

First-Principles Lattice Energy Calculation of Urea and Hexamine Crystals by a Combination of Periodic DFT and MP2 Two-Body Interaction Energy Calculations

Seiji Tsuzuki,* Hideo Orita, Kazumasa Honda, and Masuhiro Mikami

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan

Received: December 21, 2009; Revised Manuscript Received: April 13, 2010

This article proposes a new method for the accurate evaluation of the lattice energies (stabilization energies associated with the formation of crystals from isolated molecules) of molecular crystals by a combination of DFT and MP2 calculations. The interactions of well-separated molecules were evaluated by periodic DFT calculations. The interactions with neighboring molecules were evaluated by MP2-level two-body interaction energy calculations with the neighboring molecules. The sublimation energies calculated for crystals of urea and hexamine using the proposed method (21.2 and 20.0 kcal/mol, respectively) were close to the experimental values (20.9–23.6 and 17.7–18.8 kcal/mol, respectively). The lattice energies calculated for the two crystals by the proposed method are significantly different from those obtained by DFT calculations, suggesting that the dispersion contribution to the lattice energy is significant even in the crystal, where molecules are bound by hydrogen bonds. Lattice energies calculated by changing the range of the neighboring molecules show that the nearest-neighboring molecules are mainly responsible for the dispersion interactions in the crystals.

Introduction

Accurate computational determination of the lattice energies of molecular crystals has paramount importance in crystal engineering, which is important in many applications such as the development of pharmaceutical products^{1–4} and optical materials.^{5–7} The critical issue in the calculation of lattice energies for molecular crystals is the appropriate description of intermolecular interactions,^{8–14} which control the structure and thermodynamic properties of the crystals. Periodic density functional theory (DFT) calculations are widely used for the first-principles lattice energy calculations of molecular crystals.^{15–21} Periodic calculations are essential for the accurate evaluation of electrostatic interactions in the crystals of polar molecules, because electrostatic interactions converge slowly with distance. DFT calculations with commonly used functionals often fail to adequately evaluate the dispersion interactions,^{22–24} which contribute significantly to the attractions in molecular crystals.²⁵ Recently reported lattice energy calculations of the urea crystal show that LDA (SVWN) overestimates the attraction, whereas calculations with the B3LYP and PW91 functionals underestimate the attraction.²⁶ The experimental sublimation energy of crystalline urea is 20.9–23.6 kcal/mol,^{27–32} as summarized in Table 1, whereas the values calculated for the crystal using the SVWN, B3LYP, and PW91 functionals are 32.0, 14.5, and 17.9 kcal/mol, respectively.²⁶ DFT calculations with an empirical correction of the dispersion energy were also applied for lattice energy calculations.^{33–35} The lattice energies calculated for crystals depend on the empirical parameters used for the corrections.³⁵ Recently reported CCSD(T) calculations of molecular clusters showed that CCSD(T) calculations provide very accurate intermolecular interaction energies, if a sufficiently large basis set is used. It has also been reported that MP2-level interaction energies are often close to the CCSD(T) values.^{36,37} These calculations suggest that periodic MP2 or CCSD(T) calculations should provide very accurate lattice energies of

TABLE 1: Experimental Sublimation Enthalpies for Urea and Hexamine Crystals

ΔH_{sub}^a	T_m^b	year	ref(s)
Urea			
20.95 ± 0.21	356	1956	28
21.1	356	1959	29, 30
22.8	361	1978	31
23.6	298	1983	30
23.2	351	1983	30
21.7 ± 0.5	381	1987	32
Hexamine			
18.0		1958	63
17.7 ± 0.2	289	1960	64
17.9 ± 0.7	298	1960	65
18.8	316	1983	30
18.4	313	1987	66

^a Sublimation enthalpy. Energy in kcal/mol. ^b Mean temperature of measurements in K. See ref 27.

molecular crystals. However, the highly computationally demanding periodic MP2 and CCSD(T) calculations of large molecular crystals containing more than 20 heavy atoms in a unit cell are not practical at present. The MP2, CCSD(T), and symmetry-adapted perturbation theory (SAPT) calculations of finite clusters have also been used for estimating lattice energies of small molecular crystals.^{38–41} However, it is difficult to accurately evaluate many-body contributions and electrostatic interactions with well-separated molecules in crystals by calculations of finite clusters. Therefore, a computationally viable first-principles calculation method for an accurate evaluation of lattice energies of large molecular crystals is strongly needed.

In this work, we propose a method for the accurate evaluation of the lattice energies of molecular crystals by a combination of a periodic DFT calculation and MP2 calculations of two-body interactions with neighboring molecules. The interactions of well-separated molecules (mainly electrostatic interactions) are evaluated by a periodic DFT calculation.⁴² The interactions

* To whom correspondence should be addressed. E-mail: s.tsuzuki@aist.go.jp.

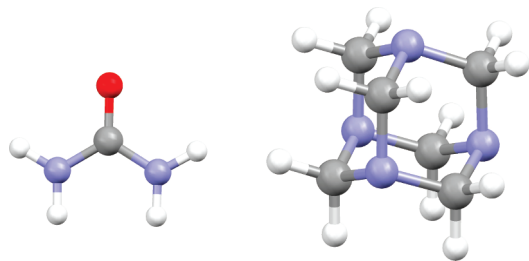


Figure 1. Urea and hexamine molecules.

with neighboring molecules, where the dispersion contributions are significant, are evaluated as the sum of the two-body interaction energies calculated by the MP2 method. The dispersion energy is approximately proportional to the inverse sixth power of the intermolecular distance. Therefore, the dispersion interactions with well-separated molecules are small.

