A Transferable Intermolecular Potential for Nitramine Crystals

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Received: April 29, 1998

We have investigated the transferability of a Buckingham repulsion−dispersion intermolecular potential previously developed [*J. Phys. Chem. B* **1997**, *101*, 798] for the explosive hexahydro-1,3,5-trinitro-1,3,5-*s*-triazine (RDX) to predict the crystal structures (within the approximation of rigid molecules) of 30 nitramines, comprising acyclic, monocyclic, and polycyclic molecules. It is shown that this potential model accurately reproduces the experimentally determined crystallographic structures and lattice energies of these crystals. For the majority of these crystals, the best agreement with experiment is obtained when the electrostatic charges are determined using ab initio methods that include electron correlation effects, namely, MP2 and B3LYP. The use of the electrostatic charges calculated at the Hartree−Fock level results in large deviations of the predicted lattice energies from the experimental values. These deviations of the lattice energies can be significantly decreased, without significantly affecting the predicted crystallographic parameters, by scaling the electrostatic charges with a constant factor.

I. Introduction

Atomistic simulation is increasingly gaining acceptance as a practical research tool in the investigation of the behavior of condensed-phase materials. In addition to providing information that is difficult or impossible to measure, prediction leads to a reduction in unnecessary measurement or synthesis of candidates in the course of design of new materials. However, the power of atomistic simulation can only be realized if the description of the molecular system is accurate. The development of accurate intermolecular potentials is not a simple, straightforward procedure. Substantial work has been directed toward determining both simple functions that make large-scale simulations feasible and correct parametrization such that the physical properties of the materials are properly described. In this work, we present an intermolecular potential that accurately describes nitramine crystals. We also investigate how the potential parameters affect its predictive ability.

In our initial studies of nonreactive processes in the nitramine explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-*s*-triazine), we developed an intermolecular potential energy function that would accurately reproduce the structure of the α-form of the RDX crystal.[1] This potential is composed of pairwise atom−atom (6-exp) Buckingham terms with explicit inclusion of the electrostatic interactions between the charges associated with the atoms of different molecules. The parametrization of the potential function was done such that molecular packing calculations (MP) reproduced the experimental structure of the crystal and its lattice energy. Isothermal−isobaric molecular dynamics simulations (NPT-MD) using this potential energy function predicted crystal structures in excellent agreement with the experimental data.[1]

We have shown that this interaction potential energy function is transferable to two other nitramine crystals: the polycyclic nitramine 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)[2] and the monocyclic nitramine 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).[3] Both MP and NPT-MD simulations predict geometrical parameters in good agreement with the experimental values for the different polymorphs of the HNIW and HMX crystals.[2,3] Furthermore, the calculations indicate a stability ranking for HNIW in agreement with experimental measurements.[4]

The success of these potential energy parameters in describing the RDX crystal and different phases of the HMX and HNIW crystals provides impetus for further investigations to determine the limits of the transferability of this interaction potential. Toward this end, we report here MP calculations of 30 nitramine crystals. This set of crystals is composed of monocyclic, polycyclic, and acyclic nitramine molecules. We were particularly interested in determining how accurately the known geometrical and energetic parameters for these crystals are reproduced by this potential model.

One of the main factors that contribute to the quantitative description of the molecular packing in a crystal is related to the representation of the electrostatic interactions. It was shown more than a decade ago[5,6] that increased accuracy in structural predictions of molecular crystals and in transferability of the potential parameters can be achieved by explicit use of electrostatic interactions between the charges associated with the atoms. For example, many of the available force fields such as Amber,[7] ECEPP,[8] or Dreiding[9] use these kinds of potential terms in models of organic, biological, and main group inorganic crystals. Further improvement of the description of the electrostatic forces between molecules, particularly in crystals with substantial anisotropies, can be achieved by using sets of point multipoles (charge, dipole, quadrupole, etc.) on every atomic site. This distributed multipole representation has been shown to be successful in the modeling of the crystal structures of polar and hydrogen-bonded molecules.[10]

In the present study we have found that, as in the cases of the RDX,[1] HNIW,[2] and HMX[3] crystals, the set of 30 crystals considered here can be accurately represented using the Buck-

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10.1021/jp9820525 CCC: $15.00
Published on Web 10/02/1998

ingham potential plus Coulombic interactions. The assignment of the electrostatic charges poses a problem in that the atom-centered monopole charge is not an observable quantity and cannot be obtained directly from either experiment or first principles calculations. Currently, there are several schemes for evaluation of charges by empirical partition or by using a quantum mechanically derived wave function.[11−13] We have determined the Coulombic terms through fitting of partial charges centered on each atom of the molecules to a quantum mechanically derived electrostatic potential.[13] We have investigated how the geometrical and energetic parameters predicted in MP calculations depend on charges determined from ab initio methods that do or do not include electron correlation effects. Specifically, we used different sets of charges derived from the Hartree−Fock (HF) wave function[14] and from methods that employ electron correlations such as second-order Möller−Plesset (MP2)[15] and B3LYP.[16,17]

The studies described here represent the first stage in the development of a general model for nitramine crystals. The main limitations of the present model are due to the assumption of rigid molecules, but further refinement of this model can be made to include the effects of intramolecular motions, particularly of low-frequency torsional motions of the nitro groups and the ring.

