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Informal Report

Estimation of the Density of Organic Explosives from Their Structural Formulas

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H. H. Cady

ESTIMATION OF THE DENSITY OF ORGANIC EXPLOSIVES FROM THEIR STRUCTURAL FORMULAS

by

H. H. Cady

ABSTRACT

The explosives community spends considerable time, effort, and money in synthesizing and determining physical properties of compounds to find better explosives. When "better" means more powerful, density is the most important property to be determined.

This report presents a technique for predicting the density of an organic (C-H-N-O-Cl-F) compound given its proposed structural formula.

I. GEOMETRICAL MODEL OF A MOLECULAR CRYSTAL

The distinguishing geometrical peculiarity of a molecular crystal is that one can single out groups of atoms within the crystal in which the distance between any atom of the group and at least one other atom of the same group is significantly less than the distance to any adjacent atom of another group. These short distances are conventionally called covalent bonds. Thus, for example, in hydrocarbon crystals the spacings between hydrogen atoms in different molecules are not less than 2.2 to 2.4 Å, but distances from these atoms to covalently bonded carbon or nitrogen atoms are about 1 Å. Intramolecular spacings between covalently bonded carbon atoms are 1.2-1.5 Å, however, the carbon atoms of different molecules are at least 3.3 Å apart.

One of the most important discoveries of crystallography is that the bond angles and distances between covalently bonded atoms can be predicted from a knowledge of the types of atoms and the nature of the bonds between them. Published tables[1-3] provide the basis for the bonded atom, interatomic distances used in this discussion.

Kitaigorodsky[4] and Bondi[5] have assembled lists of van der Waals nonbonded atomic radii of the nonmetallic elements for use in calculating molecular volumes. I used the values chosen by Bondi, which consider both physical properties and intermolecular distances. Kitaigorodsky's discussion of the principles involved is lucid, and I strongly recommend it.

II. CALCULATIONAL TECHNIQUE

Calculation of the displacement or hard-sphere volume of a proposed molecule is feasible given the bond lengths and van der Waals radii. The total volume of the molecule comprises increments contributed by each individual atom. These volume increments V_j are calculated from the van der Waals sphere volumes by correcting for the volumes of overlapped segments with

$$V_j = (4/3)\pi R_j^3 - \sum_i (1/3)\pi h_i^2 (3R_j - h_i) \quad , \qquad (1)$$

where R_j is the van der Waals radius of the atom concerned; the R_i are the van der Waals radii of the atoms that are valence bonded with atom j and positioned at distance d_i from it. The heights of the cut-off segments are

$$h_i = R_j - \frac{R_j^2 + d_i^2 - R_i^2}{2d_i} \quad . \tag{2}$$

The displacement volume of a molecule is

$$V = \sum_j V_j \tag{3}$$

over all atoms in the molecule.

Figure 1 illustrates the model used in this calculation; the shaded portion indicates the segment volume subtracted because of overlap with atom i.

Scale drawings of molecules (such as trimethylamine, in which a small nitrogen atom is surrounded by large carbon atoms) have a systematic error caused by overlapping of subtracted segments; that is, the central atom is calculated as smaller than it should be. However, this error is almost exactly compensated for by that of neglecting the overlap between the nonbonded (carbon) atoms surrounding this small atom, so both errors are ignored. Overlap volumes caused by steric hindrance between more distant nonbonded atoms or between hydrogen-bonded atoms are impossible to estimate at present and are also ignored in the volume calculations.

Interatomic distances and radii are usually published in angstrom units. Multiplying volumes calculated in cubic angstroms per molecule by 0.60226 gives volumes in cubic centimeters per mole (C_{12} = 12.000).

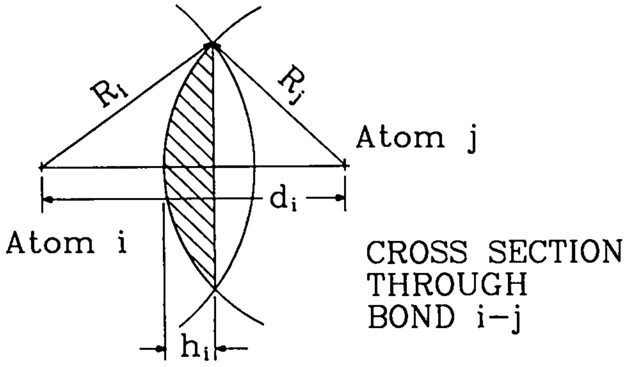


Fig. 1.
Volume of atom j.

Densities are estimated by dividing the gram molecular weight by the calculated volume in cubic centimeters per mole, which gives the theoretical maximum density, and then multiplying by the assumed packing coefficient. The packing coefficient is, thus, the displacement volume of a molecule divided by the volume that the molecule occupies in a crystal.

Kitaigorodsky[4] has pointed out that the packing coefficient (k) for the overwhelming majority of crystals is between 0.65 and 0.77, i.e., of the same order as the close-packing coefficients of spheres. If the shape of the molecule precludes packing with k above 0.6, a temperature drop will cause a melt to vitrify instead of crystallizing.

Studies have shown that benzene, napthalene, and anthracene are solid when k is above 0.68. When these materials change from a solid phase to a liquid phase, k instantly drops to 0.58. Raising the liquid temperature to the boiling point further decreases k, in napthalene to 0.51. At $k \leq 0.5$ these substances become gaseous.

As another example, the moduli of compressibility of tolane, dibenzyl, and stilbene crystals are, respectively, 4.07, 4.54, and 6.50 (in 10^{10} dynes/cm^2), and their packing coefficients are 0.69, 0.71, and 0.72. Thus, in analogous structures, compressibility is inversely related to the packing coefficient.

III. INPUT PARAMETERS

Table I lists the van der Waals radii selected for the atoms most frequently encountered in secondary explosives. Radii of many other atoms are given in Bondi's article.[5]

A table of covalent-bond lengths is not so easily condensed because, even to a first approximation, bond lengths depend on the environments and elements at both ends of the bond. Table II lists approximate bond lengths that can be used to construct models of most organic explosives. It also lists a volume-correction increment that is explained later. Bond lengths between unlisted atoms and groups usually can be found in Refs. 1-3.

TABLE I

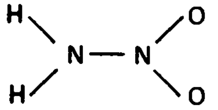
VAN DER WAALS RADII

Atom	Environment	Radius (Å)
C	Aromatic	1.77
C	Triply bonded	1.78
C	All other bond types	1.70
N	Triply bonded	1.60
N	All other bond types	1.55
O	Polyalkane ether	1.48
O	Polyphenyl ether	1.49
O	Carbonyl and other C=O	1.50
O	All other bond types	1.52
H	Bonded to aromatic C	1.00
H	All other bond types	1.20
F	All covalent	1.47
Cl	All covalent	1.75

The displacement volume of a compound can be calculated from the parameters in Tables I and II and a relatively simple computer code that sums the incremental atom volumes. Or one can develop a table in which the volumes of common groups of atoms are already calculated so that only an adding machine is required to calculate the displacement volume of a molecule composed of several groups. The connection points of an atom group present a minor difficulty because the volume of the group depends on both the attached atom(s) and the valence bonds within the group. This difficulty is overcome by calculating the volume of the group assuming a standard attached atom. One can then tabulate volume increments corrected for the length of the attachment bond and for the kind of attached atom as an additivity correction. Table II lists the additivity corrections associated with changes from the standard attachment atom (a quaternary carbon atom for single bonds, an olefinic carbon for double bonds, an acetylenic carbon for triple bonds, and an aromatic carbon for aromatic bonds).

Table III lists the volumes of most groups needed for calculating the displacement volumes of organic explosives. Bonds without termination atoms in the group illustrations are assumed to be the above carbon atom types, but the listed volumes do not include any contributions from these carbon atoms. The table includes the corresponding gram-molecular weights for use in calculating theoretical maximum densities (TMD).

