Accurate Predictions of Crystal Densities Using Quantum Mechanical Molecular Volumes

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Received: April 23, 2007; In Final Form: August 15, 2007

A quantum mechanically based procedure for estimation of crystal densities of neutral and ionic crystals is presented. In this method, volumes within 0.001 electrons/bohr^3 isosurfaces of electron density for the constituent isolated neutral and ionic molecules are calculated to define the molecular volume or formula unit volumes used in predicting the crystal density. The B3LYP density functional theory in conjunction with the 6-31G** basis set were employed to generate the electron densities. The suitability of this method of crystal density prediction was assessed by subjecting a large number (289) of molecular and ionic crystals to the procedure and comparing results with experimental information. The results indicate that, for neutral molecular crystals, the root-mean-square (rms) deviation from experiment is within 4%, whereas the rms deviation is somewhat larger for the 71 ionic crystals evaluated (within 5%).

1. Introduction

A diverse set of predictive methodologies has been produced for the design and development of energetic materials (EM).[1−3] These modeling tools have varying degrees of accuracy and sophistication and span time and spatial regimes ranging from atomistic to the continuum. The majority of the methods are designed to predict either the performance of a material in a weapons system or its potential hazard. The motivating force behind the development of these models is an increasingly important need to reduce the often-inordinate time and costs required to synthesize, test, and field a new material. Recent advances in weapons design as well as new threats requiring rapid response have demanded that resources be expended only on extremely promising candidates. Thus, it is imperative that modeling tools be developed that will rapidly and reliably identify properties of EM that are indicative of either potential performance or possible hazard, thus preventing the expenditure of limited resources on materials that will not be fielded.

One of the most important physical properties of a solid EM that is used to initially assess potential performance in a weapon is its density. Therefore, substantial efforts have been directed toward developing a procedure that will accurately predict this property without a priori knowledge of the crystal structure. Numerous approaches have been developed,[4−26] several of which utilize Quantitative Structure Property Relationships (QSPR).[8−15] In many of these studies, the "molecular volume" is used in the development of the QSPR description of the crystal density. The quantity "molecular volume" is somewhat arbitrarily defined; for example, the molecule volume reported in the Cambridge Structural Database (CSD)[27] is the volume of the measured unit cell divided by the number of molecules within the cell. Molecular volume is also often approximated using group or atom additivity, in which the molecular volume (V_{VA}) is defined as:

$$V_{\mathrm{VA}} = \sum n_i V_i \tag{1}$$

where n_i and V_i are the number and volume respectively, of the ith atoms or functional groups contained within the molecule. The atomic or group volumes are defined in a variety of ways (e.g., van der Waals volume[7] or similar assignment[9,28,29]) or can be determined by parametrizing eq 1 to a large set of experimental information.[12,14,16−21] An alternative QSPR-like approach to density prediction has been developed by Politzer using a quantum mechanically based General Interaction Properties Function (GIPF).[30−32] In this approach, a macroscopic property of a material is described by a GIPF that uses statistical or geometric features of electrostatic potentials (ESP) mapped onto a molecular surface. In Politzer's work, the molecular surface is defined to be the 0.001 electrons/bohr^3 isosurface of electron density of an isolated molecule; both ESPs and the electron densities are calculated using quantum mechanical methods. Crystal densities for numerous compounds were predicted using a GIPF whose molecular descriptors consisted of the area of the molecular surface and the variance of the surface ESP, calculated using Hartree Fock theory and the STO-3G basis set.[15] The authors note that the GIPF could be modified to use the molecular volume within the isosurface rather than molecular surface area, but concluded that such a modification was unnecessary because their results were in adequate agreement with experiment. Other studies have modified the original GIPF approach for crystal density prediction[7,10,11] by replacing the surface area term with the molecular volume, where the molecular volume is defined as that contained within the 0.001 electrons/bohr^3 isosurface of electron density (as prescribed by Politzer) or using the van der Waals volume.[7] Additionally, the original GIPF derived by Politzer did not accurately predict crystal densities for cyclic and cage compounds[11] without reparameterization of the equations. A subsequent study in which experimental electron densities were used to generate the surface ESPs required for the GIPF showed that the molecular volume alone is sufficient to predict crystal density; inclusion of surface variance term in the original Politzer GIPF did not enhance the correlation.[10] In a similar fashion, Xiao and co-workers[22−26] have used quantum mechanical or semiempirical molecular orbital calculations to estimate crystal densities for several notional and actual energetic materials. In this procedure, geometry optimiza-