The organization of the paper is as follows. In section II the intermolecular potential used to simulate the nitramine crystals is presented. In sections III and IV the molecular packing methods and results, respectively, are described. The main conclusions are summarized in section V.

II. Intermolecular Potential

The central problem in classical simulations of molecular crystals is the construction of realistic potentials that accurately predict the structural and thermochemical parameters. In this paper we employ the same general model for the atom−atom potentials that proved to be successful in modeling of the RDX, HNIW, and HMX crystals.[1−3] In particular, we assume that (a) the intermolecular interactions depend only on the interatomic distances, (b) the interaction potential can be separated in contributions identified as van der Waals and electrostatic, and (c) the same type of van der Waals potential is used for the same type of atoms, independent of their valence state. Moreover, in the present case we assume the transferability of the potential parameters between similar molecules; i.e., we extend the validity of the potential parameters determined for the case of RDX crystal to all the nitramines considered in this study.

In the present treatment, we approximate the intermolecular interactions between the molecules of the crystal as sum of pairwise Buckingham (6-exp) (repulsion and dispersion) and Coulombic (C) potentials:

$$V_{\alpha\beta}^{6-\exp}(r) = A_{\alpha\beta}\exp(-B_{\alpha\beta}r) - C_{\alpha\beta}/r^6 \qquad (1)$$

and

$$V_{\alpha\beta}^{C}(r) = \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r} \qquad (2)$$

where r is the interatomic distance between atoms α and β, q_α and q_β are the electrostatic charges on the atoms, and ϵ_0 is the dielectric permittivity constant of vacuum.

The parameters for the 6-exp potential in eq 1 are those determined for the RDX crystal.[1] We use the same combination rules for calculation of the heteroatom parameters from homoatom parameters as previously reported.[1]

The assignment of the electrostatic charges is made by using the set of atom-centered monopole charges for the isolated molecule that best reproduces the quantum mechanically derived electrostatic potential, which is calculated over grid points surrounding the van der Waals surface of the molecules. This method of fitting the electrostatic potential was proposed by Breneman and Wiberg[13] and is incorporated in the Gaussian 94 package of programs[18] under the keyword CHELPG (electrostatic-potential-derived atomic charges). This method has the advantage of a higher density of points and a better selection procedure, which ensures a significant decrease in orientation effects compared to those observed with similar methods.[12] The CHELPG charges were found to be invariant to either the rotation of the molecular coordinates or internal bond rotations. These calculations have been done at both the HF[14] and at the MP2[15] levels to investigate the electron correlation effects.

For the purpose of comparison and as an alternative to the computationally demanding MP2 method, we have also used density functional theory (DFT) in the Kohn−Sham formulation.[19] The DFT methods offer a less expensive but still accurate computational alternative to ab initio methods for including the electron correlation in post-HF treatments. In particular, we employed the exchange functional described by the fitted three-parameter hybrid of Becke[16] and the correlation functional of Lee, Yang, and Parr (B3LYP).[17] All the above theoretical calculations were done using a reasonable quality basis set, i.e., 6-31G** (split-valence plus d-type and p-type polarization functions).[20]

It has been shown previously[21,22] that the neglect of electron correlation in self-consistent wave functions overestimates the electrostatic interactions; however, this is mainly a scaling effect. Cox and Williams[21] have suggested that a scaling factor of 0.9 can be used to improve agreement between the calculated and experimental values of the dipole moments for a set of eight small molecules. The same factor has been justified in a study of the electrostatic interactions of a dipeptide[22] as well as in a more recent work related to the role of electrostatic interactions in determining the crystal structures of polar organic molecules.[10] We have employed such an electrostatic model to further evaluate the effects of this scaling procedure. Specifically, four electrostatic models were tested for each of the 30 crystals. Two of them use electron correlation methods, namely MP2 and B3LYP, the third one uses unscaled HF charges, and the last the HF charges scaled by 0.9 (denoted as 0.9HF).