Lattice energy calculations by the proposed method have several advantages: (1) Dispersion interactions with neighboring molecules are included in the lattice energy calculation without the use of any empirical parameters. (2) This method does not require a highly computationally demanding periodic MP2 calculation. (3) The accuracy of the lattice energy calculated by this method can be improved systematically by increasing the range of the neighboring molecules and by improving the approximation (choice of basis set and electron correlation correction procedure) used for calculating the two-body interactions with the neighboring molecules. (4) The contributions of many-body interactions such as hydrogen-bond cooperativity are included in the lattice energy through the periodic DFT calculation. (5) The lattice energy can be evaluated by this method, even if the positions of hydrogen atoms in the crystal have some uncertainty in experiments, because the positions of atoms in the crystal are optimized by the periodic DFT calculation.

We applied this method for lattice energy calculations of crystals of urea and hexamine (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]-decane) (Figure 1). The sublimation energies calculated for the crystals from the calculated lattice energies were compared with experimental values to assess the accuracy of the calculated lattice energies. We selected urea and hexamine crystals to examine the performance of this method for evaluating the lattice energies of two types of molecular crystals. Urea molecules are bound by hydrogen bonds in the crystal. It is expected that these hydrogen bonds are mainly responsible for the cohesive energy of the crystal. On the other hand, there are no hydrogen bonds in the hexamine crystal. It is therefore expected that dispersion interactions are the major source of attraction in this crystal. We studied how the range of neighboring molecules taken into consideration affects the calculated lattice energy. We also studied the dependence of the lattice energies on the basis set used for calculating the two-body interaction energies with the neighboring molecules.

Computational Methods

DFT calculations were performed with the program package DMol³ in Materials Studio (version 4.3) of Accelrys Inc. In the DMOL³ method,^{43–45} the physical wave functions are expanded in terms of accurate numerical basis sets. We used the double-numerical-quality basis set with polarization functions (DNP) for geometry optimizations. The triple-numerical quality basis set with polarization functions (TNP) was used for energy calculations, unless noted otherwise. The PW91 functionals were used for the DFT calculations.⁴⁶ The positions of atoms in the

crystal were optimized by the periodic DFT calculations. The experimental lattice parameters^{47,48} were fixed during the optimization.⁴⁹ The lattice energy [$E_{\text{lattice(DFT)}}$] was calculated by the DFT method as

$$E_{\text{lattice(DFT)}} = \frac{1}{Z} E_{\text{crystal(DFT)}} - E_{\text{mono(DFT)}} \quad (1)$$

where Z is the number of molecules in one unit cell. The Z value for crystals of each urea and hexamine is 2. The energy of the crystal per unit cell [$E_{\text{crystal(DFT)}}$] was calculated by the periodic DFT method using the optimized crystal structure.^{50,51} The energy for an isolated molecule [$E_{\text{mono(DFT)}}$] was calculated using the optimized geometry of the isolated molecule. (Periodic boundary conditions were not imposed in the monomer energy calculations.) Two-body interaction energies with the neighboring molecules in the crystal were calculated by the HF and MP2 methods.^{52–55} The Gaussian program⁵⁶ was used for the HF and MP2 calculations. The aug-cc-pVTZ basis set was used for the calculations, unless noted otherwise. The basis-set superposition error (BSSE)⁵⁷ was corrected by the counterpoise method.⁵⁸ The energy of the crystal [$E_{\text{crystal(DFT)}}$] and the two-body interaction energies at the DFT, HF, and MP2 levels (E_{DFT} , E_{HF} , and E_{MP2} , respectively) were calculated using the optimized geometry of the crystal by periodic DFT calculations. The lattice energy [$E_{\text{lattice(MP2+DFT)}}$] was also calculated using periodic DFT calculations and MP2-level two-body interaction energies with neighboring molecules as in the equation

$$E_{\text{lattice(MP2+DFT)}} = E_{\text{long(DFT)}} + E_{\text{short(MP2)}} \quad (2)$$

$E_{\text{long(DFT)}}$ was obtained by eq 3

$$E_{\text{long(DFT)}} = E_{\text{lattice(DFT)}} - E_{\text{short(DFT)}} \quad (3)$$

$E_{\text{short(DFT)}}$ is the sum of the DFT-level two-body interaction energies with the neighboring molecules (E_{DFT})

$$E_{\text{short(DFT)}} = \frac{1}{2} \sum E_{\text{DFT}} \quad (4)$$

$E_{\text{long(DFT)}}$ is mainly the DFT-level interaction energies with well-separated molecules in the crystal. $E_{\text{long(DFT)}}$ includes the contributions of many-body interactions, because $E_{\text{long(DFT)}}$ was obtained by subtracting the two-body interaction energies with the neighboring molecules from the lattice energy obtained by the periodic DFT calculations, which captures the many-body interactions. The deformation energy of a molecule associated with the crystal formation is also included in $E_{\text{long(DFT)}}$. $E_{\text{short(HF)}}$ and $E_{\text{short(MP2)}}$ are the sums, respectively, of the HF- and MP2-level two-body interaction energies with the neighboring molecules (E_{HF} and E_{MP2}) as follows

$$E_{\text{short(HF)}} = \frac{1}{2} \sum E_{\text{HF}} \quad (5)$$

$$E_{\text{short(MP2)}} = \frac{1}{2} \sum E_{\text{MP2}} \quad (6)$$

The electron correlation contribution to the MP2-level two-body interaction energies with the neighboring molecules [$E_{\text{short(corr)}}$] was obtained from the equation

$$E_{\text{short(corr)}} = E_{\text{short(MP2)}} - E_{\text{short(HF)}} \quad (7)$$

