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A Procedure for Estimating the Crystal Densities of Organic Explosives

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by

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ABSTRACT

High density is an important property for a military explosive. The quantity of material that can be carried in a space-limited warhead, and performance parameters such as detonation pressure and velocity, increase with density. An accurate and reliable method for calculating the solid state (crystal) density from the molecular formula of an energetic material would permit predictions to be made of explosive performance and serve as a valuable adjunct to any synthesis program aimed at producing improved explosive compounds.

Existing methods of density prediction, which primarily involve the summation of appropriate atomic or group volumes of parts of a molecule, yield what we call a "normal" density for a particular chemical composition. However, the compounds of most interest as military explosives often have densities significantly above the norm and predicted densities for members of this group frequently are substantially underestimated. A new procedure has been developed that allows a possible crystal packing arrangement for a molecule to be determined, from which a crystal density, usually accurate to within 2%, can be calculated. The technique consists of three parts: (1) determination of a reasonable three-dimensional molecular structure; (2) determination of several possible crystal packing arrangements (crystal structures) for this molecular structure; (3) refinement of the unit cell parameters, molecular orientation and position for each of the potential crystal structures. The lowest energy arrangement from step (3) is used to calculate the crystal density.

The crystal densities predicted for both bicyclo-HMX and octanitrocubane are lower than those obtained from additivity methods. This result should be considered when establishing priorities for further attempts to synthesize these currently unknown compounds. This work was supported by the NAVSEA Energetic Materials (Explosives) Research Program, SR 024-03, with Horst G. Adolph and George D. Edwards as project monitors.

I. INTRODUCTION

High density is an important property for a military explosive because more material can be carried in a space-limited warhead, and performance parameters such as detonation pressure and velocity increase with density. The work of Kamlet and Jacobs[1] indicates that the Chapman-Jouget pressure behind a detonation front is approximately proportional to the square of the solid state density. Consequently, high density is sought in the development of improved explosives. Fortunately, high density and sensitivity to accidental ignition are independent of each other[2]. An accurate method for the calculation of crystal density from the molecular formula of an energetic material would permit more reliable estimates of explosive performance to be made and, thereby, serve as a valuable guide to synthetic programs aimed at producing improved explosive compounds.

The two methods developed previously in this program for the estimation of densities, one by Cichra, Holden and Dickinson [3] and another by Stine [4], are similar to earlier work reported by Tarver [5], Cady [6] and Immirzi and Perini [7]. All of these studies approach the problem by deriving average volumes for various atoms and/or groups of atoms to fit the observed densities from large data bases of organic molecules. They differ mostly in parameter specification and in data base selection. Stine used a large number of compounds selected from the Cambridge Crystallographic Data File, whereas the parameters for the Cichra-Holden-Dickinson method were derived from a collection of 807 solids intentionally biased toward high energy compounds. We call these estimates "normal" densities because they are based on averages over a large number of compounds.

Both methods are convenient to apply and reproduce the measured densities of known solid energetic compounds with an average error of about 3%. The Cichra Holden-Dickinson procedure can also be used to predict liquid densities with parameters derived from 307 liquids. The performance of these programs is probably as good as can be expected from such additivity methods.

These methods, however, may not provide sufficiently accurate density estimates to be of real utility to synthetic programs, because the compounds of most interest as high performance explosives are frequently exceptional cases whose densities can be seriously underestimated by "normal" density

predictions. For example, the densities of two of the most useful current explosives, TATB and β-HMX, are calculated about 9.5% too low by additivity methods. Such estimates might have caused these compounds to be overlooked as potential candidates for synthesis.*

The approach we have taken depends not so much on average properties of atoms, or groups of atoms, but more on specific interactions between non-bonded atoms. In this way better estimations of density can be made for those molecules which pack efficiently by virtue of shape and/or strong intermolecular interactions.

II. THE METHOD

There are three parts to our density prediction method:

1. Determination of the molecular structure and probable conformation of an isolated molecule. Program MM2 [8] or other.
2. Determination of a number of trial crystal structure models. Program MOLPAK.
3. Minimization of the energy of these trial models with respect to the unit cell parameters and the orientation and position of the molecule within the unit cell. The resulting unit cell volume is used to calculate the crystal density. Program WMIN [9].

The principle computer program used in Step 1, MM2, can be obtained from the Quantum Chemistry Program Exchange (see Ref. 8). The program for Step 2, MOLPAK, can be obtained from Dr. James R. Holden or Dr. Ruth M. Doherty, Naval Surface Weapons Center, Silver Spring, MD 20903-5000. Step 3, WMIN, is available directly from its author, Dr. William R. Busing (see Ref. 9). CRAY and VAX versions of WMIN can be obtained from D. T. Cromer at Los Alamos and H. L. Ammon at the University of Maryland, respectively. The MM2, MOLPAK and WMIN programs are discussed in turn and a prediction of the density of a presently unknown compound, bicyclo-HMX, serves as an example of their use. Results of their application to both known and other unknown compounds are also included.

*Table 1 is a list of abbreviations for compounds used in this study.

III. STRUCTURES OF ISOLATED MOLECULES (Step 1)

The generation of a suitable molecular structure (set of atomic coordinates) for a subsequent crystal packing analysis can be accomplished in several ways. The coordinates of essentially planar molecules, such as substituted aromatics, are easily derived. However, coordinate generation for nonplanar structures, such as β-HMX, bicyclo-HMX or octanitrocubane, normally requires the assistance of some kind of modeling or coordinate manipulation computer program, followed by structure refinement (energy minimization) to regularize bond lengths, bond angles, torsion angles, etc. Structure generation can be accomplished most conveniently by the use of portions of known structures to form the nucleus of the new structure.

Computer assisted modeling and graphics programs, such as CHEMGRAF or CHEM-X (Chemical Design Ltd.) or Macro Model (Columbia University), can also be used for molecular structure generation. At the University of Maryland, CHEMGRAF is executed on a DEC MicroVAX II computer linked to a Lundy S-5688 color graphics terminal equipped with a data tablet. This configuration allows one to create a structure from scratch, or to begin with a preformed fragment, such as a benzene ring or cyclohexane chair. The coordinates of frequently used fragments, such as nitro, nitramine or trinitromethyl groups, can be created and stored for future use. Existing fragments can be joined, or a structure can be built one atom at a time. Bond lengths, angles and dihedral angles can be specified. Atom types can be readily changed. For example, a quick way to produce the 1,3,5-triazine ring of RDX is to replace three of the carbon atoms in cyclohexane by nitrogen.

Preliminary structures can be refined by molecular mechanics (MM) or other energy minimization computer programs. We use the MM2 program developed by Allinger and associates at the University of Georgia[8] for this purpose. A drawback of the presently available MM2 program is the absence of parameterization for many of the functional groups common to energetic materials. For example, parameters are not available for heterocyclic rings or for either C-nitro or N-nitro groups. These parts of a molecule are constructed with typical bond lengths and angles from x-ray diffraction studies and not refined, or refined with modified parameters estimated from other atom and bond types. For example, by treating nitro group oxygen atoms as carbonyl oxygens, reasonable conformations can be obtained. Although calculated strain energies are not accurate on an absolute scale, relative values probably

are good enough to identify the most stable stereoisomer or conformer from among several possibilities. It has recently come to our attention that R. D. Gilardi[10] and E. D. Stevens[11] have determined some of the pertinent parameters for MM2.

A detailed description of the input and output of MM2 is not given here because an adequate description is available in the QCPE program write-up[8]. It is worth noting that MM2 is remarkably tolerant of starting coordinates provided, of course, that the connectivity table is correct.

IV. TRIAL CRYSTAL STRUCTURES (Step 2)

Generation of trial structures is done with the program MOLPAK which can produce structures in triclinic space groups, in all primitive monoclinic space groups and in orthorhombic space groups with four molecules in the unit cell. Although a detailed discussion of the manner in which MOLPAK searches for packing patterns in each of the various space groups will be given in a separate Naval Surface Weapons Laboratory report by J. R. Holden, a brief discussion is given here. In this procedure, coordination spheres containing the specified space group symmetry are built around a central molecule in various orientations with respect to the lattice to be generated. A few general comments will be made about this method for determining crystal structures, followed by a detailed description for space group P $\bar{1}$ as an example.

Crystal structures with one molecule per asymmetric unit are usually described by giving the size and symmetry of the unit cell followed by the orientation and placement of the molecule within the cell. This is the order in which the information is usually acquired when determining a crystal structure by x-ray or neutron diffraction. However, the entire structure can also be characterized by specifying the coordination sphere of any one central molecule. Therefore, an equivalent way to describe a crystal structure is to place the centroid of one molecule at the origin of an orthogonal coordinate system and give the coordinates of the centroids of surrounding molecules along with their orientational relationship to the central molecule. Our approach to building crystal structures is this second, equivalent way.

