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First Principles Calculation of the Mechanical Compression of Two Organic Molecular Crystals

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The mechanical compression curves for the organic molecular crystals 1,1-diamino-2,2-dinitroethylene and β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β-HMX) are calculated using the Hartree−Fock approximation to the solutions of the many-body Schrödinger equation for a periodic system as implemented in the computer program CRYSTAL. No correction was made for basis set superposition error. The equilibrium lattice parameters are reproduced to within 1% of reported experimental values. Pressure values on the isotherm also agree well with reported experimental values. To obtain accurate results, the relaxation of all the atomic coordinates as well as the lattice parameters under a fixed volume constraint was required.

Introduction

The theoretical prediction of equations of state is important in many fundamental and practical problems, in fields as far ranging as planetary science and military applications, where experimental data may be difficult, expensive, or, in some cases, impossible to obtain. In this regard, there is great interest in computing the equation of state for a class of organic molecular crystals which are the ingredients of materials often referred to as energetic materials. While fits of experimental data to analytic equations of state have achieved some success, ab initio calculations hold the promise for calculating the equation of state as well as a number of other chemical and physical properties of these materials in cases in which experimental data are not available or are not easy to obtain.

In recent years there has been a large body of research devoted to the determination of optical, mechanical, and reactive properties of materials from numerical solutions of the many-body Schrödinger equation. In particular, the equation of state of many solids has been determined in this manner: metals such as iron, copper, and aluminum; elementary solids such as silicon; metal oxides; ionic solids such as NaCl. Not much work has been done on the equation of state of more complex materials such as organic molecular crystals. Ab initio calculations for organic crystals require large computational resources due to both the typically large size of the molecules and the complexity of the crystal structure. However, state of the art computer power has progressed to the point where it becomes practical to study these more complex materials. Unfortunately, there are still many difficulties. The Hartree−Fock method, unless modified with a specific correlation method, does not include electron correlation energies beyond exchange correlation, and while density functional theory (DFT) methods[1,2] do include electron correlation effects, they rely on functionals which only approximately describe the electronic density. Also, dispersion forces, including van der Waals interactions, are significant in molecular crystals. DFT methods treat them somewhat poorly, and Hartree−Fock methods treat them not at all.

Most of the recent investigations performed at the ab initio level use DFT methods and only a few studies have been based on the Hartree−Fock method.

Miao et al.[3] studied the molecular crystal structure and the molecular dissociation of iodine, bromine, and chlorine under high pressure with pseudopotential plane wave LDA (local density approximation) and GGA (generalized gradient approximation) methods. They found that GGA overestimates the interlayer distance but describes geometry parameters within the plane much better than LDA. The calculated unit cell volumes differ by 10−20% from experimental values, and the bulk moduli obtained by LDA differ from experimental values by 5−36%, and those obtained by GGA are within 5% of experimental values.

Civalleri et al.,[4] in a study of the structure of silica polymorphs, using both Hartree−Fock and DFT methods with a number of atom-centered Gaussian type basis sets,[5] concluded that geometrical parameters are “scarcely” sensitive to the presence of polarization functions so that for the optimization of large unit cells the Hartree−Fock method with a 6-21G basis (Pople’s notation[5]) is good enough. However, determination of the relative stability of the polymorphs required calculation of the final energy with at least a 6-31G(d) basis.

Ojamăe et al.,[6] in one of the first calculations with a periodic structure Hartree−Fock method for molecular crystals, determined the mechanical compression curve for ice VIII. (The term “mechanical compression” is used to indicate that no vibrational or electronic contributions are included. Thus, the “mechanical compression curve” is not strictly equivalent to the “0 K isotherm” which would include a zero point energy contribution.) They used a 6-31G** basis, optimized the atomic coordinates and cell parameters, and found that the calculations slightly overpredicted the pressure under compression. They also

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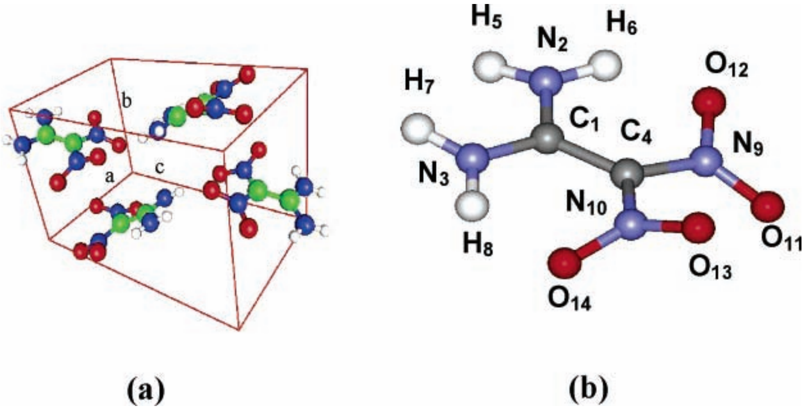

Figure 1. FOX-7 unit cell (a) and molecular unit (b). The entire molecule comprises the irreducible asymmetric unit.

