

# First Principles Computation of Lattice Energies of Organic Solids: The Benzene Crystal

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**Abstract:** We provide a first-principles methodology to obtain converged results for the lattice energy of crystals of small, neutral organic molecules. In particular, we determine the lattice energy of crystalline benzene using an additive system based on the individual interaction energies of benzene dimers. Enthalpy corrections are estimated so that the lattice energy can be directly

compared to the experimentally determined sublimation energy. Our best estimate of the sublimation energy is  $49.4 \text{ kJ mol}^{-1}$ , just over the typical experimentally reported values of 43–

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$47 \text{ kJ mol}^{-1}$ . Our results underscore the necessity of using highly correlated electronic structure methods to determine thermodynamic properties within chemical accuracy. The first coordination sphere contributes about 90% of the total lattice energy, and the second coordination sphere contributes the remaining 10%. Three-body interactions are determined to be negligible.

## Introduction

Understanding intermolecular interactions is the foundation of molecular recognition and crystal engineering. Crystal engineering can capitalize on the understanding of such interactions to design and manipulate crystal properties by making chemical modifications on the molecular level.<sup>[1–3]</sup> Often, when crystal structures are predicted for a given molecular structure, multiple stable crystal structures with similar energies can be generated. Accurate computational determination of the lattice energy of such crystal structures would aid in energetically ranking the structures and offer the ability to select structures of a particular energy. Such computations and energy rankings could help identify competing low-energy structures that might complicate synthesis and production of pharmaceutical products<sup>[2]</sup> and could also aid in the prediction of the resolution behavior of racemic mixtures, by providing a method to rank the energy of the mixture versus single-enantiomer crystal structures.<sup>[4]</sup>

Interest in calculating the lattice energy of crystalline benzene can be found as early as 1966.<sup>[5]</sup> Calculations of the lattice energy have generally proceeded by using atom–atom potentials, with parameters fit to experimental observations. Recent work on drug crystals suggests that the lattice energy can be quite sensitive to the chosen parameters;<sup>[6]</sup> moreover, the need to fit to experimental data to deduce many different atom–atom potentials makes it harder to apply these approaches to a wide variety of systems. Recently, methods have been proposed to take into account intermolecular interactions, rather than just simpler atom–atom interactions.<sup>[7]</sup> However, the accuracy of these methods is still governed by the quality of the intermolecular parameters and the flexibility of the assumed functional form; when simple model potentials are used, the global minimum crystal structure is predicted only about a third of the time.<sup>[2]</sup>

Nonempirical models are preferred for their wider applicability and their potential for yielding more accurate results. One successful nonempirical approach is the PIXEL method,<sup>[3,8–10]</sup> which is based the determination of molecular densities and using this information to determine the different physical contributions (coulombic, polarization, dispersion, and repulsion) to the intermolecular interaction energies. Results from the PIXEL method have been compared to some first-principles electronic structure calculations that include electron correlation and can perform comparably to second-order perturbation theory (MP2).<sup>[10]</sup>

To investigate methods that would remove the dependence of lattice energy determination on empirical parame-

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ters, Schweizer and Dunitz<sup>[11]</sup> performed ab initio MP2 electronic structure calculations on the benzene dimer to determine the lattice energy of crystalline benzene and compared these results to those from the PIXEL method. The benzene dimer and the methods required to achieve converged results for its interaction energy have been the subject of significant computational effort,<sup>[12–20]</sup> but using correlated electronic structure methods to determine the lattice energy of crystalline benzene was largely unexplored. Schweizer and Dunitz proposed an additive scheme in which the interaction energy of only the four unique symmetry-related nearest-neighbor dimers is determined. MP2 greatly overestimated the interaction energy of the dimers, and the overestimation grew worse with increasing the size of the basis set and did not provide convergent results. Counterpoise corrections lowered the interaction energy to less than half of the uncorrected MP2 values, indicating that the largest basis set employed, 6–31++G(d,p), is not nearly large enough to approach basis-set convergence. These findings are in agreement with other studies documenting the need to use coupled-cluster methods in conjunction with very large basis sets to achieve reliable results for noncovalent interactions between aromatic molecules.<sup>[13, 15, 18, 21, 22]</sup> In contrast, the PIXEL energies converged towards a value of 42.1 kJ mol<sup>-1</sup> (incorrectly given as 43.8 kJ mol<sup>-1</sup> in the paper by Schweizer and Dunitz<sup>[11]</sup> because of an arithmetical error) for the estimated lattice energy with increasing basis-set size.

