

Structure and Density Predictions for Energetic Materials

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The discovery of new energetic materials could be facilitated, accelerated and made more cost effective with the use of computer modeling and simulations for the identification of compounds that have significant advantages over materials currently in use. The quantitative estimation of properties, such as the heat of formation, density, detonation velocity, detonation pressure and sensitivity, to screen potential energetic candidates would permit the selection of only the most promising substances [1] for laboratory synthesis, measurement of properties, scale-up, testing, etc. The most significant properties or characteristics of a high performance energetic material are the molecular structure, elemental composition, heat of formation, solid-state density and microstructure. Performance characteristics such as the detonation velocity and pressure are proportional to the density. The detonation velocity, for example, increases linearly with density while the Chapman-Jouguet pressure is proportional to the square of the initial density [2]. An increase in the solid-state density also is desirable in terms of the amount of material that can be packed into a volume-limited warhead or propulsion configuration. Density has been termed "the primary physical parameter in detonation performance" [3]. Microstructure is a catchall term that refers to the three-dimensional structure with various dislocation motifs and imperfections. The sensitivity of a material in response to impact or shock stimuli is associated with a number of factors, among which are the molecular and micro structures.

Initial efforts were directed to density prediction. Without question, the simplest method is by so-called "group or volume additivity." This is truly a back-of-the-envelope or spreadsheet calculation and involves the summation of appropriate atom and functional group volumes to give an effective solid-state volume for a molecule, then a density. Overall, volume additivity parameterization cannot readily account for molecular conformation, crystal packing efficiency or positional isomerism. The cyclic nitramine explosives RDX and the three HMX polymorphs with CH_2NNO_2 as the basic structural unit are a case in point. The experimental crystal densities are 1.806 (RDX), 1.839 (α -HMX), 1.902 (β -HMX) and 1.759 (δ -HMX) g cm^{-3} . The additivity densities of 1.838 for RDX and 1.847 g cm^{-3}

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for RDX and the HMX's, are somewhat different by the use of separate CH₂ parameters for different ring sizes [4]. The experimental densities are due in part to the molecular conformations in the crystals reflected by the point group symmetries of C_s for RDX and C₂, C₁ and C_{2v} for the three HMX's.

A procedure to predict the most likely crystal structure for a substance was developed to replace basic volume additivity. The principal advantages are: (1) information on the molecular structure, conformation and positional isomerism are automatically introduced because the three-dimensional structure of a molecule forms the essential starting point; (2) the procedure routinely handles (different) packing efficiencies. Note that the densest crystals have both high packing efficiencies and molecular densities.

Excellent reviews of the state-of-the-art in organic structure prediction are available from two blind test studies hosted in 1999 and 2001 by the Cambridge Crystallographic Data Center and a recent dissertation [5].

Structure Prediction

The model-MOLPAK-WMIN procedure consists of three steps: (1) construction of a reasonable three-dimensional model for the compound of interest (the search probe) followed by *ab initio* quantum mechanical geometry optimization (usually B3LYP/631G* or 631G**); (2) determination of thousands of possible crystal structures for the search probe (MOLPAK program [6]); (3) refinement (WMIN [7], DMAREL [8] or other programs) of the unit cell parameters, search probe orientation and position by lattice energy minimization for the best of the crystal structures derived in step 2.

In step 2, the search probe is used as a rigid packing moiety for the construction of hypothetical crystal structures with the MOLPAK (MOLEcular PAcKing) program. Typically, several hundred of the most dense, hypothetical structures for each of 29 possible coordination geometries are passed to the step 3 refinement. The most probable structure is identified by a combination of (lowest) crystal lattice energy and (highest) density.

MOLPAK was designed to reproduce the molecular coordination geometries observed in the most common triclinic, monoclinic and orthorhombic space groups. In addition, molecules with C₁, C₂ and C_s point group symmetries can be examined in space groups in which the appropriate molecular and unit cell symmetries coincide. The 29 molecular coordination geometries presently encoded in MOLPAK can fit the known crystal structures of approximately 94% of all C-H-N-O-F containing compounds with one molecule per asymmetric unit. The space groups and numbers of coordination geometries used routinely by MOLPAK are shown in Table 1 and a flow chart illustrating the various steps in the

crystal structure predictions process is shown in Fig. 1.