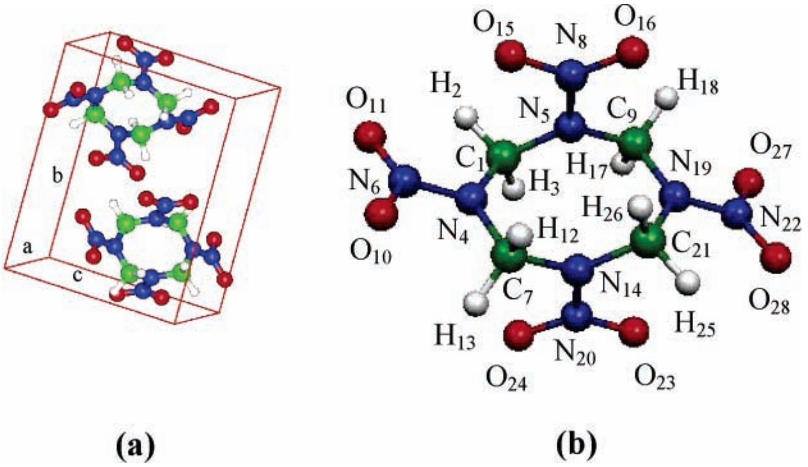

Figure 2. β-HMX unit cell (a) and molecular unit (b). The irreducible asymmetric unit consists of atoms 1−14.

found that correction for basis set superposition errors[7] did not change the results significantly.

The mechanical hydrostatic compression of the energetic molecular crystal, pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$, was recently investigated by Gan et al.[8] They used density functional theory with the Perdew−Burke−Ernzerhof functional[9] and a 6-31G** Gaussian basis set with optimization of atomic positions and fixed volume optimization of the c/a lattice parameter ratio. They obtained results that agree remarkably well with experiment, although they did not correct for basis set superposition errors.

In this article, we describe a reasonably accurate calculation of the mechanical compression curve for several organic molecular crystals, including 1,1-diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$) and β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($C_4H_8N_8O_8$). These materials are representative of the large class of organic molecular crystals known as high explosives because of their propensity for rapid explosive decomposition under shock conditions.

Bemm and Östmark[10] determined the crystal structure of 1,1-diamino-2,2-dinitroethylene, which they named FOX-7, to be monoclinic with space group $P2_1/n$ and 4 molecules/unit cell. They reported the values of the lattice parameters $a = 6.9410$ Å, $b = 6.5690$ Å, $c = 11.315$ Å, and $\beta = 90.55°$. Gilardi[11] has also studied the structure of FOX-7 and found the values $a = 6.9396$ Å, $b = 6.6374$ Å, $c = 11.3406$ Å, and $\beta = 90.611°$. The unit cell and molecular conformation are depicted in Figure 1. The irreducible asymmetric unit consists of the entire molecule.

β-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($C_4H_8N_8O_8$), also known as β-HMX, has a monoclinic $P2_1/c$ structure with 2 molecules/unit cell.[12] The cell parameters for the $P2_1/c$ structure, $a = 6.54$ Å, $b = 11.05$ Å, $c = 8.70$ Å, and $\beta = 124.3°$, were reported by Cady, Larson, and Cromer,[13] who transformed the measured values of Eiland and Pepinsky[14] from the $P2_1/n$ structure. The unit cell and molecular unit are depicted in Figure 2. In this case, the irreducible asymmetric unit consists of half the molecular unit (atoms 1−14 in the figure).

In previous work[15] we reported the results of calculations for FOX-7 using a rigid molecule approximation as well as performing optimization of molecular structure at several levels including optimization of the fractional atomic coordinates.

It turns out that the Hartree−Fock approximation with a periodic structure code using a linear combination of atomic orbitals (LCAO) Gaussian basis at the 6-21G level gives very good results for this type of calculation. The Hartree−Fock calculations reproduce the equilibrium lattice parameters within about 1% and the corresponding unit cell volume within 3%. Because no correction was made for basis set superposition errors[7] inherent with LCAO basis sets that are less than complete, the good agreement for the equilibrium configuration is probably the result of compensation for the absence of dispersion forces by errors introduced from basis set truncation. But it is interesting that this compensation of errors seems to occur for a number of organic molecular crystals.

Optimization Procedure

To obtain results that can be compared to hydrostatic compression experiments, it is necessary not only to optimize the atomic coordinates of the molecules within the unit cell but also to optimize the lattice parameters under a fixed volume constraint. The basic quantum calculations for a periodic structure were performed with the CRYSTAL98[16] computer program, developed by the Theoretical Chemistry Group at the University of Torino. More recent calculations were performed with CRYSTAL03.[17] All calculations with CRYSTAL were performed with a $4 \times 4 \times 4$ Monkhorst–Pack[18] grid in the irreducible wedge of the Brillouin zone. The truncation criteria for CRYSTAL's calculation of the bielectronic integrals was set as follows: overlap threshold for Coulomb integrals, penentration threshold for Coulomb integrals, overlap threshold for Hartree–Fock exchange integrals, and pseudo overlap for the Hartree–Fock exchange series, all set to 10^{-7}; second pseudo overlap for the Hartree–Fock exchange series, set to 10^{-14}. Optimizations of the atomic coordinates and lattice parameters were done separately and iteratively. For the calculations with CRYSTAL98, the atomic coordinates were first optimized using Zicovich–Wilson's LoptCG script,[19] which calls CRYSTAL98 to calculate the energy for each configuration. The lattice parameters then were optimized under a fixed volume constraint using a locally written program based on the downhill simplex method of Nelder and Mead.[20,21] This was repeated until satisfactory convergence was achieved. In general, the second repetition did not significantly improve the results, most likely due to the presence of modes of displacement in which the energy changes very little while the displacement continues to increase. We have not identified or investigated these modes in this work.