Other than this recent work, ab initio determinations of the lattice energies of crystals have been primarily been limited to Hartree–Fock and density functional methods (DFT), which do not always give qualitatively similar results for the lattice parameters and bond lengths of the crystals when compared to experimental values.<sup>[23]</sup> Recent work which adds an empirical van der Waals correction to DFT has shown an improvement in the determination of unit cell parameters (although lattice energies were not reported).<sup>[24]</sup> The only ab initio determination of a crystal energy that used highly correlated electronic structure methods, such as coupled-cluster theory through perturbative triples [CCSD(T)],<sup>[25]</sup> computed the electron correlation energies of a series of small LiH crystals and determined the cohesive energy of the crystal by extrapolating these results.<sup>[26]</sup>

In this work, we employ state-of-the-art quantum mechanical methods to determine the lattice energy of crystalline benzene with high accuracy. Specifically, we use the CCSD(T) and MP2 methods in conjunction with very large basis sets to obtain dimer energies that should provide accurate dimer binding energies to within a few tenths of a kcal mol<sup>-1</sup>.<sup>[12]</sup> to enable a more accurate determination of the lattice energy of crystalline benzene by using the additive system of Schweizer and Dunitz. Going beyond their model, we also consider the effects of including longer range dimer interactions, as well as three-body interactions among nearest-neighbor trimers. To compare our calculated lattice energy to experimental estimates for the heat of sublimation, corrections must also be included to account for the enthalpy change of the crystal from 0 K to the measurement

temperature of the sublimation energy (around 250 K) as well as a zero-point vibrational energy correction to account for the lattice mode vibrations of the crystal. By making these comparisons, we seek to demonstrate that state-of-the-art quantum chemistry is capable of computing the lattice energy of organic crystals like benzene to a high accuracy and to provide a definitive methodology for obtaining converged results for the lattice energy of neutral organic crystals.

## Computational Methods

The coordinates for the benzene dimers were taken from the neutron diffraction crystal structure of Bacon et al. and were not otherwise optimized. These are the coordinates used in recent work by Schweizer and Dunitz,<sup>[11]</sup> and we chose to use the same coordinates for consistency and to enable comparison to the methods used in their study. A more recent neutron diffraction study by Jeffery et al.<sup>[27]</sup> determined a very accurate structure for deuterated benzene and reported very similar mean bond lengths to the structure of Bacon et al., but with much smaller uncertainties. However, using the coordinates of this improved structure would have made very little difference in the computation of the lattice energy, as the interaction energy of a typical dimer differs by only 0.01 kcal mol<sup>-1</sup> for the two structures.

For each dimer, the total counterpoise-corrected interaction energy was determined by MP2 in conjunction with the correlation consistent basis sets augmented with diffuse functions, aug-cc-pVXZ (in which X = D, T, and Q), and CCSD(T) with the aug-cc-pVDZ basis set. From the aug-cc-pVTZ and aug-cc-pVQZ results, the MP2 correlation energy was extrapolated to the complete basis-set (CBS) limit using the procedure of Halkier et al.<sup>[28]</sup> This extrapolation procedure should almost entirely eliminate any basis-set incompleteness error from the determination of the dimer interaction energies and thus the lattice energy. To account for additional electron correlation, the counterpoise-corrected CCSD(T) interaction energy was determined using the aug-cc-pVDZ basis set, and a correlation correction term was determined as the difference between the MP2 and CCSD(T) energies determined in the aug-cc-pVDZ basis. This change, denoted  $\Delta$ CCSD(T), was then added to the MP2/CBS results, giving an estimated CCSD(T)/CBS interaction energy. Previous work<sup>[21]</sup> indicates that the  $\Delta$ CCSD(T) correction term is quite insensitive to basis-set effects, so that  $\Delta$ CCSD(T) corrections are probably converged within a few hundredths of a kcal mol<sup>-1</sup> when the aug-cc-pVDZ basis is used. All computations were performed using MOLPRO.<sup>[29]</sup>

