of explosives with specific properties. Consequently, methods for the estimation of molecular properties, which might seem quite crude by other standards, can be of considerable practical value.

We present in this paper some of our recent efforts at extending and developing molecular models for explosives. These efforts fall into three main areas. The first is the estimation of crystal densities of organic nitrates and perchlorates by an entirely empirical group additivity method. The second is the calculation of molecular heats of formation and bond dissociation energies (BDE's) by a semi-empirical molecular orbital method, AM1. Third and last is the electronic structure of nitrobenzene as obtained from non-empirical (sometimes called ab initio) molecular orbital calculations.

Parameters for Estimating Crystal Densities

Stine derived parameters to be used in the prediction of crystal densities some time ago.[2] For a wide range of organic compounds, predictions accurate to about $\pm 5\%$ can be easily obtained using his method. Consequently, Stine's method has been frequently used for estimating densities of new potential explosives.

Ionic compounds, however, were not considered in Stine's investigations and density predictions were not possible for new potential explosives that are ionic. Interest in ionic compounds as explosives has increased recently and, as a result, we have derived the required parameters for organic nitrates and perchlorates to be used in conjunction with Stine's method.

Unit cell dimensions from X-ray crystal structures in the literature were used to obtain densities of known nitrates and perchlorates. For consideration, compounds were required to be unsolvated C,H,N,O containing ionic nitrates or perchlorates of integral stoichiometry with an even number of electrons.

These requirements were satisfied by a large range of compound types including acid adducts, quaternary ammonium salts, and carbonium ions. No error checking was performed for the data set, as errors are expected to be random and, consequently, their effect is presumably negligible. It is unfortunate that the number of compounds for which there is data is quite small.

The rules in Table 1 were applied to calculate a molecular volume of the organic moiety in the manner Stine suggests in LA–8920. No claim other than that these rules were consistently applied is made.

Parameters for ionic compounds were then derived by obtaining molecular volumes, V_{mol}, from Equation 1 for the literature compounds.

$$V_{mol}(\text{Å}^3) = \frac{\text{molecular weight}}{\rho_{obs}(g/cc)\ 0.6023} \tag{1}$$

Subtracting the volume of the organic moiety, as described by Stine and in Table 1, from V_{mol} yields the volume parameter of the anionic moiety required to reproduce the observed crystal density. These derived volumes, V_{anion}, were then averaged to yield one parameter each for nitrate and perchlorate ions.

Using the data shown in Tables 2 and 3, we obtained volumes of 57.183 Å^3 and 76.561 Å^3 for nitrate and perchlorate ions, respectively. The average error in the calculated density for the compounds studied is quite small, being 0.017 g/cc and 0.027 g/cc for nitrates and perchlorates, respectively, despite large variations in V_{anion}. This occurs in part because of the relatively small volume of the anion relative to the molecular volume. Additionally, the small errors must be judged with due regard to the limited data sets from which they were derived. Nevertheless, these results suggest that density calculations for ionic compounds do not yield errors significantly larger than those for non-ionic compounds.

An example of the application of the method is shown in Table 4 for two compounds that came to our attention after the nitrate parameters had been derived. The results are satisfactory.

Heats of Formation and Bond Dissociation Energies from AM1

The AM1 semi-empirical molecular orbital method[3] has proved useful in a number of connections. Reasonable results have been obtained for a wide variety of molecular properties including heats of formation, molecular geometries, ionization potentials, proton affinities, and others.[3,4] We wished to apply the AM1 method to determine if heats of formation and molecular geometries could be obtained for explosive molecules. Although additivity methods are capable of providing the same information,[5] we prefer the MO method because the MO approach allows greater generality. In addition, there are observed heats of formation for several explosives to test the calculations.

