# Chapter 8
# Relationship Between Atomic Contact and Intermolecular Interactions: Significant Importance of Dispersion Interactions Between Molecules Without Short Atom–Atom Contact in Crystals

**Seiji Tsuzuki**

**Abstract** Intermolecular interactions in crystals of polycyclic aromatic molecules, *n*-hexane, and hexamine were analyzed by dispersion-corrected DFT calculations. The origin of the attraction and the relationship between short atom–atom contact and magnitude of attraction were discussed. The calculations show that the dispersion interactions are the primary source of the attraction between adjacent molecules in the crystals. The strong attraction by the dispersion interactions often exists between adjacent molecules in the crystals, even if the adjacent molecules do not have short atom–atom contact. Although intermolecular interactions in crystals have been discussed based on the presence or absence of atom–atom contact at short distances, our analysis shows that it is often dangerous to discuss the intermolecular interactions in crystals solely based on crystal structures.

**Keywords** Intermolecular interaction · DFT calculations · Dispersion interaction · Short atom–atom contact · Crystal structure

## 8.1 Introduction

The intermolecular interactions control the arrangement of molecules in organic crystals and greatly affect the physicochemical properties of the organic crystals. For this reason, detailed information on intermolecular interactions is increasingly required in the development of organic materials. With regard to the structures of organic crystals, a huge amount of data obtained by crystal structure analysis has been accumulated. On the other hand, it is not easy to directly elucidate the nature (magnitude, directionality and origin of attraction) of the intermolecular interactions between molecules in crystals solely by experimental methods. For this reason, until now, intermolecular interactions in organic crystals have often been discussed

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S. Tsuzuki (✉)
National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Ibaraki, Japan
e-mail: s.tsuzuki@aist.go.jp

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based on the presence or absence of atomic contact at short distances (contact at interatomic distances less than the sum of the van der Waals radii). Recently, high-level ab initio molecular orbital calculations and dispersion-corrected DFT (density functional theory) calculations can evaluate intermolecular interaction energies in organic crystals sufficiently accurately. Recently reported calculations show that strong attraction owing to the dispersion interactions often exists between molecules in crystals which do not have short atom–atom contact. For example, in crystals of polycyclic aromatic molecules such as thienoacenes [1], strong attraction owing to dispersion interactions exist between adjacent molecules which do not have short atom–atom contacts. Here, the intermolecular interactions in the crystals of polycyclic aromatic molecules, *n*-hexane, and hexamine analyzed by dispersion-corrected DFT calculations are shown. They are compared with HF calculations which cannot evaluate the dispersion interactions to estimate the contribution of the dispersion interactions to the attraction. We also point out the danger of the discussion on intermolecular interactions in organic crystals based solely on the presence or absence of contact of atoms at short distances.

## 8.2 Intermolecular Interactions

There exist several intermolecular interactions which have different origins between interacting molecules [2]. The intermolecular interactions classified by physical origins are shown in Table 8.1. The intermolecular interactions can be classified into two groups. The first one is long-range interactions, which have their origin in Coulomb interactions. The long-range interactions can work even when molecules are well separated. The second one is short-range interactions, which have their origin in interactions between molecular orbitals. The short-range interactions only work at short distances where the overlap of molecular orbitals is significant. The electrostatic, that is the Coulomb interaction between the static charge distributions of molecules, the induction, that is the attraction due to induced polarization, and the dispersion, that is the attraction due to the correlated motion of electrons, are the

**Table 8.1** Intermolecular interactions

| Intermolecular interactions | Feature |
|---|---|
| *Long-range interactions* (*Coulombic interactions*, $E \sim R^{-n}$) | |
| Electrostatic | Attraction or repulsion, directional |
| Induction (polarization) | Attraction |
| Dispersion (van der Waals attraction) | Attraction |
| *Short-range interactions* (*overlap of molecular orbitals*, $E \sim \exp(\alpha R)$) | |
| Exchange-repulsion | Strong repulsion at short distance |
| Charge-transfer | Attraction |

long-range interactions. The magnitude of the energies of the long-range interactions are proportional to some inverse power of the intermolecular distance, and therefore, the energies of the long-range interactions decrease slowly with the increase of the intermolecular distance. On the other hand, the exchange-repulsion, that is the strong repulsion at short distance, and the charge-transfer, that is the attraction due to the interactions between molecular orbitals, are the short-range interactions. Since the energies of the short-range interactions are approximately proportional to the overlap integral, they decrease rapidly as the intermolecular distance increases. For this reason, the short-range interactions do not work at long distance.

