

Predicting Lattice Energy of Organic Crystals by Density Functional Theory with Empirically Corrected Dispersion Energy

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Abstract: Calculation of the lattice energy of organic crystals is needed for predicting important structural and physicochemical properties such as polymorphism and growth morphology. Quantum mechanical methods that can be used for calculating typical organic crystals are unable to fully estimate van der Waals energies in a crystal. A method by augmenting the density functional theory with an analytical, nonelectronic approach for accounting for the dispersion energy was tested for selected organic crystals. The results illustrate the feasibility of this method for the prediction of the lattice energy of organic crystals. It is also shown that the dispersion energy is a dominant component of the lattice energy, particularly for those organic crystals that have no hydrogen bonds.

Introduction

Organic or molecular crystals play a central role in the pharmaceutical and fine chemical industry. Their structures and particulate properties greatly affect the handling and processing of materials and considerably control the performance of final products.¹ Because of the relatively weak intermolecular interactions, organic crystals are susceptible to the formation of polymorphs due to a change or disruption in the crystal growth environment.² Solvents, additives, impurities, supersaturation, and temperature are among key factors that affect how organic molecules pack in the solid state. Crystal packing of the same molecules may vary dramatically, resulting in different physical and chemical properties. Lattice energies of different polymorphs, however, can have similar values, making the prediction a very challenging task.³ Consequently, calculation of the lattice energy not only offers a possible way for polymorph prediction but may also help understand the supramolecular chemistry and self-assembly during the nucleation and crystal growth processes.

A few methods can be used for calculating the lattice energy of molecular crystals. One often used is molecular

mechanics based upon empirical force fields, which are constituted by a set of analytical equations using the positions and types of atoms as well as their bonding information for estimating interatomic interactions with the help of empirical parameters. Many have been developed for small molecules and biomolecules, such as Amber⁴ and Dreiding.⁵ Several potential models have been developed for periodic systems.⁶ Nonetheless, being a totally empirical method, a force field has inherited difficulties for providing reliable energy estimations, especially for those structures that vary greatly from those used to develop the force field. Because the lattice energy of molecular crystals is relatively small, in particular, the difference between polymorphs can be as small as 2 kJ/mol,² or even smaller, which is beyond the typical accuracy of force-field based methods, calculating the lattice energy with force fields alone may pose a significant challenge for the polymorph prediction.

Quantum mechanical methods, on the other hand, may be capable of producing highly accurate energy estimations for a molecular system. However, one of the biggest challenges for calculating organic crystals in practice stems from the difficulty of fully considering the long-range van der Waals (vdW) energy.^{7–9} As a quantum-mechanical phenomenon, vdW energies indicate mutually induced or correlated motions of electrons by the Coulomb interactions between atoms, even when the atoms are distantly apart.⁷ The Hartree–Fock (HF) theory considers no such correlation

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energies; the density functional theory (DFT),^{10–12} in principle, gives the exact description of ground-state energy, including the vdW energy. However, practical implementations relying on estimation strategies for the exchange-correlation functionals, including local density approximation (LDA)¹¹ and generalized gradient approximation (GGA),^{13–15} cannot satisfyingly predict the vdW energies.⁸ Using localized electron densities or their gradients fails to reproduce the physics of vdW interactions at large separations between atoms where there is little or no overlap of their electron densities. Higher-level quantum mechanical theories, such as MP2 (second-order Møller–Plesset perturbation theory¹⁶), are able to do a better job in considering the vdW energies, but they are very computationally demanding, making their applications for organic crystals impractical (except for a few simple crystal systems, such as C₂H₂ and CH₃OH^{17,18}).

There have been many efforts for improving the quantum mechanical methods to account for the long-range vdW energies, including the introduction of vdW functionals to the traditional DFT methods.^{7,19} One interesting approach among the efforts for the practical calculation of intermolecular interactions is to augment the HF and DFT methods with analytical models of vdW potentials parametrized empirically, in a similar way as those being used in molecular mechanics.²⁰ The augmentation, not part of the electronic calculations and only based on positions and types of nuclei, accommodates the quantum mechanical methods posteriorly through the adjustment of the empirical vdW models. It was applied to the HF^{21–23} and recently to the DFT.⁹ It appears to be a practical and flexible approach for considering the vdW energies at large interatomic distances but to damp or tune down at small distances where the HF or DFT takes over and can carry out reliable calculations of intermolecular energies.