AM1 calculates a heat of formation appropriate for an isolated molecule in field-free space. Most experimental data for explosives, however, are measured in the crystal phase. The difference between these two numbers is a heat of sublimation, which is of non-negligible size. To facilitate comparison of calculated and observed data, we developed from data available in the literature a completely *ad hoc* correlation equation relating heats of formation in the gas phase to those in the crystal phase. This was accomplished simply by a least squares treatment of the data for nitro-group containing compounds shown in Table 5. The result, Equation 2, furnishes a convenient means of correlating gas phase and crystal data; the ad hoc nature of this correlation makes its use for compounds dissimilar from those in Table 5 unjustifiable.

$$H_f(g) = 0.886 * H_f(c) + 20.4$$
$$N = 23,\ r = 0.987,\ SD = 4.4\ kcal \qquad (2)$$

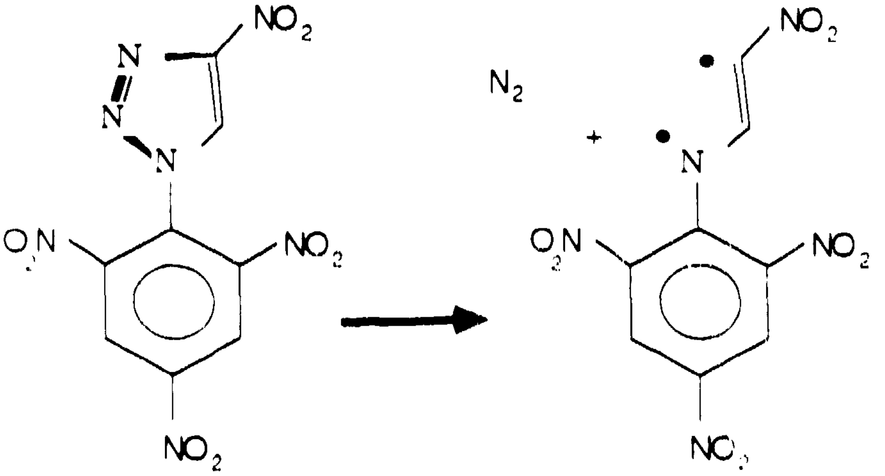
AM1 calculations were then performed for the explosive molecules shown in Table 6. Complete geometry optimizations were performed in each case. The resulting geometries are in reasonable agreement with experimental data, but discussion of these results is postponed for reasons of space here.

The results of the calculations and observed data when available are presented in Table 7.

Comparison of experimentally based heats of formation obtained from Equation 2 with calculated heats of formation from AM1 indicate that systematic errors occur in the theory. To correct this error it is recommended that 10 kcal for each C-NO_2 group and 23 kcal for each N-NO_2 group present in the molecule be subtracted from the AM1 heats of formation. O-NO_2 groups do not require a correction. When the systematic deficiencies of AM1 are corrected in this fashion, heats of formation of explosives can be obtained with an average error of about 5–10 kcal; i.e., that normally found for AM1. HMX still has a large error, however, and its conformational surface is being examined more carefully to insure that the global minimum was obtained.

Bond dissociation energies (BDE's) were obtained from corrected AM1 heats of formation of the closed shell molecule and the organic radical resulting from the loss of NO_2. The experimental H_f of NO_2 of 7.9 kcal was used also. The results appear in Table 7. Although there is a lack of experimental data with which to compare the data, several apparent trends seem quite reasonable. The agreement with the observed C-NO_2 BDE[6] of nitrobenzene is fair. Additionally, NH_2 substitution on the trinitrobenzene ring results in increased C-NO_2 bond strength.