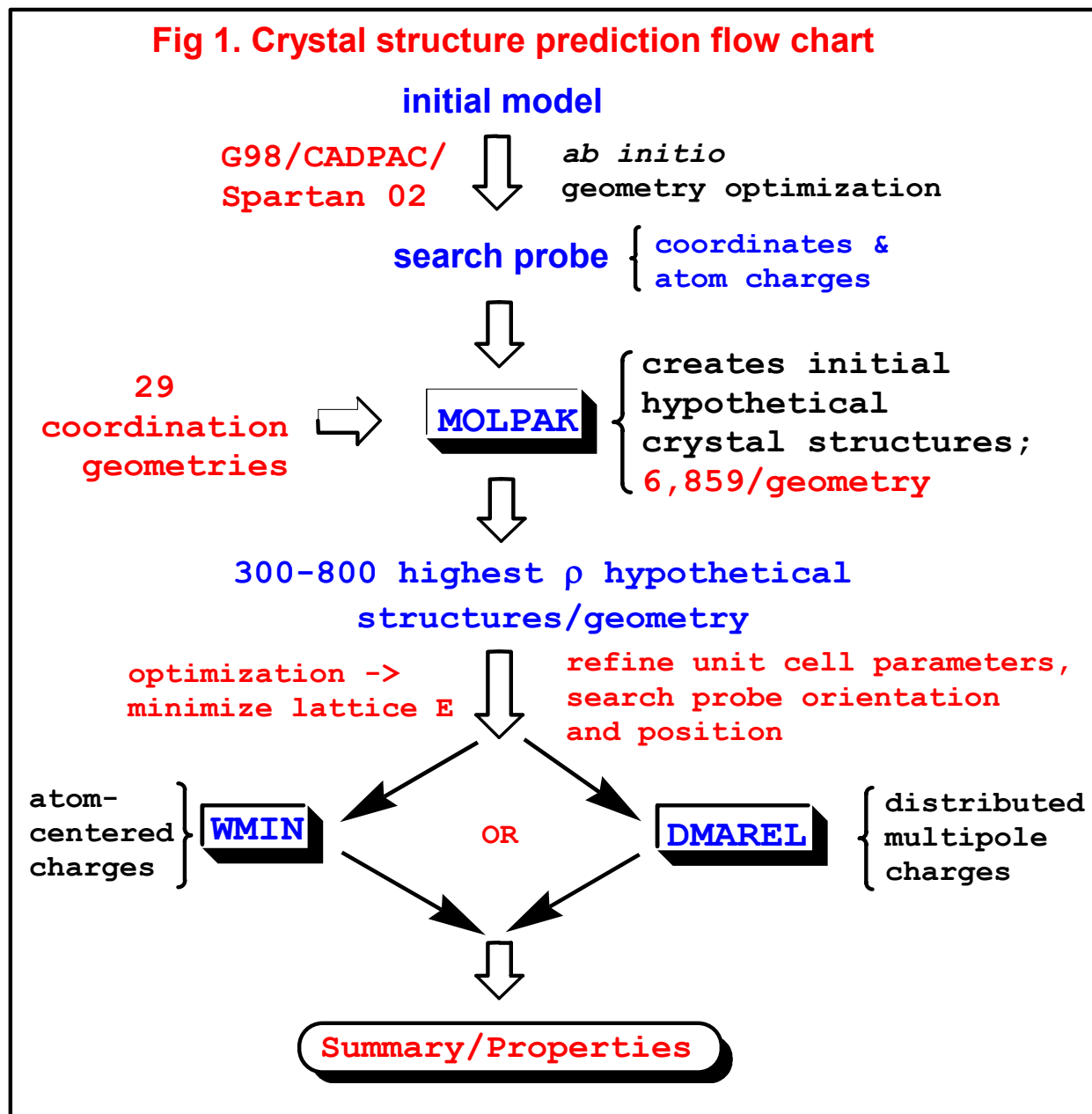


Table 1. Space Groups, numbers of structures (N) and percentages (%) for triclinic to Z = 8 orthorhombic unit cells with one molecule per asymmetric unit*

| # | Symbol | Space Groups | | | | | |
|---|----------------|--------------|-------------|----|------------------|------------|------------|
| | | N | % | # | Symbol | N | % |
| 1 | P1 [1] | 58 | 0.4 | 21 | C222 | 1 | 0.01 |
| 2 | P-1 [2] | 1747 | 12.6 | 23 | I222 | 2 | 0.01 |
| 4 | P21 [2] | 1507 | 10.9 | 29 | Pca21 [2] | 137 | 1.0 |
| 5 | C2 [1] | 125 | 0.9 | 33 | Pna21 [3] | 253 | 1.8 |

| | | | | | | | |
|----|--------------------|-------------|-------------|----|-----------------|------------|------------|
| 7 | Pc | 46 | 0.3 | 34 | Pnn2 | 2 | 0.01 |
| 9 | Cc [1] | 135 | 1.0 | 41 | Aba2 | 10 | 0.1 |
| 13 | P2/c | 12 | 0.1 | 45 | Iba2 | 9 | 0.1 |
| 14 | P21/c [5] | 5157 | 37.2 | 52 | Pncn | 1 | 0.01 |
| 15 | C2/c [3] | 557 | 4.0 | 56 | Pccn | 35 | 0.3 |
| 18 | P21212 [3] | 57 | 0.4 | 60 | Pbcn [2] | 62 | 0.4 |
| 19 | P212121 [2] | 3210 | 23.2 | 61 | Pbca [2] | 714 | 5.2 |
| 20 | C2221 | 14 | 0.1 | | | | |

*The numbers in brackets indicate the number of MOLPAK coordination geometries used for each space group.