Table III also gives the TMD of the groups obtained by dividing their weights per mole by their displacement volumes per mole. These densities cannot be used for estimating densities of compounds, but they are useful in choosing groups to consider, as when a dense explosive is desired. The example calculation below shows the use of the tables. The volume of nitramide (H_2NNO_2) can be calculated from the structural formula



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the van der Waals radii (R) (listed in Table I and below), and the interatomic distances (d) as follows.

$d_{H\text{-}N} = 1.01$ Å $\quad R_H = 1.20$ Å

$d_{N\text{-}N} = 1.36$ Å $\quad R_N = 1.55$ Å

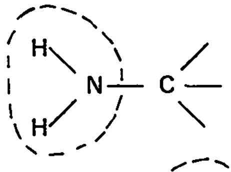
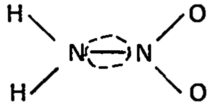
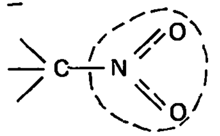
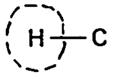
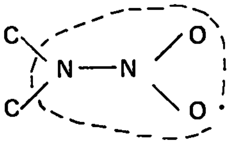
$d_{N\text{-}O} = 1.23$ Å $\quad R_O = 1.52$ Å

The atom sphere volumes and subtracted segment volumes are

Atom	Sphere Volume (Å^3) [(4/3 πR^3)]	Segment Volumes (Å^3)
H	7.238	−3.490 (N at 1.01 Å)
N (N-$\underline{N}H_2$)	15.598	−1.381, −1.381, −2.996
N (N-$\underline{N}O_2$)	15.598	−2.996, −3.166, −3.166
O	14.710	−3.365 (N at 1.23 Å)

The total displacement volume of two hydrogens, two nitrogens, and two oxygens is 46.298 Å^3/molecule or, multiplying by 0.60226, 27.88 cm^3/mole.

The volume can also be obtained from entries in Tables II and III as follows.

Group	Group Volume (cm^3/mole) (Table III)	Additivity Correction (cm^3/mole) (Table II)
	10.02	 0.84
	17.02	
	OR	
	1.85	 1.80
	20.58	

The first group volume calculation gives 10.02 + 17.02 + 0.84, or 27.88 cm^3/mole; the second gives (1.85) (2) + 20.58 + (1.80) (2), and again, 27.88 cm^3/mole.

Once the gram molecular weight and the displacement volume of a material are known, the only additional parameter needed to estimate the crystal density is the packing coefficient. Kitaigorodsky[4] states that the packing coefficient for the overwhelming majority of crystals is between 0.65 and 0.77. I rechecked this range because the radii I used are not identical with Kitaigorodsky's and because the compounds of interest for explosives usually contain nitrogen and oxygen, which may skew the packing coefficient distribution. Packing coefficients (k) were calculated ($k_{obs} = \rho meas/\rho TMD$) for all organic materials whose crystal densities are listed in handbooks by Brigitta Dobratz,[6] Rudolf Meyer,[7] and the U.S. Army Materiel Command;[8] those listed by Michael Coburn;[9] and several additional explosives and hydrocarbons. These "observed" packing coefficients are reported in Table IV.

Table IV indicates a rough trend of decreasing packing coefficient with an increasing number of hydrogen atoms attached to carbon atoms. This trend does not seem to apply to other hydrogen atoms, possibly because the proton of a covalently bonded hydrogen is partly exposed since its electron is drawn into the bond. The more electronegative the adjacent atom, the more the proton is exposed. Hydrogen atoms thus appear as positive electrostatic charges and tend to repel each other. Exposed oxygen, fluorine, chlorine, and nitrogen atoms tend to appear as negative charges, so they would be attracted to hydrogen atoms. When this attraction is strong, it is called a hydrogen bond. Hydrogen atoms attached to carbon atoms classically cannot form hydrogen bonds, so they must have nearly shielded protons.

The packing coefficient that results from this electrostatic effect can be modified by counting the number and strength of exposed charges and adjusting the packing coefficient accordingly; however, this technique involves too many quantum

TABLE II

SINGLE BOND LENGTHS (d in Å) AND GROUP ADDITIVITY CORRECTIONS FOR VOLUME CALCULATIONS (ΔV in cm³/mole)

A—C⟨ + ⟩C—B → A—B : $V_{A-B} = V_A + V_B + \Delta V$

C—B d	⟩—C⟨ 1.54	⟩—C″– 1.51	⟩—C⟨ 1.51	⟩—C≡ 1.46	⟩—N⟨ 1.47	⟩—NO₂ 1.47	⟩—N= 1.47	⟩—O–H 1.43	⟩—O–R 1.43	⟩—O–ϕ 1.43	⟩—H 1.09	⟩—F 1.33	⟩—Cl 1.77	
A—C⟨ d														
⟩C—⟨ 1.54	1.54 0.00	1.51 −0.07	1.51 −0.43	1.46 −0.82	1.47 0.54	1.47 0.54	1.47 0.54	1.43 0.60	1.43 0.76	1.43 0.75	1.09 1.58	1.33 0.89	1.77 0.28	d ΔV
–C″—⟨ 1.51		1.46 −0.22	1.49 −0.45	1.45 −0.59	1.36 0.17	1.47 0.61	1.33 0.05	1.36 0.40	1.36 0.57	1.36 0.55	1.08 1.82	1.33 0.76	1.72 0.14	d ΔV
⟩C—⟨ 1.51			1.52 −0.71	1.44 −1.07	1.43 0.15	1.47 0.31	1.34 −0.23	1.36 0.11	1.41 0.54	1.42 0.55	1.08 0.84	1.33 0.48	1.70 −0.29	d ΔV
⟩C—⟨ 1.51					1.34 −0.23	— N(H)⟍ ORTHO TO NITRO								d ΔV
≡C—⟨ 1.46				1.37 −1.38	1.46 0.24	1.47 0.37	1.44 0.24	1.36 0.16	1.36 0.35	1.36 0.32	1.06 1.50	1.32 0.50	1.64 −0.52	d ΔV
⟩N—⟨ 1.47					1.45 1.16	1.36 0.84	1.36 0.84	1.41 1.22	1.41 1.83	1.41 1.75	1.01 1.80	1.36 1.46	1.75 0.95	d ΔV
O₂N—⟨ 1.47						1.75 2.16	1.36 0.84	1.36 1.05	1.36 1.66	1.36 1.58	1.01 1.80	1.36 1.46	1.97 1.71	d ΔV
=N—⟨ 1.47							1.36 0.84	1.41 1.22	1.41 1.83	1.41 1.75	1.01 1.80	1.36 1.46	1.97 1.71	d ΔV
H–O—⟨ 1.43								1.48 1.66	1.48 2.27	1.48 2.19	0.96 1.82	1.42 1.85	1.70 0.97	d ΔV
R–O—⟨ 1.43									1.48 2.88	1.48 2.80	0.96 2.43	1.42 2.46	1.70 1.58	d ΔV
ϕ–O—⟨ 1.43										1.48 2.72	0.96 2.35	1.42 2.38	1.70 1.50	d ΔV

e.g. $>N\underset{1.47}{—}\in \; + \; \ni\underset{1.09}{—}H \longrightarrow >N\underset{1.01}{—}H$

The normal N–C single bond length is 1.47 Å(Row 5), the C–H bond length is 1.09 Å(Col. 11), and the N–H bond length is 1.01 Å(Row 5, Col. 11 intersection). The volume of the N–H group is estimated from V_{N-C}(2.72), V_{C-H} (1.85) and ΔV(1.80) to be 2.72 + 1.85 + 1.80 or 6.37 cm³/mole. The values 2.72 and 1.85 cm/mole come from Table III.