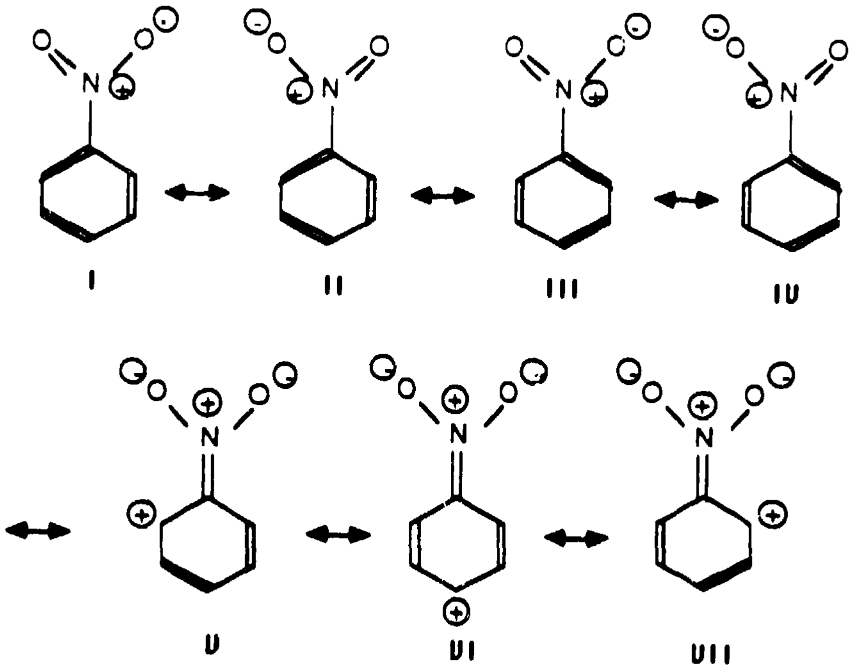
An interesting result is found from further calculations of the 1- or 2-picryl-1,2,3-triazoles. These two compounds are isomeric and thus have equal oxygen balance. Despite this, they have drastically different impact sensitivities: 1PkTz=11 cm and 2PkTz=200 cm. AM1 calculations reveal similar C-NO_2 BDE's, giving no explanation for the different behavior. It has been suggested that 1PkTz may lose N_2 in the manner illustrated below, thus resulting in its greater sensitivity.[7]



AM1 calculations for the resulting biradical show it to be only about 20 kcal above the 1PkTz. This is an especially low-energy decomposition pathway, even allowing for significant errors in the calculation.

Electronic Structure of Nitrobenzene

The traditional description of the reactivity of nitrobenzene invokes resonance structures I-VII, below.[8]



Structures V-VII are generally considered to be important because of the strong [pi] withdrawing ability of the nitro group. In these structures, the nitro group carries a full negative charge, with the corresponding positive charge appearing at the ortho and para positions of the benzene ring.

Table 8 shows results from three different basis sets for geometries of nitrobenzene in which the nitro group is in the plane of the ring (termed planar) and the nitro group is held perpendicular to the ring (termed perpendicular).[9] At the best level of theory (6–311G**), which includes a triple split of the valence orbitals, d functions on heavy atoms, and p functions on hydrogen, the barrier for C-NO_2 rotation is 6.9 kcal. This is considerably higher than the observed barrier of 2.8–3.0 kcal.[10] Nevertheless, the barrier is dropping with increasing basis set size and the 6–311G** calculations may be taken as a reasonable description of these structures.

We believe that these calculations do not support the involvement of resonance structure V-VII in the ground state description of nitrobenzene. Calculated charges for the nitro group, obtained by summing the N and twice the O charges, provide some of the strongest evidence. It is found that the planar-perpendicular difference in charge borne by the nitro group is nowhere near -1 as structures V-VII suggest; indeed, at the best level of theory, the nitro group actually bears more negative charge in the perpendicular form than it does in the planar form. Consequently, the contribution of resonance structures V-VII must be quite small in the ground state of nitrobenzene.

Conclusions

Several molecular properties can be obtained from molecular modeling. As the complexity of the property increases, the theoretical models become increasingly empirical so that results can be obtained with reasonable or possibly no computer time. Also, the accuracy with which complex properties can be calculated and the detail provided by the theory necessarily decreases. In spite of this, useful results can be obtained to provide a rational approach to explosives design, development, and application.

Despite these advances, experimental data are invaluable. We thus welcome any new structural, thermodynamic, and kinetic data for explosives as it becomes available.

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TABLE 1

Rules for Assigning Atom Types in the Calculation of Densities for Nitrates and Perchlorates

1. Always consider acid proton, if present, as bound to N.

2. When two or more nitrogens are present in a molecule, protonate in the following order: sp before sp^2 before sp^3. For N's of the same hybridization, protonate N bearing fewer hydrogens first.

3. N(+) is the value of N bearing a formal +1 charge in the most important resonance structure. Its value is always 0.232 $Å^3$. Non-charge bearing nitrogens are treated in the usual manner.

4. Protons are not distinguished with separate values. They are treated in the usual fashion; for example all hydrogen in $NH_4^{\oplus}$ are treated as hydrogens bound to nitrogen.