## Results and Discussion

**Lattice energy determination:** The symmetry-related dimers used in the lattice energy determination are described in Table 1, including the distance between the centers of mass of the two benzene molecules. The total interaction energies of each of the symmetry-related dimers (**A–D**; see Figure 1) of the first coordination sphere are given in Table 2. These dimers are produced by glide-reflection symmetry operations (**A**, **B**, and **C**) and the *c*-translation operation (**D**). Our CCSD(T)/CBS estimate for the lattice energy contribution from these dimers is –52.1 kJ mol<sup>-1</sup>. By comparison, the computationally inexpensive PIXEL method, using MP2/6–31++G(d,p) densities, provides a reasonably good (given the computational cost) estimate of –43.8 kJ mol<sup>-1</sup>.<sup>[11]</sup> Around 90% of the lattice energy comes from the contribu-

Table 1. Interacting dimer pairs in crystalline benzene.

pair	symmetry operation	$N^{[a]}$	$R^{[b]}$
<b>A</b>	<i>a/c</i> glide reflection	4	5.02
<b>B</b>	<i>c/b</i> glide reflection	4	5.81
<b>C</b>	<i>b/a</i> glide reflection	4	5.99
<b>D</b>	$\pm c$ translation	2	6.81
<b>E</b>	$\pm a$ translation	2	7.39
<b>F</b>	$\pm b$ translation	2	9.42
<b>G</b>	$\pm c$ translation and <i>b/a</i> glide reflection	8	9.07
<b>H</b>	$\pm a$ translation and <i>c/b</i> glide reflection	8	9.40

[a] Number of symmetry-related pairs involving a given reference.

[b] Distance [in Å] between the centers of mass of the two molecules.

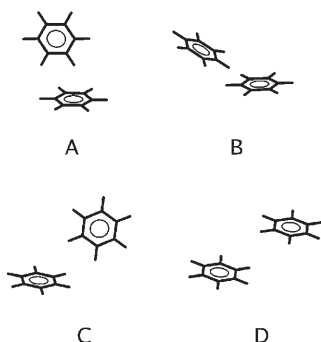


Figure 1. Dimer interactions in the first coordination sphere.

tions of these dimers, but smaller contributions result from interactions outside this first coordination sphere. The largest of these smaller contributions (those that have a total interaction energy greater than  $0.25 \text{ kJ mol}^{-1}$  at the MP2/aug-cc-pVDZ computational level, and an intermonomer separation of less than  $9.5 \text{ \AA}$ ) come from the dimers produced by the *a* and *b* translations, the *c* translation followed by the *b/a*-glide reflection, and the *a* translation followed by the *c/b*-glide reflection. The interaction energies for these dimers (**E–H**, respectively; see Figure 2) and their contribution to the lattice energy are summarized in Table 3.

Given that the majority of the lattice energy comes from the interaction energy of the symmetry-related dimers in the first coordination sphere, one might also consider the contributions of the three-body interactions within the first coordination sphere. In the study of Tauer et al.,<sup>[30]</sup> the authors found that the cyclic benzene trimer had a three-body contribution to the interaction energy of over  $1 \text{ kJ mol}^{-1}$ . However, when we examined the cyclic trimers that would be found in the first coordination sphere for the benzene crystal, the three-body effect was always less than  $0.1 \text{ kJ mol}^{-1}$ . The benzenes in the crystal are further apart than in the