III. Computational Approach

A general procedure for testing intermolecular potential energy functions for organic crystals is based on the use of molecular packing calculations.[5,6] The basic idea is to minimize the lattice energy with respect to the structural degrees of freedom of the crystal. For crystals with one molecule in the asymmetric unit occupying an arbitrary position, the maximum number of degrees of freedom is 12 and corresponds to the six unit cell constants (a, b, c, α, β, γ), the three rotations (θ_1, θ_2, θ_3), and the three translations (τ_1, τ_2, τ_3) of the rigid molecule. A reduced number of structural degrees of freedom might be involved, depending on the symmetry restrictions of different space groups. For crystals with more than one molecule in the asymmetric unit, additional degrees of freedom are introduced to describe the rotation and translation of the additional molecules.

Assuming that the crystal energy is known as a function of the structural lattice parameters, the equilibrium crystal configuration is determined by the conditions of zero force and torque, together with the requirement that there is a minimum. The search for such a minimum can be done using a combination of steepest-descent and Newton−Raphson procedures.[23,24]

In the present study, we assume that the crystals can be represented as an ensemble of rigid molecules. The minimization of the lattice energy with symmetry constraints has been performed using the molecular packing program PCK91[25] by taking the experimentally observed geometries as starting configurations. This program employs an accelerated convergence method[1,24] for accurate evaluation of the crystal Coulombic and dispersion lattice sums, with the first and second derivatives of the crystal energy evaluated analytically. In all calculations a cutoff distance of 19 Å has been used with the parameters η that determines the relative contributions of the real- and reciprocal-space terms as defined in ref 1 having the values $\eta_1 = 0.1861$ Å^{-1} and $\eta_6 = 0.2304$ Å^{-1}. The space-group symmetry is maintained throughout the energy minimization. This reduces the number of independent variables in the minimization procedure, resulting in a significant decrease in the computational time compared to unconstrained energy minimization. For example, for the β phase of HMX crystal with space group $P2_1/n$ ($Z = 2$), the crystallographic parameters that were varied in the minimization using the PCK91 program are the three dimensions of the unit cell and the angle β, while the angles α and γ were frozen at 90°. Since the molecule in the asymmetric unit occupies an inversion center, only the three rotations of this molecule were allowed to vary, while the three translations were not modified to maintain the symmetry imposed by the inversion center. We have shown previously[1,2,26] that, despite the symmetry restrictions imposed in the PCK91 program, the final lattice energies and crystallographic parameters are in good agreement with those obtained when symmetry constraints were removed; i.e., the predicted crystals maintained the observed space-group symmetry.

The quality of the predicted geometrical crystallographic parameters relative to the experimental values has been done using a structural shift factor of the form[24,27]

$$F = (\Delta\theta/2)^2 + (10\Delta x)^2 + (100\Delta a/a)^2 + (100\Delta b/b)^2 + (100\Delta c/c)^2 + (\Delta\alpha)^2 + (\Delta\beta)^2 + (\Delta\gamma)^2 \quad (3)$$

where $\Delta\theta$ is the total root-mean-square (rms) rigid-body rotational displacement (in degrees) after minimization; Δx is the rms total rigid-body translational displacement (in angstroms); and a, b, c and α, β, γ are respectively the lengths of the edges and the angles of the unit cell.

An important test of the validity of the model is the accuracy of the predicted lattice energies of the crystals. The lattice energies determine the relative stabilities of the different crystallographic phases. The calculated static lattice energy can be compared to the experimental sublimation enthalpy by using the relationship[28] $-\Delta H_{\mathrm{subl}} = E + K_0 + 2RT$, where E is the lattice energy and K_0 is the zero-point energy. Often a rough estimation of the lattice energy is obtained by neglecting the K_0 term. Kitaigorodski[5] has pointed out that, considering the inaccuracy involved in the experimental determination of ΔH_{subl} and with the neglect of zero-point energy, discrepancies up to 3−4 kcal/mol between the calculated and the observed enthalpies of sublimation are expected.[5] In the case of RDX crystals we found using this approximation that the predicted lattice energy ($E = -130.09$ kJ/mol) is in very close agreement with the experimental sublimation enthalphy ($-\Delta H_{\mathrm{subl}} = -130.1$ kJ/mol).[1]

IV. Results and Discussions

The 30 nitramine molecules considered in this study are shown in Figure 1. They were chosen as representative examples of important acyclic and cyclic nitramines. We have included different types of mono- and polycyclic nitramines, particularly crystals that are important energetic materials. The structures of most of these crystals have been determined by X-ray diffraction techniques. Despite the generally poorer resolution of hydrogen atom positions obtained by these techniques, we have not done any additional adjustment of these positions to give, for example, the standard bond lengths.[29] The crystal structures in Figure 1 are denoted first by the common names of the molecules. Where available, the crystal abbreviation from the original reference is also included with the corresponding crystal "*refcode*" used in the Cambridge Structural Database[30] and indicated by the term in the second set of parentheses. The structures used for the HNIW[31l] and β-HMX[31e] crystals are not in the Cambridge database so they do not have a *refcode*. In addition, we have studied different crystallographic phases of HMX and HNIW crystals; these are detailed in Supporting Information Table 1S. The specific references for each of the 30 crystals in Table 1S are given in ref 31.