5. In cyclopropenium ions, ring carbons are C(1,-5,-5). In triphenyl methyl ions, phenyl carbons are C(1,-5,-5), and the methyl carbon is C(7,1,1) on the basis of its structure in important resonance structures.

TABLE 2

Data and Results for the Indicated Nitrates

Ref.	Name	Molecular Formula	ρ_{obs}	$V_{(derived)}$	ρ_{calc}	$\Delta\rho$
A	urea nitrate	$CH_5N_3O_4$	1.684	58.052	1.696	0.012
B	monoacetamide nitrate	$C_2H_6N_2O_4$	1.585	52.390	1.527	-0.057
C	glycine nitrate	$C_2H_6N_2O_5$	1.632	58.451	1.647	0.015
D	N-methyl urea nitrate	$C_2H_7N_3O_4$	1.571	54.854	1.546	-0.025
E	methyl guanidinium nitrate	$C_2H_8N_4O_3$	1.459	58.469	1.471	0.012
F	glycylglycine nitrate	$C_4H_9N_3O_6$	1.627	59.760	1.648	0.021
G	morpholinium nitrate	$C_4H_{10}N_2O_4$	1.444	54.849	1.425	-0.019
H	pyridinium nitrate	$C_5H_6N_2O_3$	1.461	57.524	1.464	0.003
I	adeninium nitrate	$C_5H_7N_7O_6$	1.775	58.808	1.799	0.023
J	dl-valine nitrate	$C_5H_{12}N_2O_5$	1.390	56.713	1.386	-0.003
K	cytidinium nitrate	$C_9H_{14}N_4O_8$	1.644	57.368	1.645	0.001
L	1-Benzylcytosine nitrate	$C_{11}H_{12}N_4O_4$	1.471	54.629	1.459	-0.012
M	1-Phenyl-3,5-dimethylpyazolium nitrate	$C_{11}H_{13}N_3O_3$	1.335	61.514	1.355	0.02
				$\overline{V}_{NO_3^{\ominus}} = 57.183$		$\lvert\overline{\Delta\rho}\rvert = 0.017$

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TABLE 3

Data and Results for the Indicated Perchlorates

Ref.	Name	Molecular Formula	ρ_{obs} (g/cc)	($\AA^3$) V_{anion}	ρ_{calc} (g/cc)	$\Delta\rho$ (g/cc)
A	monomethylammonium perchlorate	$CH_6NO_4C\ell$	1.705	79.242	1.741	0.036
B	pyrazine perchlorate	$C_4H_5N_2O_4C\ell$	1.718	77.255	1.725	0.007
C	1,5-bis(dimethylamino) pentamethenium perchlorate	$C_9H_{17}N_2O_4C\ell$	1.285	85.111	1.320	0.035
D	1,3-bis(dimethylamino) trimethinium perchlorate	$C_7H_{15}N_2O_4C\ell$	1.353	78.249	1.360	0.008
E	acetylcholine perchlorate	$C_7H_{16}NO_6C\ell$	1.377	77.689	1.382	0.005
F	4-azoniaspiro[3.5] nonane perchlorate	$C_8H_{16}NO_4C\ell$	1.338	89.483	1.403	0.065
G	1,2,3-tris(dimethylamino) cyclopropenium perchlorate	$C_9H_{18}N_3O_4$	1.318	82.121	1.340	0.022
H	N,N,N′,N′-tetramethye-p-diaminobenzene perchlorate	$C_{10}H_{17}N_2O_4C\ell$	1.416	64.342	1.362	-0.054
I	1,4,8,11-tetraazacyclo-tetraclecane perchlorate	$C_{10}H_{26}N_4O_8C\ell_2$	1.509	76.290	1.486	-0.023
J	a polyfunctional [3.2.1] bicyclooctane perchlorate	$C_{13}H_{20}NO_9C\ell$	1.493	74.223	1.485	-0.008
K	an alkaloid perchlorate	$C_{13}H_{23}N_2O_6C\ell$	1.401	75.392	1.397	-0.004
L	N-phenly-2,4,6-trimethyl-pyridinium perchlorate	$C_{14}H_{16}NO_4C\ell$	1.294	100.157	1.379	0.085
M	a Lupin alkaloid perchlorate	$C_{14}H_{21}N_2O_5C\ell$	1.414	74.846	1.396	-0.018
N	1-ethyl-1-methyl-4-phenyl pyridine perchlorate	$C_{14}H_{22}NO_4C\ell$	1.304	73.710	1.294	-0.010
O	Succinylcholine perchlorate	$C_{14}H_{30}N_2O_{12}C\ell_2$	1.435	71.275	1.409	-0.026
P	Anhydro-N-hydroxy-methyldeoxygustifoline perchlorate	$C_{15}H_{25}N_2O_4C\ell$	1.341	72.510	1.328	-0.013
Q	Lupamine-N-oxide perchlorate	$C_{15}H_{25}N_2O_6C\ell$	1.467	73.718	1.457	-0.010
R	a lupamine perchlorate	$C_{15}H_{27}N_2O_4C\ell$	1.367	66.920	1.335	-0.032
S	7-hydroxy-β-isosparteine perchlorate	$C_{15}H_{27}N_2O_5C\ell$	1.413	65.947	1.378	0.035
T	α-isosparteine diperchlorate	$C_{15}H_{28}N_2O_8C\ell_2$	1.492	74.014	1.476	-0.016