The first step in the development of structure building methods was to use known structures to characterize the coordination spheres to be built. Here,

the coordination sphere is defined as consisting of molecules in (or nearly in) contact with a central molecule. With the use of van der Waals radii of 1.80, 1.17, 1.40, 1.50 and 1.50 Å for carbon, hydrogen, nitrogen, oxygen and fluorine[12], plots like Figure 1a or 1b were made for 136 known structures. For each structure, the molecules surrounding a central molecule were first sorted in order of increasing minimum distance between Van der Waals spheres. The minimum distances were then plotted against their sequence numbers in the sorted list.

All plots contain a break or ramp near sequence number 14, as illustrated by Figs. 1a and 1b. In 40%, a break occurs as shown in Fig. 1a with no minimum distance between 0.2 and 1.0Å. In the remaining structures, of which Fig. 1b is an extreme case, an S-shaped curve is found in place of a break. For these cases, an arbitrary cutoff of 0.75Å was chosen to define the size of the coordination sphere. With this definition, the number of molecules in the spheres of the 158 independent molecules investigated are distributed as follows: 1 below 12, 25 at 12, 30 at 13, 99 at 14 and 3 above 14. Therefore methods were developed designed to find coordination spheres consisting of 14 molecules.

Furthermore, the compositions of the coordination spheres form distinct patterns for the various space groups. That of the simplest one, P1, indicates why 14 is a logical number; 2 molecules along each of the three axes, 2 along each of the three face diagonals, and 2 along the body diagonal. In P $\bar{1}$ the coordination sphere contains 6 molecules with the same orientation as the central molecule (identities or I's related by a translation) and 8 molecules related by a center of symmetry (C's).

In monoclinic space groups with two symmetry related molecules per unit cell (Z = 2), the coordination sphere contains 6 identities and 8 molecules related by a twofold axis along the b axis (A2's) or 8 molecules related by a mirror plane perpendicular to the b axis (P2's). In Z = 4 monoclinic space groups, the coordination sphere contains 2 identities, 4 plane, 4 axis and 4 center related molecules (2I + 4P2 + 4A2 + 4C).

Two general classes of Z = 4 orthorhombic space groups have been found. In the first, the coordination sphere contains 2 I's and 4 A's or P's related to each of the three unit cell axes. The distribution depends on the space group. For example, a coordination sphere in space group, $P2_12_12_1$, would contain 2I + 4A1 + 4A2 + 4A3. In the second class of orthorhombic space groups, the

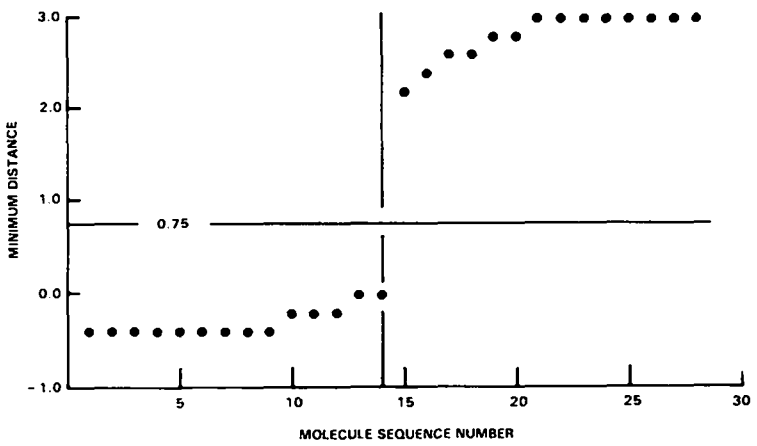

Fig. 1a. Determination of the size of the coordination sphere, example 1.

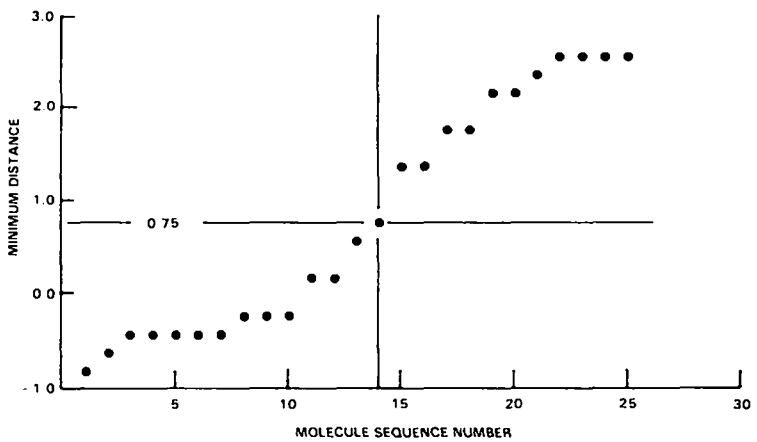

Fig. 1b. Determination of the size of the coordination sphere, example 2.

coordination sphere contains 6 I's and 4 A's or P's related to two of the three unit cell axes.

Programs have been written to construct coordination spheres for each of these structure types around molecules of a given conformation. Analysis of known crystal structures in space group, P $\bar{1}$, shows that the centroids of the 6 identity molecules in the coordination sphere lie in a plane which contains the centroid of the central molecule. The centroids of 4 center related molecules lie in a parallel plane above the central molecule, and the remaining 4 in a parallel plane below. This is then the packing pattern we must build; so we establish reference, orthogonal coordinates with axis 1) and axis 2) in the plane of the 6 identities.

As shown in Figure 2, a structure line is established by bringing an identity molecule in along axis 1) until the selected closeness criterion (see below) is satisfied. This also places another molecule at an equal distance on the negative axis, because the roles of this and the central molecule are merely reversed. Axis 'a' of the triclinic cell has now been determined. Axis 'b' and angle 'gamma' are next determined by bringing a line of identity molecules in along the axis 2) direction (see Figure 3). This is done at intervals (perhaps 8) along the axis 1) direction from one molecule directly on axis 2) to the molecule one interval short of the already established line spacing. At each position, the axis 2) separation is stopped when the closeness criterion is met between the central molecule and the molecules of the approaching line. The position giving the minimum separation is accepted (e.g. at the position "+"), and the placement along axis 1) is refined. The length and direction of the triclinic 'b' axis has now been determined as the vector between the origin and the centroid of a molecule in the offset line.

A two-dimensional grid of identity positions in triclinic space has now been established. This is also the spacing of the center-related molecules in the planes above and below, as shown in Figure 4. The remaining triclinic cell dimensions are determined by bringing this grid of center-related molecules in along the axis 3) direction (perpendicular to the plane of the paper) until the closeness criterion is met between these molecules and the central molecule. The position of this grid must be established in both the axis 1) and axis 2) directions; therefore, this must be done at all points of a 2-D interval grid. This time the range to be covered is from one molecule on axis 3) to one interval

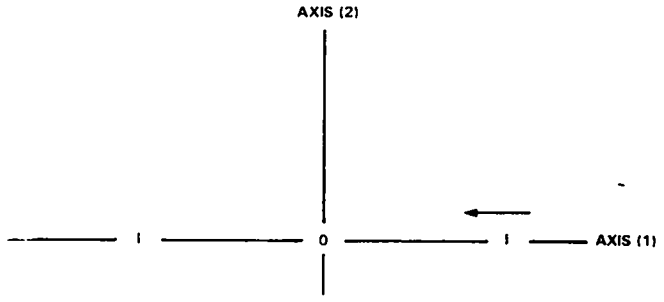

Fig. 2. Establishing a "structure line".

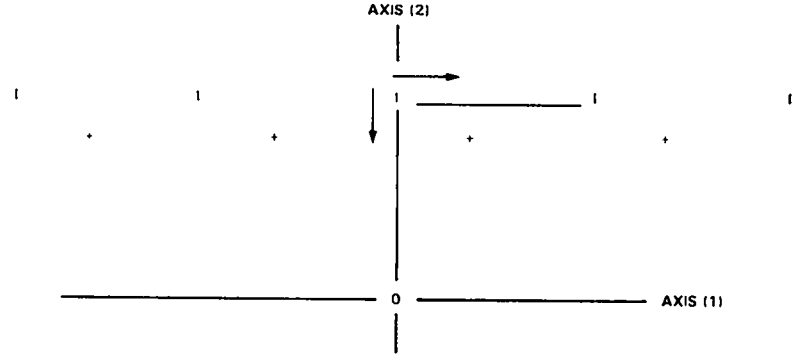

Fig. 3. Placing a "structure line" to form a 2-D grid.