The results of MP calculations using the PCK91 program are presented in Table 1S. The predicted structural lattice parameters for the great majority of these crystals deviate by less than 2% from the experimental structures. Also, for the majority of the crystals there are small rotations and practically no translations of the molecules in the asymmetric unit cell. The accuracy of the predictions can be seen in Figure 2 where the overall structural drift factors described in eq 3 are given. Only 10% of the total number of crystals considered here have a structural shift factor larger than 2.0, and practically half of the crystals have shift factors that are less than 1.0.

It is important to point out that ideally the predicted lattice structural parameters should be compared with the values determined at zero temperature. However, this is not possible due to the lack of data at low temperatures. Consequently, the above comparison considers the deviations of the predicted geometrical parameters from the experimental values obtained at room temperature. We can observe from the data given in Table 1S that the predicted lattice dimensions either underestimate or overestimate the experimental values. Consequently, there is not a general trend of the relationship between the predicted and the experimental geometric lattice periods despite the small deviations between the two sets of values.

The influence of the level of ab initio calculations on the final crystallographic parameters is also illustrated by the results in Table 1S. The difference in the predicted geometrical parameters is less than 1.0% when correlated and uncorrelated ab initio methods are used. In addition, there is not a clear trend of the degree of accuracy with the ab initio level of calculations. In 19 of the systems, the accuracy increases when the HF charges are replaced with those obtained at the B3LYP and MP2 levels, but in the other 11 cases the accuracy decreases. The maximum difference of the structural shift factors with the different levels of calculation is less than 0.27%.

We can also see from the results in Table 1S that when the electrostatic charges calculated at the HF level are scaled by 0.9 factor, the corresponding predicted geometrical parameters are very close to those obtained at the MP2 level. Moreover,