DOUBLE BOND LENGTHS (d in Å) AND GROUP ADDITIVITY CORRECTIONS FOR VOLUME CALCULATIONS (ΔV in cm³/mole)

A═C⟨ + ⟩C═B → A═B : $V_{A=B} = V_{A=} + V_{=B} + \Delta V$

⟩C═B d	⟩═C 1.33	⟩═N– 1.30	⟩═O 1.21	
A═C⟨ d				
C═⟨ 1.37	1.33 0.00	1.30 0.76	1.21 0.89	d ΔV
–N═⟨ 1.30		1.25 1.84	1.14 1.31	d ΔV

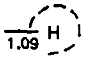
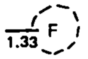
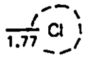
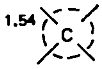
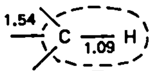
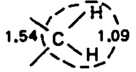
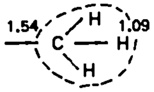
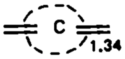
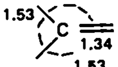
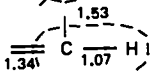
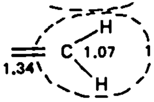
TRIPLE BOND LENGTHS (d in Å) AND GROUP ADDITIVITY CORRECTIONS FOR VOLUME CALCULATIONS (ΔV in cm³/mole)

A≡C– + –C≡B → A≡B : $V_{A\equiv B} = V_{A\equiv} + V_{\equiv B} + \Delta V$

–C≡B d	–≡C– 1.20	–≡N 1.16	
A≡C– d			
–C≡– 1.20	1.20 0.00	1.16 1.21	d ΔV

TABLE III

VOLUMES OF COMMON GROUPS

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
		1.01	1.85	0.54
		19.00	5.57	3.41
		35.45	11.66	3.04
Alkane		12.01	3.30	3.64
		13.02	6.73	1.94
		14.03	10.16	1.38
		15.04	13.59	1.11
Olefinic		12.01	6.95	1.73
		12.01	5.08	2.37
		13.02	8.48	1.54
		14.03	11.87	1.18

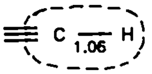
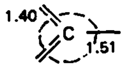
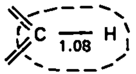
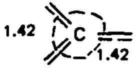
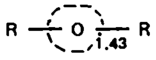
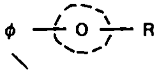
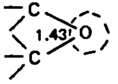
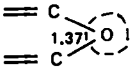
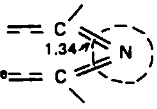
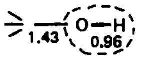
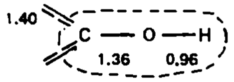
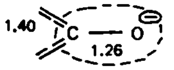
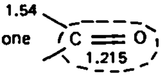
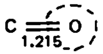
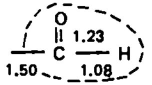
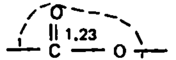
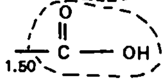
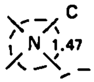
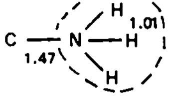
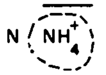
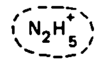
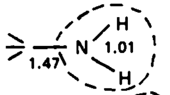
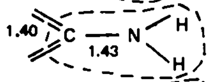
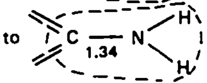
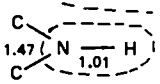
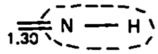
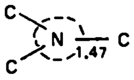
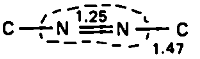
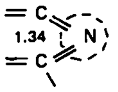
	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Acetylenic		12.01	8.06	1.49
		13.02	11.42	1.14
Aromatic		12.01	5.46	2.21
		13.02	8.15	1.60
		12.01	4.95	2.42
Ether poly alkane		16.00	3.77	4.25
poly phenyl		16.00	3.25	4.93
		16.00	3.51	4.59
aliphatic heterocycle		16.00	4.31	3.71
conjugated hetero-cycle		16.00	4.01	3.99
aromatic heterocycle		14.01	3.53	3.96

TABLE III (cont)

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Alcohol		17.01	7.97	2.13
		29.02	13.53	2.14
		28.01	11.73	2.39
Ketone		28.01	11.69	2.40
		16.00	5.70	2.81
Aldehyde		29.02	15.09	1.92
Ester		44.01	16.40	2.68
Acid		45.02	19.97	2.25
Quaternary Nitrogen		14.01	0.49^a	28.59
		17.03	11.44	1.49

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Quarternary		18.04	15.10	1.19
		33.05	22.56	1.47
Amine		16.02	10.02	1.60
		28.03	15.62	1.79
Ortho to Nitro		28.03	15.25	1.84
		15.02	6.37	2.36
		15.02	8.16	1.84
		14.01	2.72	5.16
		14.01	4.52	3.10
		28.01	10.32	2.72
		14.01	3.53	3.96

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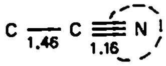
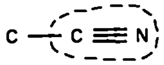
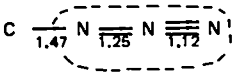
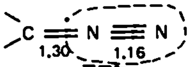
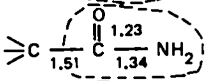
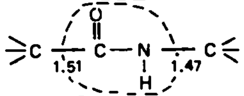
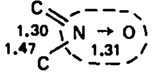
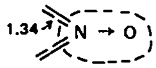
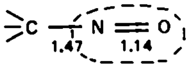
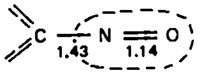
^{a}Fictitiously low due to neglect of overlapped segments, but compensated during calculations of molecular volume.

TABLE III (cont)

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Nitrile		14.01	6.69	2.10
		26.02	15.95	1.63
Azide		42.02	18.41	2.28
		40.03	18.54	2.16
Amide		44.03	21.72	2.03
		43.03	18.07	2.38
		30.01	9.73	3.08
		30.01	8.76	3.43
Nitroso		30.01	11.75	2.55
		42.02	17.36	2.42

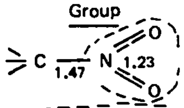
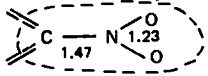
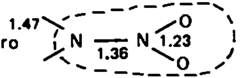
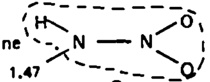
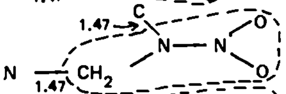
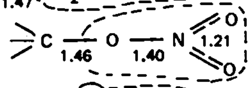
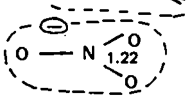
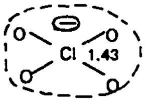
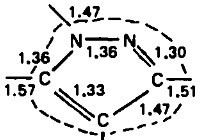
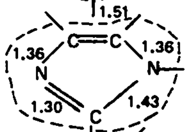
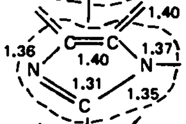
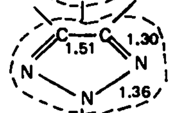
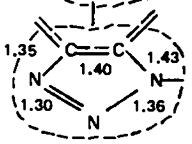
	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Nitro		46.01	17.02	2.70
		58.02	22.79	2.55
N-Nitro		60.01	20.58	2.92
Nitramine		61.02	24.23	2.52
		74.04	31.82	2.33
Nitrate		62.00	22.44	2.76
		62.00	24.06	2.58
	HNO_3	63.01	25.34	2.49
Perchlorate		99.45	32.18	3.09

TABLE III (cont)

5-Member rings

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Pyrazol		64.05	23.72	2.70
		64.05	23.67	2.71
Imidazole		64.05	23.79	2.69
1,2,3–Triazole		66.04	24.88	2.65
		66.04	24.94	2.66

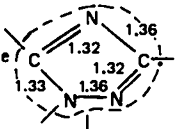
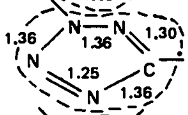
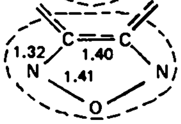
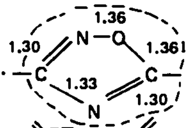
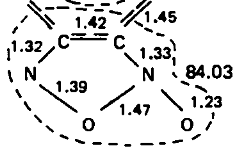
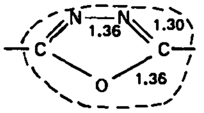
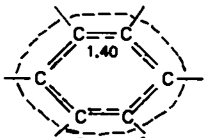
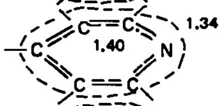
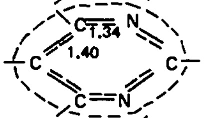
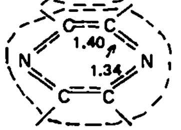
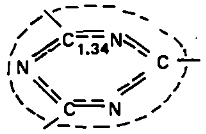
	Group	g/mole	cm^3/mole	TMD (g/cm^3)
1,2,4–Triazole		66.04	24.41	2.71
		66.04	24.37	2.71
Tetrazole		68.04	25.12	2.71
Furazan		68.04	27.23	2.50
		68.04	26.92	2.53
1,2,4 Oxadia-zolyl		68.04	26.27	2.59
Benzfuroxan		84.03	32.37	2.60