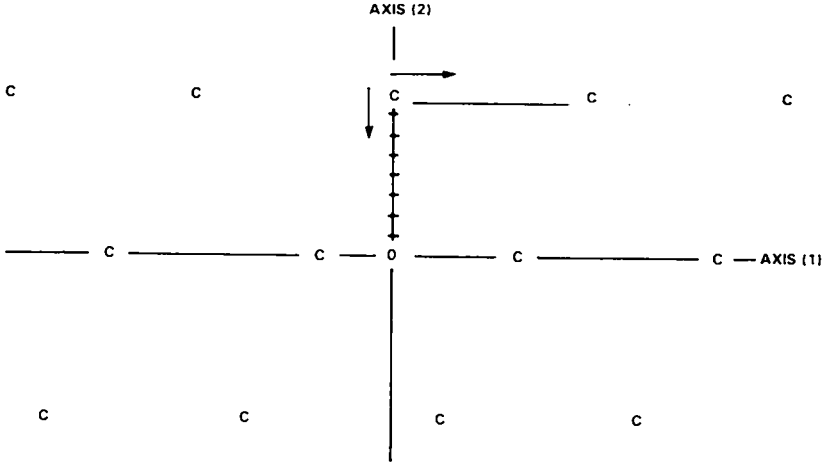

Fig. 4. Placing a 2-D grid to form a "crystal structure".

short of the triclinic 'a' spacing and the triclinic 'a-b' altitude. The position of minimum height is accepted, and refined in both the axis 1) and 2) directions. The grid placement operation is then repeated in the negative axis 3) direction. The length and direction of the triclinic 'c' axis has now been established as the vector from a center-related molecule on the grid below the central molecule to a center-related molecule on the grid above the central molecule.

A "crystal structure" has been determined by this procedure. It is the P $\bar{1}$ structure of minimum volume for one orientation of the central molecule with respect to the triclinic pattern. To find all possible P $\bar{1}$ structures, the entire process is repeated as the central molecule is rotated at intervals around three orthogonal axes which specify its orientation. The output of the program, when instructed to find P $\bar{1}$ structures, is a three-dimensional grid of unit cell volumes versus rotations of the central molecule like those shown later in this report. Note that there are a number of minima of about the same volume. Due to computer time constraints, such searches are usually carried out at relatively coarse angular intervals, followed by minimum search procedures at finer intervals.

The "closeness criterion" chosen for the MOLPAK program, a compromise between flexibility and computational speed, is a threshold energy of repulsion between pairs of molecules. This energy is evaluated as the sum of repulsion energies between the atoms of the molecules. The following modified 6-12 potential energy function is used:

$$E_{ij} = -A_{ij}D_{ij}^{-6} + B_{ij}D_{ij}^{-12} - E(D_{min})$$

where E is the repulsion energy between atoms i and j at a distance D, and $E(D_{min})$ is the energy at the distance at which the function goes through a minimum. Interactions between atoms at distances greater than D_{min} are ignored; that is, entered as zero. Inclusion of the last term makes the function continuous; its value becomes zero at the distance at which atomic interactions are entered as zero. Default values of the parameters A_{ij} and B_{ij} will be given in the planned report on MOLPAK.

When MOLPAK is run on compounds of known structure, the true unit cell volumes are reproduced with threshold repulsion energies set in the range of about 0.2 to 1.2 kcal $mole^{-1}$, depending on the compound treated. The

MOLPAK default value, 0.5 kcal $mole^{-1}$, will produce structures which can be refined in Step 3 by WMIN.

P $\bar{1}$ uses one of the most simple, straightforward structure search routines, and $P2_1/c$ requires one of the most complex. Similar routines have been developed for P1, all Z = 2 and Z = 4 monoclinic space groups, and all Z = 4 orthorhombic space groups. A few nonprimitive space groups which have been encountered have also been treated. All require significant amounts of computer time, but packing patterns can be found which can be refined with programs such as WMIN into reasonable crystal structures for organic compounds.

MOLPAK will construct structures in all, one, or any combination of space groups during each step of rotation of the central molecule. The default condition is a search of space groups in which about 70% of all reported crystal structures are found. MOLPAK is usually run in two passes (Steps 2A and 2B). In the first pass, the central molecule is rotated in large steps (e.g., 10-30°) about the three axes which specify its orientation. Several minima will be found in the resulting cell volume versus rotation grid. Some of these minima are then located more precisely using smaller incremental rotations of the central molecule (e.g., 2-5°). Crystal structures corresponding to these local minima then are used as starting points for the third step of the procedure.

V. ENERGY MINIMIZATION OF TRIAL STRUCTURES (Step 3)

Energy minimization of trial structures is done with Dr. William R. Busing's program, WMIN[9]. An equivalent program which might be used, PCK83 by Dr. Donald E. Williams, is distributed by QCPE. Since most of our experience has been with WMIN, only this program is discussed below.

WMIN is very flexible. The portions of interest to this work are least-squares refinement of energy parameters, with several experimental crystal structures as observations, and the minimization of the lattice energy of a given structure with respect to the unit cell constants and the translational and rotational parameters of a molecule treated as a rigid body. The latter minimization can be done by least-squares, steepest descent, or by a modified Rosenbrock search (which is the method we have generally used).

The lattice energy of a crystalline compound is calculated as a potential energy sum of all atom-to-atom interactions between a molecule and other

molecules that surround it in the crystal. The atom-to-atom potential function used in WMIN can be specified in user-defined subprograms, or the calculations may utilize the built-in potential illustrated below:

$$WT = [1/2Z] \sum_{i}^{n} \sum_{j \neq i}^{N} \{-A_iA_j/r_{ij}^6 + B_iB_j \exp[-(C_i+C_j)r_{ij}] + q_iq_j/r_{ij}\}$$

In this equation, WT is the total lattice energy per molecule, n is the number of atoms in a central unit cell, N is the number of atoms in all unit cells, Z is the number of molecules per cell, r_{ij} is the distance between atom i and atom j, q is the effective charge on an atom, and A, B and C are energy parameters. The three terms in WT describe attractive and repulsive Van der Waals and coulombic interactions. The several energy parameters, A, B and C, depend on the type of atom, such as carbon, nitrogen, oxygen or hydrogen, although there is no reason why structurally different atoms, such as the sp^3-carbons in HMX and sp^2-carbons in TNT, could not have somewhat different values for these parameters.

Initially, we used the potential parameters of Mirsky[13] and/or those of Williams and coworkers[14]. Efforts were made to obtain atomic charges by fitting crystal structures with the WT equation in WMIN with charges as parameters (variables). Attempts were also made to determine effective atomic charges with the methods of Cox, Williams and coworkers[15]. Basically, the procedure involves: (1) an *ab initio* molecular orbital calculation for the molecule of interest, (2) use of the wave functions to compute the electrostatic potential in a grid surrounding the molecule, and (3) use of the electrostatic potential grid to calculate point charges on the atoms. Unfortunately, the molecular orbital calculations required substantial amounts of computer time (computations at the STO-3G level for molecules such as RDX and HMX on a VAX 11/780 required 10-15 hours of CPU time), making the use of atomic charges determined in this manner impractical for routine density predictions. Furthermore the results were no more useful for density predictions than other, less rigorous methods.

The A, B and C parameters are correlated with the q values and, to a large extent, the effects of the charges can be compensated for by appropriate adjustment of the other parameters. Furthermore, B and C are highly correlated. Therefore, the least-squares features of WMIN were used to

develop a set of A and B parameters. Values of C were held constant and the Coulombic terms were omitted. The results are shown in Table 2, along with a list of the 17 compounds whose structures were used as observations in the least-squares calculations (compound abbreviations are defined in Table 1). The sublimation energies of five of these compounds (TATB, RDX, β-HMX, α-HMX, DATB) were used as heavily weighted observations in order to force the parameters to approximate an absolute scale.

The calculations to determine the various A and B energy parameters did not procede smoothly. Severe damping of the changes was required and convergence, in the usual least-squares sense, never was completely achieved. Convergence problems are perhaps the result of round-off errors in the calculation of numerical derivatives. In practice, after a few cycles, the potential parameters were used to refine the stuctural parameters of each of the compounds with WMIN and the calculated and experimentally observed densities compared. The process was then iterated. It eventually was noted that the density was calculated increasingly too high as the number of hydrogen atoms per molecule increased. Further least-squares cycles did not materially change this situation. Inspection of the individual pair interactions indicated that the repulsive parameter B for hydrogen was too small. Trial and error adjustments were made on all of the B parameters, leading to the final set shown in Table 2. It is not possible to give standard deviations of the parameters because the final adjustments were made by trial and error. However, previous least-squares calculations gave standard deviations of A_i and B_i for C, N, and O of about 5% of their values and 15% of the values for H.