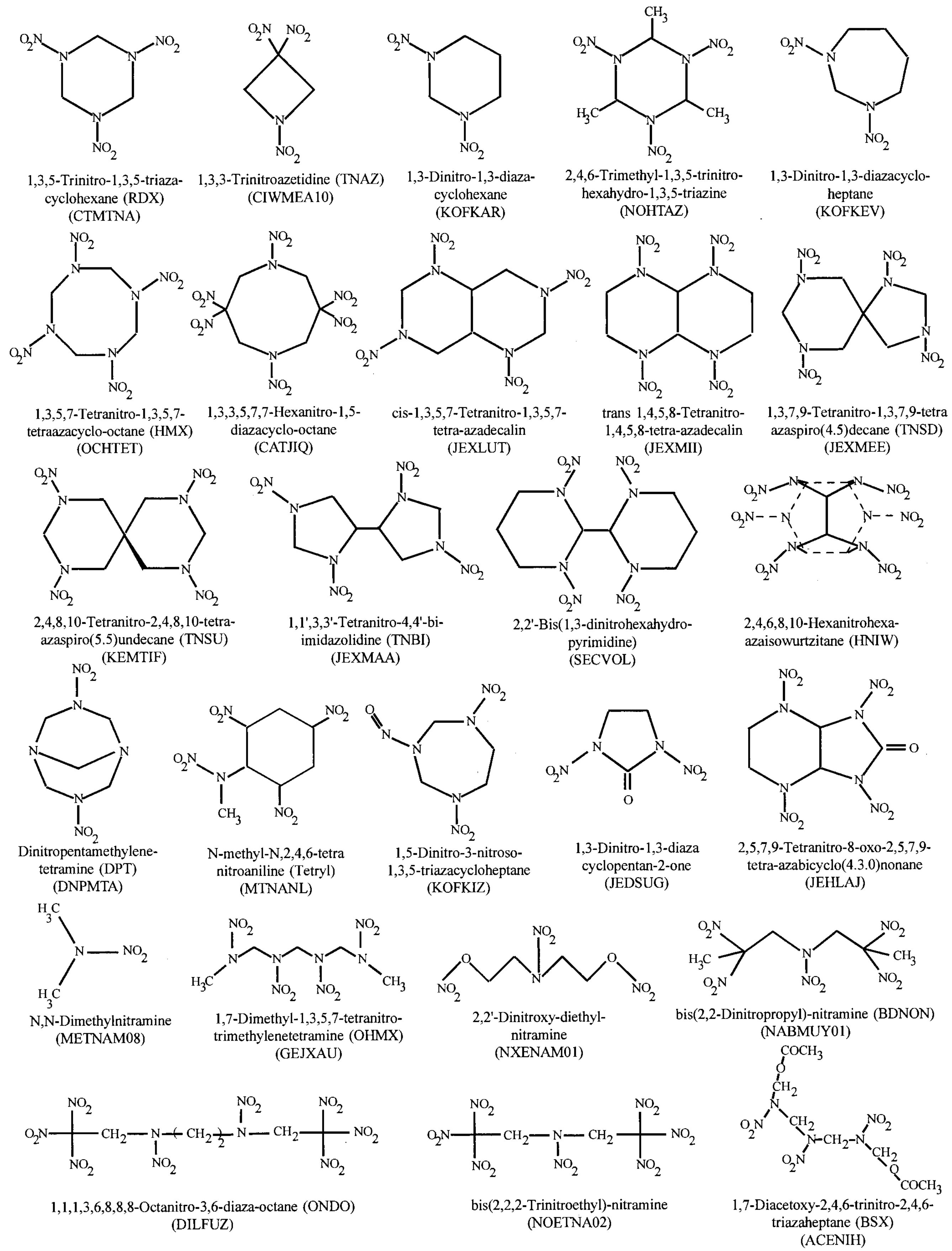

Figure 1. Illustration of the 30 molecules for which crystal structures were calculated. The common abbreviation of the crystal name is given in the first set of parentheses, and the *refcode* entry of the Cambridge Structural Database[30] is given in the second set of parentheses.

the corresponding structural shift factors generally have values intermediate between the MP2 and HF values.

The lattice energies predicted by the different models are given in Table 1. As can be seen by comparing the results for

TABLE 1: Comparison of the Experimental and Calculated Lattice Energies for Different Sets of Electrostatic Charges

			lattice energy (kJ/mol)			
no.	crystal	ΔH_{sub} (kJ/mol)	MP2/6-31G**	B3LYP/6-31G**	0.9 HF/6-31G**	HF/6-31G**
1	CTMTNA	130.1[a]	−130.09	−133.68	−136.05	−148.18
2	CIWMEA10		−113.01	−116.40	−118.81	−129.07
3	KOFKAR		−116.55	−119.40	−119.61	−129.26
4	NOHTAZ		−141.45	−145.35	−145.99	−157.25
5	KOFKEV		−120.00	−122.66	−122.20	−131.95
6	β-HMX	175.2[a]	−180.23	−185.02	−187.01	−204.45
7	OCHTET		−179.15	−184.66	−188.74	−208.75
8	OCHTET03	161.9[b]	−168.24	−173.44	−178.11	−197.67
9	CATJIQ		−182.50	−187.59	−196.88	−213.26
10	JEXLUT		−178.54	−184.32	−186.70	−200.43
11	JEXMII		−169.22	−172.11	−177.36	−190.98
12	JEXMEE		−172.98	−178.48	−179.86	−196.13
13	KEMTIF		−184.42	−190.46	−192.56	−208.80
14	JEXMAA		−176.33	−182.29	181.97	−196.64
15	SECVOL		−187.66	−192.30	−193.63	−209.42
16	HNIW (ϵ-phase)		−186.77	−192.82	−196.52	−210.88
17	HNIW (β-phase)		−181.29	−186.28	−190.54	−201.81
18	HNIW (γ-phase)		−175.31	−180.90	−186.15	−198.61
19	DNPMTA		−140.60	−142.78	−142.60	−154.30
20	MTNANL	133.8 ± 1.6[c]	−149.53	−153.81	−158.30	−170.57
21	KOFKIZ		−262.18	−267.98	−265.78	−288.98
22	JEDSUG		−124.22	−128.89	−131.24	−145.14
23	JEHLAJ		−180.70	−187.76	−192.29	−209.63
24	METNAM08	69.87[d]	−70.26	−71.20	−70.21	−76.25
25	GEJXAU		−171.87	−174.31	−175.69	−191.41
26	NXENAM01		−131.84	−134.80	−137.57	−148.40
27	NABMUY01		−169.28	−173.70	−180.86	−196.26
28	DILFUZ		−216.09	−220.50	−209.57	−241.50
29	NOETNA02		−166.55	−163.68	−172.29	−181.04
30	ENIH		−186.20	−188.32	−191.61	−205.65

[a] Rosen and Dickinson, ref 32a. [b] Taylor and Crookes, ref 32b. [c] Cundall et al., ref 32c. [d] Bradley et al., ref 32d.