The classification of intermolecular interactions by structural features is also often used. Typical intermolecular interactions classified by structural features are shown in Fig. 8.1. When a hydrogen atom bonded to an electronegative atom (oxygen, nitrogen, etc.) is in contact with another electronegative atom or $\pi$-electron system and there exists attraction between them, the interaction is called hydrogen bond. When aromatic rings are in contact and there exists attraction, the interaction is called $\pi/\pi$ interaction. The contact between C-H bonds and aromatic rings is often observed in organic crystals and the interaction between C-H bond and aromatic ring is called CH/$\pi$ interaction. Further, it is known that there exists strong attraction between halogen atom such as iodine or bromine and Lewis base, the interaction is called halogen bond.

The classification of intermolecular interactions by structural features has many problems, although it is widely used to discuss intermolecular interactions due to the abundance of crystal structure data. For example, the structure of CH/$\pi$ interaction is similar to the structure of $\pi$ hydrogen bond between water and benzene. For this reason, it was believed that the CH/$\pi$ interaction was weak hydrogen bond and its properties were similar to hydrogen bonds [3]. However, high-level ab initio calculations revealed that the nature of the CH/$\pi$ interactions is completely different form hydrogen bonds [4, 5]. The major source of the attraction in hydrogen bonds is the highly directional electrostatic interactions, and therefore, hydrogen bonds have

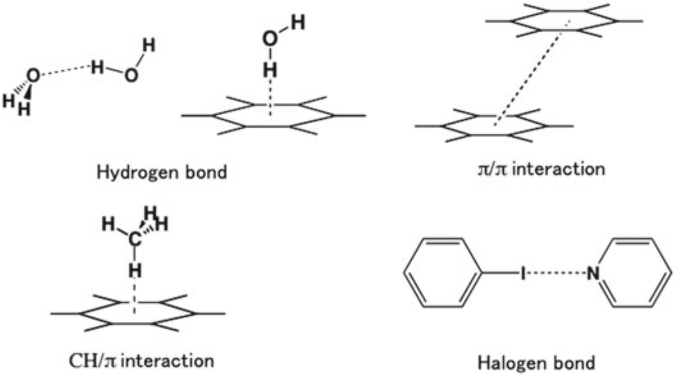


**Fig. 8.1** Intermolecular interactions classified by structural feature

strong directionality. On the other hand, the major source of the attraction in the CH/$\pi$ interactions is the dispersion interactions. The contribution of the electrostatic interaction is very small. Therefore, the directionality of the CH/$\pi$ interactions is very weak. The directionality of hydrogen bonds is important for controlling orientation of molecules in crystals and supermolecules [6]. The weak directionality of the CH/$\pi$ interactions suggests that the CH/$\pi$ interactions are difficult to play important roles in controlling arrangement of molecules in molecular assemblies as in the cases of hydrogen bonds. Another example is the interactions between benzene and aromatic cations. The structure of the benzene-*N*-methylpyridinium complex is similar to the structure of the $\pi$-stacked benzene dimer. But the nature of the interactions in the benzene-*N*-methylpyridinium complex is completely different from that in the benzene dimer [7]. The interactions in the benzene-*N*-methylpyridinium complex are significantly stronger than that in the benzene dimer owing to the strong electrostatic and induction interactions. On the other hand, the dispersion interactions are the major source of the weak attraction in the benzene dimer.

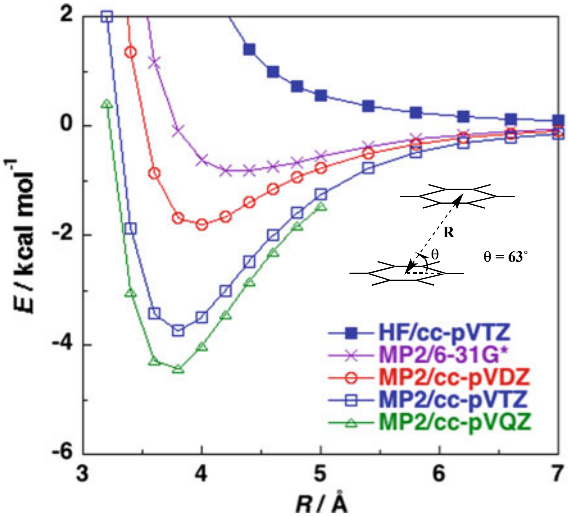
## 8.3 Calculation of Intermolecular Interaction Energy