VI. TESTS OF THE METHOD ON KNOWN STRUCTURES

Table 3 lists space group and density information for a number of crystal structures. The calculated densities were obtained by WMIN refinement of the observed crystal structures with the use of the energy parameters in Table 2. The refinement variables were appropriate combinations of unit cell constants, molecular orientation and position. The sets of calculated densities, one obtained with the procedures described in this report, and the others calculated with volume additivity techniques, show the clear superiority of the first method.

Footnotes i, j and k to Table 3 indicate that substantially improved density calculations can be realized by expanding the energy parameter set to include

different atom types. A dramatic improvement was observed in the case of MNDIOL and p-NPHOL by modifying the energy parameters for hydrogen linked to oxygen (i.e., -O-H) to more properly account for -O-H···O intermolecular interactions. Special hydrogen parameters were also implemented for TNHCUBE and MNFXN (see footnote k).

It had been demonstrated previously (see below) that a MOLPAK search in space groups P1 and P $\bar{1}$, followed by WMIN structure refinement, gave calculated densities that were close to those obtained from refinement of the actual space groups. Table 4 lists calculated densities, for eleven of the Table 3 compounds, obtained in the following manner: (1) MOLPAK searches in P1 and P $\bar{1}$ with a 10° orientation step, (2) a 3° MOLPAK search about the smallest unit cell volume found in (1), and (3) a WMIN structure refinement of the smallest volume crystal structure found in (2). As might be expected, the agreement between the calculated and observed densities is not as good as that observed when the real crystal structures are subjected to WMIN structure refinement.

The influence of the C-H bond distance, used for the molecular model, on the predicted density is illustratred for β-HMX and TNHCUBE in Table 4. In both cases, an increase in the bond distance from 1.08 to 1.11 Angstroms resulted in an increase in the calculated volume that translated to a 0.004 g cm^{-3} decrease in the crystal density. This density change is sufficiently small to eliminate small variations in X-H distances as a significant source of error in the calculated unit cell volumes and densities.

The data given in Table 5 represent a partial list of tests that were conducted to determine the sensitivity of the calculated density to the assumed crystal space group. Here, known compounds were subjected to the following procedure: (1) adjust the molecular structure to a form such as would be produced by MM2; (2) MOLPAK search; (3) WMIN refinement of several of the best crystal structures obtained in step (2). As indicated by these results, there are many ways, almost equally efficient and of almost equal energy, in which molecules can be packed. Reliable determination of the one of lowest energy, actually chosen by nature, would require more complete and accurate measures of atomic and molecular interactions than those used in MOLPAK or in WMIN. For the purpose of predicting density, a search for efficient packing in space group P $\bar{1}$ is generally sufficient. When denser structures are found in other space groups, the difference is usually marginal. These data suggest

that MOLPAK searches can be limited to space group P $\bar{1}$ for a preliminary density evaluation of an unknown compound.

As indicated, the methods outlined in this report produce a number of structures with about the same packing efficiency and calculated lattice energy. In almost all of the known compounds we have studied, one is the approximate true structure and the resulting calculated crystal density is within 2% of true. One notable exception is 3,5-dinitroisoxazole (DNIOZL, see Table 5) in which the true structure is complex with inefficient packing. A more ordinary crystal structure with an 11% higher density is predicted by the methods described in this report. This unusual failure of the method might have encouraged an unproductive synthetic effort but would not have caused a potentially useful compound to be overlooked. It should be noted that this discrepancy between the observed and calculated densities is most probably due to our inability to predict unusual packing arrangements of this type. The crystals used for structure determination were prepared by sublimation; it is suggested that solvent recrystallization might produce a higher density polymorph.

VII. DENSITY PREDICTION FOR PROPOSED (UNKNOWN) COMPOUNDS

Table 6 gives calculated density data for seven currently unknown compounds. The procedure used was the same as described above with an additional preliminary step that involved the construction and energy minimization of a hypothetical structure. The procedure was: (1) construct a molecular structure with the desired atomic connectivity; (2) MM2 refinement to regularize bond lengths, dihedral angles, etc.; (3) MOLPAK search; (4) WMIN structure refinement. In six of the seven cases in which several space groups were investigated, the highest crystal density was associated with P $\bar{1}$. HNAZWUR is unique in that the 1.965 g cm^{-3} density obtained for $P2_1/c$ is substantially higher (ca. 0.04 g cm^{-3}) than the 1.927 g cm^{-3} P $\bar{1}$ value. In the case of the P $\bar{1}$ structures, the 10° MOLPAK search grid could have been too coarse to locate the smallest unit cell (highest density structure), or investigations of other P $\bar{1}$ structures may have lead to higher density crystal structures following WMIN refinement.

In Table 6, there is good agreement (i.e. within 2%) between the present predictions and those of Stine[4] in four of the seven cases and in only one case is the agreement good with the predictions of Cichra et al.[3]

The RDX "dimer", RDXDMR, gave a predicted density 2.05% greater than RDX, but 2.69% lower than HMX. A similar increase in density with a decrease in the hydrogen percentage is found in the case of the oxygen bridged-HMX molecule HMXO, which is predicted to be 0.95% more dense than β-HMX. Dinitrooxadiazole(DNODZL) and hexanitroazadamantane(HNAZADMAN) are, perhaps, the most interesting of the proposed compounds listed in Table 6 with predicted densities of 2.007 and 2.032 g cm^{-3}, respectively. 1,4-Diamino-2,3,5,6-tetranitrobenzene(DATENB) is predicted to be 2.85% less dense than 2,3,4,6-tetranitroaniline(TENA) and thus would be of little interest from this standpoint. Considerable effort has already been expended on attempts to develop a synthesis for octanitrocubane, ONCUBE. The density predicted by our method, 1.984 g cm^{-3}, although lower than predictions by other methods, might still justify this effort.

VIII. DETAILED ILLUSTRATION OF THE METHOD WITH BICYCLO-HMX

The procedures for density prediction described in this report are illustrated with the currently unknown bicyclo-HMX, a compound that can be envisaged as being derived from HMX by linking two carbon atoms on opposite sides of the eight-membered ring. Models with *cis* and *trans* ring fusions were developed. The initial coordinates for the *cis*-isomer were produced starting with the known structure of β-HMX modified to contain the appropriate transannular C-C bond. The model was forced to have C2 symmetry. A starting model for the *trans*-isomer was developed in a similar manner, with the requirement for C2 symmetry replaced by that of inversion symmetry. The initial and MM2-minimized model coordinates for the *cis*-isomer are given in Table 7. Because of the substantial difference in the MM2-predicted strain energies in the *cis* and *trans*-isomers, 39.13 and 51.84 kcal $mole^{-1}$, no further work was done with the *trans*-compound. The atomic positions for the *cis* conformation then served as input for step 2, the search for trial crystal structures using MOLPAK.

The output from the first MOLPAK pass (Step 2A) for the *cis*-isomer (see Figure 5 and Table 7) is given in Table 8. Sixteen minima in the unit cell volume versus central molecule rotation grid were singled out for the second