TABLE III (cont)

	Group	g/mole	cm^3/mole	TMD (g/cm^3)
1,3,4–Oxadiazolyl		68.04	26.43	2.57
6–Member rings				
Benzene		72.07	32.73	2.20
Pyridine		74.06	33.07	2.24
Pyrimidine		76.06	33.40	2.28
Pyrazine		76.06	33.40	2.28
Triazine		78.05	33.73	2.31

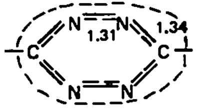
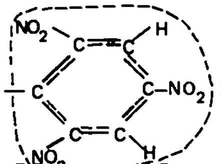
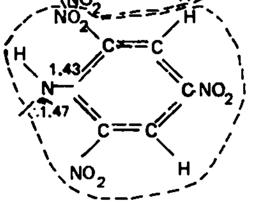
	Group	g/mole	cm^3/mole	TMD (g/cm^3)
Tetrazine		80.05	33.68	2.38
Picryl		212.10	90.12	2.35
Picryl Amino		227.11	96.64	2.35

TABLE IV

OBSERVED AND CALCULATED DENSITIES

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div\sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
Nitramide	$H_2N_2O_2$	1.783	0.80	0.77	–1.0	1.71	2.03	1.88
Ammonium perchlorate	H_4NO_4Cl	1.95	0.78	0.77	–0.4	1.91	2.05	1.95
Ammonium nitrate	$H_4N_2O_3$	1.73	0.85	0.77	–2.6	1.57	1.76	1.70
Ammonium azide	H_4N_4	1.346	0.80	0.77	–1.0	1.29	1.26	1.46
Hydrazine perchlorate	$H_5N_2O_4Cl$	1.83	0.76	0.77	0.3	1.86	2.01	1.94
Hydrazine nitrate	$H_5N_3O_3$	1.64	0.80	0.77	–1.0	1.57	1.76	1.73
Nitroguanidine	$CH_4N_4O_2$	1.72	0.80	0.77	–1.0	1.65	1.76	1.65
Urea nitrate	$CH_5N_3O_4$	1.65	0.73	0.77	1.3	1.75	1.79	1.70
Methylamine nitrate	$CH_6N_2O_3$	1.422	0.75	0.74	–0.4	1.40	1.56	1.49
Triaminoguanidine nitrate	$CH_9N_7O_3$	1.5	0.74	0.77	0.9	1.56	1.68	1.66
Hexanitroethane	$C_2N_6O_{12}$	1.81^{12}, 2.00^{10}, 2.25^{12}	0.68	0.77	2.9	2.06	2.14	2.06
4–Nitro–1,2,3–triazole	$C_2H_2N_4O_2$	1.72	0.75	0.75	0.0	1.73	1.83	1.75
Ethylenedinitramine	$C_2H_6N_4O_4$	1.71	0.79	0.74	–1.7	1.58	1.75	1.66
Ethanolamine dinitrate	$C_2H_7N_3O_6$	1.53	0.72	0.74	0.6	1.58	1.70	1.62
Ethylenediamine dinitrate	$C_2H_{10}N_4O_6$	1.577	0.78	0.75	–1.1	1.51	1.66	1.57
Cyanurictriazide	C_3N_{12}	1.54	0.67	0.77	3.2	1.75	1.71	1.53
2,4–dinitroimidazole	$C_3H_2N_4O_4$	1.76	0.73	0.76	0.9	1.84	1.88	1.85
Ammonium 2,4,5–trinitroimidazole	$C_3H_4N_6O_6$	1.835	0.76	0.77	–0.3	1.86	1.90	1.80
RDX	$C_3H_6N_6O_6$	1.806	0.78	0.73	–1.6	1.71	1.86	1.87
4,4'–dinitro–3,3'–bi-furazanyl	$C_4N_6O_6$	1.85	0.73	0.77	1.2	1.96	2.05	1.86
5,5'–dinitro–3,3'–bi–1,2,4–triazole	$C_4H_2N_8O_4$	1.76	0.72	0.75	1.0	1.83	1.94	1.85
Sorguyl	$C_4H_2N_8O_{10}$	2.03	0.78	0.76	–0.7	1.97	2.10	2.15
4–Amino–3,5–dinitro–1–methyl-pyrazole	$C_4H_5N_5O_4$	1.70	0.76	0.75	–0.4	1.68	1.77	1.72
Dinitrodimethyloxamide	$C_4H_6N_4O_6$	1.523	0.69	0.73	1.3	1.60	1.68	1.62
Erythritoltetranitrate	$C_4H_6N_4O_{12}$	1.6	0.67	0.74	2.2	1.78	1.91	1.74
Dioxiethylnitraminedinitrate	$C_4H_8N_4O_8$	1.488	0.78	0.73	1.8	1.60	1.73	1.62
Beta – HMX	$C_4H_8N_8O_8$	1.90	0.82	0.73	–2.5	1.71	1.85	1.84
Alpha – HMX	$C_4H_8N_8O_8$	1.84	0.79	0.73	–1.9	1.71	1.85	1.84
Gamma – HMX	$C_4H_8N_8O_8$	1.78	0.76	0.73	–0.9	1.71	1.85	1.84
Delta – HMX	$C_4H_8N_8O_8$	1.79	0.76	0.73	–0.9	1.71	1.85	1.84