Examples of several predictions in which the smallest calculated lattice energy corresponded to the correct structure are shown in Fig. 2 and several failures are illustrated in Fig. 3.

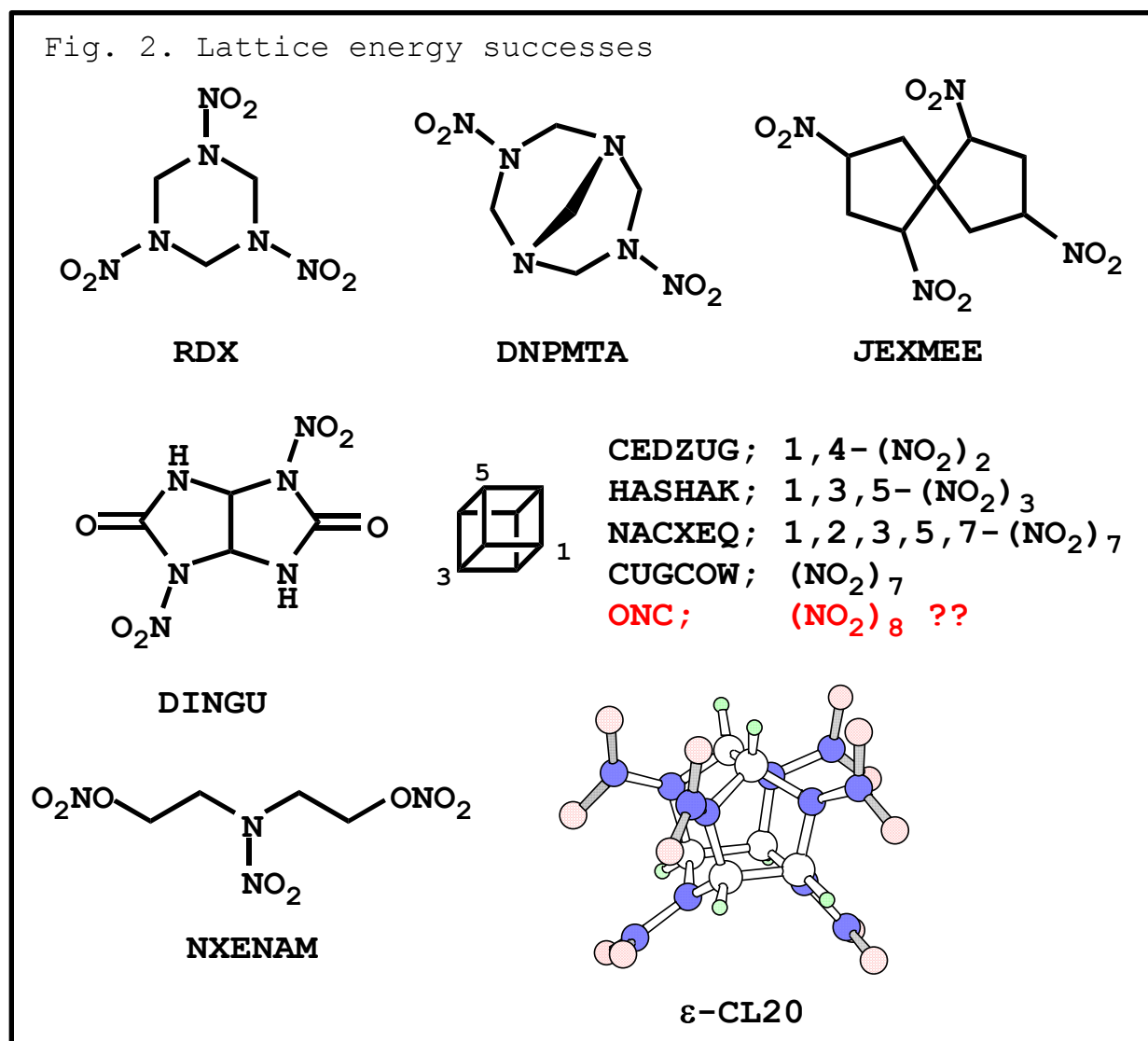
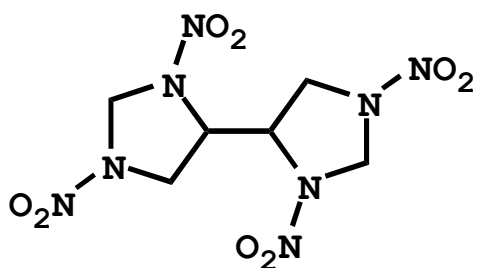
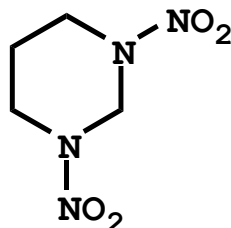