The energies of molecules and dimers obtained by molecular orbital calculations and DFT calculations are the stabilization energies by the formation of molecules and dimers from isolated nuclei and electrons. Therefore, the intermolecular interaction energy ($E_{\mathrm{int}}$) can be obtained by subtracting the sum of the energies of monomers ($E_{\mathrm{A}} + E_{\mathrm{B}}$) from the energy of dimer ($E_{\mathrm{AB}}$) as shown in Eq. 8.1. This method for the calculation of intermolecular interaction energy is called supermolecule method. Since the intermolecular interaction energy calculated by the supermolecule method is overestimated by the basis set superposition error (BSSE), the BSSE is corrected by the counterpoise method.

$$E_{\mathrm{int}} = E_{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}}) \tag{8.1}$$

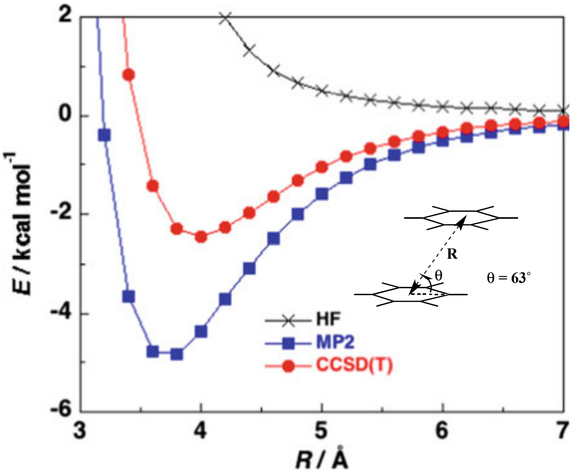
Ab initio molecular orbital calculation is an approximation, although it does not use any empirical parameter based on experimental measurements. The level of approximation is mainly determined by the choice of basis set and electron correlation correction procedure used for the calculation. Molecular orbital is described as a linear combination of gauss functions located on atoms of the molecule in ab initio molecular orbital calculation. The set of gauss functions (basis function) is called as basis set. The accuracy of the calculated intermolecular interaction energy strongly depends on the number and the angular flexibility of gauss functions used for the calculation. The calculated intermolecular interaction energy also depends strongly on the choice of electron correlation correction procedure. Therefore, sufficiently large basis set and electron correlation correction by a proper method are necessary for an accurate evaluation of intermolecular interaction energy. Figure 8.2 shows the intermolecular interaction energies calculated for the slipped-parallel benzene

**Fig. 8.2** Effects of basis set on calculated interaction energy for benzene dimer



dimer at HF and MP2 levels using several basis sets. The HF level interaction energy potential does not have a potential minimum, while the attraction is calculated when the electron correlation is corrected by the MP2 method, which clearly shows that the primary source of the attraction in the benzene dimer is the dispersion interactions. The dispersion interactions have their origin in electron correlation, and therefore, HF calculation cannot evaluate the dispersion interactions. The magnitude of the attraction calculated by the MP2 method depends strongly on the basis set. Small basis sets such as the 6-31G* basis set underestimates the attraction significantly compared with large basis sets such as the cc-pVQZ basis set. Figure 8.3 shows the calculated interaction energies for the slipped-parallel benzene dimer by the HF, MP2

**Fig. 8.3** Effects of electron correlation correction on calculated interaction energy for benzene dimer. MP2 and CCSD(T) interaction energies are the estimated interaction energies at the basis set limit



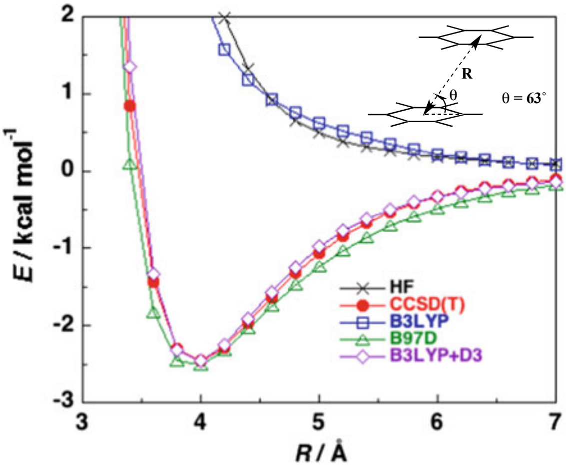


**Fig. 8.4** Comparison of interaction energies calculated for benzene dimer using dispersion-corrected DFT methods with those obtained by HF and CCSD(T) methods

and CCSD(T) methods. The MP2 and CCSD(T) level interaction energies are the estimated interaction energies at the basis set limit. The MP2 method overestimates the attraction compared with more accurate CCSD(T) method.

