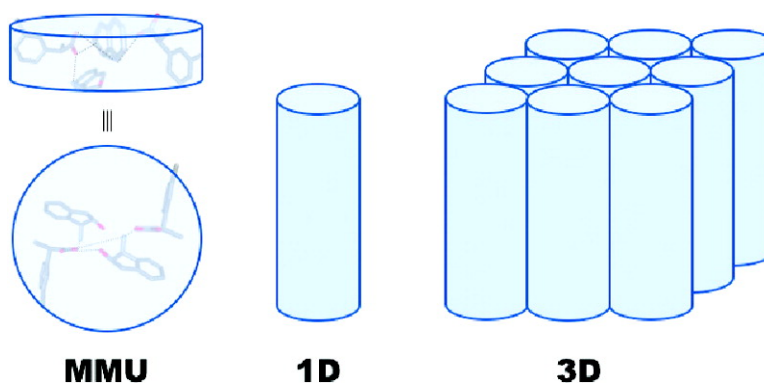Article

Periodic ab Initio Approach for the Cooperative Effect of CH/ Interaction in Crystals: Relative Energy of CH/ and Hydrogen-Bonding Interactions

Yuka Kobayashi, and Kazuhiko Saigo

MMU   **1D**   **3D**

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Periodic ab Initio Approach for the Cooperative Effect of CH/π Interaction in Crystals: Relative Energy of CH/π and Hydrogen-Bonding Interactions

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Abstract: The bonding property of the CH/π interaction in organic crystals has been investigated by the means of a periodic ab initio method. The energy of the $CH(sp^2)/\pi$ interaction in crystals, estimated with periodic RHF/6-21G*, showed a reasonable attractive $CH(sp^2)/\pi$ interaction owing to a cooperative effect, whereas the results calculated with RHF/cc-pVDZ indicate a negligibly small or repulsive interaction. The relative contribution of the $CH(sp^2)/\pi$ interaction to the column packing energy was found to be roughly half of the energy of a conventional hydrogen bond. The calculation of the charge distributions on the aromatic rings participating in the $CH(sp^2)/\pi$ interaction in crystals revealed that the atoms were more ionic than those in the gas phase. These theoretical calculations suggest a hydrogen-bonding characteristic for the $CH(sp^2)/\pi$ interaction in crystals, which does not occur in solution nor gas phase. We present computational evidence of the existence of the cooperative effect of $CH(sp^2)/\pi$ interaction in crystals.

Introduction

Synthesis of functional supramolecules is today one of the most challenging fields in chemistry. In contrast to pure covalent chemistry, supramolecular chemistry is often based on self-assembly, utilizing nonbonding interactions such as hydrogen-bonding, π/π, CH/π, and van der Waals interactions. These weak nonbonding interactions are powerful tools for the development of future nanosystems. It is very important to foster the understanding of the characteristic and energetic contribution of nonbonding interactions. In the first stage, it would be very valuable to evaluate the relative energies, which includes the cooperative effect of nonbonding interactions in organic crystals. In these systems, it is expected that the cooperative interactions are dominant for the determination of molecular arrangement and packing.[1] Results concerning the cooperative effects apply not only to crystalline structures but also to a class of very usual self-assembling supramolecules.

Among nonbonding interactions, CH/π systems have attracted the keen interest of researchers studying different areas, such as conformational preference of DNA,[2-4] molecular recognition,[5-8] and chiral recognition.[9-11] Chakrabarti et al.[12] reported about CH/π interactions in various cofactors. They investigated the existence of the CH/π interaction in the packing of the adenine ring of DNA or RNA in protein structures and concluded that the CH/π interaction has an important role for the recognition of DNA and RNA molecules by a protein, in addition to conventional hydrogen-bonding interaction. Up to now, the energetic contribution of the CH/π interaction has been considered to be small, compared with that of hydrogen-bonding interaction. This assumption is strongly supported by theoretical studies on CH/π interactions by using model systems in gas phase, and further investigations revealed that the origin of the CH/π interaction is not an electrostatic force, which is a main force for the stabilization by hydrogen-bonding interaction, but a dispersion force.[13-18] This means that the energy of CH/π interactions may be closer to van der Waals than hydrogen-bonding interactions.[19] In contrast, there are several papers that report the high influence of CH/π interactions in organic