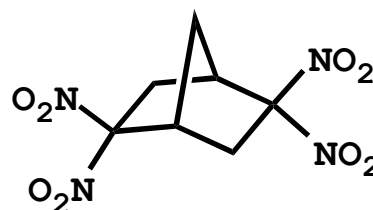
Fig. 3. Lattice energy failures*



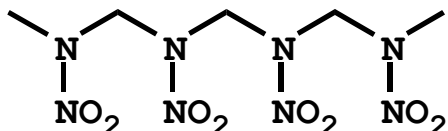
JEXMAA
(5th lowest,
1.0 kcal/mol)



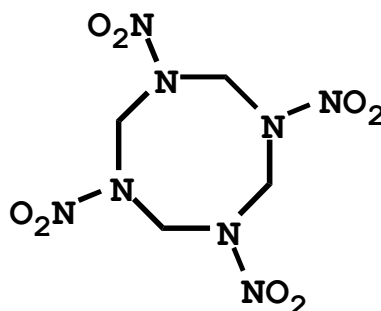
KOFKAR
(6th, 1.3)



JUVMIV
(3rd, 3.3)



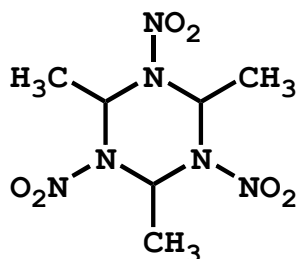
GEJXAU
(3rd, 0.6)



β -HMX
(2nd, 0.2)

*The quantities in parentheses indicate the lattice energy rank. For JEXMAA, the correct structure had the 5th lowest lattice energy and was 1.0 kcal/mol higher than the lowest energy structure.

A Good Example: NOHTAZ, $P2_12_12_1$, $\rho_{\text{obs}} = 1.580 \text{ g cm}^{-3}$.



The search probe file consisted of an adjusted model (C-H and N-O distances set to the standard values of 1.098 and 1.22 Å, respectively) plus electrostatic potential charges for the refinement step. MOLPAK created the highest density packing arrangements for all unique probe orientations (typically 180° rotation about three Eulerian axes in 10° increments) for each of the 29 coordination geometries. The 400 smallest volume

hypothetical structures per geometry were passed to WMIN for structure optimization. An abbreviated energy/density summary is given in Table 2. This is an extremely favorable example in

Table 2. Summary of Predictions for NOHTAZ

| # | ρ_{calc} (g cm^{-3}) | E_{min} (kcal mol^{-1}) | Space Group |
|----|--|--|--------------|
| 1 | 1.590 | -34.81 | $P2_12_12_1$ |
| 2 | 1.584 | -32.20 | $P2_1/c$ |
| ~ | ~ | ~ | ~ |
| 29 | 1.515 | -27.19 | P1 |

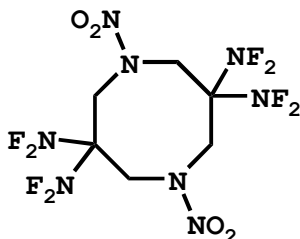
which the correct structure has both the lowest energy and highest density. Additionally, the lattice energy difference of $2.6 \text{ kcal mol}^{-1}$ between the best and next best-predicted structures is relatively large in comparison to most predictions.

A Close Example: β -HMX, $P2_1/c$, $Z = 2$, $\rho_{\text{obs}} = 1.893 \text{ g cm}^{-3}$.

β -HMX crystallizes in the monoclinic $P2_1/c$ space group with two molecules per unit cell; the molecule has C_i point group symmetry and is positioned on a crystallographic inversion center. MOLPAK + WMIN structure predictions were performed for the validated coordination geometries in space groups with centers of symmetry, P-1, $P2_1/c$, $C2/c$ and Pbcu. On the basis of lattice energy, however, the lowest energy predicted structure ($P2_1/c$, $E = -45.34 \text{ kcal mol}^{-1}$, $\rho_{\text{calcd}} = 1.856 \text{ g cm}^{-3}$) was incorrect. Rather, the correct structure had the second lowest energy ($P2_1/c$, $E = -45.13 \text{ kcal mol}^{-1}$, $\rho_{\text{calcd}} = 1.891 \text{ g cm}^{-3}$). Note the small energy difference of $0.2 \text{ kcal mol}^{-1}$ between the incorrect and correct structures.