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10.1021/jp073117j CCC: $37.00

tions of isolated molecules are first performed, and the volumes within the 0.001 electrons/bohr^3 isosurfaces of electron densities of the optimized structures are then used to estimate the crystal densities. In their latest study, a set of 45 acyclic, monocyclic, polycyclic, and caged nitramines were subjected to this methodology, using a variety of modest basis sets and either density functional theory or semiempirical methods.[26] All results using the B3LYP density functional[33,34] are in reasonably good agreement with experiment, with the best predictions resulting from the utilization of the 6-31G** basis set.[35] The predicted crystal densities produce average and rms deviations from experimental values of 0.3% and 5%, respectively, with maximum deviations ranging from 0.26 to 0.38 g/cm^3 for the three flurorinated nitramines that were included in this set. Elimination of these three systems from the set of calculations produced average and rms deviations of −0.8% and 3.1%, respectively, and a maximum deviation of 0.19 g/cm^3. Predictions using various semiempirical methods were in poorer agreement with experiment than those generated using the density functional methods, and produced volumes that were systematically larger than the DFT results.

The use of quantum mechanically generated electron densities to define molecular volumes is quite appealing, because quantum mechanical methods can be generally applied to a wide variety of systems, whereas other methods (e.g., volume additivity or the GIPF approach utilizing molecular surface descriptors) usually have a limited applicability, and that to systems where experimental information was used for parametrization. Further, the survey study performed by Qiu et al.[26] suggests that accurate results can be obtained using a modest level of quantum mechanical theory and basis set (B3LYP/6-31G**). In contrast, Jenkins et al., in their study of inorganic salts (mainly metallic and halogenated compounds), concluded that B3LYP volumes of isolated species “are typically lower than experimental solid-state values by 10−40%.”[36] Before either conclusion can be accepted for a broader application to systems other than nitramines or the inorganic salts explored by Jenkins et al.,[36] a larger and more diverse set of crystals should be assessed, as we shall do in the present work. We present crystal density predictions using molecular volumes within isosurfaces of electron densities calculated using quantum mechanical methods (B3LYP/6-31G**) for a large number of systems (289) for which experimental crystallographic information exists. Additionally, we will explore the suitability of the method for density predictions of ionic molecular crystals that have a substantially different chemical composition than those examined by Jenkins et al.[36]

Organization of this paper is as follows: Section 2 describes the computational approaches used in this study. Results and discussion will be presented in section 3, and concluding remarks will be given in section 4.

2. Details of the Calculations

For all results presented here, the term “molecular volume” will be defined as that contained within the 0.001 electrons/bohr^3 isosurface of electron density of an isolated molecule calculated at the B3LYP/6-31G** level.[33−35] Also, in the case of ionic systems, “molecular volume” will correspond to the volume of the formula unit of the crystal. All calculations were performed using the Gaussian 03 suite of quantum mechanical software;[37] default settings were used in all calculations except for the SCF convergence, which was set to 10^{-8}. For both neutral and ionic systems, two sets of molecular volumes were generated. The first set contains volumes that correspond to the molecular structures found in the experimental crystals (i.e., no geometry optimization is performed) and will be denoted as V_{Expt}. The majority of the experimental information was obtained from the Cambridge Structural Database (CSD).[27] The second set of volumes, denoted hereafter as V_{Opt}, were generated using molecular structures obtained through geometry optimizations at the B3LYP/6-31G** level. The initial structures used in the geometry optimizations were those of the experimental crystal. For all optimized geometries presented here, normal-mode analyses were performed to confirm that each optimized structure corresponds to a local minimum on the potential energy surface. We note that our approaches to generating both molecular structures and volumes differ from those of Qiu et al.;[26] in that study, the initial molecular structures used in the geometry optimizations were generated using commercial chemical graphical software, rather than utilizing experimental information of the conformer in the crystalline state. It is possible that through such a choice of initial configuration, the resulting optimized molecular conformer might be substantially different from that observed in the experimental crystal. Thus, we have chosen to use the experimental information for our initial molecular structures in the geometry optimizations, to minimize error due to an incorrect choice of molecular conformation. However, in the case of notional compounds, one is not able to rely on experimental information, and thus the approach used by Qiu et al.[26] is reasonable.