$E_{\text{short(corr)}}$ is mainly the dispersion energy. $E_{\text{lattice(MP2+DFT)}}$ can be calculated as

$$E_{\text{lattice(MP2+DFT)}} = E_{\text{lattice(DFT)}} + E_{\text{short(MP2-corr)}} \quad (8)$$

where $E_{\text{short(MP2-corr)}}$ is the difference between $E_{\text{short(MP2)}}$ and $E_{\text{short(DFT)}}$, that is

$$E_{\text{short(MP2-corr)}} = E_{\text{short(MP2)}} - E_{\text{short(DFT)}} \quad (9)$$

$E_{\text{short(MP2-corr)}}$ can be regarded as the correction of the MP2-level interaction energies with the neighboring molecules. The two-body interaction energies with the neighboring molecules, where the shortest atom–atom distance (R_{min}) is less than 10 Å, were calculated, unless noted otherwise. The accuracy of the calculated lattice energies can be evaluated by comparing them with experimental values. Unfortunately, however, experimental lattice energies of urea and hexamine crystals have not been reported. Therefore, we compared calculated sublimation enthalpies with experimental values to judge the accuracy of the lattice energies calculated for the crystals. The sublimation enthalpy at 298 K was calculated as

$$E_{\text{sub}} = -E_{\text{lattice(DFT+MP2)}} - 2RT \quad (10)$$

where $2RT$ is the enthalpy correction term.⁵⁹

Results and Discussion

Sublimation Enthalpy and Lattice Energy. The sublimation enthalpy calculated for the urea crystal (21.2 kcal/mol) by the proposed method agrees well with the experimental values (20.9–23.6 kcal/mol) summarized in Table 1.^{27–32} The intermolecular interactions in crystalline urea have been studied using first-principles calculations by several groups.^{17,26,35,60–62} Civalieri et al. reported that periodic DFT calculations using the SVWN, B3LYP, and PW91 functionals did not accurately reproduce the experimental lattice energy.²⁶ They reported that the lattice energy obtained by a periodic DFT (B3LYP) calculation with an empirical dispersion correction (26.6 kcal/mol) was close to the experimental value.³⁵ The sublimation enthalpy calculated for hexamine crystal (20.0 kcal/mol) by the proposed method is close to the experimental values (17.7–18.8 kcal/mol).^{27,29,63–66} A larger sublimation enthalpy was reported for a periodic DFT (B3LYP) calculation with an empirical dispersion correction (21.7 kcal/mol).³⁵

The lattice energy of hexamine crystal was significantly underestimated, when the interactions with the neighboring molecules were not calculated by the MP2 method. The values of $E_{\text{lattice(DFT+MP2)}}$ calculated for the urea and hexamine crystals are –22.4 and –21.2 kcal/mol, respectively, and the $E_{\text{lattice(DFT)}}$ values for the two crystals are –20.4 and –7.0 kcal/mol.^{67,68}

Interactions with Neighboring Molecules. The interaction energies with the neighboring molecules calculated by the MP2 and HF methods [$E_{\text{short(MP2)}}$ and $E_{\text{short(HF)}}$] are summarized in Table 2. The $E_{\text{short(MP2)}}$ values calculated for the urea and hexamine crystals are –26.8 and –22.4 kcal/mol, respectively. The $E_{\text{short(HF)}}$ values calculated for the two crystals are –14.7 and 4.4 kcal/mol, respectively. The HF-level interaction energies are mainly the sums of the exchange-repulsion and electrostatic

TABLE 2: Lattice Energies, Intermolecular Interaction Energies and Sublimation Enthalpies Calculated for Urea and Hexamine Crystals^a

	urea	hexamine
$E_{\text{lattice(DFT)}}^b$	–20.4	–7.0
$E_{\text{long(DFT)}}^c$	4.4	1.2
$E_{\text{short(DFT)}}^d$	–24.8	–8.2
$E_{\text{short(MP2)}}^e$	–26.8	–22.4
$E_{\text{short(HF)}}^f$	–14.7	4.4
$E_{\text{short(corr)}}^g$	–12.1	–26.8
$E_{\text{short(MP2-corr)}}^h$	–2.0	–14.2
$E_{\text{lattice(MP2+DFT)}}^i$	–22.4	–21.2
E_{sub}^j	21.2	20.0