TABLE 3 (CONTINUED)

Data and Results for the Indicated Perchlorates

Ref.	Name	Molecular Formula	ρ_{obs} (g/cc)	($\AA^3$) V_{anion}	ρ_{calc} (g/cc)	$\Delta\rho$ (g/cc)
U	S-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate	$C_{16}H_{19}N_4O_6C\ell$	1.458	82.569	1.476	0.020
V	a novel lycopodium alkaloid perchlorate	$C_{16}H_{25}N_2O_6C\ell$	1.502	58.157	1.438	-0.064
W	auramine perchlorate	$C_{17}H_{22}N_3O_4C\ell$	1.358	83.797	1.347	-0.011
X	triphenylemethyl perchlorate	$C_{19}H_{15}O_4C\ell$	1.347	90.348	1.392	0.045
Y	tri(p-aminophenyl) carbonium perchlorate	$C_{19}H_{13}N_3O_4C\ell$	1.426	70.352	1.407	-0.019
Z	Panamine diperchlorate	$C_{20}H_{35}N_3O_8C\ell$	1.464	72.860	1.446	-0.018
				$\overline{V} = 76.561$		$\lvert\overline{\Delta\rho}\rvert = 0.027$

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TABLE 4

Examples of Density Calculations of Organic Nitrates

Ethylene Diamine Dinitrate
($C_2H_{10}N_4O_6$, $MW = 186.1252$)

$$\begin{array}{lclcr} 2(\mathrm{CH_2}) & = & 2 \times 25.35 & = & 50.70 \\ 2\mathrm{N}^+ & = & 2 \times 0.232 & = & 0.46 \\ 6\mathrm{H}_N & = & 6 \times 5.199 & = & 31.19 \\ 2\mathrm{NO_3^-} & = & 2 \times 57.183 & = & \underline{114.37} \\ & & & & 196.72 \end{array}$$

$$\rho_{calc} = \frac{186.1252}{196.72(0.6023)} = 1.571\ g/cc$$

$$\rho_{obs} = 1.595\ g/cc$$

Diethylene Triamine Trinitrate
($C_4H_{15}N_6O_9$, $MW = 291.1989$)

$$\begin{array}{lclcr} 4(\mathrm{CH_2}) & = & 4 \times 25.35 & = & 101.400 \\ 3(\mathrm{N}^{\oplus}) & = & 3 \times 0.232 & = & 0.696 \\ 7\mathrm{H}_N & = & 7 \times 5.199 & = & 36.393 \\ 3\mathrm{NO_3^-} & = & 3 \times 57.183 & = & \underline{171.549} \\ & & & & 310.038 \end{array}$$

$$\rho_{calc} = \frac{291.1989}{310.038(0.6023)} = 1.559\ g/cc$$

$$\rho_{obs} = 1.57\ g/cc$$

TABLE 5

Heats of formation (H_f in kcal) measured in the gas (g) and crystal (c) phases.[a]