Because the London dispersion force is a major, universal contributor to the vdW force,²⁴ dispersion energy is often equally quoted as the long-range vdW energy. It is argued, however, that the vdW interactions also include the Keesom force (due to the orientation effect between permanent dipoles) and the Debye force (due to the induction effect between a permanent dipole and an induced dipole),²⁴ which may be trivial as compared to the dispersion force. For our purpose to study the lattice energies of organic crystals, we will use the two concepts, dispersion energy and long-range (attractive) vdW energy, exchangeably.²⁵ As the lattice energy of an organic crystal consists of short-range, electrostatic, induction (polarization), and dispersion energies,²⁶ the dispersion energy is believed to be significant, especially for crystals with no hydrogen bonds present. In this study, we present calculation results of lattice energies of selected organic crystals by using the empirically augmented DFT method and discuss possible future improvements.

Methodology

Lattice energy, E_{latt} , of an organic crystal is the energy difference between the bulk crystal, E_{xtal} , and isolated molecule, E_{mol} , of the same compound:

$$E_{\text{latt}} = E_{\text{xtal}} - E_{\text{mol}} \quad (1)$$

It is the energy requirement for vaporizing a crystal, representing the cohesive or intermolecular interactions in the solid state. Negative values of lattice energy indicate attractive intermolecular interactions of a crystal. Conversely, positive values indicate repulsive interactions. The calculation of lattice energy of selected organic crystals was carried out in two separated steps. Nondispersive energies were calculated by DFT first, followed by estimation of the dispersion energy with an empirical method.

For selected organic crystals, their crystal structures were obtained from Cambridge Structural Database.²⁷ Single-point energy calculations were conducted with DFT after the structural optimization where lattice parameters were kept the same as experimental values, while the system energy was minimized with respect to the fractional coordinates of atoms. DFT with B3LYP exchange-correlation functional^{13,28} was used for the structural optimization and energy calculation. When calculating the energy, the basis set superposition error (BSSE)²⁹ was considered by the counterpoise method.³⁰ Fifty ghost atoms were typically placed around each atom within 5 Å in order to obtain acceptable BSSE corrections. Furthermore, the single molecule of each compound was optimized independently with the DFT-B3LYP method so that the possible energy reduction due to conformational change of the molecule from the solid state to the gas phase could be considered. The effect of basis sets was studied as well. A periodic ab initio program, Crystal 03,³¹ was used for the optimization and single-point electronic calculations. The energy convergence of the structural optimizations and single-point electronic calculations was set as 10^{-7} Hartree. The root-mean-squares (RMS) of energy gradient and atomic displacement were set to 0.0003 and 0.0012 atomic units, respectively. All calculations were performed on a 16-CPU Linux cluster.

The dispersion energy between a pair of atoms at long range can be evaluated by a power series of the interatomic distance, R ²⁶

$$E_{\text{disp}}(R) = - \sum_{n=6}^{\infty} C_n R^{-n} \quad (2)$$

where n are even numbers, and C_n are dispersion coefficients. The first term, $C_6 R^{-6}$, is the dominant contribution, representing the instantaneous dipole-instantaneous dipole interaction,⁸ and is often used in practice as the only term of dispersion energy. The subsequent terms ($C_8 R^{-8}$, $C_{10} R^{-10}$, etc.) are attributed to interactions between higher-order fluctuating multipole moments.

To preserve the true nature of dispersion energy that is not infinite at $R = 0$, a damping function is often used to correct the power series in eq 2 for calculating the dispersion energy.²⁶ A general form of the damping functions remains one at long range and decays to zero when $R = 0$. Various types of damping functions have been reported.^{9,21,23,32,33} In this study, the form of dispersion energy is given by

$$E_{\text{disp}}(R) = -f_d(R)C_6 R^{-6} \quad (3)$$

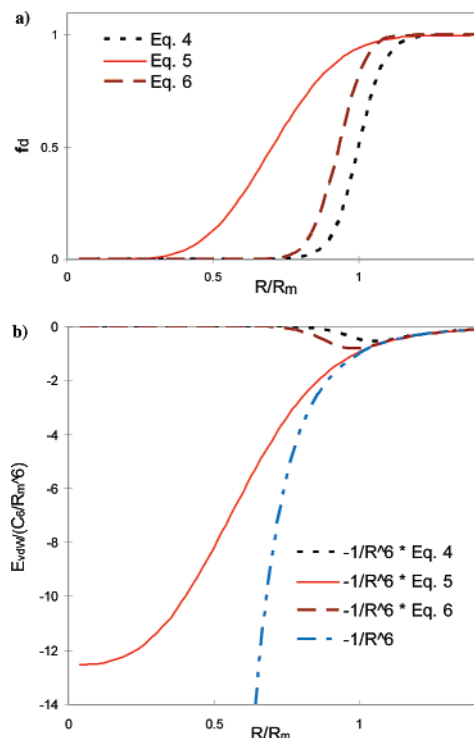


Figure 1. Plots of the three damping functions (a) and their influences on the van der Waals interaction (b).