The DFT calculations do not require large computation time compared with ab initio calculations. The required computational time for DFT calculations are proportional to the cubic of the number of basis functions. On the other hand, the computational time for MP2 and CCSD(T) calculations are proportional to the 5th and 7th power of the number of basis functions, respectively. For this reason, the DFT calculations of large molecules are relatively easy. However, the DFT calculations using functionals such as B3LYP [8] cannot evaluate the attraction by the dispersion interactions as shown in Fig. 8.4. The intermolecular interaction potential calculated for the slipped-parallel benzene dimer using the B3LYP functional does not have a minimum as in the case of the HF level potential. For this reason, the dispersion-corrected DFT methods have been developed. The energy of dispersion interactions is corrected by empirical parameters in the dispersion-corrected DFT methods. In calculations using functionals such as B97D [9], the dispersion-corrected calculations are performed. It is also possible to carry out B3LYP calculations with Grimme's D3 dispersion correction [10] (B3LYP + D3). The calculated interaction energies by the dispersion-corrected DFT methods are often close to those obtained by high-level ab initio calculation (CCSD(T) calculation using a large basis set near the basis set limit). The comparison of the calculated interaction energies using B97D and B3LYP + D3 methods with those obtained by the CCSD(T) method is shown in Fig. 8.4.

## 8.4 Intermolecular Interactions of Naphthalene

Herringbone structures are often observed in the crystals of polycyclic aromatic molecules such as the crystal of naphthalene as shown in Fig. 8.5. A naphthalene molecule interacts strongly with six adjacent molecules in the crystal. Two adjacent molecules are $\pi$-stacked and arranged in parallel orientation. The remaining four adjacent molecules are molecules in adjacent $\pi$-stacked columns and arranged in tilted T-shape configuration. The short atom–atom contact less than the sum of van der Waals radii is shown by arrows in Fig. 8.5. Short atom–atom contact exists between adjacent molecules in tilted T-shape configuration. On the other hand, there is no short contact between adjacent molecules arranged in parallel.

The interaction energies between adjacent naphthalene molecules in the crystal ($E_{\mathrm{B97D}}$) calculated by the dispersion-corrected DFT method (B97/6-311G**) are shown in Table 8.2. The interaction energy with the tilted T-shape adjacent molecule was calculated as −4.83 kcal/mol. The magnitude of the attraction is close to the

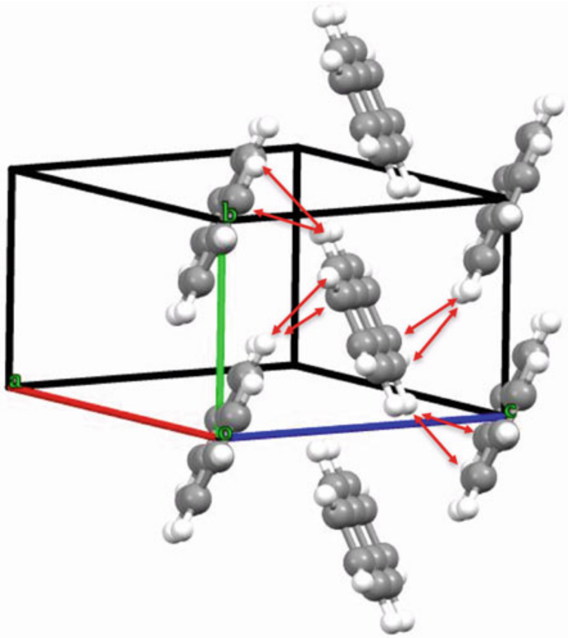


**Fig. 8.5** Crystal structure of naphthalene

**Table 8.2** Intermolecular interaction energies between adjacent naphthalene molecules in crystal. Energy in kcal $\mathrm{mol}^{-1}$

| | $E_{\mathrm{B97D}}$ | $E_{\mathrm{HF}}$ | $E_{\mathrm{disp}}$ |
|---|---|---|---|
| Tilted T-shape | −4.83 | 3.31 | −8.14 |
| Parallel | −3.62 | 0.41 | −4.03 |

hydrogen bond of water dimer (about −5 kcal/mol). The interaction energy with parallel adjacent molecule was calculated as −3.62 kcal/mol. These results show that there exists strong attraction not only between the tilted T-shape adjacent molecules, but also between the parallel adjacent molecules, although there is no short atom–atom contact between the parallel adjacent molecules.