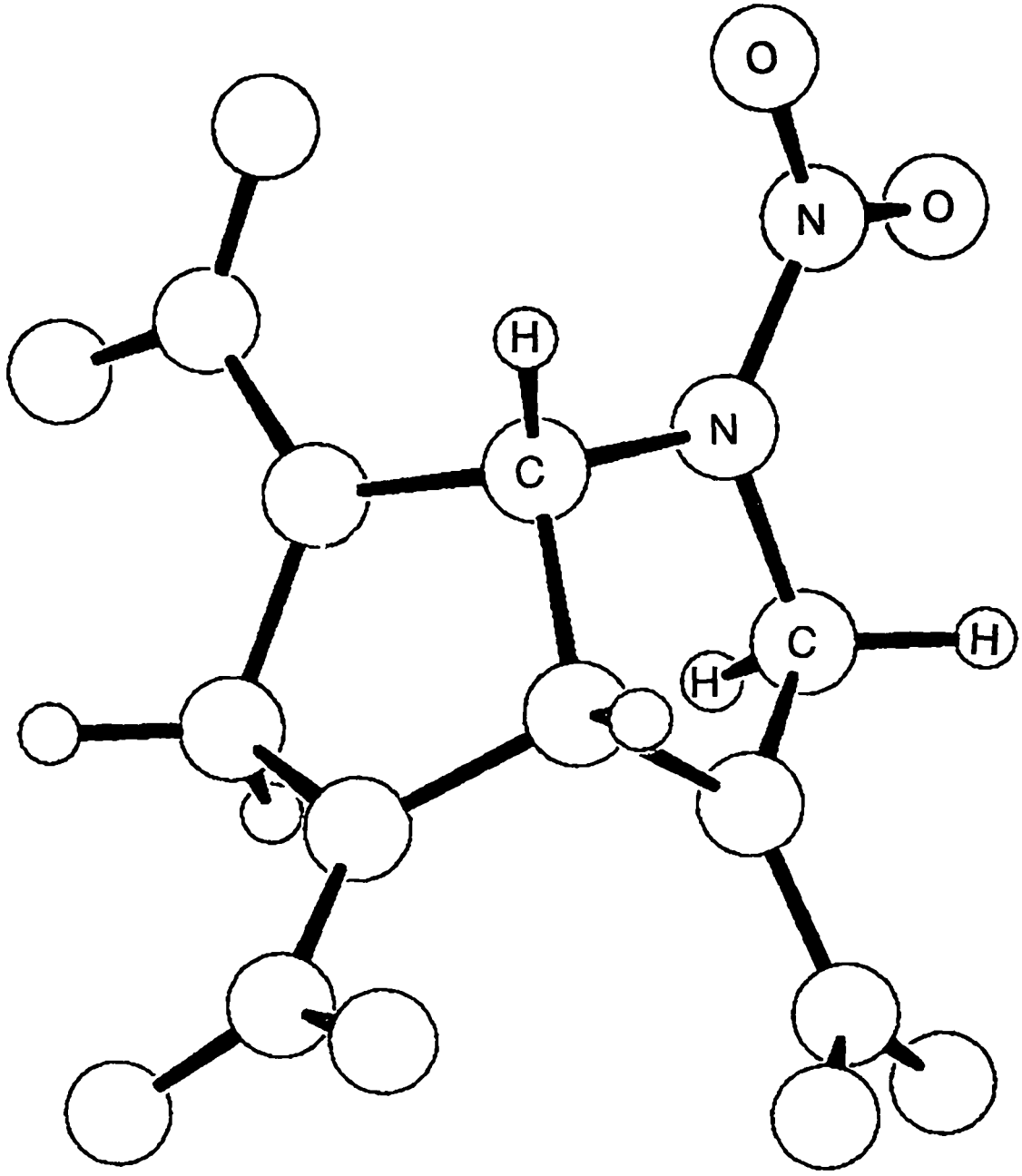

Fig. 5. *Cis*-bicyclo-HMX.

MOLPAK pass (step 2B). The results of the 5° interval minima location step are summarized in Table 9.* The cell dimensions of the structures produced are given to show similarities and variations among them. The complete output for each structure also includes atomic positions within the unit cell; that is, all information which would result from a crystal structure determination by x-ray or neutron diffraction is available. This information is the input for step 3 of our density prediction method, energy minimization using WMIN.

The right-hand columns of Table 9 give results of WMIN refinement of the "structures" chosen from the MOLPAK packing search. Note that refinement of the 15th structure results in both the smallest cell volume and the lowest lattice energy. The unit cell dimensions for this structure, after refinement, are given at the bottom. Its cell volume would give a predicted crystal density of 1.851 g cm^{-3}. However, this results from searches for P $\bar{1}$ structures only. The results of a more complete structure search are given in Table 10. The highest density obtained from the calculations is 1.870 g cm^{-3}.

IX. COMMENTS AND FUTURE DIRECTIONS

As stated in the introduction, a major goal of the work described in this report was to formulate an accurate, reliable method for density prediction. It was our hope to provide chemists with a computational tool that could be used, along with other considerations, to guide the selection of unknown energetic compounds for synthesis and evaluation. We believe that this goal has been realized, on the whole, with a method that takes into account molecular shape and packing efficiency and is accurate to 2% or less. The major drawbacks of the method are its complexity and the amount of computer time required for implementation. Volume additivity methods will continue to provide rough estimates of density and should be used for preliminary screening.

Energy parameters for use with WMIN (Step 3) presently are available only for carbon, hydrogen, nitrogen and oxygen. Work is now under way to extend the method and parameterization to fluorine-containing compounds. In addition, the currently available C-H-N-O parameter set is being refined to

*We usually perform a -90-90° search in 10° increments about each of the model coordinate axes, followed by a 3° step refinement around several minima. The coarser search illustrated here was done in the interest of space conservation.

improve the fit of the WMIN-minimized crystal structures. The accuracy of the WMIN calculations is limited, to an extent, by the simplicity of the computational model and the use of a single set of parameters for all carbon atoms, another set for all nitrogen atoms, etc. We hope to be able to extend the WMIN parameterization to take account, at the very least, of different types of oxygen (e.g., nitro, hydroxyl, ether and carbonyl), nitrogen (e.g., nitro and amino) and hydrogen atoms.

The present version of WMIN uses numerical differentiation for both energy parameter and structure refinement. This technique requires the use of double-precision arithmetic functions, etc. for all derivative computations. The major computational disadvantages of double-precision are an increase in computer memory requirements, longer execution times and increased charges. The DEC Microvax-II used currently at the University of Maryland for structure refinement is not equipped with double-precision hardware resulting in a four to sixfold increase in WMIN run times for calculations that require derivatives. This deficiency is presently being addressed for energy parameter refinement with the introduction of analytical derivatives into the WMIN code.

The search for molecular packing patterns (Step 2 with MOLPAK) is presently the weakest link in the overall procedure on the basis of computer-time usage. Modifications to the packing algorithm have been made leading to a threefold increase in speed and tests are under way to evaluate the overall applicability of the new program.

An additional problem with the current status of the density prediction method outlined in this report is that the required computer programs can not be used easily by chemists unfamiliar with crystallography. The programs should be consolidated into a single package that is executable from start to finish from minimum input data.

It should be mentioned that extensive efforts have been made to develop syntheses for two of the proposed (unknown) compounds treated in this report, bicyclo-HMX (BCHMX) and octanitrocubane (ONCUBE). Neither of these compounds has a predicted density as high as estimated by additivity (see Tables 6 and 10). The predicted density of bicyclo-HMX, 1.871 g cm^{-3}, is somewhat lower than the the known density of β-HMX, 1.894. Although the bicyclic compound has a higher molecular density, its molecular shape is more like the α polymorph of HMX, which has a known density of 1.839 g cm^{-3}. The predicted density of octanitrocubane, 1.985 g cm^{-3}, is high, but not spectacular

as estimated by additivity (see Table 6). From the standpoint of crystal density, our work would indicate that oxygen bridged bicyclo-HMX (HMXO), with a predicted density of 1.912 g cm^{-3}, would be a better target compound for synthesis; however, the difference, only about 2%, is within the range of possible density prediction error.

The authors would welcome inquiries and requests for density predictions on potential energetic materials.

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TABLE 1.

Compound Abbreviations and Structures·

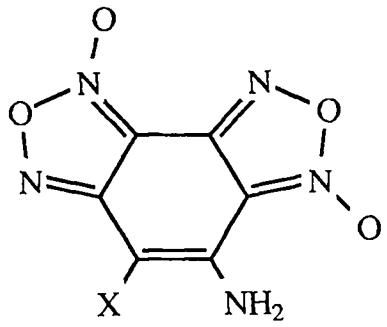
Abreviation	Chemical Name
ANBBOD	4-Amino-5-nitrobenzo bis(oxadiazole)-3,8-dioxide
BCHMX	Bicyclo-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
BTNEOX	Bis(2,2,2-trinitroethyl)oxamide
BZTFXN	Benztrifuroxan (Hexanitrosobenzene)
DADN	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane
DATB	1,3-Diamino-2,4,6-trinitrobenzene
DATBA	3,5-Diamino-2,4,6-trinitrobenzoic acid
DATENB	1,4-Diaminotetranitrobenzene (unknown)
m-DNB	1,3-Dinitrobenzene
o-DNB	1,2-Dinitrobenzene
p-DNB	1,4-Dinitrobenzene
DNIOZL	3,5-Dinitroisoxazole
DNODZL	Dinitro-1,2,5-oxadiazole (Dinitrofurazan) (unknown)
α-HMX	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane - α polymorph
β-HMX	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane - β polymorph
HMXO	Oxygen bridged bicyclo-HMX (unknown)
HNABI	2,2',4,4',6,6'-Hexanitroazobenzene - crystal polymorph I
HNB	Hexanitrobenzene
HNAZWUR	Hexanitrohexaazaisowurtzitane (unknown)
HNOAB	2,2',4,4',6,6'-Hexanitrosoazobenzene
HNAZADMAN	Hexanitrohexaazaadamantane (unknown)