where the damping function, $f_d(R)$, may take the following forms⁹

$$f_d(R) = \frac{1}{1 + \exp\left[-D_1\left(\frac{R}{R_m} - 1\right)\right]} \quad (4)$$

$$f_d(R) = \left(1 - \exp\left[-D_2\left(\frac{R}{R_m}\right)^3\right]\right)^2 \quad (5)$$

where R_m is the damping radius, taken as the sum of atomic van der Waals radii³⁴ of the pair of atoms. The coefficients, D_1 and D_2 , are associated with the quality of the damping functions; they were assigned to 23.0 and 3.54, respectively, by Wu and Yang.⁹ Eq 5 was used by Mooij et al as well but with D_2 as 7.19.³⁵ Other formats of damping functions include one by Elstner et al³³

$$f_d(R) = \left(1 - \exp\left[-D_3\left(\frac{R}{R_m}\right)^7\right]\right)^4 \quad (6)$$

where D_3 was assigned as 3.0. These three damping functions are shown in Figure 1, along with their effects on a general C_6R^{-6} term. It appears that the damping strength by eq 6 is between those by eqs 4 and 5 with eq 4 being the strongest. All these functions were tested in this study.

Accurate values of intermolecular C_6 coefficients can be obtained experimentally from the dipole oscillator strength distributions^{36,37} or computationally from the frequency-dependent polarizabilities.^{38,39} It is not a trivial task, however, to decompose the intermolecular C_6 coefficients into interatomic C_6 coefficients. Most often, interatomic C_6 coefficients are produced by data fitting, either directly to intermolecular C_6 coefficients⁹ or indirectly to molecular

polarizabilities.^{20,40} In this study, the interatomic C_6 coefficients reported by Wu and Yang were used without modification in our calculations of dispersion energies. In their method,⁹ interatomic C_6 coefficients were obtained by least-squares fitting to intermolecular C_6 coefficients that were accurately determined experimentally.^{36,37} It was assumed that an intermolecular coefficient was the additive sum of interatomic coefficients of all atom pairs of the molecules. It was also assumed that different molecules could use the same set of atomic C_6 coefficients. Their tests of evaluating molecular pairs indicated that the interatomic C_6 coefficients developed in their study were able to produce satisfying results for augmenting the DFT method. Nonetheless, it is argued that these empirically derived interatomic dispersion coefficients, generalized over atom types, may be limited and inflexible in dealing with other systems in which the molecular environment is greatly varied from the training sets.⁴¹

In this study, dispersion energies of bulk crystals were evaluated atom–atom pairwisely with eq 3. The cutoff distance for considering an atom pair was set to 25 Å, which only had a difference of 0.01 kJ/mol or less when compared to energy values calculated without any cutoff. Urea and benzene were used for evaluating the effects of basis sets, BSSE, and conformational change of molecules between the crystal and gas phase. Thirty-three organic crystals were selected for testing the method. Experimentally determined sublimation enthalpies of these compounds available in the literature were used for providing experimental estimates of calculated lattice energies. Sublimation enthalpy, $\Delta H_{\text{sub}}(T)$, and lattice energy, E_{latt} , are related to each other by the following equation

$$\Delta H_{\text{sub}}(T) = -E_{\text{latt}} - E_0 + \int_0^T \Delta C_p dT \quad (7)$$

where T is the temperature at which the sublimation enthalpy is measured, E_0 is the zero-point energy, and ΔC_p is the difference in heat capacity between the gas and solid phases. As the sublimation enthalpy of a crystal is typically determined from its vapor pressures at different temperatures, using the above equation to derive the lattice energy is practically difficult. ΔC_p is temperature-dependent; the heat capacity of solids is very small at low temperature, requiring more than routine instrumental methods. The equation implies that the lattice energy is a quantity determined at the absolute zero, disregarding the thermal contributions. By ignoring the zero-point energy (normally less than 1% of E_{latt} ⁴²) as well as making assumptions that the gas phase is ideal and contributions from intramolecular vibrations are equal in the solid and gas phases, an approximation form to derive lattice energy from sublimation enthalpy is given by⁴³

$$\Delta H_{\text{sub}}(T) = -E_{\text{latt}} - 2RT \quad (8)$$

where R is the gas constant. In this study, experimental values of lattice energies were estimated by the above equation from literature data of sublimation enthalpies.