The HF level (HF/6-311G**) interaction energies ($E_{\mathrm{HF}}$) between the tilted T-shape adjacent molecules and between the parallel adjacent molecules are 3.31 and 0.41 kcal/mol, respectively, as summarized in Table 8.2. The HF method cannot evaluate the dispersion interactions, therefore the contributions of the dispersion interactions ($E_{\mathrm{disp}}$) can be estimated approximately by subtracting $E_{\mathrm{HF}}$ from $E_{\mathrm{B97D}}$ as shown in Eq. 8.2.

$$E_{\mathrm{disp}} = E_{\mathrm{B97D}} - E_{\mathrm{HF}} \tag{8.2}$$

The contributions of the dispersion interactions ($E_{\mathrm{disp}}$) calculated for the interactions between the tilted T-shape and parallel adjacent molecules are −8.14 and −4.03 kcal/mol, respectively (Table 8.2). The contributions of the dispersion interactions are significant. The calculated positive values of $E_{\mathrm{HF}}$ suggest that the contributions of the electrostatic interactions to the attractions are not large, since the attraction by the electrostatic interactions can be evaluated by the HF calculations. These calculations show that the dispersion interactions are the major source of the attraction between adjacent naphthalene molecules in the crystal. Although there is no short atom–atom contact between parallel adjacent molecules, there exists strong attraction by the dispersion interactions. This indicates that the strong attraction between parallel adjacent molecules due to the dispersion interactions will be overlooked, if the intermolecular interactions in the crystal are discussed based solely on the presence of short atom–atom contact in crystals.

## 8.5 Intermolecular Interactions of Other Polycyclic Aromatic Molecules

Not only in the crystal of naphthalene, but also in the crystals of other polycyclic aromatic molecules, there exist strong attraction between adjacent molecules. The intermolecular interaction energies between parallel adjacent molecules in the crystals of anthracene, tetracene, pentacene, and pyrene (Fig. 8.6) were calculated by the dispersion-corrected DFT method (B97D/6-311G**) and by HF method (HF/6-311G**) The calculated interaction energies ($E_{\mathrm{B97D}}$ and $E_{\mathrm{HF}}$) are summarized in Table 8.3. Although there is no short atom–atom contact between the parallel adjacent molecules in these crystals, there exists strong attraction.

As the number of aromatic rings increases, the magnitude of the intermolecular interaction ($E_{\mathrm{B97D}}$) increases. The intermolecular interaction energy between parallel adjacent pentacene molecules is −9.68 kcal/mol, and that for parallel adjacent pyrene