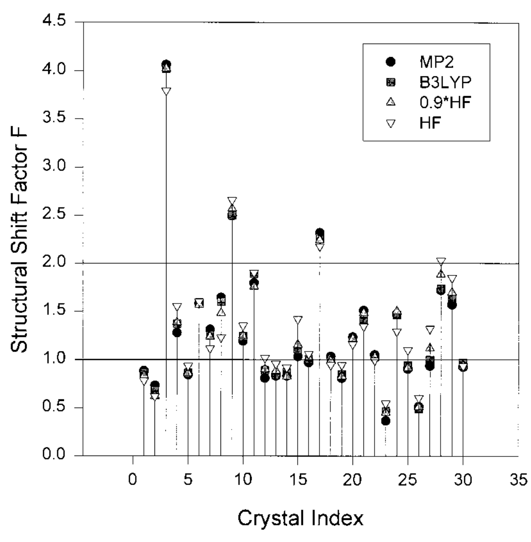

Figure 2. Calculated structural shift factor *F* (eq 3) for the crystal structures. The crystal index corresponds to the number of the crystal given in Table 1. The horizontal lines at 1 and 2 are marked for a more clear view of the distribution of points.

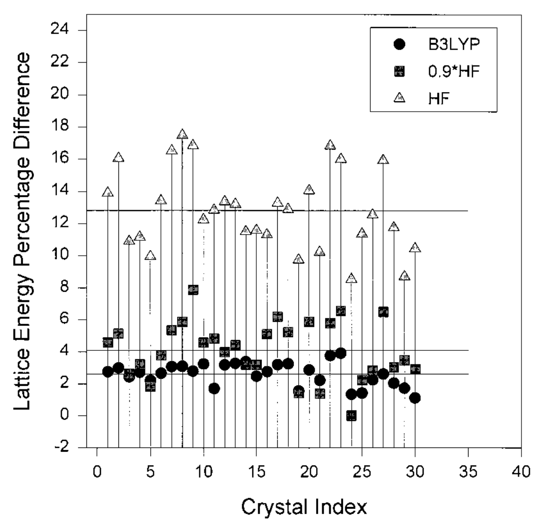

Figure 3. Percent differences between the lattice energies and those based on the MP2 values. The crystal index corresponds to the number of the crystal given in Table 1. The three horizontal lines indicate the average deviations for the energies calculated using the B3LYP ($\langle p1\rangle = 2.6\%$), 0.9*HF ($\langle p2\rangle = 4.1\%$), and HF ($\langle p3\rangle = 12.8\%$) sets of charges.

the MP2, B3LYP, and HF methods, the use of the correlated methods results in a decrease in the absolute lattice energy. This effect can be understood as a consequence of the decrease in the absolute value of the electrostatic energy, which is attractive. The variations in the absolute values of the HF lattice energies are between 8.5 and 17.5% relative to the MP2 energies, with the average deviation 12.8% (see Figure 3). The use of the 0.9 scaling factor reduces these deviations to the range 0−7.8% with the average deviation 4.1%. Finally, the B3LYP lattice energies are, as expected, much closer to the MP2 energies, with the range of variations 1.5−3.9% and average deviation 2.6%. These results indicate that the lattice energies differ significantly for sets of electrostatic charges calculated with ab initio methods that do not include electron correlation. These differences can be decreased by a factor of ∼3 by scaling the HF charges. Another important result is that DFT can provide charges that give an accuracy (within 2.6%) for the lattice energy that is comparable to those determined at the MP2 level. These results are important since the computational times for B3LYP calculations are significantly lower than those for MP2.

We also compare the calculated lattice energies to experimental sublimation enthalpies in Table 2. For RDX (CTMTNA), HMX (β-HMX, OCHTET03), and dimethylnitramine (METNAM08) crystals the agreement of the MP2 energies to the experimental values is very good, while for tetryl (NTNANL) the difference of 15.7 kJ/mol is within the range 12−17 kJ/mol considered acceptable by Kitaigorodsky.[5] Despite the limited number of experimental values available for comparisons, it can be seen that a significant improvement in the accuracy of the predicted lattice energies can be obtained by using the electrostatic charges determined by electron correlated methods. The scaling of the HF charges also leads to improvements of the predicted energies, but the differences from the experimental values are larger than those obtained when the charges are calculated with electron correlation methods.