Table 2. Interaction energies [in  $\text{kJ mol}^{-1}$ ] for interacting dimers in the first coordination sphere and lattice energy contributions at several computational levels.<sup>[a]</sup>

pair	$N^{[b]}$	MP2/DZ	CCSD(T)/DZ	MP2/TZ	MP2/QZ	MP2/CBS	$\Delta\text{CCSD(T)}$	Est.'d CCSD(T)/CBS
<b>A</b>	4	-12.9	-9.8	-14.0	-14.4	-14.6	3.1	-11.5
<b>B</b>	4	-8.1	-6.6	-8.7	-8.9	-9.1	1.5	-7.6
<b>C</b>	4	-6.4	-5.2	-6.9	-7.0	-7.1	1.1	-6.0
<b>D</b>	2	-2.4	-1.9	-2.4	-2.4	-2.4	0.4	-1.9
lattice energy contribution		-57.1	-45.1	-61.6	-63.0	-64.0		-52.1

[a] Calculations performed using the aug-cc-pVXZ basis set. [b] Number of symmetry-related pairs involving a given reference molecule.

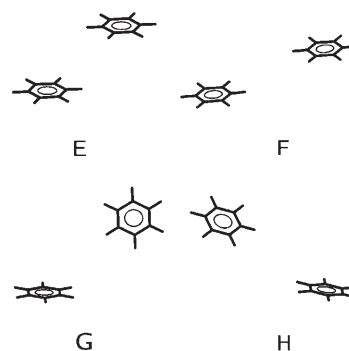


Figure 2. Important dimer interactions beyond the first coordination sphere.

Table 3. Interaction energies [in  $\text{kJ mol}^{-1}$ ] for selected interacting dimers beyond the first coordination sphere lattice energy contributions at several computational levels.<sup>[a]</sup>

pair	$N^{[b]}$	MP2/DZ	CCSD(T)/DZ
<b>E</b>	2	-1.4	-1.2
<b>F</b>	2	-0.3	-0.3
<b>G</b>	8	-0.5	-0.4
<b>H</b>	8	-0.4	-0.3
lattice energy contribution		-5.2	-4.3

[a] Calculations performed using the aug-cc-pVXZ basis set. [b] Number of symmetry-related pairs involving a given reference molecule.

gas-phase configurations of Tauer et al., and the three-body contribution diminishes rapidly with increasing intermonomer separation.

The total lattice energy is obtained by multiplying our best estimate of the interaction energy for each dimer by the number of symmetry-related pairs involving a given reference molecule (these multiplicities are given in Table 1), summing these products and dividing by two (as a result of the counting method<sup>[11]</sup>). Using the four dimers from the first coordination sphere (**A–D**; estimated CCSD(T)/CBS results) and the four energetically significant dimers from the second coordination sphere (**E–H**; CCSD(T)/aug-cc-pVDZ results), our best estimate for the lattice energy of the benzene crystal is  $-56.4 \text{ kJ mol}^{-1}$ .

**Enthalpy corrections:** To compare our calculated lattice energy to experimental values for the sublimation energy, corrections must be included for the enthalpy changes that would occur between the temperature of the gas-phase calculations (0 K) and the measurement temperature of the sublimation energy (around 250 K). The sublimation energy is  $\Delta H_{\text{sub}} = H_{\text{vapor}} - H_{\text{crystal}}$ . The enthalpies of both phases in-

clude the intramolecular electronic energy of the benzene monomers as well as intramolecular vibrational energy contributions. In the gas phase, there are additional translational and rotational enthalpy contributions. In the crystalline phase, there are additional intermolecular (lattice) enthalpy contributions: namely, the intermolecular electronic energy (lattice energy), the zero-point energy of the lattice vibrations, and the finite-temperature ( $T > 0$ ) contribution of the lattice vibrations.