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div \sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
2,3,6–Trinitropyridine–1–oxide	$C_5H_2N_4O_7$	1.87	0.75	0.75	0.0	1.87	1.89	1.86
3,5–Dinitro–2,4,6–triaminopyridine	$C_5H_6N_6O_4$	1.88	0.85	0.77	–2.6	1.70	1.81	1.73
PETN	$C_5H_8N_4O_{12}$	1.77	0.76	0.73	–0.9	1.69	1.82	1.68
PETRIN	$C_5H_9N_3O_{10}$	1.54	0.69	0.73	1.3	1.63	1.73	1.60
n-Pentane	C_5H_{12}	0.879	0.70	0.68	–0.7	0.85	0.87	0.86
Benzotrifuroxan	$C_6N_6O_6$	1.901	0.73	0.77	1.2	2.00	2.14	2.11
Hexanitrobenzene	$C_6N_6O_{12}$	2.00	0.78	0.77	–0.4	1.98	2.02	1.97
Trinitrotriazidobenzene	$C_6N_{12}O_6$	1.81	0.76	0.77	0.3	1.83	1.83	1.73
Trinitrochlorobenzene	$C_6H_2N_3O_6Cl$	1.797	0.74	0.75	0.5	1.84	1.86	1.81
Diazodinitrophenol	$C_6H_2N_4O_5$	1.63	0.72	0.75	1.1	1.79	1.82	1.77
Pentanitroaniline	$C_6H_2N_6O_{10}$	1.77	0.71	0.77	1.9	1.91	1.98	1.92
Dinitrochlorobenzene	$C_6H_3N_2O_4Cl$	1.70	0.73	0.74	0.5	1.75	1.74	1.70
1,3,5–Trinitrobenzene	$C_6H_3N_3O_6$	1.68	0.72	0.75	0.9	1.75	1.76	1.73
1,2,4–Trinitrobenzene	$C_6H_3N_3O_6$	1.73	0.75	0.75	0.0	1.72	1.76	1.73
Picric acid	$C_6H_3N_3O_7$	1.77	0.75	0.76	0.2	1.76	1.83	1.76
Styphnic acid	$C_6H_3N_3O_8$	1.829	0.77	0.76	–0.3	1.81	1.90	1.78
Tetranitroaniline	$C_6H_3N_5O_8$	1.867	0.78	0.76	–0.6	1.82	1.90	1.84
1,3–Dinitrobenzene	$C_6H_4N_2O_4$	1.575	0.73	0.74	0.2	1.60	1.61	1.60
1,2–Dinitrobenzene	$C_6H_4N_2O_4$	1.565	0.72	0.74	0.5	1.60	1.61	1.60
1,4–Dinitrobenzene	$C_6H_4N_2O_4$	1.625	0.75	0.74	–0.4	1.60	1.61	1.60
2,3–Dinitrophenol	$C_6H_4N_2O_5$	1.681	0.76	0.75	–0.5	1.64	1.76	1.69
2,4–Dinitrophenol	$C_6H_4N_2O_5$	1.683	0.76	0.75	–0.5	1.64	1.76	1.69
3,4–Dinitrophenol	$C_6H_4N_2O_5$	1.672	0.75	0.75	0.0	1.64	1.76	1.69
3,5–Dinitrophenol	$C_6H_4N_2O_5$	1.702	0.77	0.75	–0.8	1.64	1.76	1.69
Picramide	$C_6H_4N_4O_6$	1.76	0.77	0.76	–0.5	1.73	1.80	1.75
2,4–Dinitroaniline	$C_6H_5N_3O_4$	1.615	0.75	0.75	0.0	1.60	1.67	1.63
DATB	$C_6H_5N_5O_6$	1.837	0.79	0.76	–0.9	1.77	1.89	1.81
4–Nitroaniline	$C_6H_6N_2O_2$	1.42	0.73	0.74	0.2	1.44	1.49	1.46
Ammonium picrate	$C_6H_6N_4O_7$	1.72	0.77	0.76	–0.4	1.69	1.76	1.71
TATB	$C_6H_6N_6O_6$	1.938	0.85	0.77	–2.6	1.75	1.76	1.79
TNETB	$C_6H_6N_6O_{14}$	1.78	0.72	0.74	0.8	1.85	1.87	1.78
Manitolhexanitrate	$C_6H_8N_6O_{18}$	1.73	0.71	0.74	1.0	1.81	1.94	1.77
Hexamethylenetriperoxidediamine	$C_6H_{12}N_2O_6$	1.57	0.80	0.71	–2.9	1.42	1.66	1.62
n-Hexane	C_6H_{14}	0.888	0.70	0.68	–0.7	0.86	0.88	0.87

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div\sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
5–Picrylaminotetrazole	$C_7H_4N_8O_6$	1.91	0.81	0.76	–1.7	1.79	1.85	1.76
TNT	$C_7H_5N_3O_6$	1.654	0.75	0.74	–0.4	1.62	1.67	1.64
2,3,4–Trinitrotoluene	$C_7H_5N_3O_6$	1.620	0.74	0.74	0.0	1.62	1.67	1.64
2,4,5–Trinitrotoluene	$C_7H_5N_3O_6$	1.620	0.74	0.74	0.0	1.62	1.67	1.64
Trinitroanisole	$C_7H_5N_3O_7$	1.61	0.72	0.74	0.6	1.66	1.72	1.66
Trinitrometacresol	$C_7H_5N_3O_7$	1.68	0.74	0.75	0.2	1.68	1.74	1.67
Tetryl	$C_7H_5N_5O_8$	1.73	0.75	0.74	–0.2	1.72	1.77	1.74
2,4– Dinitrotoluene	$C_7H_6N_2O_4$	1.52	0.73	0.73	0.0	1.51	1.53	1.51
2,2–Dinitropropyl–4,4,4–trinitrobutyrate	$C_7H_9N_5O_{12}$	1.68	0.70	0.73	1.1	1.75	1.73	1.66
n-Heptane	C_7H_{16}	0.872	0.68	0.68	0.0	0.87	0.89	0.87
4–Nitro–1–picryl–1.2.3–triazole	$C_8H_3N_7O_8$	1.85	0.78	0.75	–0.9	1.80	1.84	1.79
4–Nitro–2–picryl–1.2.3–triazole	$C_8H_3N_7O_8$	1.75	0.73	0.75	–0.8	1.77	1.84	1.79
3–Nitro–1–picryl–1.2.4–triazole	$C_8H_3N_7O_8$	1.75	0.73	0.75	0.8	1.81	1.84	1.79
3–Nitro–4–picrylaminofurazan	$C_8H_3N_7O_9$	1.81	0.75	0.76	0.3	1.84	1.89	1.81
1–(3,4–dinitrophenyl)–4–nitro–1.2.3–triazole	$C_8H_4N_6O_6$	1.73	0.75	0.75	0.0	1.73	1.75	1.71
1–(3,5–dinitrophenyl)–4–nitro–1.2.3–triazole	$C_8H_4N_6O_6$	1.74	0.75	0.75	0.0	1.73	1.75	1.71
1– Picryl–1.2.3–triazole	$C_8H_4N_6O_6$	1.695	0.74	0.75	0.2	1.71	1.75	1.71
2–Picryl–1.2.3–triazole	$C_8H_4N_6O_6$	1.69	0.74	0.75	0.2	1.71	1.75	1.71
1–Picryl–1.2.4–triazole	$C_8H_4N_6O_6$	1.78	0.78	0.75	–0.9	1.72	1.75	1.71
2–Picrylamino–1.3.4–oxadiazole	$C_8H_4N_6O_7$	1.76	0.75	0.75	0.0	1.76	1.81	1.74
1–(3–Amino–2.4.6–trinitrophenyl)–1.2.3–triazole	$C_8H_5N_7O_6$	1.75	0.76	0.75	–0.2	1.73	1.79	1.73
4–Picrylamino–1.2.3–triazole	$C_8H_5N_7O_6$	1.78	0.78	0.75	–0.9	1.73	1.79	1.73
3–Picrylamino–1.2.4–triazole	$C_8H_5N_7O_6$	1.936	0.84	0.75	–2.8	1.73	1.79	1.73
4–Picrylamino–1.2.4–triazole	$C_8H_5N_7O_6$	1.78	0.78	0.75	–0.9	1.72	1.79	1.73
3–Amino–4–picrylaminofurazan	$C_8H_5N_7O_7$	1.77	0.77	0.76	–0.3	1.75	1.84	1.75
3–Amino–6–picrylamino–s–tetrazine	$C_8H_5N_9O_{16}$	1.78	0.77	0.76	–0.3	1.75	1.81	1.70
Trinitrophenoxethylnitrate	$C_8H_6N_4O_{10}$	1.68	0.73	0.74	0.3	1.70	1.78	1.69
Trinitrophenylnitraminoethylnitrate	$C_8H_6N_6O_{11}$	1.75	0.75	0.74	0.2	1.74	1.82	1.75
1,1'–Dimethyl–3,3',5,5'–tetranitro–4,4'–bipyrazolyl	$C_8H_6N_8O_8$	1.75	0.75	0.74	–0.2	1.73	1.77	1.75