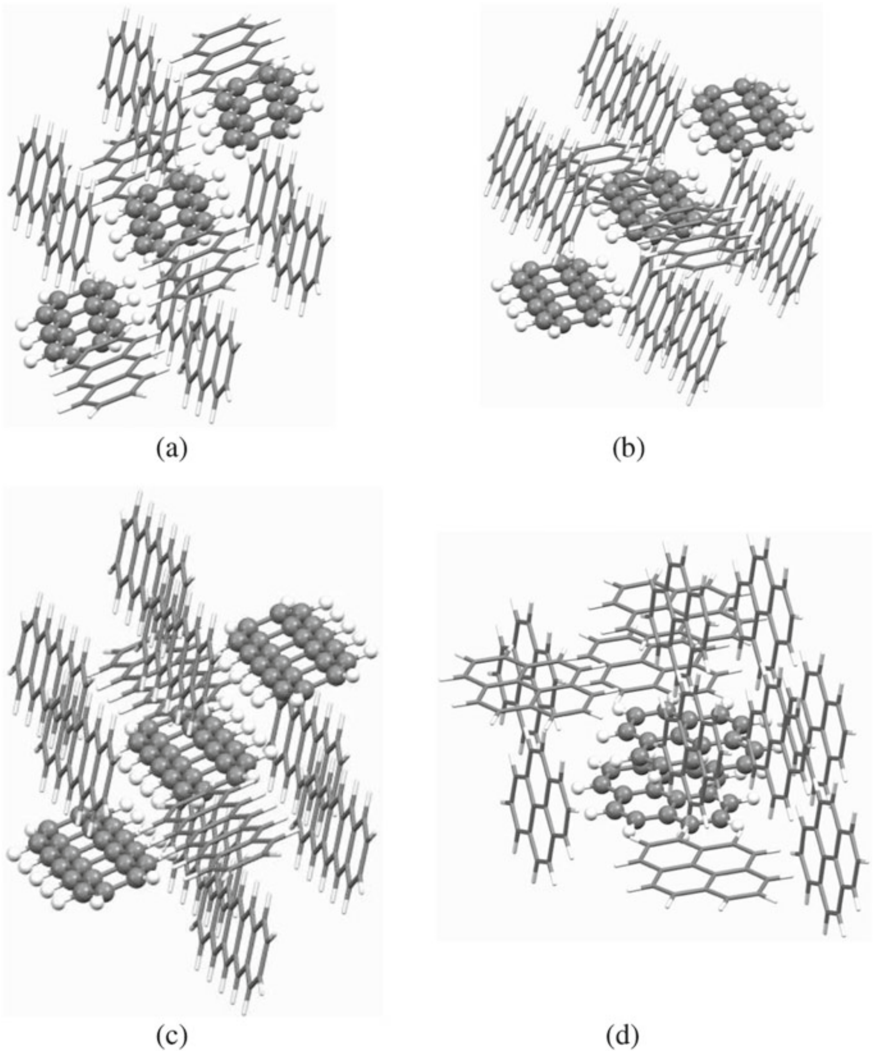


**Fig. 8.6** Crystal structures of **a** anthracene; **b** tetracene; **c** pentacene; **d** pyrene. Parallel adjacent molecules in crystals are shown in ball and stick model

**Table 8.3** Intermolecular interaction energies between parallel adjacent molecules in crystals of polycyclic aromatic molecules. Energy in kcal mol$^{-1}$

| | $E_{\mathrm{B97D}}$ | $E_{\mathrm{HF}}$ | $E_{\mathrm{disp}}$ |
|---|---|---|---|
| Naphthalene ($P2_1$/c) | −3.62 | 0.41 | −4.03 |
| Anthracene ($P2_1$/a) | −5.25 | 0.17 | −5.42 |
| Tetracene ($P^{-}1$) | −7.55 | 0.56 | −8.11 |
| Pentacene ($P^{-}1$) | −9.68 | 1.61 | −11.29 |
| Pyrene ($P2_1$/a) | −12.06 | 15.63 | −27.69 |

molecules is −12.06 kcal/mol. They are about the double of the hydrogen bond of the water dimer. The calculated $E_{\mathrm{disp}}$ show that the strong dispersion interactions exist between parallel adjacent molecules in the crystals. The analysis of the intermolecular interactions in the crystals of polycyclic aromatic molecules also shows that it is dangerous to discuss the intermolecular interactions in crystals solely based on the presence or absence of short atom–atom contact.

## 8.6 Intermolecular Interactions of *n*-hexane

The arrangement of *n*-hexane molecules in the crystal is shown in Fig. 8.7a. The long axes of *n*-hexane are aligned in parallel in the crystal. The molecular arrangement seen from the C-axis direction of the crystal is shown in Fig. 8.7b. The calculated intermolecular interaction energies in three pairs of adjacent molecules arranged in parallel in the crystal are shown in Table 8.4. Although there is no short atom–atom contact between any parallel adjacent molecules, there exists considerable attraction between parallel adjacent molecules. The calculated intermolecular interaction energy ($E_{\mathrm{B97D}}$) between molecules A and B is −5.19 kcal/mol, which is nearly identical to the interaction energy of hydrogen bond in water dimer. The calculated $E_{\mathrm{disp}}$ shows that the strong dispersion interactions are responsible for the attraction. The analysis of the intermolecular interactions in the *n*-hexane crystal also indicates that the strong attraction owing to the dispersion interactions exists between molecules without short atom–atom contact.

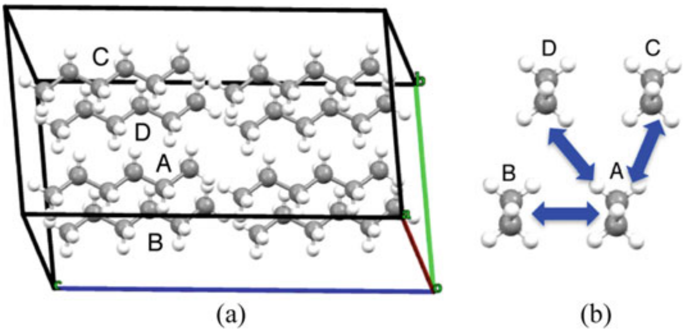


**Fig. 8.7** Crystal structure of *n*-hexane

**Table 8.4** Intermolecular interaction energies between adjacent *n*-hexane molecules in crystal. Energy in kcal mol$^{-1}$

| | $E_{\mathrm{B97D}}$ | $E_{\mathrm{HF}}$ | $E_{\mathrm{disp}}$ |
|---|---|---|---|
| A-B | −5.19 | 3.06 | −8.25 |
| A-C | −2.87 | 1.73 | −4.60 |
| A-D | −2.04 | 0.93 | −2.97 |