Results and Discussion

Using the DFT-B3LYP/6-31G** method, the lattice energy of urea was calculated as −95.14 kJ/mol. The conformational

change alone of urea from the crystal to gas phase accounted for 20.09 kJ/mol. The symmetry, C_{2v} , of urea in the solid state was reduced to C_2 during the optimization of the single molecule, the most stable conformer in the gas phase.⁴⁴ If the symmetry was kept, the energy contribution of the conformational change was 12.88 kJ/mol instead. Therefore, full optimization of single molecules in the gas phase seems to be essential and was carried out for other crystals as well in this report. The BSSE that was associated with DFT-B3LYP/6-31G** was estimated with 94 ghost atoms as 32.00 kJ/mol. After considering the BSSE, the lattice energy of urea calculated by DFT was -63.14 kJ/mol. Furthermore, based on the optimized urea crystal structure, dispersion energies were calculated by eq 3 with the three damping functions defined by eqs 4–6 as -39.03, -57.09, and -43.30 kJ/mol, respectively. Added together from values calculated by DFT and each of the three analytical methods, lattice energies were -102.17, -120.23, and -106.44 kJ/mol. The experimental value of sublimation enthalpy of urea was reported as 98.6 kJ/mol,⁴⁵ leading to its lattice energy estimated by eq 8 as -103.6 kJ/mol. The calculation results of the lattice energies appear to be acceptable, particularly using the dispersion energies calculated by the damping functions, eqs 4 and 6. More importantly, it is clearly indicated that the lattice energy calculated by DFT alone is greatly underestimated. In the case of urea, the dispersion energy accounts for about 40% of the total lattice energy.

The effect of basis sets was studied with urea and benzene. Lattice energies of urea calculated by DFT-B3LYP with 6-21G, 6-21G**, 6-31G, 6-31G**, 6-311G, and 6-311G** after BSSE corrections of 86.72, 88.41, 34.92, 32.00, 27.64, and 28.69 kJ/mol were -79.50, -54.96, -80.88, -63.14, -81.24, and -59.54 kJ/mol, respectively. The absolute values of nondispersive energies were significantly smaller by the polarized basis sets (6-21G**, 6-31G**, and 6-311G**) than those by the nonpolarized basis sets (6-21G, 6-31G, and 6-311G). This resulted in the fact that the polarized basis sets had the total energy of the single molecule decreased more than that of the crystal. The less sensitive effect by the Gaussian type basis sets on the energies of periodic systems stems from the “real” basis sets used in the calculation being Bloch functions, which have the periodicity of the crystal lattice and have their “local” functions built up with linear combinations of the Gaussian type basis sets. For the same reason, extended basis sets with diffuse orbitals can cause numerical instabilities and are suggested not to be used. Moreover, lattice energies of benzene calculated with 6-21G, 6-21G**, 6-31G, 6-31G**, 6-311G, and 6-311G** after BSSE corrections of 27.33, 28.26, 18.15, 18.93, 9.02, and 8.45 kJ/mol were 13.78, 13.83, 16.26, 15.47, 17.43, and 16.41 kJ/mol, respectively. Positive values imply repulsive intermolecular interactions (without the consideration of dispersion energy). Polarized basis sets gave similar energy values and trend lines as those by nonpolarized basis sets, likely due to the nonpolar feature of the benzene molecule. It is interesting to note that the HF/6-21G** and HF/6-31G** gave smaller BSSE values of urea and benzene than ours.⁴⁶ Balancing the accuracy and computing time,

therefore, the 6-21G** basis set was used for the calculations of other organic crystals.