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div\sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
3–Amino–5–picrylamino–1,2,4–triazole	$C_8H_6N_{11}O_{12}$	1.85	0.81	0.76	–1.6	1.75	1.82	1.75
2,4,6–Trinitro-m-xylene	$C_8H_7N_3O_6$	1.604	0.75	0.73	–0.6	1.56	1.60	1.57
2,3,6–Trinitro-p-xylene	$C_8H_7N_3O_6$	1.590	0.74	0.73	–0.3	1.56	1.60	1.57
Dinitrophenoxiethylnitrate	$C_8H_7N_3O_8$	1.60	0.72	0.73	0.5	1.63	1.68	1.69
n-Octane	C_8H_{18}	0.858	0.66	0.68	0.7	0.88	0.90	0.88
2,4–Dinitro–1–picrylimidazole	$C_9H_3N_7O_{10}$	1.75	0.72	0.74	1.4	1.84	1.86	1.83
2–Nitro–1–picrylimidazole	$C_9H_4N_6O_8$	1.75	0.74	0.75	0.3	1.76	1.78	1.76
4–Nitro–1–picrylimidazole	$C_9H_4N_6O_8$	1.75	0.74	0.75	0.3	1.76	1.78	1.76
4–Nitro–1–picrylpyrazole	$C_9H_4N_6O_8$	1.70	0.73	0.75	0.6	1.75	1.78	1.76
1–Picrylimidazole	$C_9H_5N_5O_6$	1.75	0.77	0.74	–0.9	1.68	1.70	1.68
1–Picrylpyrazole	$C_9H_5N_5O_6$	1.60	0.71	0.74	1.1	1.67	1.70	1.68
4–Nitro–3–picrylaminopyrazole	$C_9H_5N_7O_8$	1.77	0.76	0.76	0.0	1.76	1.81	1.78
3–Picrylaminopyrazole	$C_9H_6N_6O_6$	1.70	0.76	0.75	–0.3	1.67	1.73	1.70
4–Picrylaminopyrazole	$C_9H_6N_6O_6$	1.70	0.76	0.75	–0.3	1.67	1.73	1.70
2–(2,2'–Dinitropropoxy)–1,3,5–trinitrobenzene	$C_9H_7N_5O_{11}$	1.69	0.74	0.74	0.0	1.70	1.76	1.70
1,3,5–Trinitro–2,4,6–tris(methylnitramino)benzene	$C_9H_9N_9O_{12}$	1.65	0.71	0.74	0.9	1.71	1.79	1.75
Tetramethylolcyclopentanonetetranitrate	$C_9H_{12}N_4O_{13}$	1.59	0.71	0.73	0.6	1.63	1.72	1.63
3,3',5,5'–Tetranitro–2,2'–azopyridine	$C_{10}H_4N_8O_8$	1.83	0.78	0.75	–0.9	1.82	1.76	1.67
4–Nitro–4–picrylamino–3,3'–bifurazanyl	$C_{10}H_3N_9O_{10}$	1.77	0.73	0.76	1.0	1.85	1.89	1.80
3,5–Dinitro–1–methyl–4–picrylpyrazole	$C_{10}H_5N_7O_{10}$	1.72	0.73	0.75	0.6	1.76	1.79	1.77
2–Picrylaminopyrimidine	$C_{10}H_6N_6O_6$	1.71	0.78	0.75	–0.9	1.66	1.69	1.63
1–Methyl–3–nitro–4–picrylpyrazole	$C_{10}H_6N_6O_8$	1.71	0.75	0.74	–0.2	1.69	1.70	1.70
3,5–Dinitro–1–methyl–4–picrylaminopyrazole	$C_{10}H_6N_8O_{10}$	1.74	0.74	0.75	0.3	1.75	1.81	1.77
Napthalene	$C_{10}H_8$	1.184	0.69	0.71	0.7	1.21	1.19	1.22
Bis(2,2–dinitropropyl)fumarate	$C_{10}H_{12}N_4O_{12}$	1.60	0.73	0.73	0.0	1.59	1.64	1.53
Ethyleneglycolditrinitrobutyrate	$C_{10}H_{12}N_6O_{16}$	1.63	0.71	0.73	0.8	1.68	1.72	1.64
Bis(2,2–dinitropropyl)succinate	$C_{10}H_{14}N_4O_{12}$	1.51	0.70	0.72	0.8	1.56	1.59	1.51
Camphor	$C_{10}H_{16}O$	0.990	0.63	0.69	3.0	1.10	1.07	1.04
DiPEHN	$C_{10}H_{16}N_6O_{19}$	1.63	0.72	0.73	0.3	1.65	1.75	1.61

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div\sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
N-picryl–7–nitro-v- triazole(4,5-C)pyridine	$C_{11}H_4N_8O_8$	1.78	0.76	0.75	–0.3	1.82	1.76	1.67
Hexanitrodiphenyloxide	$C_{12}H_4N_6O_{13}$	1.70	0.71	0.75	1.4	1.79	1.83	1.79
TACOT	$C_{12}H_4N_8O_8$	1.85	0.79	0.75	–1.2	1.77	1.82	1.68
4,6–Dinitro–1–picrylbenzotriazole	$C_{12}H_4N_8O_{10}$	1.86	0.78	0.75	–0.9	1.80	1.74	1.63
5,6–Dinitro–1–picrylbenzotriazole	$C_{12}H_4N_8O_{10}$	1.77	0.74	0.75	0.4	1.80	1.74	1.63
5,7–Dinitro–1–picrylbenzotriazole	$C_{12}H_4N_8O_{10}$	1.74	0.73	0.75	0.8	1.80	1.74	1.63
HNAB-I	$C_{12}H_4N_8O_{12}$	1.799	0.75	0.75	0.0	1.80	1.81	1.74
HNAB-II	$C_{12}H_4N_8O_{12}$	1.750	0.73	0.75	0.8	1.80	1.81	1.74
HNAB-III	$C_{12}H_4N_8O_{12}$	1.718	0.72	0.75	1.1	1.80	1.81	1.74
Hexanitrodiphenylamine	$C_{12}H_5N_7O_{12}$	1.64	0.70	0.75	1.8	1.77	1.88	1.78
DIPAM	$C_{12}H_6N_8O_{12}$	1.79	0.76	0.76	0.0	1.79	1.81	1.80
3,5–Bis(picrylamino)–1,2,4–triazole	$C_{12}H_7N_{11}O_{12}$	1.81	0.77	0.76	–0.4	1.78	1.83	1.78
Dinitrodiphenylamine	$C_{12}H_9N_3O_4$	1.42	0.70	0.73	1.0	1.49	1.49	1.48
Diphenyl	$C_{12}H_{10}$	1.185	0.70	0.71	0.3	1.19	1.17	1.18
Diphenylamine	$C_{12}H_{11}N$	1.16	0.67	0.73	1.9	1.23	1.20	1.22
1,3–Bis(2,2–dinitropropoxy)–2,4,6–trinitrobenzene	$C_{12}H_{11}N_7O_{16}$	1.67	0.72	0.74	0.6	1.70	1.76	1.68
Bicyclohexylidine	$C_{12}H_{20}$	1.07	0.73	0.69	–1.3	1.01	1.02	1.06
HNS	$C_{14}H_6N_6O_{12}$	1.74	0.76	0.75	–0.4	1.72	1.73	1.70
2–Picryl–3–picrylamino–1,2,4–triazole	$C_{14}H_6N_{10}O_{12}$	1.80	0.77	0.75	–0.5	1.77	1.81	1.77
1–Picryl–4–picrylamino–1,2,3–triazole	$C_{14}H_6N_{10}O_{12}$	1.75	0.74	0.75	0.2	1.77	1.81	1.77
3,4–Bis(picrylamino)furazan	$C_{14}H_6N_{10}O_{13}$	1.86	0.79	0.76	–1.1	1.78	1.84	1.79
3,5–Bis(picrylamino)–1,2,4–oxadiazole	$C_{14}H_6N_{10}O_{13}$	1.70	0.72	0.75	1.1	1.79	1.82	1.78
3,6–Bis(picrylamino)–s–tetrazine	$C_{14}H_6N_{12}O_{12}$	1.82	0.77	0.76	–0.4	1.78	1.81	1.70
Anthracene	$C_{14}H_{10}$	1.248	0.71	0.72	0.2	1.26	1.23	1.27
1,4–Dipicrylpyrazole	$C_{15}H_6N_8O_{12}$	1.71	0.74	0.75	0.3	1.74	1.77	1.74
4–Nitro–1–picryl–3–picrylaminopyrazole	$C_{15}H_6N_{10}O_{14}$	1.72	0.73	0.75	0.8	1.79	1.82	1.79
5–Nitro–1–picryl–4–picrylaminopyrazole	$C_{15}H_6N_{10}O_{14}$	1.72	0.73	0.75	0.8	1.79	1.82	1.79
1–Picryl–3–picrylaminopyrazole	$C_{15}H_7N_9O_{12}$	1.67	0.72	0.75	1.0	1.75	1.72	1.69
1–Picryl–4–picrylaminopyrazole	$C_{15}H_7N_9O_{12}$	1.73	0.75	0.75	0.0	1.75	1.72	1.69
1–Picryl–5–picrylaminopyrazole	$C_{15}H_7N_9O_{12}$	1.67	0.72	0.75	1.0	1.75	1.72	1.69
3,5–Bis(picrylamino)pyrazole	$C_{15}H_8N_{10}O_{12}$	1.70	0.74	0.75	0.5	1.74	1.80	1.76
TRIPEON	$C_{15}H_{24}N_8O_{26}$	1.58	0.70	0.73	0.8	1.63	1.73	1.59