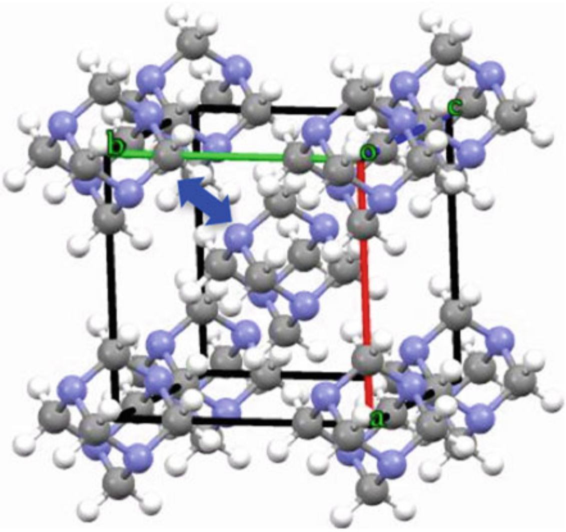


**Fig. 8.8** Crystal structure of hexamine

**Table 8.5** Intermolecular interaction energies between adjacent hexamine molecules in crystal. Energy in kcal mol$^{-1}$

| | $E_{\mathrm{B97D}}$ | $E_{\mathrm{HF}}$ | $E_{\mathrm{disp}}$ |
|---|---|---|---|
| Hexamine | −4.64 | 0.31 | −4.95 |

## 8.7 Intermolecular Interactions of Hexamine

The arrangement of hexamine molecules in the crystal is shown in Fig. 8.8. There is no short atom–atom contact between adjacent molecules in the hexamine crystal. However, there exists significant attraction between adjacent molecules. The adjacent molecule pair indicated by arrow in Fig. 8.8 has the strongest interaction. The intermolecular interaction energy ($E_{\mathrm{B97D}}$) calculated for this pair is −4.64 kcal/mol as shown in Table 8.5. The calculated $E_{\mathrm{disp}}$ shows that the dispersion interactions are again responsible for the strong attraction.

## 8.8 Why Strong Attraction Exists Between Molecules Without Short Atom–Atom Contact?

Analysis of intermolecular interactions in the crystals of organic molecules shows that the strong attraction caused by the dispersion interactions exists between adjacent molecules in crystals, even if there is no short atom–atom contact. Therefore, the question arises why strong attraction owing to the dispersion interactions exists between adjacent molecules without short atom–atom contact. Intermolecular interactions in crystals have been discussed mainly based on the presence or absence of short atom–atom contacts in crystals. The short atom–atom contact is observed mainly in the cases where single atom of one molecule is in contact with an atom or atoms of another molecule such as the interactions of hydrogen bonds and halogen bonds. By comparing with hydrogen bonds, we would like to discuss the reason why short atom–atom contact is not observed between adjacent molecules even when there exist strong dispersion interactions.

The interatomic distance between adjacent molecules is determined by the balance between attractive and repulsive interactions acting between molecules. In hydrogen bonds and halogen bonds, the major source of the attraction is the electrostatic interactions, and therefore, strong attraction due to the electrostatic interactions acts between positively charged atoms (hydrogen bond or halogen bond donor) and negatively charged atoms (hydrogen bond or halogen bond acceptor). The structure of the hydrogen bonded cluster of methanol dimer is shown in Fig. 8.9a. The equilibrium distance between the hydrogen atom of the donor molecule and the oxygen atom of the acceptor molecule is determined by the balance between the attractive electrostatic interactions and the exchange-repulsion interactions. The distance between the hydrogen atom and the oxygen atom needs to be considerably short to increase the repulsive interactions that can balance the strong attraction by the electrostatic interactions, since only one hydrogen atom and one oxygen atom can contribute to the repulsion. For this reason, in the cases of hydrogen bonds and halogen bonds, the short atom–atom contact between adjacent molecules is necessary when strong attraction exists between molecules.