Table 1 lists the results of lattice energies of 33 organic crystals, including nondispersive energies calculated by DFT-B3LYP/6-21G** with the BSSE correction, dispersion energies by the three damping functions, and experimental values of sublimation enthalpy and derived lattice energy data. The reference codes of the crystals and the temperatures under which crystals structures were determined are listed in Table 2. Dispersion energies calculated with the damping function, eq 6, produced absolute values between larger ones by eq 5 and smaller ones by eq 4 and gave the closest lattice energies to experimentally derived data. From the percentage in the lattice energies, the dispersion energies are a major component of intermolecular interactions of the organic crystals. Cyanamide in Table 1 has the smallest value, 42%, which is already a significant number. Most crystals that have hydrogen bonds have the dispersion energy between 40 and 65% of their lattice energies. The percentage is significantly higher for crystals that have no hydrogen bonds between their molecules in crystal. For those crystals whose percentages of dispersion energy are more than 100%, their nondispersive energies ($E_{\text{DFT}} + \text{BSSE}$) are positive, meaning that the conformation of individual molecules in the crystals is likely to be energy-unfavorable due to close contacts. It can be further noticed that the crystals that have positive or very absolutely small nondispersive energies have no hydrogen bonds. The integrity of the crystals is likely to be kept solely by the dispersion energy. It should be noted that the optimization of crystal structures was carried out without the consideration of dispersion energy; it was done purely based on nondispersive energies. It is believed that the nondispersive energies calculated by DFT in an organic crystal are responsible for the conformation of individual molecules, while the dispersion energy plays a key role in deciding the volume of unit cell, especially for a crystal that has no hydrogen bonding. In fact, compared to the system energy of a crystal calculated by DFT, the dispersion energy is trivial (e.g., the dispersion energy is about 3×10^{-5} of the total DFT energy of urea). It is very likely that the introduction of dispersion energy during the structural optimization of a crystal may have little influence on the fractional coordinates of atoms, but affect the lattice constants. Consequently, the lattice constants of a crystal were kept the same as the experimental values during optimizations. As shown in Table 2, the root-mean-square (RMS) values due to the optimization of atomic Cartesian coordinates of all crystals studied are small, indicating that the optimization method is sound and the exclusion of dispersion energy is acceptable. The major contribution to the RMS values appears to be a result of position changes of H atoms. This is not surprising since most X-ray diffraction measurements are not able to directly determine fractional coordinates of H atoms. Thus, it is thought that during the optimization, especially when the lattice parameters are kept constant and the space group is maintained, the close contacts or short-range interactions between atoms, not the long-range, collective van der Waals energy, play a more important role in determining the fractional coordinates of atoms. Still, the

Table 1. Calculated Energy Values of Selected Organic Crystals, Including Nondispersive (E_{DFT}), BSSE, Dispersion (E_{disp}), and Lattice Energies (E_{latt})^m