Qiu et al.[26] determined the molecular volumes of their compounds from averaging 100 single-point molar volume calculations per molecule generated using a Monte Carlo integration scheme as implemented in the Gaussian 03 program package[37]. This work took a different tack and employed the use of the Visualization Toolkit (VTK)[38] to measure the volume associated with the 0.001 electrons/bohr^3 isosurface of electron density. VTK is a freely available, open-source software system that provides an application programming interface (API) to implementations of commonly used algorithms for 3D graphics, image processing, and visualization. Using the VTK API, we developed a custom tool that generated the desired isosurface from the electron density information generated in a Gaussian 03[37] cubegen utility calculation, and we measured the corresponding volume. To measure the volume, VTK implements an algorithm based on the discrete form of the divergence theorem. Additional details about the algorithm and an evaluation of its accuracy may be found in Lancaster et al.[39] and Alyassin et al.[40]

While it is straightforward to use this procedure to calculate the molecular volumes for neutral species, assessing the formula unit volumes of ionic systems in a similar fashion is problematic if there is no a priori knowledge of the crystal structure. In the case of neutrals, we would simply assume an initial molecular structure and subject it to a geometry optimization, from which we would determine the molecular volume. For the case of ionic systems in the absence of crystal structure information, we are faced with the problem of how to determine the most probable relative separations and orientations of the ionic partners in the formula unit that would correspond to the crystalline phase, because this would affect the resulting molecular volume. Simply calculating and ranking formula units whose ionic partners are arranged in a variety of orientations and relative separations might not necessarily produce a result that is consistent with the experimental crystal structure, because the packing of the ionic partners would be strongly influenced by the crystalline field. Such field effects cannot be captured in quantum mechanical calculations of isolated formula units. Also, geometry optimizations of the isolated ionic partners can result in spontaneous reaction (e.g., proton transfer[41,42]), and the preservation of charge separation cannot be assured. Such problems can be circumvented by assuming additivity to define formula unit volumes.[21,29,36] In this approach, the volume of the formula unit M_pX_q of an ionic crystal is simply the sum of the volumes of the ions contained in the formula unit:

$$\text{volume} = pV_{M+} + qV_{X-} \tag{2}$$

where M denotes the cation and X denotes the anion. Because we are able to evaluate volumes of individual ions using the QM procedure described above, we use eq 2 to calculate formula unit volumes for ionic crystals. For several systems studied, there were also neutral solvent molecules included in the crystal lattice. For these systems, the total formula unit volume including the solvent molecules are assumed to be:

$$\text{volume} = pV_{M+} + qV_{X-} + rV_{\text{solvent}} \tag{3}$$

where r denotes the number of solvent molecules in the formula unit.

3. Results and Discussion

Neutral Molecular Crystals. We evaluated two sets of molecular volumes (V_{Expt} and V_{Opt} as defined in section 2) for 180 CHNO species for which experimental crystallographic information exists. All experimental information was obtained from the CSD.[27] The majority of these compounds had previously been subjected to the ab initio crystal structure prediction method for calculating densities by Rice and Sorescu (RS),[43] and the set contains mainly nitroaliphatic, nitroaromatic, nitramine, or nitrate ester compounds. The chemical names, the CSD entry identifier (refcode), temperature at which the measurements were taken, molecular volumes, and crystal densities as reported in the CSD are given in Table 1S. Also, the crystal densities predicted using the method of ab initio crystal structure prediction[43] are given in Table 1S.

The results of the calculations using the approach described in this Article are presented in Table 1S, and a graphical comparison of the predicted V_{Opt} values with the experimental molecular volumes as defined in the CSD is given in Figure 1a. Molecular volumes calculated using the experimental structures (V_{Expt}) had average and rms deviations from experiment of −4.2% and 5.8%, respectively. The average and rms deviation of the molecular volumes using the optimized geometries (V_{Opt}) are −0.9% and 3.7%, respectively. The molecular structures generated through geometry optimization represent a 0 K result and do not include any thermal expansion of the intramolecular bonds that might be present in the experimental structures. To explore whether imposing estimated thermal effects on V_{Opt} might bring the predicted values into better agreement with experiment, we assume that the volume V_{Opt} will vary linearly with temperature:[12]

$$V_{\text{Opt,Corrected}} = V_{\text{Opt}}\,(1 + \alpha T) \tag{4}$$

where T denotes the temperature at which the crystal structure is measured and α is a thermal expansion coefficient, determined by fitting eq 4 to the experimental molecular volumes listed in Table 1S. Application of the thermal correction to V_{Opt} produced average and rms deviations from experiment of 1.3% and 3.8%, indicating thermal effects on the molecular structure are minimal and no significant improvement to the predictions was gained by its application. For the set of molecules whose configurations correspond to the experimental structure (V_{Expt}), thermal effects (as well as crystal field effects) that might affect the molecular structure are already inherently included; therefore, no thermal correction was imposed on molecular volumes or densities calculated using these structures.