The dispersion interaction has its origin in molecular polarization. For this reason, the dispersion interactions between molecules with large polarizabilities are strong. The polarizability of molecule composed of a large number of atoms is large, since the polarizability of molecule is approximately the sum of the polarizabilities of the atoms constituting the molecule. In hydrocarbons, carbon atoms are mainly responsible for the dispersion interactions, since the polarizability of hydrogen atoms is small. The dispersion interactions between one carbon atom and one carbon atom are small. For example, the intermolecular interaction energy of methane dimer is

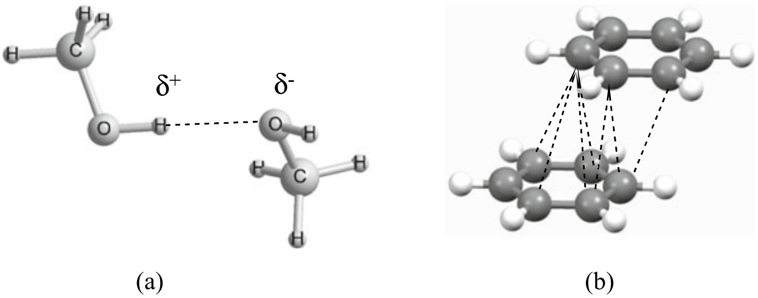


**Fig. 8.9** Attraction in hydrogen bonded complex and dispersion-dominated complex

about −0.5 kcal/mol [11]. On the other hand, a number of carbon atoms interact at distances close to the sum of the van der Waals radii in the crystals of polycyclic aromatic molecules and saturated hydrocarbon molecules (Fig. 8.9b), so that the strong dispersion interactions exist between adjacent molecules. In this case, the attractive interaction between each atom pair is weak, so the attractive interaction can be balanced with exchange-repulsion even when the atoms do not contact at short distance less than the sum of the van der Waals radii. For this reason, no short atom–atom contact is observed, even if strong attraction owing to the dispersion interactions exists between adjacent molecules.

## 8.9 Importance of Dispersion Interactions in Organic Crystals

The dispersion interactions are famous as the origin of the weak attraction between rare gas atoms. For this reason, it is often misunderstood that the dispersion interactions between organic molecules are also weak. However, the analysis of intermolecular interactions shows that the strong dispersion interactions exist between adjacent molecules in the organic crystals. The polarizabilities of organic molecules are significantly large compared with rare gas atoms such as neon and argon. For this reason, the strong dispersion interactions exist between adjacent molecules in the organic crystals.

The structures of organic crystals also suggest the importance of the dispersion interactions for the stabilization of the crystals. The crystal structure of water (Fig. 8.10a) is characterized by large vacant space. The highly directional electrostatic interactions are the major source of the attraction (hydrogen bond) between water molecules. Hydrogen bonds have strong orientation dependence owing to the large contributions of the electrostatic interactions. For this reason, neighboring molecules have to locate at specific positions advantageous to increase the attraction by the highly directional electrostatic interactions for the stabilization of water

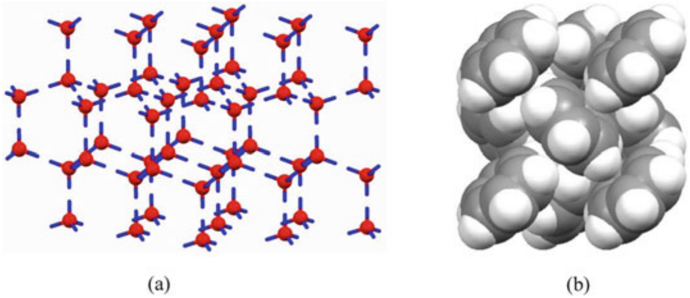

(a) (b)

Fig. 8.10 Crystal structure of water and benzene crystal. Therefore, the water crystal has large vacant space, which is not advantageous for the stabilization by the dispersion interactions.

On the other hand, the crystal structure in which the vacant space is reduced and the average intermolecular distance is shortened like the benzene crystal in Fig. 8.10b is advantageous for the stabilization of the crystal, if the major source of the attraction between adjacent molecules in the crystal is the dispersion interactions. Most of organic crystals have structures which have few vacant spaces. This result suggests that the dispersion interactions are the primary source of attraction in most of organic crystals.

## 8.10 Summary

Ab initio molecular orbital calculations and dispersion-corrected DFT calculations are becoming powerful methods for studying intermolecular interactions in organic crystals. We can obtain detailed information on the intermolecular interactions in crystals (magnitude and origin of attraction). The intermolecular interactions in crystals have been mainly discussed based on the presence or absence of atom–atom contact at short distances. However, analysis of intermolecular interactions in organic crystals show that the strong attraction by the dispersion interactions often exists between adjacent molecules in crystals, even if adjacent molecules do not have short atom–atom contact. The analysis shows that we should remember the significant importance of the dispersion interactions in organic crystals and the danger to discuss the intermolecular interactions in crystals solely based on crystal structures. The analysis of intermolecular interactions in crystals by theoretical calculations is important for understanding structures and properties of organic crystals.

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