^a Energy in kcal/mol. The nearest atom–atom distance with the neighboring molecule (R_{min}) is less than 10 Å. See text. ^b Lattice energy calculated by the DFT method [= $(1/Z)E_{\text{crystal(DFT)}} - E_{\text{mono(DFT)}}$]. ^c Interactions with well-separated molecules calculated by the DFT method [= $E_{\text{lattice(DFT)}} - E_{\text{short(DFT)}}$]. This term also includes some other terms (contributions of many-body interactions and deformation energy of the molecule in the crystal). ^d Sum of the interaction energies with the neighboring molecules calculated by the DFT method. ^e Sum of the interaction energies with the neighboring molecules calculated by the MP2 method. ^f Sum of the interaction energies with the neighboring molecules calculated by the HF method. ^g Contribution of electron correlation to the interaction energies with the neighboring molecules. This term is mainly the dispersion energy. ^h Correction term for the MP2-level interaction energies with the neighboring molecules [= $E_{\text{short(MP2)}} - E_{\text{short(DFT)}}$]. ⁱ Lattice energy calculated by a combination of the periodic DFT calculation and MP2-level calculations of the two-body interaction energies with the neighboring molecules [$E_{\text{long(DFT)}}$] + [$E_{\text{short(MP2)}}$]. ^j Sublimation enthalpy [= $-E_{\text{lattice(MP2+DFT)}} - 2RT$].

energies. The MP2-level interaction energies include the dispersion energies. The difference between the MP2- and HF-level interaction energies [$E_{\text{short(corr)}}$] is mainly the dispersion energy. Substantial attraction was calculated for the urea crystal at the HF level, which shows that the electrostatic interactions contribute largely to the attraction. The $E_{\text{short(corr)}}$ value for the urea crystal (–12.1 kcal/mol) is significant, which shows that the dispersion interaction is also important for the attraction in the hydrogen-bonded crystal. On the other hand, the $E_{\text{short(HF)}}$ value calculated for the hexamine crystal is repulsive. The large negative $E_{\text{short(corr)}}$ value (–26.8 kcal/mol) shows that the dispersion interaction is mainly responsible for the attraction in the hexamine crystal. Because of the large dispersion interactions in the hexamine crystal, the MP2 calculations of the two-body interaction energies with the neighboring molecules significantly change the lattice energy for the hexamine crystal.

The interaction energies with the neighboring molecules calculated for the urea and hexamine crystals by the DFT method [$E_{\text{short(DFT)}}$] are –24.8 and –8.2 kcal/mol, respectively, whereas the $E_{\text{long(DFT)}}$ values for the two crystals are positive (4.4 and 1.2 kcal/mol, respectively). $E_{\text{long(DFT)}}$ includes the contribution of many-body interaction and the deformation energy of a molecule in the crystal. The deformation energies of urea and hexamine in the crystals calculated by the DFT method are 3.8 and 0.2 kcal/mol, respectively. The deformation energy is mainly responsible for the large positive $E_{\text{long(DFT)}}$ value for the urea crystal.

Effect of Basis Set for Evaluating Interactions with Neighboring Molecules. To confirm the effects of the basis set used for the MP2 calculations of the two-body interaction energies with the neighboring molecules, the $E_{\text{lattice(DFT+MP2)}}$ values for the urea and hexamine crystals were calculated using several basis sets, as summarized in Table 3. Small basis sets

TABLE 3: Dependence of Lattice Energies [$E_{\text{lattice}}(\text{MP2}+\text{DFT})$] Calculated for Urea and Hexamine Crystals on the Basis Set Used for the MP2-Level Two-Body Interactions with Neighboring Molecules^a

basis set ^b	urea	hexamine
6-31G*	−15.6	−10.8
6-311G*	−14.7	−13.3
6-311G**	−15.4	−14.9
cc-pVDZ	−14.6	−12.7
cc-pVTZ	−19.9	−18.8
aug-cc-pVDZ	−20.3	−19.8
aug-cc-pVTZ	−22.4	−21.2

^a Energy in kcal/mol. The nearest atom–atom distance with the neighboring molecule (R_{mim}) is less than 10 Å. See text. ^b Basis set used for the MP2-level calculations of the two-body interaction energies with the neighboring molecules.

underestimate $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ compared with large basis sets. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ values calculated for the two crystals using the

6-31G* basis set are −15.6 and −10.8 kcal/mol, respectively. Because of the larger electrostatic energy, the basis-set effects on the $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ values calculated for the urea crystal are smaller than those for the hexamine crystal.

The basis-set effects on the intermolecular interaction energies calculated for small molecular clusters have been studied extensively.^{24,69} The intermolecular interaction energies calculated for the clusters agree well with the experimental values in the gas phase, as long as a sufficiently large basis set is used and electron correlation is taken into account properly. Small basis sets underestimate molecular polarizability and, therefore, underestimate dispersion interactions significantly. Because of this reason small basis sets underestimate $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ for the two crystals. Especially small basis sets greatly underestimate $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ for the hexamine crystal because of the large dispersion interactions in this crystal. It has also been reported that the intermolecular interaction energies for molecular clusters calculated using the aug-cc-pVTZ basis set are close to the estimated value at the basis-set limit, which shows that the aug-