Table 1 continued

MNDIOL	2-Methyl-2-nitropropan-1,3-diol
MNFXN	3-Methyl-4-nitrofuroxan
p-NPHOL	4-Nitrophenol
NTO	3-Nitro-1,2,4-triazole-5-one
NQ	Nitroguanadine
ONCUBE	Octanitrocubane (unknown)
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane
RDXDMR	RDX Cage Dimer (unknown)
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TENA	2,3,4,6-Tetranitoaniline
TNA	2,4,6-Trinitroaniline
TNB	1,3,5-Trinitrobenzene
TNHCUBE	6,6,8-Trinitropentacyclodecane (trinitro-bis-homocubane)

Table 1 continued

Structural Formulae



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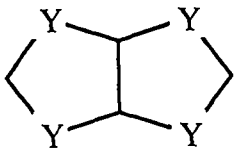
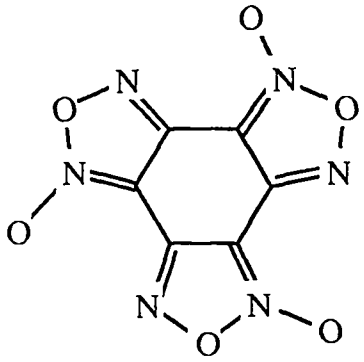


BCHMX



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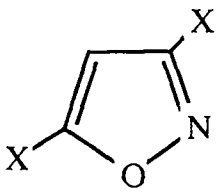
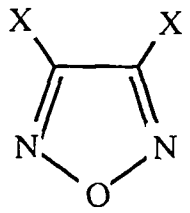


DNIOZL



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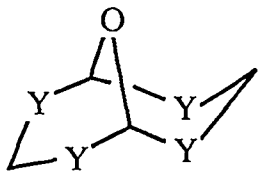
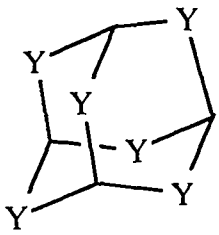


HMXO



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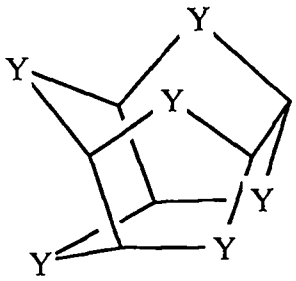

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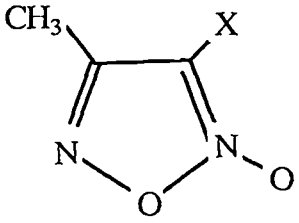
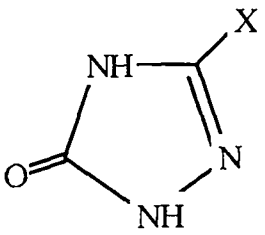


MNFXN



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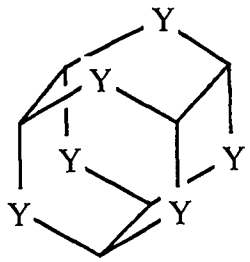
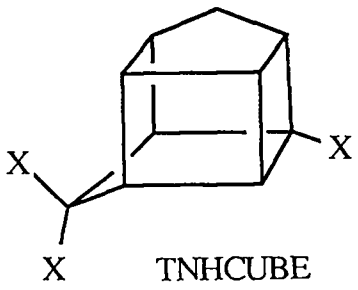


RDXDMR



TNHCUBE

$X = NO_2$, $Y = N\text{-}NO_2$

TABLE 2.

Parameters for the Calculation of Crystal Lattice Energies with WMIN

$$WT = [1/2Z] \sum_{i \neq j}^{n} \sum^{N} \{-A_i A_j / r_{ij}^6 + B_i B_j \exp[-(C_i + C_j) r_{ij}]\}$$

Atom Type	A (kcal mole^{-1})$^{1/2}$	B (kcal mole^{-1})$^{1/2}$	C (Å)$^{-1}$
C	17.01	324	1.80
H	2.51	13	1.87
N	20.72	150	1.805
O	28.87	390	1.98

These parameters were derived from the known crystal structures of the following compounds

DADN	α-HMX	β-HMX	DATB	HNABI
BZTFXN	HNB	m-DNB	p-DNB	MNFXN
NQ	p-NPHOL	RDX	TATB	TENA
TNA	TNB			

C-H distances were fixed at 1.08 Å and N-H distances at 1.05 Å

TABLE 3.

Observed and Calculated Densities(g cm^{-3}) for Known Compounds

Cpd.[a]	Space Group	X-ray Dens.	Calc. Dens.[b,c]	Delta %[d]	Add. Dens.[e]	Delta %	Add. Dens.[f]	Delta %
BZTFXN	$Pna2_1$	1.901	1.876	+1.32	2.070	-8.89	2.061	-8.42
DADN	$P2_1/c$	1.636	1.604	+1.96	1.513	+7.52	1.553	+5.07
DATB	Pc	1.835	1.820	+0.82	1.770	+3.65	1.784	+2.89
m-DNB	$Pna2_1$	1.575	1.581	-0.38	1.578	-0.19	1.596	-1.33
p-DNB	$P2_1/n$	1.616	1.587	+1.79	1.578	+2.35	1.596	+1.24
α-HMX	Fdd2	1.839	1.846	-0.38	1.800	+1.42	1.784	+2.99
β-HMX	$P2_1/c$	1.893	1.915	-1.16	1.800	+9.27	1.784	+5.81
HNAB-I	$P2_1/c$	1.795	1.726	3.84	1.763	+1.78	1.803	-0.45
HNB	I2/c	1.988	1.998	-0.50	1.957	+1.56	2.016	-1.41
MNFXN	$P2_12_12_1$	1.659	1.765	-6.39	1.724	-3.92	1.899	-14.47
p-NPHOL	$P2_1/a$	1.491	1.452	+2.62	1.465	+1.74	1.520	-1.95
NQ	Fdd2	1.760	1.776	-0.91	1.682	+5.51	1.664	+6.52
RDX	Pbca	1.806	1.814	-0.44	1.805	+0.06	1.784	+1.22
TATB	$P\bar{1}$	1.937	1.948	-0.57	1.794	+7.43	1.801	+7.07
TENA	$P2_1/c$	1.860	1.864	-0.22	1.837	+1.29	1.870	-0.48
TNA	$P2_1/c$	1.773	1.780	-0.39	1.744	+1.64	1.765	+0.45
TNB	Pbca	1.676	1.654	+1.31	1.716	-2.63	1.744	-4.31
ANBBOD	$P2_12_12_1$	1.932	1.898[g]	+1.76	1.957	-1.29	1.942	-0.52
BTNEOX	$P\bar{1}$	1.798	1.808	-0.56	1.834	-2.00	1.842	-2.45
DATBA	$P2_1/c$	1.863	1.880[g]	-0.91	1.799	+3.44	1.849	+0.75
o-DNB	$P2_1/c$	1.580	1.586	-0.38	1.578	+0.13	1.596	-1.01
MNDIOL	Cc	1.316	1.171	+11.01	1.331	-1.14	1.432	-8.81
MNDIOL	Cc	1.316	1.337[j]	-1.60				
MNFXN	$P2_12_12_1$	1.659	1.678[h,i]	-1.15	1.724	-3.92	1.899	-14.47
p-NPHOL	$P2_1/a$	1.491	1.491[k]	+0.02	1.465	+1.74	1.520	-1.95
TNHCUBE	$P2_1/c$	1.610	1.675	-4.04	1.665	-3.42	1.688	-4.84
TNHCUBE	$P2_1/c$	1.610	1.593[j]	+1.13	1.665	-3.42	1.688	-4.84

Table 3 continued

[a] Compound abbreviations are defined in Table 1.

[b] Calculated densities were derived from crystal volumes obtained from WMIN refinement of the observed crystal structures.

[c] C-H distances = 1.08 Å unless noted otherwise.

[d] Delta % = 100 x (x-ray Dens. - Calc. Dens.) / X-ray Dens.

[e] Calculated by additivity method of Cichra, Holden and Dickinson[3].

[f] Calculated by additivity method of Stine[4].

[g] C-H distances = 1.02 Å.

[h] Use of the x-ray determined methyl group hydrogen positions (C-H = 0.86, 0.86, 0.94 Å) gave a calculated density of 1.78 g cm^{-3} and a delta of -7.3%. Movement of the hydrogen atoms along the C-H bond vectors to give the more realistic C-H of 1.10 Å gave a calculated density and delta of 1.748 g cm^{-3} and -5.3%.

[i] The densities reported here for MNFXN and TNHCUBE were obtained with hydrogen energy parameters of A = 4.417 and B = 34.036 kcal $^{1/2}mol^{-1/2}$. It is suggested that the A and B parameters for hydrogen atoms adjacent to electron withdrawing substituents should be significantly different from those for other hydrogen atoms.