LoptCG is a flexible script, allowing the choice of the method of steepest descents or the Polak–Ribiere conjugate gradient method or some combination of these methods to find the minimum energy.[20,22] LoptCG calculates derivatives numerically and will automatically adjust the self-consistent field (scf) convergence criterion to the precision required to calculate the first derivative. These criteria ranged from a low of 10^{-6} hartree for the root-mean-square change in energy eigenvalues and 10^{-5} hartree for the change in absolute value of the total energy during one scf cycle to a high of 10^{-15} hartree and 10^{-12} hartree, respectively. It also takes advantage of the ability of CRYSTAL to start an scf calculation with the initial guess taken from density matrixes calculated on a previous run. In the calculations reported here, the conjugate gradient method was used exclusively to optimize the fractional coordinates, with a convergence criterion of 10^{-3} hartree in the gradient norm.

The simplex optimization routine, SOPT, which was used for the lattice parameter optimization under a fixed volume constraint, also calls CRYSTAL to determine the energy of a configuration and has the advantage of not requiring the calculation of derivatives. SOPT also starts successive energy computations from the density matrix of the previous computation but does not alter CRYSTAL's scf convergence tolerances. The lattice parameter optimization was considered converged when the root-mean-square of the lattice parameter change during one iteration was less than 10^{-5} Å.

CRYSTAL uses a set of basis functions composed of linear combinations of Gaussian type atomic orbitals. Kunz[23] determined that a modified 6-21G split valence basis set affords a good compromise between accuracy of the computations and required computer resources in the case of the energetic solids RDX (*cyclo*-trimethylenetrihydramine) and TATB (1,3,5 triamino-2,4,6 trinitrobenzene). Our own tests confirm this, and we have chosen to utilize this basis set in the computations reported here. As these basis functions are optimized for isolated, nonperiodic systems, scaling factors are introduced that reduce the range of the outer orbitals to better adapt them for use in periodic systems. The scaling factors (1.05 for C, N, H; 1.00 for O) for Hartree–Fock computations were determined by minimizing the energy in test calculations and are similar to values obtained previously.[23,24] No correction for basis set superposition error was made as there is disagreement in the literature as to the efficacy of the principal method of correction, the counterpoise method of Boys and Bernardi,[25] in producing reliably more accurate results than no correction at all. It does appear, however, that there is some basis set superposition error which tends to compensate for the absence of van der Waals forces.

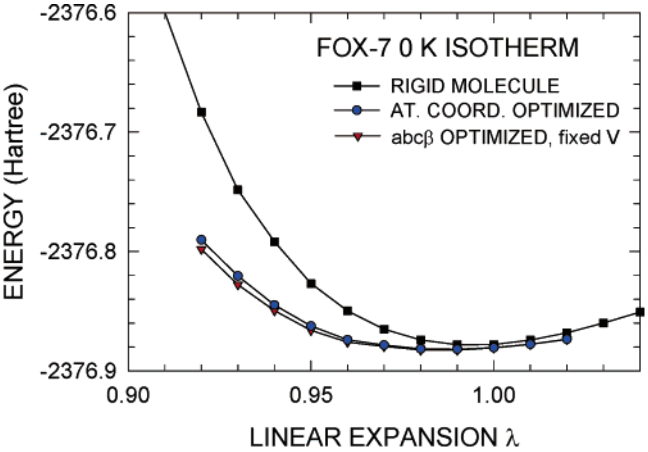

Figure 3. Energy along the 0 K isotherm for FOX-7. The squares show the energy in the rigid molecule approximation, the circles show the energy after the atomic coordinates have been relaxed, and the triangles show the energy after a further relaxation of the lattice parameters under the fixed volume constraint.

FOX-7 Mechanical Compression

The energy along the mechanical compression curve for FOX-7 is shown in Figure 3 as a function of mean linear expansion $\lambda = (V/V_0)^{1/3}$. In the figure, a linear expansion of 1 corresponds to Gilardi's experimental values for the lattice parameters and an associated unit cell volume V_0 of 522 Å^3. For comparison, the energy calculated under uniform compression of the lattice with the assumption of rigid molecules is shown. (The rigid molecule structure is that for which the 13 bond lengths have been optimized for lattice parameters equal to 99% of Gilardi's parameters.) A considerable improvement in the energy occurs when the molecules are no longer treated as rigid and the fractional atomic coordinates are relaxed. In this relaxation, only the coordinates of the 14 irreducible atoms in the unit cell are considered, preserving the symmetry of the space group. A further, small but significant, improvement in the energy occurs when the lattice parameters, *a*, *b*, *c*, and *β*, are relaxed under a fixed volume constraint, where the volume $V = \lambda^3 V_0$. Relaxation under the fixed volume constraint corresponds to true hydrostatic compression.