If the monomer geometry of the benzene molecules were identical in both phases, the intramolecular electronic energy of one mole of benzene molecules would be the same in both phases and would therefore cancel in the computation of the sublimation energy. Jeffrey et al.<sup>[27]</sup> report a slight deformation from  $D_{6h}$  to  $C_{3v}$  symmetry in crystalline benzene, and so to examine the effect of this small distortion, we determined the molar intramolecular electronic energy for the 15 K neutron diffraction structure of Jeffrey et al. (the most precise crystal structure taken for crystalline benzene) and compared it to molar intramolecular electronic energy for gas-phase benzene. There are inherent difficulties in comparing structures from neutron diffraction studies to gas-phase studies due to differences in the quantities measured. The bond lengths determined from the neutron diffraction data are inferred from the difference between the average nuclear positions of the atoms and should thus be compared to similar measurements for the gas phase ( $r_z$  values). The  $r_z$  values for benzene have been determined experimentally<sup>[31]</sup> and theoretically,<sup>[32]</sup> with good agreement. Using the  $r_z$  values for the C–C and C–H bond lengths of Tamagawa et al.<sup>[31]</sup> (1.3976 and 1.085 Å, respectively) for the gas-phase determination of the molar intramolecular electronic energy of benzene, both phases agree within 0.01 kcal mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVDZ level. We also assume that the internal intramolecular vibrational frequencies are nearly the same in the gas and solid phase, so the enthalpy contribution due to intramolecular vibrations would also cancel in both terms. (The validity of this assumption will be discussed below.) Neglecting the quantities that appear in both phases, the sublimation energy is now given as Equation (1):

$$\Delta H_{\text{sub}} = H_{\text{vapor,trans\&rot}} - (\text{lattice energy} + \text{ZPVE}_{\text{solid,lattice}} + H_{\text{solid,lattice}}^{\text{finite-}T}) \quad (1)$$

The molar enthalpy corrections to the vapor and solid phases can be easily estimated if one assumes that the temperature is sufficient that equipartition of energy applies. In the vapor phase, the translational motions contribute  $\frac{5}{2}RT$  to the enthalpy correction and the rotational degrees of freedom contribute  $\frac{3}{2}RT$ , giving a total of  $4RT$ , or 8.3 kJ mol<sup>-1</sup> at 250 K. For the solid phase, the finite-temperature enthalpy correction is  $6RT$  (by the Dulong–Petit approximation), or 12.5 kJ mol<sup>-1</sup> at 250 K. The zero-point contribution of the lattice vibrational, modes which would only be present in the solid phase (the  $\text{ZPVE}_{\text{solid,lattice}}$  term), is de-

scribed by Nakamura and Miyazawa,<sup>[33]</sup> who calculated the lattice vibrational frequencies for the benzene crystal structure determined by Bacon et al.<sup>[34]</sup> and determined the frequency distribution of the vibrations. From this distribution, the zero-point energy correction to the sublimation energy was determined as 0.67 kcal mol<sup>-1</sup>, or 2.8 kJ mol<sup>-1</sup>. Substituting these values, along with our best estimation of the lattice energy, into the equation above gives our best estimate of the sublimation energy, 49.4 kJ mol<sup>-1</sup>. The results are summarized in Table 4.

Table 4. Estimation of the sublimation energy [in kJ mol<sup>-1</sup>] for crystalline benzene.

calculated lattice energy	
contribution from the first coordination sphere	
estimated CCSD(T)/CBS results	-52.1
contributions for selected dimers	
beyond the first coordination sphere	
CCSD(T)/aug-cc-pVDZ results	-4.3
total calculated lattice energy	-56.4
vapor-phase enthalpy correction	8.3
solid-phase enthalpy correction	12.5
ZPVE <sub>lattice</sub>	2.8
<b>sublimation energy</b>	<b>49.4</b>
typical experimental values	43–47