[j] This discrepancy, shown in the previous line for MNDIOL, arises from the short intermolecular H...O contacts of about 1.66 Å in the crystal structure which have a large repulsive component. A correction was applied to the (O-H) hydrogen A and B values to give no net O...H interaction at a distance of ca. 2.4 Å; A=0.360, B=0.3576 kcal$^{1/2}mol^{-1/2}$. The necessity for such a correction reflects the inadequacy of our potential energy model in this instance.

[k] The normal A and B hydrogen coefficients gave a calculated density of 1.470 g cm^{-3} and a delta of +1.38%. The table value was obtained by replacing the (O-H) hydrogen parameters with those derived for MNDIOL (see footnote j).

TABLE 4.

Results of MOLPAK 10° Step Search in Triclinic Space Groups
Followed by 3° Step Search Around Minimum and WMIN Refinement

Compound[a]	P $\bar{1}$ [b]	P1 [b]	MOLPAK	WMIN Minimum[c]	Density Calc.[d]	Delta%[e]
α-HMX	276.25	276.60	274.2 [f]	266.75	1.843	-0.22
β-HMX		269.60	269.47[g]	254.05	1.935	-2.24
			254.58[h]		1.931	-2.03
RDX	209.30	208.47	208.47[h]	202.06	1.825	-1.06
o-DNB	160.59	171.04	159.55[g]	180.21	1.549	+1.97
m-DNB	164.25	168.61	164.25[f]	182.26	1.531	+2.77
p-DNB		156.08	155.49[g]	177.04	1.577	+2.44
TATB	214.63	212.46	212.46[g]	226.32	1.894	+2.23
DATBA	262.90	260.91	258.48[g]	256.48	1.859	-1.30
ANBBOD	214.47	213.13	213.13[g]	224.59	1.878	+2.76
BTNEOX		399.40	399.40[g]	378.81	1.815	-1.82
TNHCUBE	269.94	282.94	269.30[f]	267.88	1.644	-2.88
			268.49[h]		1.640	-2.63

[a]Compound abbreviations are defined in Table 1.

[b]Minimum cell volume per molecule (Å^3) from 10° MOLPAK search.

[c]Cell volume per molecule (Å^3) after WMIN refinement of crystal structure found by MOLPAK.

[d]Crystal density (g cm^{-3}) calculated from WMIN cell volume.

[e]Delta % = 100 (Vcalc - Vobs)/Vobs.

[f]Minimum cell volume after 3° step search at P $\bar{1}$ minimum.

[g]Minimum cell volume after 3° step search at P1 minimum.

[h]X-ray crystallographic structure with C-H distances set to 1.11Å.

TABLE 5.

Density Predictions on Known Compounds

Compound	Space Group	Volume/Molecule ($Å^3$)	Delta %[a]	WMIN Energy (kcal $mole^{-1}$)
TATB	$P\bar{1}$	221.24	Observed	
	$P\bar{1}$	219.0*	+0.99*	-36.48*
	P1	225.7	-2.04	-34.33
	P1	225.0	-1.73	-34.52
	Pc	225.7	-2.04	-33.10
	$P2_1$	223.0	-0.81	-34.94
	$P2_1$	220.3	+0.40	-35.68
	Pn	220.3	+0.40	-35.68
DATB	Pc	219.65	Observed	
	$P\bar{1}$	219.9*	-0.10*	-32.52*
	$P\bar{1}$	217.3	+1.09	-31.33
	$P\bar{1}$	223.0	-1.52	-31.33
	$P\bar{1}$	220.5	-0.40	-31.74
	$P\bar{1}$	218.8	+0.40	-30.83
	$P2_1/c$	217.7	+0.89	-32.06
	$P2_1/c$	218.6	+0.50	-31.46
	$P2_1/c$	220.1	-0.20	-31.73
	$P2_1/c$	220.3	-1.21	-30.74
	$P2_1/c$	217.5	+0.99	-31.71
	$P2_1/c$	219.0	+0.30	-31.80
	$P2_1/c$	217.3	+1.09	-32.13
	$P2_1/c$	230.2	-4.82	-29.04
	$P2_1/n$	223.4	-1.73	-30.64
	$P2_1/n$	225.5	-2.67	-29.94
	$P2_1/n$	224.1	-2.04	-30.32
	$P2_1/n$	228.3	-3.95	-30.03
o-DNB	$P2_1/c$	176.66	Observed	
	$P\bar{1}$	177.2	-0.30	-17.19
	$P\bar{1}$	183.4	-3.84	-15.89
	$P2_1/c$	190.6	-7.87	-15.65
	$P2_1/c$	183.8	-4.06	-16.18
	$P2_1/c$	182.5	-3.31	-16.36
	$P2_1/c$	179.5	-1.63	-16.76
	$P2_1/c$	174.7*	+1.09*	-18.18*
NTO	$P\bar{1}$	112.3	Observed	
	$P\bar{1}$	112.6	-0.27	-20.56
	$P\bar{1}$	112.5	-0.18	-20.70
	$P\bar{1}$	113.1*	-0.71*	-20.86*

Table 5 continued

DNIOZL	$P\bar{1}$	153.57	Observed	
	$P\bar{1}$	138.0	+10.14*	-24.73*
	$P\bar{1}$	137.4	+10.53	-24.47
	$P\bar{1}$	137.4	+10.53	-24.44
	$P\bar{1}$	140.4	+8.58	-24.17

[a]Delta % = 100 x (Obs. Vol. - Calc. Vol.)/ Obs. Vol.
*Structure with lowest calculated lattice energy.

TABLE 6.

Prediction of Densities of Unknown Compounds

Compound	Space Group	Calc. Density ($g\ cm^{-3}$)	WMIN Energy ($kcal\ mole^{-1}$)	Additivity Densities ($g\ cm^{-3}$)[a]	($g\ cm^{-3}$)[b]
DATENB	$P\bar{1}$	1.808*	-35.14*	1.882	1.860
	$P\bar{1}$	1.798	-34.83		
	$P2_1/c$	1.779	-33.98		
	$P2_1/c$	1.761	-33.19		
	$P2_1/c$	1.748	-33.73		
	$P2_1/c$	1.812	-34.98		
	$P2_1/c$	1.761	-33.19		
	$P2_1/c$	1.733	-32.70		
	$P2_1/n$	1.784	-34.37		
	$P2_1/n$	1.776	-33.60		
	$P2_1/n$	1.756	-32.98		
DNODZL	$P\bar{1}$	2.007*	-26.49*	1.970	1.936
	$P\bar{1}$	1.972	-25.60		
	$P2_1$	1.924	-24.56		
	$P2_1$	1.937	-24.87		
	$P2_1$	1.947	-24.80		
	Pn	1.942	-24.77		
	$P2_1/c$	1.925	-24.46		
	$P2_1/c$	1.990	-25.86		
	$P2_1/c$	1.939	-24.60		
	$P2_1/n$	1.970	-25.24		
RDXDMR	P1	1.766	-43.63	1.989	2.036[c,e]
	$P\bar{1}$	1.827	-48.41		
	$P\bar{1}$	1.801	-45.63		
	$P\bar{1}$	1.801	-45.63		
	$P\bar{1}$	1.801	-45.63		
	$P\bar{1}$	1.843*	-48.20		
	$P2_1$	1.767	-43.71		
	$P2_1/c$	1.803	-45.67		
HMXO	P1	1.858	-37.20	1.898	1.929
	$P\bar{1}$	1.912*	-40.67*		
	$P2_1$	1.804	-35.84		
	$P2_1/c$	1.904	-40.44		
	$P2_12_12_1$	1.900	-38.07		
	Aa	1.892	-38.03		
ONCUBE	$P\bar{1}$	1.984	-52.84	2.124	2.104[d,e]
	$P\bar{1}$	1.985*	-52.86*		
	$P2_1/c$	1.942	-51.05		
	$P2_12_12_1$	1.845	-45.75		

Table 6 continued

HNAZADMAN	$P2_12_12_1$	1.964	-46.43	2.048	2.149[c,e]
	$P2_1/c$	1.976	-50.53		
	$P\bar{1}$	2.032*	-53.55		
HNAZWUR	P1	1.886	-47.10	1.989	2.036[c,e]
	$P\bar{1}$	1.902	-48.26		
	$P\bar{1}$	1.903	-48.34		
	$P\bar{1}$	1.927	-48.46		
	$P2_1$	1.858	-45.30		
	$P2_1/c$	1.965*	-51.42*		

[a] Method of Stine[4].

[b] Method of Cichra, Holden and Dickinson[3].

[c] Four ring corrections applied.

[d] Five ring corrections applied.

[e] The derived ring correction parameters do not really apply to cage compounds. The number chosen is that which properly accounts for the number of bonds allottted to the included atom types.

*Structure with lowest calculated lattice energy.

TABLE 7.