The experimental observations[10,11] are done at room temperature (300 K). The thermal expansion coefficient for FOX-7 has not yet been experimentally determined but was calculated by Sorescu et al.,[26] using molecular dynamics. They determined an average linear expansion coefficient of 6.8×10^{-5} K^{-1} at 273 K. A similar material, TATB ($C_6H_6N_6O_6$), has a measured linear thermal expansion coefficient[27] of the order of 5×10^{-5} K^{-1} at 300 K. The thermal expansion decreases to zero at 0 K. Thus, the correction for the temperature difference should amount to about 1%. This would shift the calculated equilibrium point up to 100.5% of Gilardi's value.

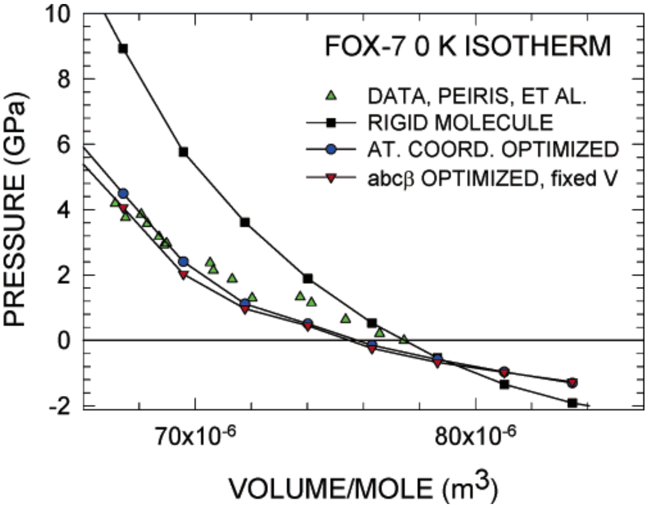

Figure 4. Pressure along the 0 K isotherm for FOX-7. The squares show the pressure in the rigid molecule approximation, the circles show the pressure after the atomic coordinates have been relaxed, and the downward pointing triangles show the pressure after a further relaxation of the lattice parameters under the fixed volume constraint. The calculated equilibrium volume is 75.8 cm^3/mol. The upward pointing triangles show the experimental data of Peiris et al.[28]

The pressure−volume dependence is calculated from the usual thermodynamic relation

$$P = -\left(\frac{\partial F(V,T)}{\partial V}\right)_T \tag{1}$$

where F is the Helmholtz free energy. At 0 K, this reduces to $P = -\mathrm{d}E_0/\mathrm{d}V$, where E_0 is the energy along the 0 K isotherm. The pressure, calculated from the energy curves in Figure 3, is shown in Figure 4, along with experimental data reported by Peiris et al.[28] It can be seen that the rigid molecule, uniform compression calculations predict much too high a pressure, while the calculations in which the atomic coordinates and lattice parameters have been relaxed are in excellent agreement. The agreement, in particular near the equilibrium (zero pressure) state, may be accidental due to cancellation of errors; while the Hartree−Fock method does not reproduce dispersion forces, including the van der Waals forces, this may be compensated by basis set superposition error arising from basis set truncation.

To make the comparison, it is necessary to take into account the fact that the experimental data corresponds to room temperature, about 300 K. Currently work is underway to determine the equation of state for nonzero temperatures. At present there is limited theoretical information and no experimental data for thermal properties of FOX-7 but some estimates are possible. The pressure difference may be determined from the thermodynamic identity

$$\left(\frac{\partial P}{\partial T}\right)_V = \rho c_V \gamma \tag{2}$$

where ρ is the density, c_V is the specific heat at constant volume, and γ is the Grüneisen parameter. The Grüneisen parameter may be determined from the relation

$$\gamma = \frac{\alpha \kappa_T}{\rho c_V} \tag{3}$$

where α is the volume coefficient of thermal expansion and κ_T is the isothermal bulk modulus. With a density of 1900 kg/m^3, assuming a specific heat of 1000 J/(kg K) and a Grüneisen parameter of 1.0, the pressure at 300 K would be about 0.6 GPa greater than the pressure at 0 K. This is very consistent with the results shown in Figure 4.