Something Better?: HNFx, R-3, $\rho_{\text{obs}} = 1.807 \text{ g cm}^{-3}$.

Difluoroamino compounds are of interest because of their potential high density and energy and properties as solid propellant oxidizers. An X-ray crystallographic determination [9] of the promising HNFx [10] revealed the disappointingly low



density of 1.807 g/cc . This value was the result of unexpected crystal packing in which three molecules form the surface of a cylinder with an empty core. Our calculations and predictions,

outlined in Table 3, show that the experimental crystal structure in space group R-3 is not the lowest energy at -39.7 kcal mol⁻¹. Rather, we predict a (presently) unknown polymorph in space group P2₁/c with a substantially lower energy of about -44 kcal mol⁻¹ and higher density of about 2.03 g cm⁻³.

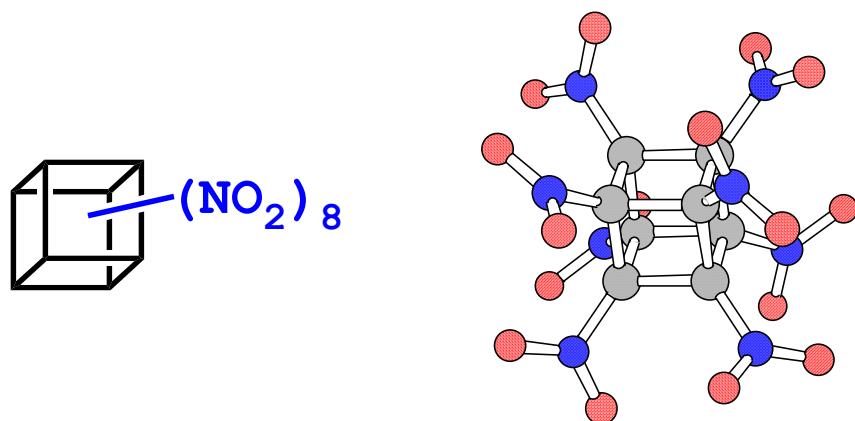
Table 3. Various HNFx models, space groups, lattice energies and densities

| Model geometry | Space group | Lattice E (kcal mol ⁻¹) | Density (g cm ⁻³) |
|---|--|-------------------------------------|-------------------------------|
| C _i , exptl xray | R-3 | -39.71 | 1.789** |
| C _i , xray model in general posn | Pca2 ₁ | -41.19 | 1.945 |
| C _i , xray model on center of symm | P2 ₁ /c | -43.39 | 2.049 |
| C _i , optim model* on center of symm | P2 ₁ /c | -44.77 | 2.027 |
| C _i , optim model* in general posn | Pca2 ₁ or P2 ₁ 2 ₁ 2 ₁ | -41.03 | 1.963 |
| C ₂ , model* in general posn | Cc | -39.38 | 1.944 |
| C ₂ , model* on 2-fold axis | C2/c | -33.33 | 1.760 |
| C ₁ model* | P2 ₁ /c | -37.72 | 1.917 |

* Gaussian98, B3LYP/631G* geometry optimization.

** $\rho_{\text{obs}} = 1.807$ g cm⁻³; $\rho_{\text{volume add}} = 1.915$ g cm⁻³.

Octanitrocubane (ONC): C2/c, z' = 0.5, $\rho_{\text{obs}} = 1.978$ g cm⁻³.



Earlier predictions of the density ranged from 2.1 to more than 2.2 g cm⁻³. The plot (Fig. 4) of densities vs. number of nitro groups suggests that extrapolation of the cubane to tetranitrocubane data would give a value of 2.2 g cm⁻³ or perhaps

larger for ONC. However, beyond five nitro groups the slope eases and has become almost flat in the 6-8 nitro group range. The successful synthesis and subsequent X-ray structure determination [11] in 2000 showed a disappointing crystal density of less than 2 g cm^{-3} . Extensive calculations, performed with the MOLPAK + WMIN procedures are summarized in Table 4. The predicted densities with both an X-ray model and Gaussian 98 optimized model for the search probe are in good agreement with experiment. The predicted structure for geometry DC corresponds to the experimental X-ray structure and is only $0.01 \text{ kcal mol}^{-1}$ higher than the lowest energy structure. Geometry DA, space group Cc, also corresponds to the experimental structure; the search probe C2 axis is aligned to generate an effective C2/c space group. Use of the X-ray structure as the search probe gives DC (experimental) as the lowest energy structure.