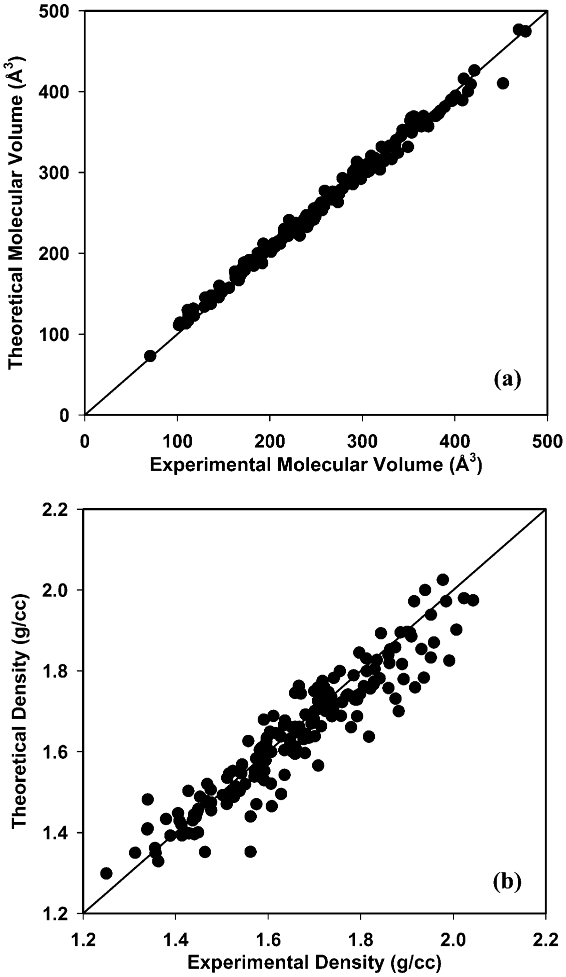

Figure 1. (a) Predicted molecular volumes within the 0.001 electrons/bohr^3 isosurface of electron density using molecular structures optimized at the B3LYP/6-31G** level versus experimental values for 180 CHNO neutral molecular crystals. (b) Predicted crystal densities using molecular volumes illustrated in (a) versus experimental values.

Because results generated using V_{Opt} are in better agreement with experiment than results using the molecular configuration corresponding to the measured crystal structure, we only compared calculated crystal densities using V_{Opt} with experiment (Figure 1b); results are given in Table 1S. Average and rms deviations of predicted crystal densities from experimental values using V_{Opt} are 1% and 3.7%, respectively. The maximum deviations of molecular volume and density from experimental results from this set are 53 Å^3 and 0.178 g/cm^3, respectively.

We also compared performance of this method against the earlier procedure used by RS in which 174 CHNO systems were subjected to ab initio crystal prediction.[43] 169 of the systems presented here were also calculated by RS; average and rms deviations of the RS results from experiment for this set of 169 molecules are 3.0% and 3.9%. Application of the procedure described herein to the same subset of systems produces results with average and rms deviations from experiment of 1.2% and 3.6%, an improvement over the previous RS density prediction method.

While the results using the current procedure are slightly better than those using the RS density prediction method (ref

43), the computational costs are substantially less. Additionally, the current method is not dependent on a classical force field (which usually is limited to accurate treatment of similar classes of compounds). On the other hand, the current method does not reveal any information about the atomic arrangement within the crystal lattice as does the RS method; it merely provides volumetric data. The method presented here requires more computational resources than QSPRs utilizing volume additivity, but allows for a broader range of applications because it is not parametrized to specific classes of chemical compounds, as will be shown hereafter.