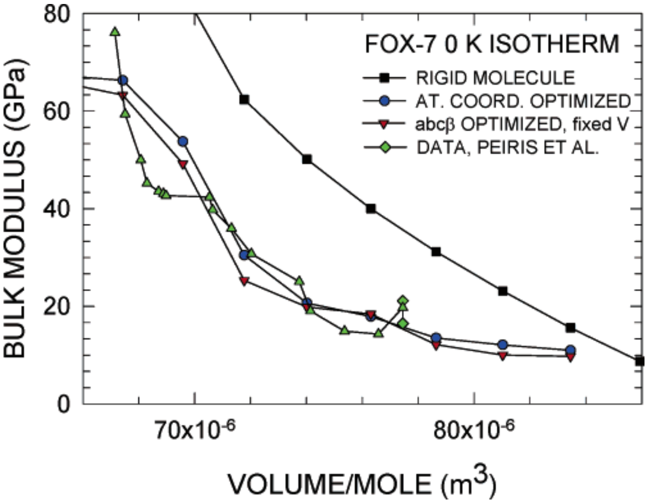

Figure 5. Bulk modulus along the 0 K isotherm for FOX-7. The squares show the bulk modulus in the rigid molecule approximation, the circles show the bulk modulus after the atomic coordinates have been relaxed, and the downward pointing triangles show the bulk modulus after a further relaxation of the lattice parameters under the fixed volume constraint. The calculated equilibrium volume is 75.8 cm^3/mol. The upward pointing triangles represent the bulk modulus obtained from the numerically differentiated pressure data of Peiris et al.[28] while the two diamond shaped points show the range of their reported bulk modulus values at atmospheric pressure.

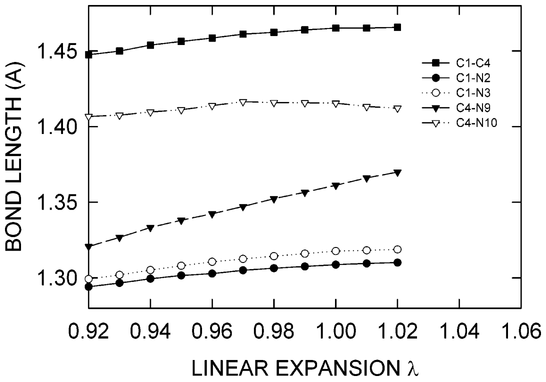

Figure 6. C−C and C−N bond lengths for FOX-7 optimized along the 0 K isotherm.

The calculated bulk modulus is shown in Figure 5, along with the zero pressure, room temperature range of values of the bulk modulus determined experimentally by Peiris et al.[28] The calculated value is a little smaller than the measured value. Further, the measured value at room temperature is presumably smaller than the 0 K value, but we do not know by how much at this point. If we assume that the room-temperature value of the bulk modulus is not much smaller than the 0 K value, then the calculated value agrees well with the experimental value. However, this may not be a good assumption. There is some evidence that the 0 K value of the bulk modulus could be as much as 50% larger than the room temperature (300 K) value according to Monte Carlo calculations for RDX ($C_3H_6N_6O_6$) reported by Sewell and Bennett.[29] Also shown in the figure are values of bulk modulus under compression obtained by differentiating the experimental pressures reported by Peiris et al. Although there is a large amount of scatter produced by the numerical differentiation of the data, it is seen that there is approximate agreement between the data and the calculation.

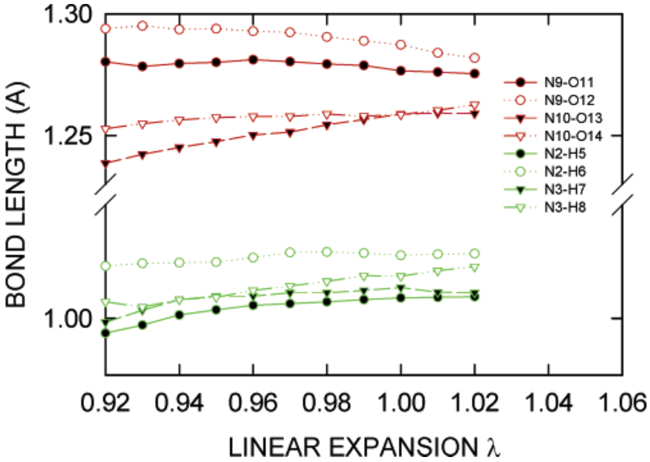

Figure 7. N−O and N−H bond lengths for FOX-7 optimized along the 0 K isotherm.

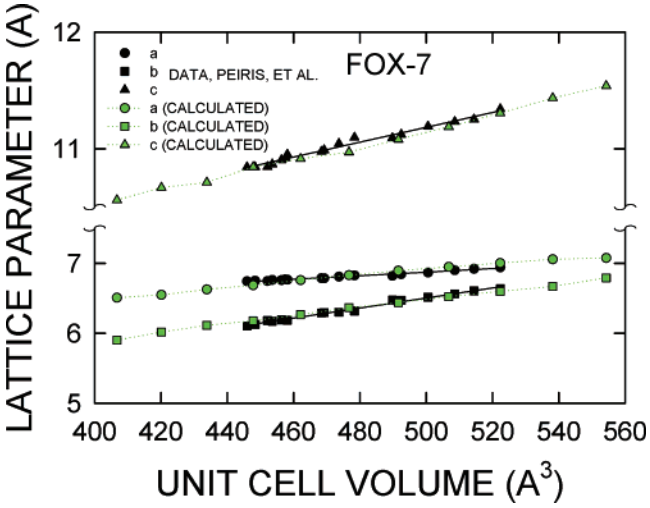

Figure 8. Calculated vs experimentally measured lattice parameters for hydrostatic compression of FOX-7.