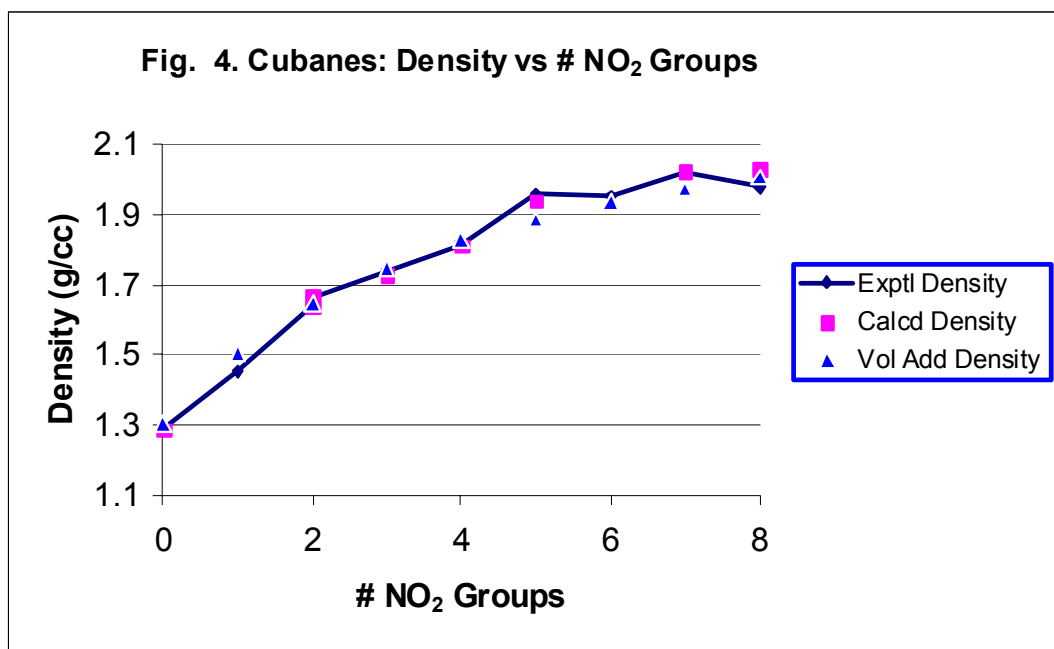


Table 4. Summary of MOLPAK + WMIN predictions for octanitrocubane; Gaussian 98 B3LYP/631G** model with C₂ symmetry