Compound Name	H_f(c)	H_f(g)
TNT	-16.1	9.4
TNB	-8.9	14.9
PkOMe	-37.7	-5.8
2,4-Dinitrophenol	-55.7	-30.6
2,6-Dinitrophenol	-50.2	-23.4
Trinitromethane	-11.4	-.2
(2,2,2-trinitroethyl)benzene	-4.4	15.7
2-ethoxy-1,3,5-trinitrobenzene	-48.9	-20.1
1,3-dinitrobenzene	-6.6	12.8
3-nitro-2isoxazoline-2-oxide	-12.2	4.8
1-methyl-2,4-dinitrobenzene	-15.8	8.0
PETN	-128.8	-92.6
Bis(2,2-dinitropropyl)-amine	-63.4	-38.3
Bis(2,2-dinitropropyl)-nitrosoamine	-46.0	-19.5
Bis(2,2,2-trinitroethyl)amine	-8.0	11.3
Bis(2,2,2-trinitroethyl)nitrosoamine	11.8	35.2
Bis(2,2,2-trinitroethyl)nitramine	-6.5	21.6
2-nitrobenzeneamine	-6.3	15.3
3-nitrobenzeneamine	-9.1	14.0
4-nitrobenzeneamine	-10.0	14.2
1-nitropiperidine	-22.2	-10.6
1-methyl-4-nitrobenzene	-11.5	7.4
hexanitroethane	20.0	39.9

[a] J. B. Pedley and J. Rylance, "Sussex - NPL Computer Analysed Thermochemical Data: Organic and Organometallic Compounds," University of Sussex, 1977.

TABLE 6

Explosives for which AM1 calculations were performed and their acronym.

ID	Name	Acronym
	C-NO$_2$ Explosives	
A	2,4,6-Trinitrotoluene	TNT
B	1,3,5-Triamino-2,4,6trinitrobenzene	TATB
C	1,3,5-Trinitrobenzene	TNB
D	Picric acid	PkOH
E	2,4,6-Trinitroanisole	PkOMe
F	1,3-Diaminao-2,4,6-trinitrobenzene	DATB
G	Hexanitrobenzene	HNB
H	2,4,6-Trinitroaniline	PkNH$_2$
I	1,3-Diaminopicric acid	DAPA
J	2-Picryl-1,2,3-triazole	2PkTz
K	1-Picryl-1,2,3-triazole	1PkTz
L	4-Nitro-2-picryl-1,2,3-triazole	4N2PkTz
M	4-Nitro-1-picryl-1,2,3-triazole	4N1PkTz
N	3,5-Dimethylpicric acid	3,5-DMPkOH
O	3-Methylpicric acid	3-MPkOH
P	Picryl chloride	PkCl
Q	1-Picryl-4-nitro-pyrazole	1-Pk-NPz
R	1-Picryl-2-nitro-imidazole	1-Pk-NIm
	O-NO$_2$ Explosives	
S	Nitroglycerine	NG
T	Dinitroglycerine	DNG
U	Nitrogylcide	NGCD
V	Nitroglycol	NGCL
W	Dimethylolnitroethane dinitrate	DNDN
X	Pentaerythritol tetranitrate	PETN
	N-NO$_2$ Explosives	
Y	1,3,5-Trinitro-1,3,5-triaxacyclohexane	RDX
Z	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX
AA	Nitroguanidine	NQ
AB	Methylenedinitramine	MEDINA
AC	Ethylenedinitramine	EDNA
AD	N-Methyl ethylenedinitramine	MEDNA

TABLE 7

Comparison of observed and calculated heats of formation (kcal/mol) and bond dissociation energies (BDE's in kcal) for some explosives.