To verify that the internal intramolecular vibrational modes of the molecules contribute nearly equivalently to both phases, one could estimate the finite-temperature component of the enthalpy of the solid phase and compare it to the  $6RT$  approximation used above. By using heat capacities determined experimentally or with more complete theoretical estimates such as the Debye function, the total finite-temperature enthalpy of the solid can be determined by integrating the heat capacity over the appropriate temperature range. Lord and co-workers made such estimates of the heat capacity using the Debye function and calculated the heat capacity of crystalline benzene at 32 discrete temperatures in the range of 0 to 270 K.<sup>[35]</sup> From these estimates for the heat capacity, the enthalpy of the crystal is estimated as 14.7 kJ mol<sup>-1</sup>. The difference between this value and the  $6RT$  estimate (2.2 kJ mol<sup>-1</sup>) is the finite-temperature contribution to the enthalpy from the intramolecular vibrational modes in the solid phase. However, if the total finite-temperature enthalpy of the crystal had been used for the solid phase, then the finite-temperature correction to the vibrational enthalpy from the intramolecular vibrational modes would have to have been included in the vapor phase as well. This correction would be determined using the vibrational frequencies of a benzene molecule and the usual harmonic oscillator partition function. By using the frequencies reported by Paige et al.,<sup>[36]</sup> this contribution is 2.3 kJ mol<sup>-1</sup> at 250 K, almost exactly canceling the difference between the  $6RT$  estimate and the more complete estimation of the  $T > 0$  part of the enthalpy of the solid phase. This indicates that the intramolecular vibrations are, in fact, extremely similar in both phases and if their effects were included, they would appear in both terms and simply cancel.

**Comparison to experiment and error analysis:** Values for the benzene sublimation energy have been reported from 38.0 to 53.9 kJ mol<sup>-1</sup>,<sup>[37,38]</sup> with the majority of values in the 43–47 kJ mol<sup>-1</sup> range, slightly below our calculated value. Even though the pair interaction energies are each converged to within a few hundredths of a kcal mol<sup>-1</sup>, this error accumulates in the summation of the lattice energy. The largest sources of error in the dimer interaction energies are basis-set incompleteness, higher order electron correlation, and correlation of core electrons.

The aug-cc-pVTZ/aug-cc-pVQZ extrapolation of the MP2 correlation energy should provide results nearly converged to the CBS limit and nearly eliminate errors associated with the incompleteness of the one-particle basis set. The approximate size of any remaining basis-set error can be estimated by comparing the MP2/aug-cc-pVQZ and MP2/CBS interaction energies for the dimers in the first coordination sphere (A–D). The difference in these interaction energies is the largest for **A** and is 0.25 kJ mol<sup>-1</sup>. The remaining basis-set error in the interaction energy is very likely to be less than this value. Additionally, the basis-set error diminishes rapidly as the intermonomer separation increases and for **D**, the difference in the MP2/aug-cc-pVQZ and MP2/CBS estimates for the interaction energy is less than 0.01 kJ mol<sup>-1</sup> and is completely negligible for **E–H**. Estimating the remaining basis-set error as the difference between the MP2/aug-cc-pVQZ and MP2/CBS interaction energies for the dimers involved in the first coordination sphere and propagating this error in the lattice energy calculation, the error introduced to the lattice energy from remaining basis-set incompleteness is at most –1.0 kJ mol<sup>-1</sup>.

The importance of higher order electron correlation is evident by the size of the  $\Delta$ CCSD(T) correction used in the determination of the lattice energy, and the contribution of the triple excitations is essential in accurately determining the interaction energy of noncovalent systems. Given the importance of the triple excitations, it is certainly possible that even higher order contributions to the electron correlation, such as quadruple or pentuple excitations, may make small, but not insignificant contributions to the interaction energies. Hopkins and Tschumper investigated the importance of quadruple excitations on the interaction energy of several small dimers.<sup>[39]</sup> For their test set of  $\pi$ – $\pi$  interacting dimers, the contribution of the quadruple excitations is between 5% and 27% that of the triple excitations. Using this guideline, we have estimated the contribution of the quadruple excitations for each of our eight dimers as these percentages of the difference between the CCSD(T)/aug-cc-pVDZ and CCSD/aug-cc-pVDZ interaction energies. (While there are certainly contributions from pentuple excitations and beyond, they will be dwarfed by the contributions from the quadruple excitations.) From these estimations, we obtain an error in the lattice energy due to contributions from higher order electron correlation of 0.6 (using the 5% estimate) to 3.2 kJ mol<sup>-1</sup> (using the 27% estimate).