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) (Eq. (4))	Deviation $\div\sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
N,N'–Dipicryl–5,5'–dinitro–3,3'–bi–1,2,4–triazole	$C_{16}H_4N_{14}O_{16}$	1.71	0.70	0.76	1.9	1.85	1.88	1.83
4,4'–Bis(picrylamino)–3,3'–bifurazanyl	$C_{16}H_6N_{12}O_{14}$	1.81	0.76	0.76	0.0	1.79	1.85	1.77
1–picryl–2–picrylimino–1,2–dihydropyrimidine	$C_{16}H_7N_9O_{12}$	1.74	0.76	0.75	0.4	1.72	1.74	1.70
5,5–Bis(picrylamino)–3,3'–bi–1,2,4–triazole	$C_{16}H_8N_{14}O_{12}$	1.80	0.77	0.76	–0.4	1.78	1.83	1.77
Hexadecanol	$C_{16}H_{34}O$	0.982	0.70	0.69	–0.5	0.96	0.97	0.94
2,6–Bis(picrylazo)–3,5–dinitropyridine	$C_{17}H_5N_{13}O_{16}$	1.86	0.78	0.76	–0.8	1.81	1.82	1.73
2,5–Bis(picrylamino)–3,6–dinitropyridine	$C_{17}H_7N_{11}O_{16}$	1.77	0.75	0.76	0.2	1.78	1.83	1.78
2,6–Bis(picrylamino)–3,5–dinitropyridine	$C_{17}H_7N_{11}O_{16}$	1.77	0.75	0.76	0.2	1.78	1.83	1.78
3,5–Bis(picrylamino)–2,6–dinitropyridine	$C_{17}H_7N_{11}O_{16}$	1.77	0.75	0.76	0.2	1.78	1.83	1.78
Diethyldiphenylurea	$C_{17}H_{20}N_2O$	1.112	0.66	0.68	0.7	1.15	1.15	1.11
2,6–Dipicrylbenzo(1,2–d: 4,5–d')bistriazole–4,8–dione	$C_{18}H_4N_{12}O_{14}$	1.85	0.77	0.76	–0.4	1.83	1.83	1.81
1,5–Dipicrylbenzo(1,2–d: 4,5–d')bistriazole	$C_{18}H_6N_{12}O_{12}$	1.79	0.75	0.75	0.0	1.78	1.80	1.77
1,7–Dipicrylbenzo(1,2–d: 4,5–d')bistriazole	$C_{18}H_6N_{12}O_{12}$	1.80	0.76	0.75	–0.2	1.78	1.80	1.77
3,5–Bis(picrylamino)–2,4,6–trinitrobenzene	$C_{18}H_7N_{11}O_{18}$	1.79	0.75	0.76	0.2	1.80	1.83	1.79
1,5–Bis(picrylamino)–2,4–dinitrobenzene	$C_{18}H_8N_{10}O_{16}$	1.78	0.76	0.75	–0.2	1.76	1.72	1.65
Tetracene	$C_{18}H_{12}$	1.300	0.73	0.72	–0.4	1.29	1.26	1.29
Terphenyl	$C_{18}H_{14}$	1.232	0.72	0.71	–0.4	1.22	1.19	1.20
1,4–Dipicryl–5–picrylamino–2–tetrazoline	$C_{19}H_6N_{14}O_{18}$	1.74	0.73	0.76	0.8	1.81	1.79	1.69
3,5–Bis(picrylamino)–1–picrylpyrazole	$C_{21}H_9N_{10}O_{18}$	1.67	0.71	0.75	1.4	1.77	1.81	1.78
2,4,5–Tris(picrylamino)–s–triazine	$C_{21}H_9N_{15}O_{18}$	1.75	0.75	0.76	0.2	1.77	1.83	1.76

TABLE IV (cont)

Compound	Formula	Density (Literature) (g/cm^3)	Packing Coefficient (k_{obs}) (ρ_L/TMD)	Packing Coefficient (k_{calc}) [Eq. (4)]	Deviation $\div \sigma_K$ $\frac{k_{calc} - k_{obs}}{0.031}$	ρ_{calc} [Eq. (6)] (g/cm^3)	ρ_{calc} (Immirizi Parameters) (g/cm^3)	ρ_{calc} (Holden Parameters) (g/cm^3)
5–Nitro–2,4,6–tris(picrylamino)-pyrimidine	$C_{22}H_9N_{15}O_{20}$	1.88	0.80	0.76	−1.4	1.78	1.84	1.78
2,4,6–Tris(picrylamino)pyrimidine	$C_{22}H_{10}N_{14}O_{18}$	1.90	0.82	0.75	−2.1	1.75	1.80	1.75
Pentacene	$C_{22}H_{14}$	1.335	0.74	0.72	−0.4	1.30	1.27	1.31
3,5–Dinitro–2,4,6–tris(picrylamino)-pyridine	$C_{23}H_9N_{15}O_{22}$	1.80	0.76	0.76	0.0	1.80	1.84	1.80
1,3,5–Trinitro–2,4,6–tris(picrylamino)-benzene	$C_{24}H_9N_{15}O_{24}$	1.82	0.76	0.76	−0.0	1.81	1.79	1.70
Quaterphenyl	$C_{24}H_{18}$	1.285	0.74	0.71	−1.3	1.22	1.20	1.21
Hexacene	$C_{26}H_{16}$	1.363	0.75	0.72	−0.6	1.31	1.28	1.33
N,N'–dipicryl–5,5'–bis(picrylamino)-3,3'–bi–1,2,4–triazole	$C_{28}H_{10}N_{20}O_{24}$	1.83	0.77	0.75	−0.5	1.80	1.80	1.74

mechanical calculations. An approximation for estimating the electrostatic term in the packing coefficient equation is to use as a parameter the atom fraction of hydrogen atoms bonded to carbon atoms. A linear fit of the 183 compounds in Table IV gives the following equation for the packing coefficient (k).

$$k = 0.7686 - 0.1280\,\underline{a} \quad , \tag{4}$$

where $\underline{a}$ is the atom fraction of hydrogen atoms bonded to carbon. The standard deviation of the intercept in Eq. (4) is 0.0036, that of the slope is 0.0154, and that of a predicted packing coefficient is 0.0309 when the goodness of fit parameter χ^2 equals 181, which is the number of degrees of freedom. Therefore, predicted densities will have an error of about 4% (0.03/0.75 x 100). Table IV lists the packing coefficients calculated using Eq. (4), as well as the deviation from the measured value expressed in multiples of the standard deviation (0.0309).

The use of Eq. (4) for estimating density is shown by continuing the nitramide example. The packing coefficient (k) is estimated by

$$k = 0.7686 - 0.1280(0/6) = 0.7686 \quad . \tag{5}$$

The density is then estimated using

$$\rho_{est} = (MW)(k)/V \quad , \tag{6}$$

where MW is the gram-molecular weight, k is the estimated packing coefficient, and V is the volume of a mole of molecules expressed in cubic centimeters as obtained by Eq. (3). Nitramide's density is estimated to be

$$\rho_{est} = (62.03)(0.7686)/(27.88) = 1.71\ g/cm^3 \quad .$$

The true crystal density is 1.783 g/cm^3, giving a 4% deviation or 0.07 g/cm^3; therefore, nitramide is an example whose estimated density is one standard deviation lower than the true density.