We have also applied the procedure presented in this study to a small set (38) of compounds that have a nitrogen content of at least 50% or are composed of nitrogen-containing rings. This was done to determine, to a limited degree, the transferability of the method to chemical systems that are somewhat dissimilar from the CHNO systems described earlier. The names and crystal densities of these compounds are reported in Table 2S. As for the larger set of CHNO systems, molecular volumes for these compounds were calculated using the 6-31G** basis set and the B3LYP density functional; all geometries were optimized at the B3LYP/6-31G** level. Densities calculated using molecular volumes within the 0.001 electrons/bohr^3 isosurfaces of electron density without any temperature correction are listed in Table 2S; visual comparisons of both volumes and densities with experimental values are given in Figure 2. Calculated crystal densities have average and rms deviations from experiment of -1.8% and 3.4%, respectively. The maximum deviations of molecular volume and density from experimental results from this set of crystals are 12 Å^3 and 0.129 g/cm^3, respectively. Despite the differences in molecular composition, this method appears to be transferable to this set of compounds.

Density Predictions: Ionic Crystals. Formula unit volumes to be used in predicting crystal densities of ionic crystals were determined using eqs 2 and 3 and calculated volumes of the various cations, anions, and solvent molecules contained in 71 salts. These salts are not representative of all classes of ionic compounds; rather, they are composed of systems of interest to the energetic materials community. As for the neutrals, the ionic volume of each individual ion is that contained within the 0.001 electrons/bohr^3 isosurface of electron density of the isolated ion. Also, two sets of ionic volumes were generated: one corresponding to experimental ionic structures and the other corresponding to optimized geometries of the ions. The chemical names, the CSD entry identifier (refcode) if available, formula unit volumes, and crystal densities are given in Table 3S.

Calculated formula unit volumes using both experimental structures and optimized geometries are compared to experimental formula unit volumes in Table 3S. Unlike what was observed for the neutral molecular crystals, the calculated formula unit volumes using the experimental structures had a lower rms percent deviation from experimental values (5.0%) than formula unit volumes calculated using optimized geometries (7.3%). A comparison of the ionic components of the formula unit volumes calculated using experimental and optimized geometries revealed the following: for those ions that had no hydrogen atoms, the differences between the ionic volumes assuming the experimental structures and those using the optimized structures were very small (fractions of Å^3). The largest differences in ionic volumes were for those ions that contained hydrogen atoms. Figure 3 shows the difference between experimental and optimized ionic volumes as a function of the number of hydrogen atoms in each of the ions evaluated in this study; the line represents a linear least-squares fit of the curve ($R^2 = 0.90$). It is clear that the differences scale approximately linearly with the number of hydrogen atoms in the ion. Examination of the optimized structures with experimental structures indicated that the X−H (X = N, C) bonds resulting from the B3LYP/6-31G** geometry optimizations were consistently larger than the experimental values by as much

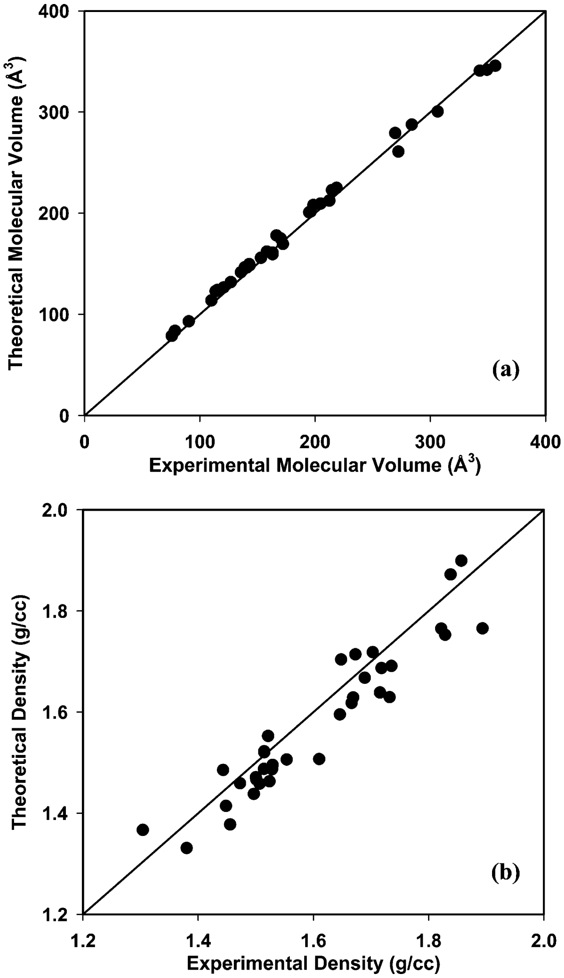

Figure 2. (a) Predicted molecular volumes within the 0.001 electrons/bohr^3 isosurface of electron density using molecular structures optimized at the B3LYP/6-31G** level versus experimental values for 38 molecular crystals with nitrogen content greater than 50% or that are composed of nitrogen-containing rings. (b) Predicted crystal densities using molecular volumes illustrated in (a) versus experimental values.