In all the computations using the aug-cc-pVXZ basis sets, all the core orbitals were doubly occupied; that is, the

frozen-core approximation was utilized. To estimate the effect of removing this restriction, MP2 interaction energies were determined using the double- $\zeta$  core-valence basis set, aug-cc-pCVDZ,<sup>[40]</sup> for dimer **A**. The interaction energy was determined within this basis set using the frozen-core approximation and again allowing the core electrons to be correlated. The difference between these two interaction energies was only 0.06 kJ mol<sup>-1</sup>. As discussed above in regards to basis-set incompleteness, as the total interaction energy of the complex decreases, so does the size of the error associated with the dimer's interaction energy. Since **A** has the greatest interaction energy of the dimers considered, and the core correlation energy for the remaining dimers will be even smaller for the other dimers, we conclude that core correlation is not a significant source of error in the determination of the interaction energies of these systems and should not introduce a sizable error in the determination of the lattice energy.

Any additional sources of error, such as errors introduced by the Born–Oppenheimer approximation or relativistic effects, are much smaller than the sources of errors just discussed. The effects of higher order electron correlation are certainly the largest source of error and give a less bound estimate of the lattice energy and a lower value for the sublimation energy. These effects would be partially countered by the error due to basis-set incompleteness, which would give a more bound estimate of the lattice energy and a larger sublimation energy. Using our estimates of –1.0 to 0 kJ mol<sup>-1</sup> for the basis-set incompleteness error and 0.6 to 3.2 kJ mol<sup>-1</sup> for the higher order correlation error, we obtain estimates of –53.2 to –56.8 kJ mol<sup>-1</sup> for the lattice energy, or 46.2 to 49.8 kJ mol<sup>-1</sup> for the sublimation energy.

Taking into account the error analysis of our calculated sublimation energy, our estimate of the sublimation energy for benzene is likely within “chemical accuracy” (within 1 kcal mol<sup>-1</sup>) of typical experimental values. Using, for instance, the most recent value included in the NIST compilation as a benchmark (45.2 kJ mol<sup>-1</sup>),<sup>[41]</sup> a “chemical accuracy” estimate could range from 41.0 to 49.4 kJ mol<sup>-1</sup>, encompassing almost our entire range of theoretical values. The computational rigor of the methods required to achieve this result underscores the need to use highly converged electronic structure methods to make high-accuracy ab initio determinations of sublimation energies.

## Conclusion

The lattice energy of crystalline benzene has been determined by using highly correlated electronic structure methods and large augmented basis sets and has been extrapolated to the CCSD(T) complete basis-set limit. This work extends previous work on ab initio lattice energy determination in several important ways. We have used correlated methods beyond second-order perturbation theory to more accurately determine the interaction energy of the dimeric interactions involved in the first coordination sphere for a



reference benzene molecule. We investigated the size of the three-body interactions in the first coordination sphere and have shown that these interactions make negligible contributions to the lattice energy. However, longer range dimeric interactions (beyond the first coordination sphere) account for almost 10% of the total lattice energy and should not be neglected if one hopes to make a high-accuracy determination of the lattice energy.

The use of converged methods is particularly important, since even small systematic errors (on the order of a few hundredths of a kcal mol<sup>-1</sup> in these calculations) result in larger errors in the determination of the lattice energy, because they accumulate in the addition of all the pair energies. Sources of such systematic errors were discussed and estimates for the sizes of these errors were included to estimate the error bars on the calculated sublimation energy. Including enthalpy corrections, the sublimation energy of benzene was estimated to be 46.2–49.8 kJ mol<sup>-1</sup> (with a best estimate of 49.4 kJ mol<sup>-1</sup>), compared to typical experimental values of 43–47 kJ mol<sup>-1</sup>. These computations demonstrate that the lattice energy can be accurately determined (to around 1 kcal mol<sup>-1</sup>) for neutral organic molecular crystals using converged ab initio electronic structure methods and establish a general methodology to make such high-accuracy determinations.

The highly accurate determination of lattice energies provides a new tool for the crystal engineer to energetically rank and compare competing crystal structures. Furthermore, it should be possible to directly obtain the most thermodynamically stable crystal structures by minimizing the lattice energy with respect to the crystal geometry, employing techniques described here or judicious approximations of them. Clearly the ability to predict the structures and energetics of crystals to a high degree of accuracy would be of great utility in crystal design.

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