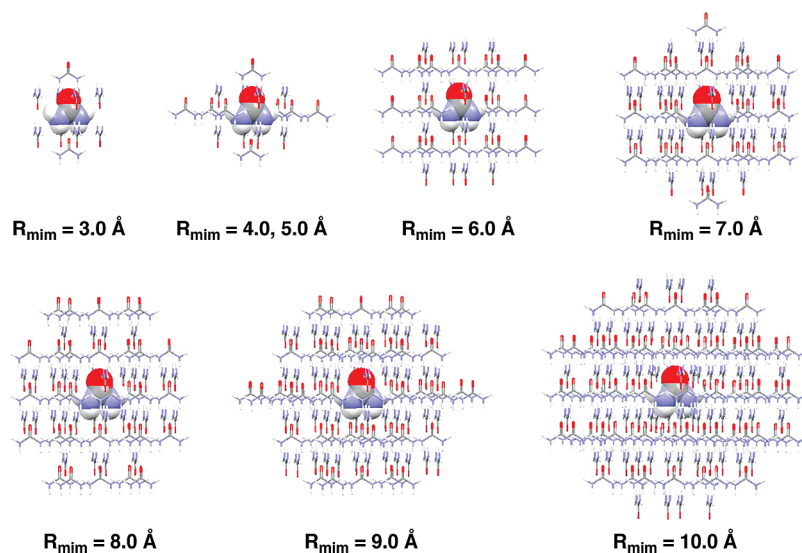
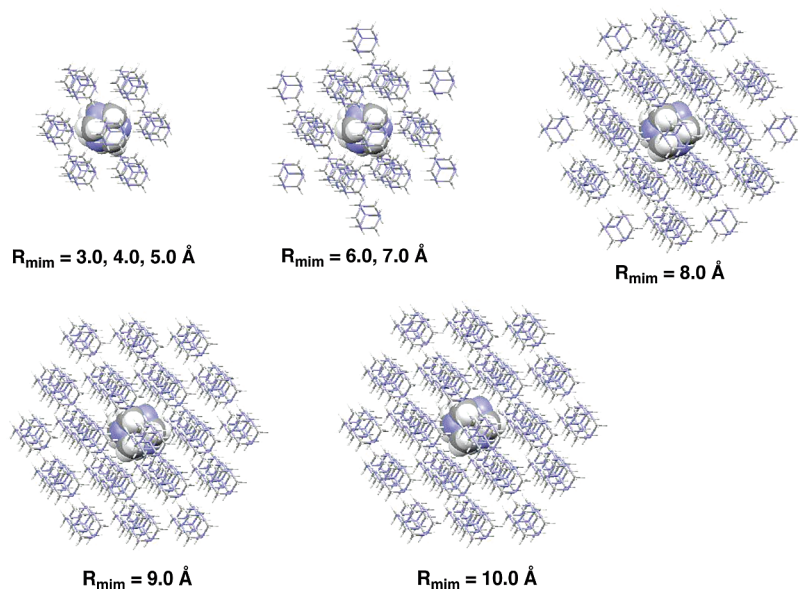
**Figure 2.** One urea molecule (space-filling) and neighboring urea molecules (skeleton) used for the MP2-level two-body interaction energy calculations. See text.**Figure 3.** One hexamine molecule (space-filling) and neighboring hexamine molecules (skeleton) used for the MP2-level two-body interaction energy calculations. See text.

TABLE 4: Dependence of Lattice Energies [$E_{\text{lattice}}(\text{MP2}+\text{DFT})$] Calculated for Urea and Hexamine Crystals on the Range of Neighboring Molecules Taken into Consideration

R_{min}^a (Å)	urea		hexamine	
	number ^b	$E_{\text{lattice}}(\text{MP2}+\text{DFT})^c$	number ^b	$E_{\text{lattice}}(\text{MP2}+\text{DFT})^c$
3	10	−21.5	14	−18.0
4	16	−21.3	14	−18.0
5	16	−21.3	14	−18.0
6	36	−21.5	26	−19.0
7	54	−21.8	26	−19.0
8	64	−21.9	50	−20.2
9	92	−22.2	58	−21.2
10	128	−22.4	64	−21.2

^a Range of neighboring molecules. The nearest atom–atom distance with the neighboring molecule is less than R_{min} . The TNP basis set was used for the periodic DFT calculations. The aug-cc-pVTZ basis set was used for calculating two-body interaction energies with the neighboring molecules. See text. ^b Number of the neighboring molecules. ^c Lattice energy in kcal/mol. See text.

cc-pVTZ basis set is nearly saturated. The effects of electron correlation beyond MP2 on the intermolecular interaction energies calculated for the urea dimer and hexamine dimer are not large.⁷⁰ Therefore, it is expected that the intermolecular interactions with neighboring molecules in the urea and hexamine crystals calculated at the MP2/aug-cc-pVTZ level are not largely different from the CCSD(T)-level interaction energies at the basis-set limit. For this reason the sublimation enthalpies for the two crystals obtained using the MP2 calculations are close to the experimental values.

Range of Neighboring Molecules. The effects of the range of the neighboring molecules were investigated by changing the value of R_{min} , as illustrated in Figures 2 and 3. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ values calculated for the urea and hexamine crystals using different values of R_{min} are summarized in Table 4. The absolute value of $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ for the urea crystal increases gradually with increasing R_{min} . The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value for $R_{\text{min}} = 10$ Å was −22.4 kcal/mol, where the interactions with 128 neighboring urea molecules were calculated by the MP2 method. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value for $R_{\text{min}} = 3$ Å was −21.5 kcal/mol, where the interactions with 10 neighboring urea molecules were calculated by the MP2 method. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value obtained by the MP2 calculations of the interactions with the nearest 10 urea molecules is very close to that obtained by the MP2 calculations of the interactions with the 128 neighboring urea molecules: the difference is only 4%. The change in R_{min} has larger effects on the $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ values for the hexamine crystal. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value for $R_{\text{min}} = 10$ Å was −21.2 kcal/mol, where the interactions with 64 neighboring hexamine molecules were calculated by the MP2 method. The $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value for $R_{\text{min}} = 3$ Å was −18.0 kcal/mol, where the interactions with 14 neighboring hexamine molecules were calculated by the MP2 method. Although the dispersion interaction is mainly responsible for the attraction in the hexamine crystal, the $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value obtained by the MP2 calculations of the interactions with the nearest 14 molecules is not significantly different from that obtained by the MP2 calculations of the interactions with the 64 neighboring hexamine molecules. The difference is 15%. These results show that the MP2 calculations of the interactions with the nearest-neighboring molecules ($R_{\text{min}} = 3$ Å) has paramount importance for an accurate evaluation of the dispersion contributions to the lattice energy. MP2 calculations of the interactions with larger numbers of neighboring molecules are not necessary if one does