TABLE 1: Calculated Lattice Parameters, Pressure, and Bulk Modulus as a Function of Unit Cell Volume for FOX-7

λ	*V* (Å^3)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg)	*P* (GPa)	*B* (GPa)
0.92	406.73	6.506	5.920	10.560	90.55	11.05	94.0
0.93	420.14	6.547	6.016	10.667	90.78	8.27	77.8
0.94	433.84	6.626	6.113	10.711	90.58	6.02	65.7
0.95	447.83	6.686	6.178	10.843	90.61	4.06	63.3
0.96	462.12	6.758	6.266	10.914	90.53	2.03	49.2
0.97	476.72	6.829	6.364	10.970	90.69	0.97	25.3
0.98	491.61	6.893	6.437	11.080	90.50	0.45	19.9
0.99	506.81	6.947	6.522	11.188	90.49	−0.24	18.4
1.00	522.33	7.003	6.598	11.306	90.52	−0.67	12.1
1.01	538.16	7.057	6.669	11.435	90.56	−0.98	10.0
1.02	554.30	7.075	6.790	11.539	90.55	−1.27	9.8

Bond lengths for the optimized molecular structure are shown in Figures 6 and 7 as a function of the effective linear expansion. Most of the bonds increase in length or increase and level off with expansion. Some bonds, notably the N9−O bonds, increase in length with compression, and one bond (C4−N9) has a strong decrease in length with compression. The sensitivity of this bond length to compression of the lattice is consistent with the observation that splitting of the NO_2 group is the first step in the explosive decomposition of this material. The calculated lattice parameters, pressure, and bulk modulus are summarized in Table 1. Figure 8 shows the calculated lattice parameters compared to those measured by Peiris et al.[28] By plotting the parameters vs unit cell volume, focus is placed on the anisotropic variation with hydrostatic compression, showing a reasonably good correlation between the calculated and experimental values.

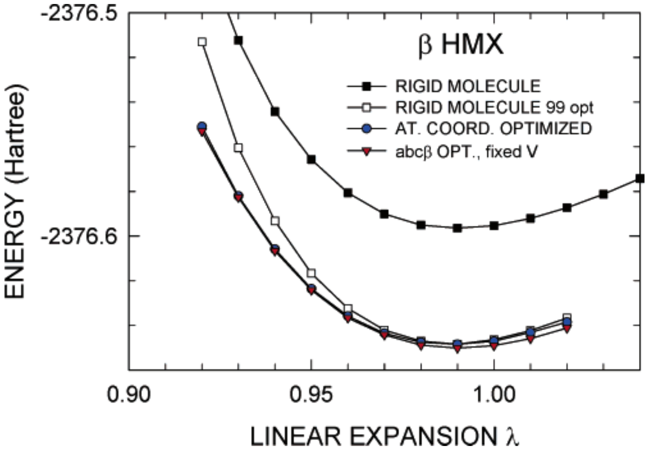

Figure 9. Energy vs effective linear expansion for *β*-HMX. The squares show the energy calculated in the rigid molecule approximation where the molecule has the experimentally determined geometry. The open squares show the energy in the rigid molecule approximation where the molecule has the optimized geometry at values of the lattice parameters equal to 99% of the experimentally measured lattice parameters. The circles show the energy after relaxing the atomic coordinates, and the triangles show the energy after a subsequent lattice parameter relaxation at fixed volume.

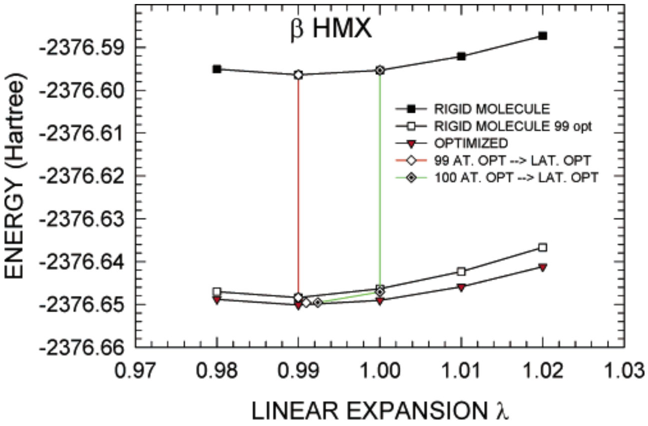

Figure 10. Illustration of two optimization paths for calculating equilibrium configuration for *β*-HMX. The diamonds with the dot in the center illustrate the path in which the atomic coordinates are first optimized starting from the experimental configuration, followed by an (unconditional) optimization of the lattice parameters. The open diamonds show the path in which the lattice parameters are optimized first, starting from the experimental configuration, followed by an optimization of the atomic coordinates, and then followed by another lattice parameter optimization.