	E_{DFT}	BSSE	$E_{\text{DFT}} + \text{BSSE}$	E_{disp} (eq 4)	E_{disp} (eq 5)	E_{disp} (eq 6)	E_{latt} (eq 6)	ΔH_{sub}	E_{latt} (eq 8)
acetamide*	-120.90	80.76	-40.14	-40.26	-55.47	-44.66	-84.80	77.2 ^a	-82.2
anthracene	-13.41	49.37	35.96	-124.18	-137.65	-133.44	-97.48	103.4 ^b	-108.4
benzene	-14.43	28.26	13.83	-58.10	-65.88	-63.63	-49.80	44.4 ^c	-49.4
1,2-benzene-dicarbonitrile	-61.19	57.09	-4.10	-71.42	-81.56	-77.28	-81.38	86.9 ^d	-91.9
benzoic acid*	-91.54	81.58	-9.96	-75.11	-94.67	-82.14	-92.10	89.7 ^b	-94.7
1,1'-biphenylene	-11.91	37.46	25.55	-99.31	-109.66	-107.07	-81.52	87.3 ^e	-92.3
chrysene	-21.12	51.57	30.45	-142.72	-154.25	-152.21	-121.76	118.8 ^f	-125.2
cyanamide*	-92.96	44.64	-48.32	-31.14	-44.17	-34.80	-83.12	75.2 ^a	-80.2
cyanacetamide*	-134.22	77.31	-56.91	-51.77	-68.45	-57.65	-114.56	100.4 ^a	-105.4
cyanuric acid*	-173.77	114.35	-59.42	-64.11	-92.07	-72.24	-131.66	133.6 ^a	-138.6
cyclohexane	3.51	22.97	26.48	-69.76	-75.00	-73.94	-47.46	46.6 ^g	-49.7
1,4-cyclohexanedione	-100.78	100.46	-0.32	-67.61	-83.67	-75.47	-75.79	84.2 ^a	-89.2
dicyanodiamide*	-154.66	75.28	-79.38	-56.77	-77.43	-62.71	-142.09	129.3 ^a	-134.3
diglycolid anhydride	-105.44	86.08	-19.36	-53.10	-65.49	-59.49	-78.85	84.0 ^a	-89.0
1,3-dinitrobenzene	-93.80	97.33	3.53	-79.93	-94.23	-88.07	-84.54	81.2 ^h	-86.2
formamide*	-116.11	73.99	-42.12	-29.84	-44.52	-33.82	-75.94	71.7 ^a	-76.7
furan 2,5-dicarboxylic acid*	-193.45	132.16	-61.29	-78.19	-104.11	-85.57	-146.86	125.7 ^a	-130.7
imidazole*	-85.31	45.70	-39.61	-48.74	-61.27	-53.35	-92.96	80.8 ^a	-85.8
maleic anhydride	-74.79	66.17	-8.62	-45.65	-55.30	-51.47	-60.09	68.1 ^a	-73.1
naphthalene	-9.93	40.46	30.53	-93.81	-105.01	-102.10	-71.57	72.6 ^b	-77.6
propanoic acid*	-93.03	69.96	-23.07	-44.36	-56.87	-47.88	-70.95	74.0 ⁱ	-77.8
pyrazine	-54.78	55.12	0.34	-53.64	-62.16	-57.77	-57.43	56.2 ^j	-61.2
pyrazole*	-70.62	41.89	-28.73	-48.04	-62.69	-54.10	-82.83	71.7 ^a	-76.7
squaric acid*	-198.30	117.19	-81.11	-55.49	-84.42	-64.20	-145.31	154.3 ^a	-159.3
succinic acid*	-190.66	143.71	-46.95	-69.98	-94.98	-77.68	-124.63	123.1 ^a	-128.1
succinic anhydride	-101.02	89.29	-11.73	-51.99	-68.04	-59.74	-71.47	82.3 ^a	-87.3
tetracyanomethane	-62.32	56.69	-5.63	-42.76	-68.16	-52.73	-58.36	61.1 ^k	-66.1
1,3,5-triazine	-55.40	54.73	-0.67	-48.39	-54.00	-52.26	-52.93	56.7 ^a	-61.7
2,4,5-trimethylbenzoic acid*	-83.38	69.69	-13.69	-92.41	-108.21	-97.75	-111.44	109.6 ^l	-114.6
1,3,5-trioxane	-100.73	99.22	-1.51	-49.96	-58.76	-55.07	-56.58	55.6 ^a	-60.6
urea	-95.14	32.00	-63.14	-39.03	-57.09	-43.30	-106.44	98.6 ^a	-103.6
urethane*	-108.71	77.40	-31.31	-49.82	-63.20	-53.72	-85.03	76.3 ^a	-81.3
utroproline	-75.43	86.95	11.52	-94.37	-101.64	-100.46	-88.94	79.0 ^a	-84.0

^a Reference 45. ^b Reference 48. ^c Reference 49. ^d Reference 50. ^e Reference 51. ^f Reference 52, $T = 383$ K. ^g Reference 53, $T = 186$ K. ^h Reference 54. ⁱ Reference 55, $T = 225$ – 238 K. ^j Reference 56. ^k Reference 57. ^l Reference 58. ^m E_{DFT} and BSSE were calculated with DFT-B3LYP/6-21G** except for urea which was calculated with 6-31G**. Crystals that have hydrogen bonds are marked with asterisks. Sublimation enthalpies (ΔH_{sub}) and derived lattice energies are also listed. Unless indicated otherwise, the sublimation enthalpies were measured at 298 K. Energy unit: kJ/mol.

full optimization by considering the dispersion energy is necessary for correcting the temperature effect on the lattice volume, since most X-ray structural determinations are typically carried out under ambient conditions or in the range of 100–200 K (Table 2).