not need very accurate lattice energies. Although the expansion of R_{min} from 3 to 10 Å changes the $E_{\text{lattice}}(\text{DFT}+\text{MP2})$ value for hexamine crystal by 3.2 kcal/mol, the expansion increases the cost of the MP2 calculations by about a factor of 4.

Conclusions

This article presents a method for the accurate evaluation of the lattice energies of molecular crystals. The proposed approach aims to accurately evaluate the dispersion interactions with the neighboring molecules, the electrostatic interactions with the well-separated molecules, and the contribution of many-body effects (hydrogen-bond cooperativity) in the larger molecular crystals without highly computationally demanding calculations. The lattice energies for the crystals of urea and hexamine were calculated in an effort to evaluate the performance of the proposed method for the calculations of hydrogen-bonded crystals and dispersion-bound crystals. The sublimation enthalpies calculated for the two crystals are close to the experimental values. The MP2 calculations of the interactions with the neighboring molecules change the calculated lattice energies of the two crystals significantly, which shows that the dispersion interactions are an important source of attraction even in the hydrogen-bonded crystals. Our calculations show that the interactions with the nearest-neighboring molecules make an important contribution to the attraction.

Acknowledgment. We thank the Tsukuba Advanced Computing Center for the provision of the computational facilities.

Supporting Information Available: Geometries of the nearest urea and hexamine molecules in the crystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Fogassy, E.; Nogradi, M.; Kozma, D.; Egri, G.; Palovics, E.; Kiss, V. *Org. Biomol. Chem.* **2006**, *4*, 3011.
- (2) Karamertzanis, P. G.; Anandamanoharan, P. R.; Fernandes, P.; Cains, P. W.; Vickers, M.; Tocher, D. A.; Florence, A. J.; Price, S. L. *J. Phys. Chem. B* **2007**, *111*, 5326.
- (3) Gourlay, M. D.; Kendrick, J.; Leusen, F. J. J. *Cryst. Growth Des.* **2007**, *7*, 56.
- (4) Price, S. L. *Adv. Drug Delivery Rev.* **2004**, *56*, 301.
- (5) Evans, O. R.; Lin, W. B. *Acc. Chem. Res.* **2002**, *35*, 511.
- (6) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91.
- (7) Kwon, O.-P.; Ruiz, B.; Chouby, A.; Mutter, L.; Schneider, A.; Jazbinsek, M.; Gramlich, V.; Gunter, P. *Chem. Mater.* **2006**, *18*, 4049.
- (8) Day, G. M.; Price, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 16434.
- (9) Day, G. M.; Chisholm, J.; Shan, N.; Motherwell, W. D. S.; Jones, W. *Cryst. Growth. Des.* **2004**, *4*, 1327.
- (10) Dunitz, J. D.; Gavezzotti, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1766.
- (11) Dunitz, J. D.; Gavezzotti, A. *Cryst. Growth Des.* **2005**, *5*, 2180.
- (12) Welch, G. W. A.; Karamertzanis, P. G.; Misquitta, A. J.; Stone, A. J.; Price, S. L. *J. Chem. Theory Comput.* **2008**, *4*, 522.
- (13) Asmadi, A.; Neumann, M. A.; Kendrick, J.; Girard, P.; Perrin, M.-A.; Leusen, F. J. J. *J. Phys. Chem. B* **2009**, *113*, 16303.
- (14) Day, G. M.; Cooper, T. G.; Cruz-Cabeza, A. J.; Hejczyk, K. E.; Ammon, H. L.; Boerrigter, S. X. M.; Tan, J. S.; Valle, R. G. D.; Venuti, E.; Jose, J.; Gadre, S. R.; Desiraju, G. R.; Thakur, T. S.; van Eijck, B. P.; Facelli, J. C.; Bazterra, V. E.; Ferraro, M. B.; Hofmann, D. W. M.; Neumann, M. A.; Leusen, F. J. J.; Kendrick, J.; Price, S. L.; Misquitta, A. J.; Karamertzanis, P. G.; Welch, G. W. A.; Scheraga, H. A.; Arnautova, Y. A.; Schmidt, M. U.; van de Streek, J.; Wolf, A. K.; Schweizer, B. *Acta Crystallogr. B* **2009**, *65*, 107.
- (15) Dan C. Sorescu, D. C.; Boatz, J. A.; Thompson, D. L. *J. Phys. Chem. A* **2001**, *105*, 5010.
- (16) Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639.
- (17) Morrison, C. A.; Siddick, M. M. *Chem.—Eur. J.* **2003**, *9*, 628.
- (18) Fortes, A. D.; Brodholt, J. P.; Wood, I. G.; Voadlo, L. *J. Chem. Phys.* **2003**, *118*, 5987.