β-HMX Mechanical Compression

The mechanical compression curve for *β*-HMX was calculated using the same procedure that was used for FOX-7. Figure 9 shows the energy as a function of mean linear expansion. In this case, the fixed volume constraint lattice parameter optimization makes only a very small improvement in the energy. An unconstrained optimization to find the absolute minimum is illustrated in Figure 10. Two paths are shown. In the first path, the experimentally determined atomic coordinates are first optimized, with the lattice parameters fixed at the experimentally determined values. This is followed by an unconstrained lattice parameter optimization. In the second path, the lattice parameters

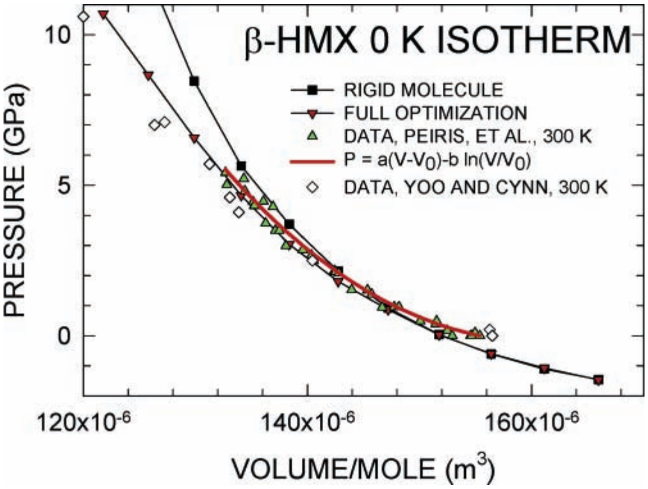

Figure 11. Calculated pressure vs volume on the 0 K isotherm for β-HMX compared to experimental data of Peiris et al.[30] (upward pointing triangles) and Yoo and Cynn[31] (diamonds). The squares show the pressure calculated in the rigid molecule approximation, the downward pointing triangles show the pressure for the fully optimized structure, and the heavy solid line is a fit to the experimental data of Peiris et al. as explained in the text.

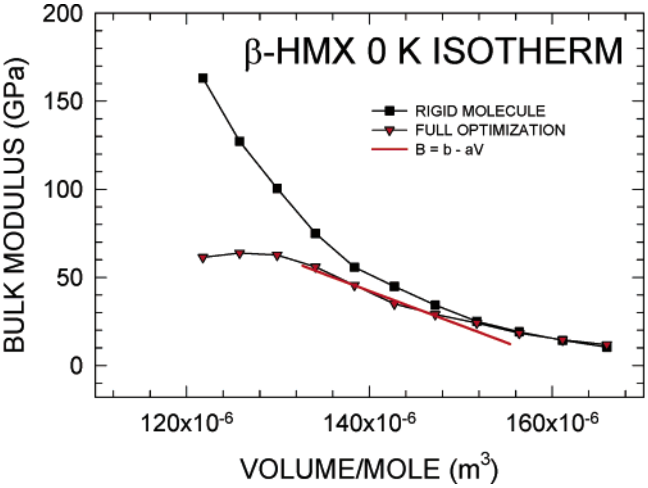

Figure 12. Bulk modulus vs volume on the 0 K isotherm for β-HMX. The squares show the bulk modulus calculated in the rigid molecule approximation, the downward pointing triangles show the bulk modulus for the fully optimized structure, and the heavy solid line is a fit to the experimental data of Peiris et al. as explained in the text.

are fixed at 99% of the experimental values, while the atomic coordinates are optimized. This is followed by an unconstrained lattice parameter optimization. Both paths lead to approximately the same result; the calculated equilibrium 0 K lattice parameters are a little less than 1% smaller than the measured 300 K lattice parameters. Taking account of the thermal expansion between 0 and 300 K, of the order of 1.5%, this puts the calculated result about 0.5% larger than the experimental result.

The calculated pressure is compared in Figure 11 with experimental results of Peiris et al.[30] and Yoo and Cynn.[31] The calculated isotherm lies below the 300 K data of Peiris et al. but above the 300 K data of Yoo and Cynn. Also shown in the figure is a fit of the relation $P = a(V - V_0) - b \ln(V/V_0)$ to the data of Peiris et al. This relation arises from the assumption that the bulk modulus is a linear function of volume, $B = b - aV$, a relation that is suggested by the plot of calculated bulk modulus shown in Figure 12. The experimental value of the bulk modulus is reasonably consistent with the calculated value, at least under equilibrium conditions.

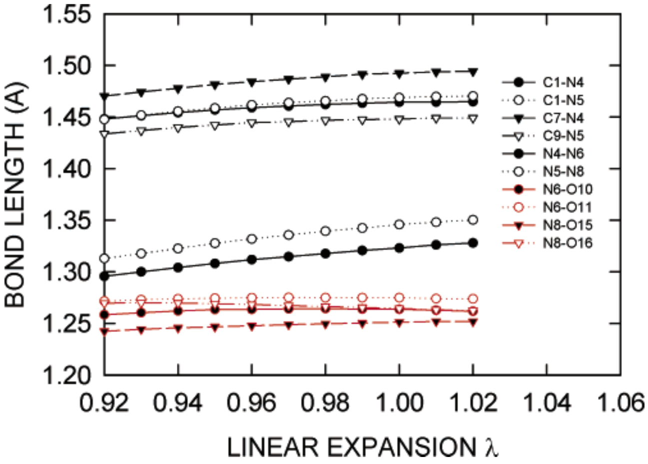

Figure 13. C−N, N−N, and N−O bond lengths for β-HMX optimized along the 0 K isotherm.