| Coord Geom | ρ (g/cc) | E (kcal/mol) | Space group |
|---------------|------------------|-----------------|-----------------------------|
| AB | 2.003 | -23.27 | P-1 |
| AK | 2.003 | -23.27 | P21/c |
| DC | 2.003 | -23.26 | C2/c <- molecule on 2-fold |
| DA | 2.003 | -23.26 | Cc <- molecule in genl posn |
| AM | 2.002 | -23.24 | P21/c |
| AH | 1.898 | -21.34 | P21 |
| AQ | 1.883 | -21.08 | P212121 |

~~~geometries deleted~~~

|    |       |        |                              |
|----|-------|--------|------------------------------|
| BF | 1.732 | -18.16 | Pna21                        |
| BB | 1.764 | -16.99 | P21212                       |
| AP | 1.647 | -15.19 | P21212 <- molecule on 2-fold |

### Now and Next Year...

#### MOLPAK + WMIN and MOLPAK + DMAREL

MOLPAK\_+ WMIN and MOLPAK\_+ DMAREL are packages of programs, C-shell scripts and data files for crystal predictions. Both use MOLPAK to produce hypothetical packing arrangements and differ primarily in the lattice energy refinement programs, WMIN and DMAREL.

The crystal lattice energy (E) is calculated as the energy sum of all atom-to-atom interactions between a central molecule and the surroundings. The terms are:  $q_i$  = Coulombic charge on atom  $i$ ;  $r_{ij}$  = atom  $i$  to  $j$  distance;  $A_{ij} = (A_i * A_j)^{1/2}$ ,  $B_{ij} = (B_i * B_j)^{1/2}$ ,  $A_i$  and  $B_i$  are empirical coefficients for atom  $i$ ;  $C_i$  is similar to a van der Waals radius for atom  $i$ . The DMAREL potential is similar, but with a distributed multipole electrostatic term (6-31G\*\* basis set) in place of the WMIN monopole).

$$E = \sum [q_i q_j / r_{ij}] - A_{ij} / r_{ij}^6 + B_{ij} \exp[-r_{ij} / (C_i + C_j)]$$

The unknowns are the various A and B coefficients; literature values are used for the C's. Ideally, a single A coefficient would be appropriate for each element type, but it has been our experience that different atom types are required such as, for example,  $\underline{H}$ -NR<sub>2</sub>,  $\underline{H}$ -C(sp<sup>2</sup>),  $\underline{H}$ -C(sp<sup>3</sup>) and  $\underline{H}$ -O for hydrogen. The parameterization process may be done either sequentially, one functional group at a time, or in a combined fashion which fits all coefficients in a single parameterization step. Limited experience suggests combined parameterizations yield better sets of coefficients, which translate into more sensitive and definitive lattice energies and structure refinements. A series of global coefficient optimizations (simplex [12] method) followed by broad testing are planned to fine-tune and extend the refinement capabilities of the WMIN and DMAREL programs.

#### MOLPAK and ROTPAK

The search probe obtained from an *ab initio* MO geometry optimization describes a molecule isolated from crystal packing effects. Although the rigid probe is adequate for most packing calculations, there are cases in which some amount of conformational flexibility is desirable. This is being addressed by the development of the ROTPAK program (ROTational PAcKing) that allows limited conformational changes to accompany the packing processes. There has been some success at this time. The development of a proper mix of the inter and

intramolecular energies necessary for determination of the total energy of a solid-state structure will be a major focus.

## After the Initial MURI Meeting

### (1) A Start on Dimethylnitramine

We have performed structure prediction calculations on one of the suggested targets, dimethylnitramine. The material crystallizes in the monoclinic space group,  $P2_1/m$ , with  $Z' = 0.5$  (1/2 molecule per asymmetric unit). The molecule has  $C_{2v}$  symmetry in the crystal and occupies the crystallographic mirror plane normal to the b-axis. The MOLPAK coordination geometry for  $P2_1/m$ ,  $Z' = 1$ , has not been implemented because the number of C-H-N-O-F-containing structures with four molecules per unit cell is close to zero. The majority of  $P2_1/m$  structures fall into the  $Z' = 0.5$  category.

Nevertheless, MOLPAK is able to handle this case by placing the  $C_s$  molecule in an appropriate position in  $P2_1$ . A summary of the MOLPAK + WMIN calculations with a  $C_{2v}$  search probe are given in Table 5. It is interesting to note that both the P-1 and  $P2_1$  structures agree with the experimental X-ray structure. In the case of the formally triclinic P-1, the unit cell angles are almost exactly those for the monoclinic system. Both the P-1 and  $P2_1$  solutions give unit cell parameters ( $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ) of 6.062, 6.192, 6.254 Å, 90, 114.96, 90°. The experimental parameters [13] are 6.129, 6.501, 6.60 Å, 90, 114.66, 90°. The P-1 and  $P2_1$  solutions differ only in the placements of the molecules along  $b$ , at  $y = 1/4$  in P-1 and  $y = 0$  in  $P2_1$ .  $P2_1$  is a polar space group and thus the  $y$  coordinate is arbitrary.

Table 5. Summary of MOLPAK + WMIN predictions for dimethylnitramine; Gaussian 98 B3LYP/631G\* model with  $C_{2v}$  symmetry

| Coord<br>Geom              | $\rho$<br>(g/cc) | E<br>(kcal/mol) | Space<br>group           |
|----------------------------|------------------|-----------------|--------------------------|
| CA                         | 1.405            | -17.65          | P-1 ← X-ray structure    |
| AH                         | 1.405            | -17.65          | $P2_1$ ← X-ray structure |
| AM                         | 1.405            | -17.65          | $P2_1/c$                 |
| AA                         | 1.389            | -17.23          | P1                       |
| FA                         | 1.398            | -17.20          | $P2_1/c$                 |
| DA                         | 1.376            | -17.01          | Cc                       |
| AQ                         | 1.379            | -16.96          | $P2_12_12_1$             |