The results of lattice energy are also plotted in Figure 2 along with experimental values. The correlation coefficient of the calculated and experimental data, r^2 , is 0.92, when eq 6 was used for calculating the dispersion energy. The coefficient became 0.79 or 0.87 if eq 4 or eq 5 was used, respectively. As shown in Figure 1, the damping function of eq 6 is not as quick as eq 4 to tune down the van der Waals interaction and is not as slow as eq 5 either when the interatomic distance decreases. The damping strength of such a function appears to be a key factor in controlling the quality of the calculation of dispersion energies. It can also be seen from Figure 2 that both crystals with and without hydrogen bonds have similar matching qualities to experimental values of the lattice energy. Crystals with hydrogen bonds may have better calculated lattice energies, except for three crystals

with the largest calculated values, furan 2,5-dicarboxylic acid, squaric acid, and dicyanodiamide, which also have the largest nondispersive energies. In addition, the majority of crystals without hydrogen bonds have their calculated lattice energies absolutely smaller than the experimental values, suggesting that the damping function, eq 6, may underestimate the dispersion energy. Consequently, the better match of crystals with hydrogen bonds to their experimental values implies that the DFT method (B3LYP/6-21G**) may overestimate the nondispersive energy, canceling out the error of dispersion energy by the damping function. Since the lattice energy accounts for the intermolecular interactions in a crystal (eq 1), the overestimation by DFT is likely due to the BSSE which may not reach the convergence because of ghost atoms being insufficient. This clearly needs to be considered in the future studies. Considering the fact that the DFT method used in this study may not be the best method and there is always a better one that can generally produce more accurate nondispersive energies, if a better DFT method is used for calculating the nondispersive energy, the damping function

Table 2. Reference Codes of the Calculated Crystals in the Cambridge Structural Database and Temperatures under Which the Crystal Structures Were Determined^a

	ref code	temp (K)	RMS (Å) (excluding H)	RMS (Å) (H only)	RMS (Å)
acetamide*	ACEMID05	23	0.142	0.195	0.174
anthracene	ANTCEN09	94	0.044	0.134	0.093
benzene	BENZEN01	138	0.197	0.373	0.298
1,2-benzene-dicarbonitrile	YUYPUD01	153	0.197	0.305	0.233
benzoic acid*	BENZAC07	20	0.134	0.169	0.149
1,1'-biphenylene	BIPHNE01	130	0.057	0.138	0.098
chrysene	CRYSEN	283–303	0.032	0.130	0.086
cyanamide*	CYANAM01	108	0.143	0.163	0.151
cyanoacetamide*	CYANAC	283–303	0.190	0.251	0.216
cyanuric acid*	CYURAC05	100	0.036	0.032	0.035
cyclohexane	CYCHEX	115	0.069	0.218	0.182
1,4-cyclohexanedione	CYHEXO	133	0.159	0.244	0.206
dicyanodiamide*	CYAMPD03	83	0.045	0.079	0.061
diglycolid anhydride	DLGYAH	283–303	0.174	0.206	0.185
1,3-dinitrobenzene	DNBENZ11	100	0.141	0.222	0.165
formamide*	FORMAM02	90	0.142	0.179	0.162
furan 2,5-dicarboxylic acid*	FURDCA	283–303	0.274	0.337	0.292
imidazole*	IMAZOL06	103	0.133	0.145	0.138
maleic anhydride	MLEICA01	130	0.163	0.269	0.191
naphthalene	NAPHTA15	100	0.086	0.142	0.114
propanoic acid*	PRONAC	178	0.168	0.344	0.278
pyrazine	PYRAZI01	184	0.035	0.208	0.134
pyrazole*	PYRZOL05	108	0.036	0.178	0.122
squaric acid*	KECYBU06	283–303	0.022	0.026	0.023
succinic acid*	SUCACB09	130	0.071	0.193	0.137
succinic anhydride	SUCANH12	100	0.265	0.251	0.260
tetracyanomethane	TCYETY11	283–303	0.283	N/A	0.283
1,3,5-triazine	TRIZIN02	283–303	0.024	0.066	0.043
2,4,5-trimethylbenzoic acid*	RUVQAA	283–303	0.116	0.200	0.164
1,3,5-trioxane	TROXAN11	103	0.039	0.128	0.095
urea	UREAXX02	148	0.025	0.046	0.037
urethane*	ECARBM01	168	0.136	0.287	0.230
urotropine	HXMTAM10	15	0.012	0.008	0.010

^a Root-mean-square (RMS) values of atomic Cartesian coordinates of each crystal due to the structural optimization are also listed. DFT-B3LYP/6-21G** was used for the optimization.

needs to be tailored with regard to diminishing the van der Waals potential than those used in this study. More suitable interatomic C_6 coefficients are also needed to be developed from various means. A recent report by Johnson and Becke suggested a general model for developing C_6 coefficients without the empirical fitting.⁴¹ Because of the empirical nature of calculating the dispersion energy as well as the lack of knowledge of the “true” value of the dispersion energy of an organic crystal, the coupling between the quantum mechanical and empirical methods for predicting the lattice energy will remain challenging, requiring significant experimental inputs.