- (19) Ju, X.-H.; Xiao, H.-M.; Chen, L.-T. *Int. J. Quantum Chem.* **2005**, *102*, 224.
- (20) Rivera, S. A.; Allis, D. G.; Hudson, B. S. *Cryst. Growth Des.* **2008**, *8*, 3905.
- (21) Lo Presti, L.; Ellern, A.; Destro, R.; Lunelli, B. *J. Phys. Chem. A* **2009**, *113*, 3186.
- (22) Hobza, P.; Spooner, J.; Reschel, T. *J. Comput. Chem.* **1995**, *16*, 1315.
- (23) Meijer, E. J.; Sprik, M. *J. Chem. Phys.* **1996**, *105*, 8684.
- (24) Tsuzuki, S.; Luthi, H. P. *J. Chem. Phys.* **2001**, *114*, 3949.
- (25) Stone, A. J.; Tsuzuki, S. *J. Phys. Chem. B* **1997**, *101*, 10178.
- (26) Civalleri, B.; Doll, K.; Zicovich-Wilson, C. M. *J. Phys. Chem. B* **2007**, *111*, 26.
- (27) Chickos, J. S.; Acree, W. E. A., Jr. *J. Phys. Chem. Ref. Data* **2002**, *31*, 537.
- (28) Suzuki, K.; Onishi, S.; Koide, T.; Seki, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 127.
- (29) Ritter Sutter, J. Ph.D. Thesis, Tulane University, New Orleans, LA, 1959.
- (30) De Wit, H. G. M.; Van Miltenburg, J. C.; De Kruif, C. G. *J. Chem. Thermodyn.* **1983**, *15*, 651.
- (31) Trimble, L. E.; Voorhoeve, R. J. *J. Analyst* **1978**, *103*, 759.
- (32) Ferro, D.; Barone, G.; Gatta, G. D.; Piacente, V. *J. Chem. Thermodyn.* **1987**, *19*, 915.
- (33) Neumann, M. A.; Perrin, M.-A. *J. Phys. Chem. B* **2005**, *109*, 15531.
- (34) Feng, S.; Li, T. *J. Chem. Theor. Comput.* **2006**, *2*, 149.
- (35) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. *Cryst. Eng. Commun.* **2008**, *10*, 405.
- (36) The MP2-level interaction energy is not always close to the CCSD(T)-level interaction energy.^{24,37} For example, the MP2 calculations overestimate the attraction between aromatic molecules compared with the CCSD(T) calculations. However, the MP2-level interaction energies for many molecular clusters (hydrogen-bonded clusters and saturated hydrocarbon dimers) are close to the CCSD(T) values.²⁴
- (37) Tkatchenko, A.; DiStasio, R. A., Jr.; Head-Gordon, M.; Sheffler, M. *J. Chem. Phys.* **2009**, *131*, 094106.
- (38) Alfredsson, M.; Ojamae, L.; Hermansson, K. G. *Int. J. Quantum Chem.* **1996**, *60*, 767.
- (39) Ikeda, T.; Nagayoshi, K.; Kitaura, K. *Chem. Phys. Lett.* **2003**, *370*, 218.
- (40) Ringer, A. L.; Sherrill, C. D. *Chem.—Eur. J.* **2008**, *14*, 2542.
- (41) Podeszwa, R.; Rice, B. M.; Szalewicz, K. *Phys. Rev. Lett.* **2008**, *101*, 115503.
- (42) The dipole moments of organic molecules obtained by DFT calculations using a basis set with polarization functions are close to the experimental values. This shows that the electrostatic interactions with well-separated molecules calculated by the DFT method do not have large errors.
- (43) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.
- (44) Delley, B. *J. Phys. Chem.* **1996**, *100*, 6106.
- (45) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.
- (46) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (47) Swaminathan, S.; Craven, B. M.; McMullan, R. K. *Acta Crystallogr. B* **1984**, *40*, 300.
- (48) Kampermann, S. P.; Sabine, T. M.; Craven, B. M.; McMullan, R. K. *Acta Crystallogr. A* **1995**, *51*, 489.
- (49) The lattice parameters for urea crystal were taken from experimental measurements at 12 K. Those for hexamine crystal were taken from experimental measurements at 15 K.
- (50) The interaction energy between the nearest urea molecules in the crystal (Figure 1S, Supporting Information) were calculated using the aug-cc-pVTZ basis set. The HF- and MP2-level interaction energies calculated for the dimer using the optimized geometry of the crystal by periodic DFT calculations are -8.87 and -10.76 kcal/mol, respectively. Those obtained using the crystal structure are -8.65 and -10.47 kcal/mol. The geometry optimization increases the attraction calculated at the HF and MP2 levels only slightly (by -0.22 and -0.29 kcal/mol, respectively). The electron correlation contribution to the interaction energy (the difference between the MP2- and HF-level interaction energies, which is mainly dispersion energy) obtained using the optimized geometry (-1.89 kcal/mol) is close to that obtained using the crystal structure (-1.82 kcal/mol). The effects of geometry optimization on the calculated interaction energies between urea molecules are not large. Probably, the very accurate hydrogen atom positions in the crystal reported from the neutron diffraction measurements are the cause of the negligible effects of the geometry optimization. However, it is well known that accurate determination of the positions of hydrogen nuclei by XRD is extremely difficult, and consequently, the positions of the hydrogen atoms in an XRD structure often have large errors. The geometry optimization of the position of atoms in the unit cell often changes the hydrogen-bonding energy significantly. Our previous study on the intermolecular interactions between α -(trifluoromethyl)lactic acid in the crystal showed that the hydrogen-bonding energy between the nearest molecules in the crystal calculated using the XRD structure (-5.03 kcal/mol) is significantly smaller (less negative) than that calculated using the optimized geometry (-8.37 kcal/mol).⁵¹ The calculations showed that the geometry of crystal must be optimized with great care, if one wants to evaluate the lattice energy of the crystal accurately.