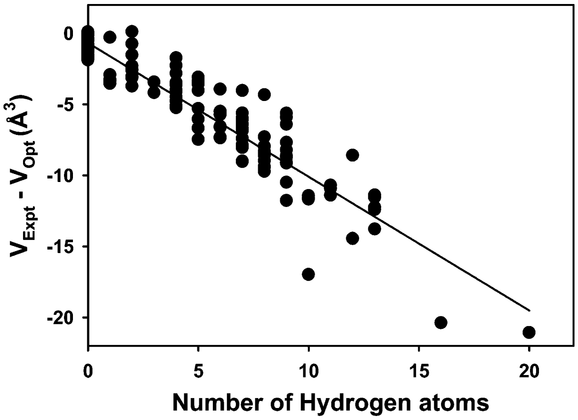

Figure 3. Difference between experimental and optimized ionic volumes versus the number of hydrogen atoms in each of the ions evaluated in this study.

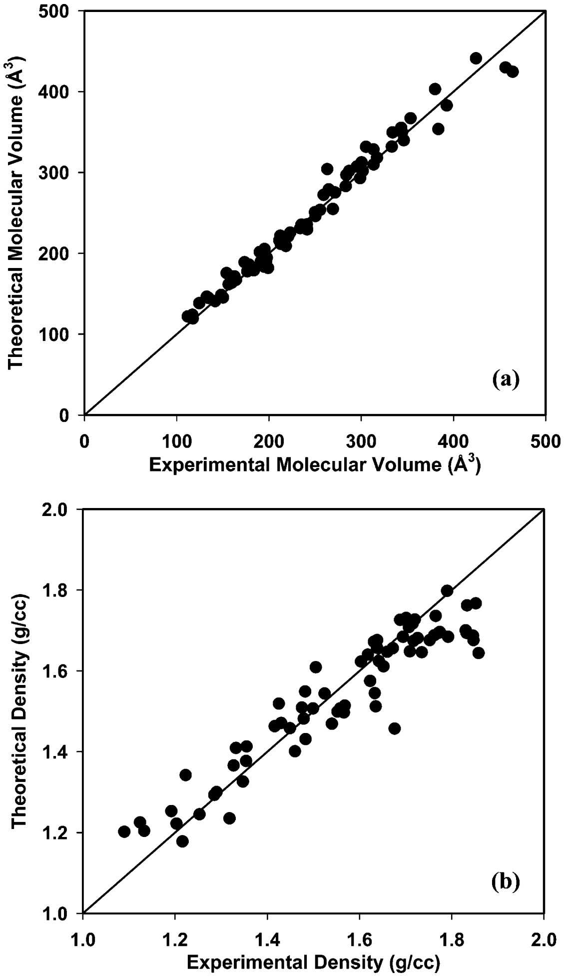

Figure 4. (a) Predicted formula unit volumes within the 0.001 electrons/bohr^3 isosurface of electron density using ionic structures optimized at the B3LYP/6-31G** level versus experimental values for 71 ionic crystals. Formula unit volumes are corrected using eq 5. (b) Predicted crystal densities using formula unit volumes illustrated in (a) versus experimental values.

as 0.354 Å. The theoretical hydrogen bond distances were on average 0.122 Å longer than the experimental values, thus producing larger molecular volumes relative to experiment. Because we are exploring methods to predict crystal densities without a priori knowledge of the crystal structure, we are, in the case of a notional compound, forced to rely upon theoretical structures. In our procedure, these will be obtained through geometry optimization at the B3LYP/6-31G** level. Therefore, we have attempted to establish a procedure to correct the overestimation of formula unit volumes for those compounds that contain hydrogen atoms, using parameters obtained from the least-squares fit of the data shown in Figure 3.