Unfortunately, there are unavoidable experimental errors and systematic variances that are associated not only with the determination of sublimation enthalpy but also with the derivation of lattice energy. It is common to see disagreement between sublimation enthalpies of the same materials in the literature.⁴⁷ The discrepancy can be caused by different instrumentations, different research groups, and even different ways to prepare the materials. Defects and impurities can greatly affect the thermodynamic properties. To directly determine the sublimation enthalpy by measuring the vapor

pressure of the solid at different temperatures may run into troubles of possible solid–solid phase transitions as well as difficulties to accurately detect the (extremely low) vapor pressure. To indirectly estimate the sublimation enthalpy by using a thermodynamic cycle and measuring the fusion enthalpy and vaporization enthalpy can be challenging due to the lack of sufficient data on heat capacity as well as the uncertainties associated with correcting the data.⁴⁷ For example, the sublimation enthalpy of anthracene at 298 K has been reported many times ranging from 85 to 105 kJ/mol, while the recommended value is 103.4 kJ/mol (Table 1).⁴⁸ Furthermore, using eq 8 adds uncertainties to the estimation of lattice energies. It is estimated that the contribution by heat capacity to the sublimation enthalpy is no more than 10% of lattice energy.⁴² Thus, given the fact that the heat capacities of most organic solids are not available at low temperature, using the correction of $2RT$ may contribute a systematic error no greater than 5% for crystals that have sublimation enthalpies ranged around 100 kJ/mol at 298 K.

Clearly, the prediction of lattice energies of organic crystals requires advances in both computational and ex-

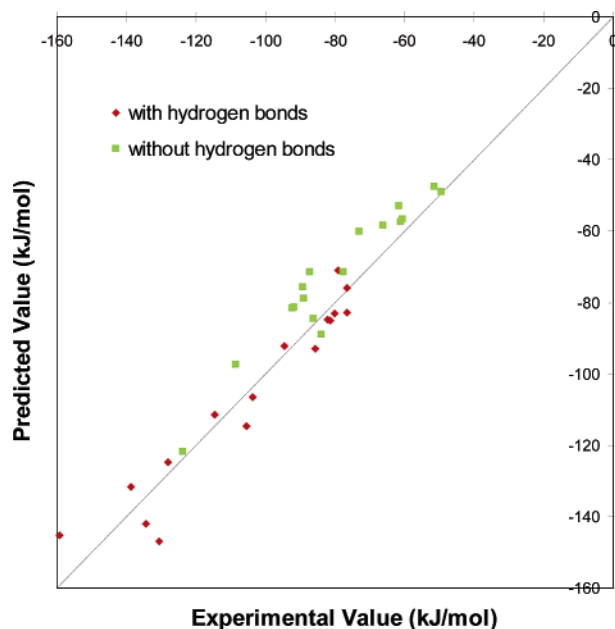


Figure 2. Comparison of calculated and experimental lattice energies. Organic crystals with and without hydrogen bonds are denoted differently. The dispersion energy was evaluated with eq 6.

perimental methods. The surprisingly good agreement between the calculated and experimental values of lattice energy (Figure 2) indicates that the prediction method of lattice energy appears to be sound and reliable. Due to the empirical nature, the damping function and the C_6 coefficients for estimating the dispersion energy should be adjusted in accordance to the DFT method that is used for calculating the nondispersive energy and, ideally, should be tailor-made for each crystal system. A recent report sheds some light in the improvement of the empirical model (eq 2).⁴¹

Conclusions

Lattice energies of selected organic crystals were calculated by DFT with subsequent corrections by empirically calculated dispersion energies. The calculated results show a good agreement with experimentally estimated values. By taking the C_6R^{-6} dispersion energy into account at large interatomic distance but diminishing it at small distance, the empirical method is likely to compensate the inability of routine DFT methods for fully describing electron correlations at the region where electron clouds are not closely overlapped. Choosing a proper analytical damping function as well as the interatomic C_6 coefficients is important for producing high-quality data. Clearly, due to the empirical nature of posterior corrections, the methodology requires both computational and experimental improvements for the prediction of lattice energies of organic crystals.

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