| ~~~~geometries deleted~~~~ |                  |                 |                          |
| BF                         | 1.371            | -16.63          | $Pna2_1$                 |
| CE                         | 1.342            | -16.32          | Pbcn                     |

Numerous diffraction determinations of dimethylnitramine, from room temperature to 4 K, have been reported. A phase transition [14] at low temperature (4 and 85 K) to the  $P2_1/c$  space group has been observed. The data are somewhat old and several of the determinations should be repeated.

## (2) Data Needed

The development of force field coefficients for crystal lattice energy calculations and structure refinements requires several kinds of experimental data of which the richest source is numerous high quality crystal structure determinations. The function we typically use is shown below. The terms are  $\Delta F$  = difference between experimental and calculated cell parameters (lengths and angles);  $\Delta E$  = difference between experimental and calculated heats of sublimation;  $\Delta d$  = difference between 50 shortest intermolecular distances;  $\langle |\delta\rho| \rangle$  = average difference in experimental and calculated densities;  $(\rho_{MAX} \dots \rho_{MIN})$  = spread of densities around the average. The terms are weighted to reflect relative importance and many use the same kind of information such as the unit cell parameters, molecule position and orientation. Heats of sublimation ( $\Delta E$ ) are in short supply (and of variable quality). Without adequate sublimation data, it is not possible to have force field coefficients give accurate estimates for the lattice energies. Can an effort be mounted to supply these?

$$\Sigma \Delta F + \Delta E + \Delta d + \langle |\delta\rho| \rangle + (\rho_{MAX} \dots \rho_{MIN})$$

Sensitivity data also are needed with clear indications of how the experiments were conducted. Particle size information should be included if available. A recent report [15] of a relationship between the frictional sensitivity of RDX and humidity is of concern as this further complicates our understanding of and ability to predict sensitivity.

## (3) Contacts

Over the years, we have collaborated with many scientists in the area of energetic materials predictions and programs. The following Table 6 probably is an incomplete list; affiliations are included. Our apologies for anyone omitted. This list does not include many to whom programs have been supplied.

Table 6. Collaborations

| <b>Person</b>     | <b>Affiliation</b> |
|-------------------|--------------------|
| A. Bashir-Hashemi | Fluorochem         |
| K. Baum           | Fluorochem         |
| R. Chapman        | China Lake         |
| W. Wilson         | China Lake (ex)    |

|                     |                   |
|---------------------|-------------------|
| B. Rice             | ARL               |
| P. Dave             | ARDEC             |
| R. Surapaneni       | ARDEC             |
| R. Damavarapu       | ARDEC             |
| H. Shechter         | Ohio State Univ.  |
| R. Bartlett         | Univ. Florida     |
| R. Miller (retired) | ONR               |
| J. Goldwasser       | ONR               |
| H. Adolph           | Indian Head       |
| A. Stern            | Indian Head       |
| W. Lawrence         | Indian Head       |
| W. Koppes           | Indian Head       |
| T. Axenrod          | CCNY              |
| A. Marchand         | Univ. North Texas |
| S. Price            | Univ. of London   |

#### (4) Research Support

Office of Naval research

MURI (Multidisciplinary Research Program of the University  
Research Initiative)

CHSSI (Common High Performance Computing Software Support  
Initiative)

#### References

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[1] R. J. Spear and W. S. Wilson, *J. Energetic Materials*, **2**, 61 (1984).

[2] M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.* **48**, 23 (1968).

[3] C. L. Mader in "Organic Energetic Compounds," P. L. Markinas, ed., Nova Science Publishers, Commack, NY, 1996, p. 193.

[4] H. L. Ammon, *Structural Chem.*, **21**, 2001, 205.

[5] W. D. S. Motherwell, H. L. Ammon, J. D. Dunitz, A. Dzyabchenko, P. Erk, A. Gavezzotti, D. W. M. Hofmann, F. J. J. Leusen, J. P. M. Lommerse, W. T. M. Mooji, S. L. Price, H. Scheraga, B. Schweizer, M. U. Schmidt, B. P. van Eijck, P. Verwer and D. E. Williams, *Acta Cryst.*, **B58**, 647 (2002); J. P. M. Lommerse, W. D. S. Motherwell, H. L. Ammon, J. D. Dunitz, A. Gavezzotti, D. W. M. Hofmann, F. J. J. Leusen, W. T. M. Mooji, S. L. Price, B. Schweizer, M. U. Schmidt, B. P. van Eijck, P. Verwer and D. E. Williams, *Acta Cryst.*, **B56**, 697 (2000); W. T. M. Mooji, *Ab Initio Prediction of Crystal Structures*,

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Ph.D. Dissertation, Utrecht University, The Netherlands, 2000.

[6] J. R. Holden, Z. Du and H. L. Ammon, *J. Comp. Chem.* **14**, 422 (1993).

[7] W. R. Busing, WMIN, A Computer Program to Model Molecules and Crystals in Terms of Potential Energy Functions, Report ORNL-5747, Oak Ridge National Laboratory, Oak Ridge, TN, 1981.

[8] D. J. Willock, S. L. Price, M. Leslie and C. R. A. Catlow, *J. Comput. Chem.*, **16**, 628 (1995).

[9] R. D. Chapman, R. D. Gilardi, M. F. Welker and C. B. Kreutzberger, *J. Org. Chem.*, **64**, 960 (1999).

[10] R. D. Chapman, M. F. Welker and C. B. Kreutzberger, *J. Org. Chem.* **63**, 1566 (1998).

[11] M. Zhang, P. E. Eaton and R. Gilardi, *Angew. Chem. Int. Ed.* **39**, 404 (2000).

[12] W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes in Fortran*, 2<sup>nd</sup> ed, Cambridge University Press, 1992, p. 402.

[13] B. Krebs, J. Mandt, R. E. Cobblestick and R. W. H. Small, *Acta Cryst.*, **B35**, 402 (1979).

[14] A. Filhol, G. Bravic, M. Rey-Lafon and M. Thomas, *Acta Cryst.*, **B36**, 575 (1980).

[15] M. Williams and M. Wingrave, *Prop. Expl. Pyrotech.* **27**, 241 (2002).