We have also investigated the relative stability of different polymorphic phases of the HMX and HNIW crystals. The calculated MP2 lattice energies for the β, α, and δ phases of HMX are −180.23, −179.15, and −168.24 kJ/mol, respectively. These values support the polymorph stability ranking $\beta > \alpha > \delta$ found experimentally by McCrone.[33] Also, the calculated lattice energies per molecule for the ϵ-, β-, and γ-HNIW phases of −186.77, −181.29, and −175.31 kJ/mol, respectively, are consistent with the stability ranking $\epsilon > \beta > \gamma$ reported by Russell et al.[4]

V. Conclusions

We have investigated the transferability of a 6-exp Buckingham potential previously developed for the α-RDX crystal[1] to 30 crystals, consisting of acyclic, monocyclic, or polycyclic nitramines. The intermolecular potential includes Coulombic interactions between electrostatic charges. These charges were determined by fitting ab initio electrostatic potentials calculated for the individual molecules in their experimental configurations.

The tests of this potential for the set of 30 crystals have been performed using molecular packing calculations. Accurate values of the crystal lattice energy have been obtained by employing an accelerated convergence technique for the dispersion and Coulombic lattice sums. We have considered four different electrostatic models, with charges determined at the HF, B3LYP, and MP2 levels and with charges obtained at the HF level uniformly scaled by a factor of 0.9. The predicted geometries indicate a good agreement with the experimental values for the great majority of the crystals in the study. For 90% of the crystals, the structural shift factor is less than 2.0, while for 50% of them it is less than 1.0.

There is only a small influence, generally below 1%, on the crystallographic parameters by the set of electrostatic charges used. However, the lattice energies are strongly dependent on the electrostatic model. In particular, the best overall agreement with experimental lattice energies was obtained by using MP2-calculated charges. The lattice energies calculated using the B3LYP charges overestimate the MP2 energies by about 2.6% while the overestimation in the case of HF charges is about 12.8%. The procedure of uniformly scaling the HF charges[10,21] decreases the differences to about 4.1%. It was also shown that this intermolecular potential correctly describes the order of stability of different phases. The predicted stability $\beta > \alpha > \delta$ for HMX is in accord with the experimental results.[33] Also, the calculated stability ranking $\epsilon > \beta > \gamma$ for HNIW agrees with the previously reported results.[4]

The success of the present potential energy parameters in describing different types of nitramines and different phases at moderate temperatures and low pressure provides incentive to further investigate the transferability of this model to other classes of crystals. Incorporation of intramolecular motion by relaxing the rigid molecular model will also be investigated in future studies.

Acknowledgment. This work was supported by the Strategic Environmental Research and Development Program (SERDP) Project PP-695. D.L.T. gratefully acknowledges support by the U.S. Army Research Office under Grant DAAG55-98-1-0089.

Supporting Information Available: A table (Table 1S) giving a comparison of the crystallographic parameters determined by molecular packing calculations and experimental values for all molecular structures considered in this paper (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Sorescu, D. C.; Rice, B. M.; Thompson, D. L. *J. Phys. Chem. B* **1997**, *101*, 798.
(2) Sorescu, D. C.; Rice, B. M.; Thompson, D. L. *J. Phys. Chem. B* **1998**, *102*, 948.
(3) Sorescu, D. C.; Rice, B. M.; Thompson, D. L. *J. Phys. Chem. B* **1998**, *102*, 6692.
(4) Russell, T. P.; Miller, P. J.; Piermarini, G. J.; Block, S.; Gilardi, R.; George, C. AD-CO48 931 (92−0134), p 155, Apr 91, CPIA Abstract No. 92, 0149. ADD604 542. C−D, Chemical Propulsion Information Agency, 10630 Little Patuxent Parkway, Suite 202, Columbia, MD 21044-3200.
(5) Pertsin, A. J.; Kitaigorodsky, A. I. *The Atom-Atom Potential Method, Applications to Organic Molecular Solids*; Springer-Verlag: Berlin, 1987.
(6) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.
(7) Weiner, S. J.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.
(8) Nemethy, G.; Gibson, K. D.; Palmer, K. A.; Yoon, C. N.; Paterlini, G.; Rumsey, S.; Scheraga, H. A. *J. Phys. Chem.* **1992**, *96*, 6474.
(9) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III *J. Phys. Chem.* **1990**, *94*, 8897.
(10) Coombes, D. S.; Price, S. L.; Willock, D. J.; Leslie, M. *J. Phys. Chem.* **1996**, *100*, 7352.
(11) See, for example: Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504 and references therein.
(12) Chirlian, L. E.; Francl. M. M. *J. Comput. Chem.* **1987**, *8*, 894.
(13) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
(14) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.
(15) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.
(16) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B41*, 785.
(18) Gaussian 94, Revision C.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Patersson, G. A.; Montgomery, J. A.; Raghavachari, K.; AL-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanyakkara, A. Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian, Inc.; Pittsburgh, PA, 1995.
(19) Hohenber, P.; Kohn, W. *Phys. Rev.* **1964**, *B126*, 864. Parr, R. G.; Yand, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(20) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(21) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2*, 304.
(22) Price, S. L.; Andrews, J. S.; Murray, C. W.; Amos, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 8268.
(23) Williams, D. E. *Acta Crystallogr.* **1977**, *A27*, 452.
(24) Williams, D. E. In *Crystal Cohesion and Confirmational Energies*; Metzger, R. M., Ed.; Springer-Verlag: Berlin, 1981; pp 3−40.
(25) Williams, D. E. PCK91, A Crystal Molecular Packing Analysis Program, Department of Chemistry, University of Louisville, Louisville, KY 40292.