Coordinates for a Hypothetical *cis*-Bicyclo-HMX Structure (Step 1)

		INITIAL (Before MM2 Refinement)			FINAL (After MM2 Refinement)		
		X	Y	Z	X	Y	Z
C	1	0.000	0.752	0.000	0.000	0.771	0.000
C	2	-2.137	0.000	0.000	-2.023	0.063	0.824
C	3	0.000	-0.752	0.000	0.000	-0.771	0.000
C	4	2.137	0.000	0.000	2.023	-0.063	0.824
N	5	1.734	2.407	0.053	2.085	1.987	-0.478
N	6	1.301	1.134	0.490	1.350	1.161	0.404
N	7	-1.734	-2.407	0.053	-2.085	-1.987	-0.478
N	8	-1.301	-1.134	0.490	-1.350	-1.161	0.404
N	9	-1.301	1.134	0.490	-0.980	1.057	1.045
N	10	-1.734	2.407	0.053	-1.424	2.396	1.125
N	11	1.301	-1.134	0.490	0.980	-1.057	1.045
N	12	1.734	-2.407	0.053	1.424	-2.396	1.125
O	13	1.343	3.341	0.756	1.466	2.788	-1.185
O	14	2.694	2.495	-0.717	3.302	2.065	-0.279
O	15	-2.694	2.495	-0.717	-2.515	2.595	1.668
O	16	-1.343	3.341	0.756	-0.597	3.284	0.906
O	17	-1.343	-3.341	0.756	-1.466	-2.788	-1.185
O	18	-2.694	-2.495	-0.717	-3.302	-2.065	-0.279
0	19	2.694	-2.495	-0.717	2.515	-2.595	1.668
0	20	1.343	-3.341	0.756	0.597	-3.284	0.906
H	21	0.000	1.021	-1.056	-0.317	1.167	-0.959
H	22	0.000	-1.021	-1.056	0.317	-1.167	-0.959
H	23	-2.802	0.000	-0.854	-2.684	0.413	0.038
H	24	-2.799	0.000	0.858	-2.582	-0.115	1.733
H	25	2.802	0.000	-0.854	2.684	-0.413	0.038
H	26	2.799	0.000	0.858	2.582	0.115	1.733

TABLE 8.

Determination of Molecular Packing of *cis*-Bicyclo-HMX (Step 2A)
Space Group P $\bar{1}$

Cell volume per molecule (Å) at rotations of A1, A2, and A3 of the 'central' molecule about orthogonal axes.

Rotation angles (°)

A1 = -60

A2 \ A3	0	30	60	90	120	150
-60	298	(291)	319	300	311	305
-30	316	329	356	314	328	335
0	305	305	(291)	319	(294)	319
30	314	303	325	314	297	320
60	300	310	306	305	310	314
90	322	340	303	335	316	309

A1 = 30

A2 \ A3	0	30	60	90	120	150
-60	338	331	305	327	315	306
-30	311	320	302	312	302	314
0	297	302	294	(294)	295	315
30	342	316	310	313	313	325
60	300	304	304	308	303	319

A1 = -30

-60	300	306	304	308	303	321
-30	336	315	305	307	305	323
0	(291)	304	294	(293)	295	300
30	307	325	302	312	306	312
60	335	334	304	327	309	304

A1 = 60

298	310	309	304	310	314
322	303	327	318	299	320
299	307	(292)	318	(293)	319
315	335	334	313	328	341
300	(291)	321	301	306	305

A1 = 0

-60	313	311	341	312	312	331
-30	320	308	321	319	304	301
0	(286)	299	296	295	(283)	301
30	325	308	321	314	304	298
60	313	309	331	312	313	331

A1 = 90

289	(283)	285	293	287	(283)
308	294	297	(287)	297	295
(285)	298	343	289	344	298
316	326	324	317	321	324
(295)	312	307	294	311	310

The volumes enclosed in parentheses are the 16 starting points for the minimum volume searches at 5° rotation intervals given in Table 4.

TABLE 9

Refinement of Molecular Packing of *cis*-Bicyclo-HMX (Steps 2B and 3)
Space Group P $\bar{1}$

	UNIT CELLS FROM 5° ROTATION INTERVAL SEARCHES										AFTER WMIN REFINEMENT	
	A1(°)	A2(°)	A3(°)	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V/mol (Å^3)	V/mol (Å^3)	Energy (kcal^{-1})
1.	-65	-60	25	9.625	13.028	4.769	82.4	104.6	85.7	284.9	267.5	-34.45
2.	-60	0	60	6.240	13.970	7.632	111.8	109.4	85.2	290.9	279.1	-31.50
3.	-55	5	110	6.234	12.513	7.805	77.3	72.6	83.3	282.9	286.3	-32.95
4.	-25	5	0	8.367	9.329	8.583	76.4	117.2	101.3	288.1	281.5	-32.00
5.	-30	-5	90	8.914	9.338	8.321	104.1	62.1	109.6	286.6	271.6	-36.13
6.	5	5	-5	8.313	8.960	8.747	80.4	72.7	110.4	278.1	174.3	-35.30
7.	0	0	130	9.625	8.043	7.953	88.4	114.6	93.8	279.4	278.3	-32.14
8.	30	5	90	8.914	9.338	8.321	75.9	62.1	70.4	286.6	267.4	-36.42
9.	65	-5	60	6.077	13.512	7.638	97.3	107.4	99.1	290.5	287.7	-30.36
10.	65	-5	120	6.617	13.720	7.142	89.1	73.2	110.3	288.6	283.4	-33.56
11.	55	60	40	9.570	13.220	4.943	91.9	111.3	97.5	187.8		
12.	90	-60	25	8.477	14.614	4.853	100.6	97.8	73.4	282.0	266.3	-35.20
13.	95	-60	155	7.894	13.998	5.235	102.9	85.9	99.7	280.9	277.4	-34.45
14.	90	-30	90	4.648	13.179	9.825	83.4	103.7	100.2	287.0	266.6	-35.33
15.	90	0	0	8.039	15.624	4.541	89.9	88.4	88.2	284.9	263.8*	-36.80
16.	90	80	15	8.859	14.562	4.616	81.4	103.9	103.2	280.0	268.7	-35.58
15.	after WMIN			8.050	15.783	4.153	90.0	89.8	89.6	263.8		

*Calculated density from structure 15 = 1.851 g cm^3.

TABLE 10.

MOLPAK-WMIN Results for *Cis*-Bicyclo-HMX in Several Space Groups

Space Group	Z	MOLPAK[a] Rotation Angles °			WMIN[b] V/Molecule Å^3	Energy kcal mole^{-1}
P1	1	0,	-30,	105	298.1	-29.32
		65,	40,	30	295.7	-29.65
		45,	0,	45	289.8	-30.94
		-60,	-45,	30	295.7	-29.65
P $\bar{1}$	2	20,	-45,	60	266.7	-35.69
		5,	-30,	30	266.0	-36.48
		-5,	-30,	150	261.9	-36.95
		-15,	45,	55	267.0	-35.69
$P2_1$	2	90,	30,	45	273.5	-34.48
		15,	45,	120	278.2	-32.60
		-60,	-15,	30	277.1	-33.00
P2	2	45,	15,	105	293.9	-29.58
		-45,	-15,	105	293.8	-29.59
		30,	-45,	75	347.5	-23.84
		0,	0,	60	286.2	-30.48
Pm	2	90,	15,	90	301.9	-28.13
		30,	-75,	120	354.3	-22.43
		45,	-75,	135	354.4	-22.43
$P2_1/c$	4	-55,	-20,	30	266.2	-36.26
		70,	20,	90	261.1	-37.17 [c,d]
		80,	20,	140	266.1	-36.06
Pn	2	0,	0,	120	271.3	-34.58
		15,	-30,	30	372.0	-22.60
		15,	15,	15	278.5	-32.27
		-15,	25,	30	331.6	-24.53
$P2_12_12$	4	-30,	-15,	120	307.0	-27.50
		-45,	30,	90	277.5	-33.66
		45,	-30,	90	279.1	-33.59
		75,	15,	15	275.3	-34.28
$P2_12_12_1$	4	90,	30,	0	282.6	-33.61
		45,	-60,	30	276.6	-34.44
		60,	15,	45	288.3	-34.78
		90,	-75,	75	276.3	-33.70

[a]30°/5° MOLPAK search.

[b]The corresponding WMIN refined molecular volumes and energies were 264.6 Å^3 and -35.02 kcal mole^{-1} for α-HMX and 255.2 Å^3 and -38.57 kcal mole^{-1} for β-HMX.

[c]Calculated density = 1.870 g cm^{-3}.

[d]"Normal" density = 1.911 g cm^{-3}.

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