A "corrected" molecular volume using a molecular structure optimized at the B3LYP/6-31G** level can be calculated using:

$$V_{\text{(corrected),Opt}} = V_{\text{(uncorrected),Opt}} - [0.6763 + 0.9418\ (\text{no. of hydrogen atoms in the ion})] \quad (5)$$

Formula unit volumes using eq 5 for 71 ionic crystals are compared to the experimental formula unit volumes in Table 3S; the comparison is illustrated in Figure 4. Formula unit volumes calculated using optimized geometries and corrected for the number of hydrogen atoms had average and rms deviations from experimental values of 1.3% and 5.0%, respectively, in much better agreement than the uncorrected values (5.6% and 7.3%, respectively). Average and rms deviations from experimental crystal densities using the volumes corresponding to the experimental structures are −0.7% and 4.9%, respectively, whereas the corresponding values using corrected formula unit volumes generated from optimized structures yield deviations in the density of −1.1% and 4.8%, respectively. Average and rms deviations from experimental crystal densities using uncorrected formula unit volumes obtained from optimized geometries are −5.1% and 6.6%, respectively. The addition of the hydrogen correction (eq 5) decreases the average and rms errors in the crystalline density by 4% and approximately 2%, respectively. This small correction yields a significant improvement in the predicted densities when using the optimized structures. Visual comparison of the predicted crystal densities (corrected for hydrogen content) with experiment is also given in Figure 4. The maximum deviations of molecular volume and density from experimental results for the corrected set are 41 Å^3 and 0.285 g/cm^3, respectively. We note that the rms deviations for the ionic materials are approximately 1% larger than those for the neutral systems. A possible explanation could be that the calculated volumes of the isolated ions might be more strongly affected by lack of the crystal field than those of the neutral molecules we examined here, because the dominant intermolecular interactions within the crystals differ in both magnitude and type (i.e., Coulombic for salts versus van der Waals for organic molecular crystals). It is reasonable to expect that the electron density of an ion within a crystal would be more strongly affected by both nearby counterions and the crystalline field than neutral neighboring molecules in the more weakly bound molecular crystals. The exclusion of these counter charges in calculating the electron density of the isolated ions could explain the larger errors as compared to neutral systems.

4. Summary and Conclusions

Crystal densities for a variety of neutral and ionic crystals of interest to the energetic materials community were predicted using volumes within the 0.001 electrons/bohr^3 isosurface of B3LYP/6-31G** calculated electron densities of the isolated molecules or ions contained within the crystals. This method was first applied to 180 CHNO neutral molecular crystals, yielding average and rms deviations of predicted crystal densities from experimental values of 1% and 3.7%, respectively. The method was also applied to 38 molecular crystals that had either a nitrogen content of at least 50% or were composed of molecules with nitrogen-containing rings. Average and rms deviations of predicted densities from experimental values are −1.8% and 3.4%, respectively. Application of the method to 71 ionic crystals, in which formula unit volumes are assumed to be the sum of volumes of the ionic constituents, produced average and rms deviations from experimental densities of −5.1% and 6.6%, respectively. However, we observed a dependence on the degree of deviation from experiment with the number of hydrogen atoms in the formula unit. This dependence appears to be due mainly to an overestimation of X−H bonds (X = N, C) resulting from the B3LYP/6-31G** geometry optimizations. To accommodate this, we applied a correction to the formula unit volumes that resulted in a significant improvement in the average and rms percent deviations of the predicted crystal densities from experiment (−1.1% and 4.8%, respectively).

The suitability of the method for predicting volumes for systems that differ significantly in chemical composition from those explored herein has not been established (e.g., metallic and halogen-containing compounds). In fact, calculations on a few such systems indicate that the error might be larger (by as much as 10−40%)[36] than for the systems explored in this Article. However, we have clearly shown that this method applied to neutral and ionic CHNO or high-nitrogen systems will generate reasonably accurate crystal densities. Therefore, the method can be used with a degree of confidence to predict crystal densities for similar compounds for which no experimental crystallographic information is available.

Acknowledgment. This work was partially supported by the Office of Naval Research and the Environmental Quality Technology Ordinance Program. All calculations were performed at either the ARL or the ASC Major Shared Resource Centers of the Department of Defense High Performance Computing Modernization Program.

Supporting Information Available: Tables 1S, 2S, and 3S containing information about the systems studied herein, including chemical names, formulas, volumes, and densities. This material is available free of charge via the Internet at http://pubs.acs.org.

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