(26) Sorescu, D. C.; Thompson, D. L. *J. Phys. Chem. B* **1997**, *101*, 3605.

(27) Starr, T. L.; Williams, D. E. *Acta Crystallogr*. **1977**, *A33*, 771.

(28) *Fundamentals of Crystallography*; Giacovazzo, C., Ed.; Oxford University Press: New York, 1992.

(29) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(30) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

(31) (a) Choi, C. S.; Prince, E. *Acta Crytallogr*. **1972**, *B28*, 2857. (b) Archibald, T. G.; Gilardi, R.; Baum, K.; George, C. *J. Org. Chem*. **1990**, *55*, 2920. (c) Pickering, M.; Rylance, J.; Small, R. W. H.; Stubley, D. *Acta Crystallogr*. **1991**, *B47*, 782. (d) Oyumi, Y.; Brill, T. B.; Rheingold, A. L.; Haller, T. M. *J. Phys. Chem*. **1985**, *89*, 4317. (e) Kohno, Y.; Maekawa, K.; Azuma, N.; Tsuchioka, T.; Hashizume, T.; Imamura, A. *Kogyo Kayaku* **1992**, *53*, 227 (in Japanese). (f) Cady, H. H.; Larson, A. C.; Cromer, D. T. *Acta Crystallogr*. **1963**, *16*, 617 (*Y* coordinate of N1 given as 0.0599 in Table 2 should be negative). (g) Cobbledick, R. E.; Small, R. W. H. *Acta Crystallogr*. **1974**, *B30*, 1918. (h) Ammon, H. L.; Gilardi, R. D.; Bhattacharjee, S. K. *Acta Crystallogr*. **1983**, *C39*, 1680. (i) Lowe-Ma, C. K.; Willer, R. L. Private communication, 1990. (j) Lowe-Ma, C. K. *Acta Crystallogr*. **1990**, *C46*, 1029. (k) Black, S. StC.; Craig, D. C.; Giitsidis, O.; Read, R. W.; Salek, A.; Sefton, M. A. *J. Org. Chem*. **1989**, *54*, 4771. (l) Gilardi, R. D. Private communication, 1997. (m) Choi, C. S.; Bulusu, S. *Acta Crystallogr*. **1974**, *B30*, 1576. (n) Cady, H. H. *Acta Crystallogr*. **1967**, *23*, 601. (o) George, C.; Flippen-Anderson, J. L.; Gilardi, R. *Acta Crystallogr*. **1990**, *C46*, 703. (p) Flippen-Anderson, J. L.; George, C.; Gilardi, R. *Acta Crystallogr*. **1990**, *C46*, 1122. (q) Filhol, A.; Bravic, G.; Rey-Lafon, M.; Thomas, M. *Acta Crystallogr*. **1980**, *B36*, 575. (r) Oyumi, Y.; Brill, T. B.; Rheingold, A. L. *Thermochim. Acta* **1987**, *114*, 209. (s) Wilkins, A.; Small, R. W. H. *Acta Crystallogr*. **1982**, *B38*, 488. (t) Bracuti, A. J. *J. Chem. Cryst*. **1997**, *27*, 67. (u) Oyumi, Y.; Brill, T. B.; Rheingold, A. L. *J. Phys. Chem*. **1985**, *89*, 4824. (v) Jinhua, C.; Shaoping, M.; Xiaotong, Z. *Jiegou Huaxue* (*J. Struct. Chem.*) **1983**, *2*, 41. (x) Cobbledick, R. E.; Small, R. W. H. *Acta Crystallogr*. **1973**, *B29*, 2795.

(32) (a) Rosen, J. M.; Dickinson, C. *J. Chem. Eng. Data* **1969**, *14*, 120. (b) Taylor, J. W.; Crookes, R. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 723. (c) Cundall, R. B.; Palmer, T. F.; Wood, C. E. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1339. (d) Bradley, R. S.; Cotson, S.; Cox, E. G. *J. Chem. Soc*. **1952**, 740.

(33) McCrone, W. C. In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Wiley: New York, 1965; Vol. II, pp 726−766.