TABLE 2: Calculated Lattice Parameters, Pressure, and Bulk Modulus as a Function of Unit Cell Volume for β-HMX

λ	V (Å^3)	a (Å)	b (Å)	c (Å)	β (deg)	P (GPa)	B (GPa)
0.92	404.44	6.052	10.055	8.058	124.43	10.70	61.4
0.93	417.77	6.128	10.099	8.209	124.68	8.67	63.8
0.94	431.39	6.159	10.289	8.225	124.14	6.58	62.7
0.95	445.31	6.241	10.444	8.245	124.04	4.66	56.0
0.96	459.52	6.302	10.543	8.340	123.97	3.04	45.6
0.97	474.03	6.337	10.649	8.443	123.70	1.81	35.0
0.98	488.84	6.380	10.761	8.501	123.11	0.87	29.0
0.99	503.96	6.469	10.868	8.553	123.06	0.03	24.1
1.00	519.39	6.521	10.987	8.618	122.73	−0.60	18.4
1.01	535.12	6.520	11.194	8.627	121.81	−1.07	14.6
1.02	551.18	6.614	11.291	8.667	121.63	−1.46	11.8

The C−N, N−N, and N−O bond lengths for the optimized β-HMX structure are plotted vs effective linear expansion in Figure 13. Again, the N−N bonds undergo the largest change with compression. The N6−O10 and N6−O11 bonds appear to reach a maximum length at $\lambda = 0.98$ and 0.97, respectively. The C−H bonds, not shown here, increase in length with expansion by about 1% over the range $\lambda = 0.92-1.02$. The calculated lattice parameters, pressure, and bulk modulus are summarized in Table 2.

Discussion and Conclusions

Hartree−Fock calculations give good results for the 0 K isotherm for the organic molecular crystals 1,1-diamino-2,2-dinitroethylene and β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine when the entire structure is relaxed under a fixed volume constraint. Calculations recently performed for solid nitromethane (orthorhombic, $P2_12_12_1$) also give good results. They yield the equilibrium lattice parameters $a = 5.0877$ Å, $b = 6.2385$ Å, and $c = 8.4270$ Å, with a unit cell volume of 267.5 Å^3. This is to be compared to the experimental values at 4.2 K, $a = 5.1832$ Å, $b = 6.2357$ Å, and $c = 8.5181$ Å, with a unit cell volume of 275.3 Å^3, reported by Trevino, Prince, and Hubbard.[32] The calculated unit cell volume is 3% lower than the measured value.

An interesting result of the atomic coordinate optimizations is that, for both FOX-7 and β-HMX, the bond length that changes most under compression is the bond that is thought to be the initial bond to break in the decomposition of the material.

Several DFT methods available in CRYSTAL98 were tried including the GGA method of Perdew and Wang[33] and Becke's[34] three-parameter hybrid method using the correlation energy of Lee, Yang, and Parr.[35] In addition, calculations with pure HF exchange energy coupled with Lee, Yang, and Parr correlation energy were performed. All DFT calculations gave similar results, underpredicting the equilibrium volume by 10−15%. When DFT PWGGA calculations for FOX-7 were corrected for basis set superposition error with the counterpoise method, the equilibrium volume was slightly overpredicted (but within 1%). However, the bulk modulus in compressed states was considerably underpredicted (by about 20 GPa at 88% of the equilibrium volume).

As for why the Hartree−Fock method gives such good results despite the absence of electron correlation energy and no treatment of van der Waals interactions, we believe that the basis set superposition error produces an artificial binding, which nearly compensates for the absent van der Waals forces. Also, although van der Waals interactions are important in molecular crystals, they are most significant for expanded states. For the moderate to highly compressed states we are dealing with here, the van der Waals forces make a relatively smaller contribution. In the case of FOX-7 with its layered structure, there is strong hydrogen bonding within the layers, reducing considerably the impact of the van der Waals forces within the layers. There is also some evidence for hydrogen bonding in β-HMX[36] although it is probably a small effect in this case. As for the correlation energy, the DFT calculations indicate that it has only a small, smooth, monotonic, and nearly linear variation over the range of compressions studied, therefore making a negligible contribution to the pressure−volume relation, except for a negative pressure contribution which drives the equilibrium volume to values approximately 10% less than experimental values. While the results reported here reproduce the behavior of these molecular crystals under hydrostatic compression, we are exploring here only a small part of the potential energy surface and it would be unwise to draw any inference concerning binding energies and chemical reactivity generally, where basis set truncation leading to basis set superposition error plays a significant role. The effect of basis set superposition error corrections on both Hartree−Fock and DFT calculations are being investigated and will be reported in future communications.

Finally, the comparison with experimental data in the case of FOX-7 and β-HMX depends on estimates of differences between the 0 K isotherm and the 300 K isotherm. Work is now underway to calculate the full $T > 0$ equation of state by constructing the free energy from the phonon frequency spectrum of the crystal.

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