- (51) Tsuzuki, S.; Orita, H.; Ueki, H.; Soloshonok, V. A. *J. Fluorine Chem.* **2010**, *131*, 461.
- (52) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (53) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.
- (54) The most computationally demanding step of the proposed method is the MP2 calculations of the interaction energies with the neighboring molecules. The MP2/aug-cc-pVTZ-level calculation of the interaction energy of a hexamine dimer requires a few days using a four-core xeon computer. We needed to calculate the interaction energies for six dimers because of the symmetry of the hexamine crystal, when we evaluated the interactions with neighboring molecules ($R_{\text{min}} = 10$ Å). The MP2-level interaction energy at the basis-set limit can be estimated by an extrapolation from the MP2-level interaction energies calculated using the cc-pVDZ and cc-pVTZ basis sets.⁵⁵ The MP2/cc-pVTZ-level calculation of a hexamine dimer requires a few hours using the same computer. The computational time required for the calculation of the interaction energy of a urea dimer is much lower than that for the calculation of the hexamine dimer.
- (55) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. *J. Chem. Phys.* **2006**, *124*, 114304.
- (56) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (57) Ransil, B. J. *J. Chem. Phys.* **1961**, *34*, 2109.
- (58) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (59) Various different correction models have been discussed in the literature;²⁷ 2RT is only one possibility. We could apply other models, such as 6RT. The values of 2RT and 6RT are 1.2 and 3.6 kcal/mol, respectively, at 298 K. The difference is as much as 2.4 kcal/mol. This shows that the calculated sublimation enthalpy has an error (about 2 kcal/mol) associated with the choice of correction model. Several experimental values have been reported for the sublimation enthalpy of urea crystal (20.9–23.6 kcal/mol). The deviations of the experimental values are larger than the error associated with the correction model. Therefore, we believe that the choice of the correction model is not a serious problem in comparing the calculated sublimation enthalpy of the urea crystal with experimental values. It can be concluded that the calculated sublimation enthalpy of urea agrees with the experimental value within the experimental error. On the other hand, the experimental sublimation enthalpies of hexamine crystal (17.7–18.8 kcal/mol) have smaller deviations. Therefore, the choice of correction model is more important in this case. The sublimation enthalpy calculated for hexamine crystal is 17.8 kcal/mol, if 6RT is used for the correction. This value is closer to the experimental values than that obtained using 2RT (20.0 kcal/mol). The 6RT correction model might be better than the 2RT correction model in this case.
- (60) Dovesi, R.; Causa, M.; Orlando, R.; Roetti, C.; Saunders, V. R. *J. Chem. Phys.* **1990**, *92*, 7402.
- (61) Ayala, P. Y.; Scuseria, G. E. *J. Comput. Chem.* **2000**, *21*, 1524.
- (62) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski, J. *J. Chem. Phys.* **2002**, *117*, 1031.
- (63) Klipping, V. G.; Stranski, I. N. *Z. Anorg. Allg. Chem.* **1958**, *297*, 23.
- (64) Budurov, S. *Izv. Khim. Inst. Bulg. Akad. Nauk* **1960**, *7*, 281.
- (65) Wada, T.; Kishida, E.; Tomiie, Y.; Suga, H.; Seki, S.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1317.
- (66) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
- (67) The lattice energy for the urea crystal was also calculated using the DNP basis set. The $E_{\text{lattice(DFT+MP2)}}$ value calculated for the crystal (-23.4 kcal/mol) was close to that calculated using the TNP basis set.
- (68) $E_{\text{lattice(DFT)}}$ was calculated by subtracting the energy of the fully optimized geometry of an isolated molecule from the energy of a unit cell per molecule. The mixing of rotamers can contribute to the average enthalpy of an isolated molecule if the molecule has large conformational flexibility. This effect was not considered in this work, because urea and hexamine are rigid molecules. The lattice energy calculation does not include the

contributions of vibrational states, phonons, and other terms. These terms might be the sources of the errors of calculated lattice energies.

(69) Dunning, T. H., Jr. *J. Phys. Chem. A* **2000**, *104*, 9062.

(70) The interaction energies between the nearest urea molecules in the crystal (Figure 1S, Supporting Information) calculated by the MP2 method using the 6-31G*, 6-311G*, 6-311G**, cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ basis sets are -9.47, -9.25, -9.14, -8.67, -9.98, and -10.18 kcal/mol, respectively. These values are close to those calculated by the CCSD(T)

method using the same basis sets (-9.43, -9.25, -9.20, -8.70, -10.04, and -10.27 kcal/mol, respectively). The interaction energies between the nearest hexamine molecules in the crystal (Figure 2S, Supporting Information) calculated by the MP2 and CCSD(T) methods using the 6-31G* basis set are -2.38 and -2.13 kcal/mol, respectively.

JP912028Q