Nitramide is not an ideal example for calculating k because it has no hydrogen-carbon bonds. Another example illustrating the use of Eq. (4) is trinitroaniline (picramide), for which

$$k = 0.7686 - 0.1280(2/20) = 0.7558 \quad .$$

IV. OTHER TECHNIQUES AND RESULTS

After I had derived and checked this model for predicting crystal density, Tarver, Coon, and Guimont[10] of the Stanford Research Institute (SRI) published a group additivity method for estimating densities. Immirizi and Perini[11] published an atom additivity method for estimating densities, and Holden[12] independently determined similar atom additivity parameters.

Attempts to correlate my technique with the SRI technique were frustrating. I could calculate the densities of their compounds, but I could not determine which of their listed densities were those of solids and which were those of liquids. Only crystal densities can be compared. I tried to use the SRI parameters and techniques to estimate my known densities, but, except for the SRI calibration compounds, I could estimate only a few compound densities in Table IV. The principal problem was that SRI had not determined the needed parameters. When I could estimate the density, it differed from the measured density much more than one would expect from a cursory reading of the SRI report.

A variance analysis of the SRI and LASL results shows that the techniques for estimating k (LASL) and group volume (SRI) fit the observed standard-compound data equally well. However, if the variances are tested to determine the estimated error of a predicted density then the difficulty with the SRI approach becomes apparent. LASL determines k with a 2-parameter fit; SRI uses 74 parameters, many of which are based on only one measurement. Although the above analysis does not invalidate the SRI approach it shows that more data are required.

Immirizi and Perini's[11] or Holden's[12] atom additivity technique is straightforward and can be used to calculate volumes for common explosives. Immirizi and Perini determined incremental volumes from 500 compounds given in Ref. 13, Vols. 5 and 6. Holden determined volumes from 354 compounds biased toward explosives. Immirizi confirmed in a private communication that Ref. 11 contains an error; the volume of a nitro group is stated to be 25.6 Å^3 in their Table 2. Calculation from the values in their Table 1 implies that the $-NO_2$ volume should be 35.2 Å, a value that Immirizi has confirmed. Densities calculated using the 35.2 Å^3 value compare favorably with measured densities.

TABLE V

VOLUME INCREMENTS FOR SOME COMMON ELEMENTS
(Different coordination numbers are considered for C, N, and O.)

Atom	Coordination Number	Volume (cm^3/mole) (Immirizi and Perini)	Volume (cm^3/mole) (Holden)
C	4	6.63	7.00
C	3	8.25	8.80
C	2	9.22	10.50
H	1	4.16	4.10
H-Bonded	1+	2.53	3.10
N	4	---	4.00
N	3	4.34	4.80
N	2	7.71	10.40
N	1	9.64	7.10
O	2	5.54	8.20
O	1	8.43	8.60
F	1	7.71	9.30
Cl	4	---	9.50
Cl	1	16.08	17.70
Br	1	19.88	20.7
I	1	27.10	27.0
S	4	14.3	14.3
S	2		16.6
Aromatic Ring		−4.22	−7.8
Saturated Ring		−1.81	−7.2

Densities calculated by my technique and by the empirical atom additivity technique are similar. My technique contains a physical model that can be refined further with the aid of a larger data set, but it is somewhat more complicated to apply than the atom additivity technique. Table V lists the volume increments for the atom additivity method. Densities are estimated by dividing the gram-molecular weight by the sum of the volume increments from Table V. The correction for packing is built into the entries of Table V, but incremental corrections are required for rings and groups that often form hydrogen bonds. Immirizi's and Holden's techniques for handling hydrogen atoms are slightly different. Holden assumes that all hydrogens attached to either nitrogen or oxygen are hydrogen bonded, but Immirizi's definition of a hydrogen-bonded hydrogen is much more restricted and cannot be predicted *a priori*. In calculating the Immirizi values I assumed that all hydrogens that are attached to nitrogens or oxygens form hydrogen bonds to exposed oxygens on a 1:1 basis until either the hydrogens or oxygens are exhausted. The density of nitramide (H_2N-NO_2) would be estimated from Table V as

$$\rho_{est} = \frac{MW}{\Sigma V} = \frac{62.03}{2(2.53) + 2(4.34) + 2(8.43)} = 2.03 \text{ g/cm}^3$$

using Immirizi and Perini's parameters, and as

$$\rho_{est} = \frac{62.03}{2(3.10) + 2(4.80) + 2(8.60)} = 1.88 \text{ g/cm}^3$$

using Holden's parameters. For comparison, the true density is 1.783 g/cm^3 and the density estimated using my technique is 1.71 g/cm^3.

Densities calculated using my technique, Immirizi and Perini's parameters, and Holden's parameters are given in Table IV. My method gives 85 compounds with densities closest to the true value, Immirizi's parameters give 49 closest values, and Holden's give 92 closest values. The total exceeds the number of compounds listed in Table IV because of ties. The average values of $(\rho - \rho_{calc})$ are essentially zero by my method [by definition of Eq. (4)] and by Holden's method. Immirizi's technique overestimates densities of these compounds by about 0.05 g/cm^3. The standard deviations of these averages are essentially equal, showing that none of these techniques offers a significant predictive advantage even after correction for systematic deviations.

Examination of tables like Table IV for unusually dense or vacuous compounds accomplishes two things. It points out compounds, like hexanitroethane, whose reported densities may be erroneous, and it can show classes of compounds whose densities deviate systematically from those predicted. These latter classes of compounds can be used to determine future parameter corrections and can lead to more accurate predictions.

Compounds in Table IV that seem to have unusually low reported densities include erythritol tetranitrate, dioxiethylnitramine dinitrate, pentanitroaniline, hexanitrodiphenylamine, and N,N-dipicryl-5,5'-dinitro-3,3'-bi-2,4,6-triazole. They probably have erroneously reported densities, or higher density polymorphs that were not reported in the references used for this work.

At the other extreme are unusually dense compounds, including 3,5-dinitro-2,4,6-triaminopyridine, TATB, 5-picrylaminotetrazole, 3-picrylamino-1,2,4-triazole, and 2,4,6-tris(picrylamino)pyrimidine. They are all aromatic with adjacent nitro and amino groups—a feature that tends to cause the substitutent groups to be coplanar with the ring and to create large local dipoles. However, Table IV lists many other molecules that have the same features but are not unusually dense.

One way to calculate better packing coefficients might be to consider the inaccessible internal voids in a molecule. Other things being equal, molecules with small internal void volumes should have high packing coefficients and relatively high densities. The internal void volume of a molecule can be estimated if the molecular shape is known. Quantum mechanical calculations may provide a way to estimate molecular shapes and charge distributions.

One important check of this molecular shape approach will be comparison of the calculated molecular geometries with those found in crystals. Most of the calculated geometries must agree with those found in crystals if this technique is to be successful. The HMX molecule will provide an interesting test of the calculations because the molecular shape in β-HMX differs significantly from that in the other three polymorphs and in the known solvates.

V. CONCLUSIONS

Two techniques can be used to predict crystal densities of explosives. The standard deviation in a predicted density is about ± 0.07 g/cm^3 by either Holden's or my technique. Immirizi's technique is essentially the same as Holden's, but Immirizi's parameters apparently contain a systematic error when used for explosives.

Density predictions with probable errors of 0.07 g/cm^3 are useful for selecting potentially useful compounds, but this tool cannot form a good basis for restricting synthesis efforts because the probable error is still too large. Compounds of special interest will continue to be those whose measured densities deviate significantly above their predicted values.

Density predictions are useful for locating compounds whose densities may have been reported erroneously and those densities should be redetermined.

VI. FUTURE WORK

It will be necessary to examine many more compounds to determine other parameters that can be used to make predictions more reliable.

The Cambridge Crystallographic Files contain information on about 24 000 compounds. This file should be processed to determine additional parameters and new values for both techniques. One point of particular interest will be to determine why the mean value obtained by averaging my calculated density with that calculated by Holden's technique is not significantly more accurate than that obtained by using either technique separately.

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