Name	AM1 actual	H_f(c) obs.	H_f(g) obs.	H_f(g) from Eq. 2	AM1[a]	BDE
C-NO_2 Compounds						
TNT	41.4	-16.1[b]	9.4[b]	6.1	11.4	56.1
TATB	20.9	-33.4[c]		-9.2	-9.1	67.0
TNB	45.3	-8.9[b]	14.9[b]	12.5	15.3	59.6
PkOH	1.2	-51.7[b]		-25.4	-28.8	60.5
PkOMe	14.3	-37.7[b]	-5.8[b]	-13.0	-15.7	60.4
DATB	25.5	-23.6[c]		-0.5	-4.5	65.5
HNB	117.2				57.2	54.3
PkNH2	34.2	-17.8[d]		4.6	4.2	63.1
DAPA	-15.2	-76.0[e]		-46.9	-45.2	65.4
2PkTz	164.0				134.0	58.3
1PkTz	159.5				129.5	57.2
4N2PkTz	179.3				139.3	56.8
4N1PkTz	172.1				132.1	56.1
3,5-DMPkOH	-3.9				-33.6	53.4
3-MPkOH	-1.1	-60.3[d]		-33.0	-31.1	57.6
PkCl	49.0				19.0	55.7
1-Pk-NPz	144.9				104.9	57.9
1-Pk-NIm	140.2				100.2	55.3
Nitromethane	-9.9		-17.9[b]		-19.9	
Nitrobenzene	25.3		16.2[b]		15.3	66.1 (71.4 obs)
O-NO_2 Compounds						
NG	-70.8	-88.7[b]	-64.8		-70.8	25.1
DNG	-102.3				-102.3	26.4
NGCD	-31.8				-31.8	26.3
NGCL	-51.0				-51.0	24.7
DNDN	-47.1	-89.5[b]		-58.9	-57.1	22.9
PETN	-96.1	-128.9[b]	-92.6[b]	-93.8	-96.1	25.2

TABLE 7 (CONTINUED)

Comparison of observed and calculated heats of formation (kcal/mol) and bond dissociation energies (BDE's in kcal) for some explosives.

Name	AM1 actual	H_f(c) obs.	H_f(g) obs.	H_f(g) from Eq. 2	AM1[a]	BDE
			N-NO_2 Compounds			
RDX	105.5	15.9[b]		34.5	36.5	30.9
HMX	145.2	11.3[c]		30.4	53.2	28.6
NQ	33.3	-22.1[b]		0.8	10.3	57.8
MEDINA	53.0				7.0	36.8
EDNA	42.0	-24.6[b]		-1.4	-4.0	40.3
MEDNA	49.0				3.0	29.9
N-nitropiperidine	8.9		-10.7[b]		-14.1	
1,4-dinitropiperzaine	53.0		14.0[b]		7.0	
Dimethylnitramine	22.5		-1.2[b]		-0.5	
Diethylnitramine	15.8		-12.7[b]		-7.2	

[a] Corrected by the addition of 10 kcal per C-NO_2 and 23 kcal per N-NO_2 group. See text.

[b] J. B. Pedley and J. Rylance, "Sussex - NPL Computer Analysed Thermochemical Data: Organic and Organometallic Compounds," University of Sussex, 1977.

[c] T. R. Gibbs and A. Popolato, Eds., "LASL Explosive Property Data," University of California Press, 1980.

[d] R. Meyer, "Explosives," Verlag Chemie, 1977.

[e] M. Stinecipher, LANL, unpublished data.

TABLE 8

Calculated Mulliken charges for nitrobenzene in which the nitro is perpendiclar to the plane of the ring (perp). Energy difference is kcal is also shown. The symbol "//" may be read "at the energy optimized geometry of." Thus, 3-21G//3-21G indicates a wavefunction obtained with the 3-21G basis set at the energy optimized geometry of the 3-21G basis set.

Parameter	3-21G // 3-21G		6-31G* // 6-31G*		6-311G** // 6-31G*	
	Planar	Perp.	Planar	Perp.	Planar	Perp.
$q(C_1)$	+0.267	+0.317	+0.153	+0.208	+0.074	+0.148
$q(C_2)$	-0.193	-0.194	-0.170	-0.177	-0.031	-0.038
$q(C_3)$	-0.247	-0.234	-0.217	-0.206	-0.105	-0.083
$q(C_4)$	-0.211	-0.226	-0.172	-0.188	-0.061	-0.087
q(N)	+0.186	+0.212	+0.521	+0.486	+0.374	+0.315
q(O)	-0.386	-0.401	-0.470	-0.449	-0.384	-0.362
δE	11.7		7.6		6.9	