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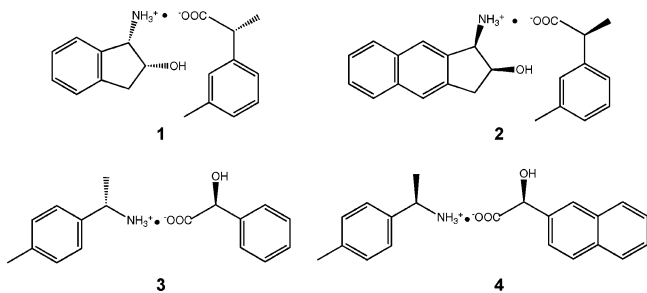
Figure 1. Organic salts applied in the present study.

crystals.[20–25] Steiner et al. proposed on the basis of the IR spectral and X-ray crystallographic studies on organic crystals that CH/π interaction energies are in the range of hydrogen-bond types.[26] Takahashi et al. reported that CH/π interactions have a hydrogen-bond-like characteristic in solid state by analyzing data sets of the Cambridge Structural Database (CSD).[27] These experimental results indicate the potential of investigating CH/π interactions in the solid state, prevented from solvation and other protection effects that usually occur in solution or gas-phase experiments. The hydrogen-bond-like characteristic of the CH/π interaction in crystals is considered to arise from a cooperative effect, induced by an electrostatic force as observed in a hydrogen bond.[28,29] From our knowledge, there is up to now no theoretical evidence for the cooperative effect of CH/π interactions.

In organic crystals, molecules often tend to optimize intermolecular interactions to realize more favorable packing, even when the conformation of each molecule is disadvantageous from an energetic point of view. Therefore, it is challenging to estimate the absolute packing energy of crystals by using a periodic ab initio method. A more efficient approach is to calculate the difference in packing energy on the basis of the X-ray crystallographic data for a pair of crystals. We have recently found that the CH/π interaction site of basic resolving agents influenced the efficiency of the enantioseparations of acidic racemates with the resolving agents.[9,11] The X-ray crystallographic analyses of the corresponding less-soluble salt crystals **1** and **2** (Figure 1) revealed that a hydrogen-bonding network with the same pattern was formed. However, the modes of the CH/π interactions are obviously different because the

aromatic group of the resolving agent (amino alcohol) components are different from each other (a phenylene in **1** and a naphthylene in **2**). A very similar phenomenon could be observed in the less-soluble diastereomeric salt crystals **3** and **4**. There, a hydrogen-bonding network exists and the modes of the CH/π interaction in the crystals **3** and **4** strongly influence the efficiency of the enantioseparations of basic racemates.[30,31] The calculations presented in this paper are based on the X-ray crystallographic structures of **1** (CCDC-140008), **2** (CCDC-255674), **3** (CCDC-RAYQOX), and **4** (CCDC-137290). These crystals are chosen because they have almost identical structure, network, and packing, but they are systematically different in their CH/π and hydrogen-bonding interactions. The results gained from periodic calculations for pairs of crystals are revealing the existence of a cooperative effect caused by CH/π interactions, and they let us derive the relative energy contribution of the CH/π and hydrogen-bonding interactions.

In this paper, we report the bonding property of the CH/π interaction, its cooperative effect, and the relative energy contribution of CH/π and hydrogen-bonding interactions to the stabilization of crystals.

Computational Methodology

From an energetic point of view, long-range interactions should be taken into account to obtain a cooperative effect, which is often observed in crystalline hydrogen-bonding systems.[32] Dovesi et al. estimated the energy of the hydrogen-bonding interaction in crystalline urea by using the periodic Hartree–Fock linear combination of atomic orbitals (LCAO) method.[33] They reported that the energy is in very good agreement with experimental data. Thus, the periodic Hartree–Fock LCAO method is applicable to a wide variety of physical and chemical systems.[34–36] Although the method cannot be directly applied to the estimation of a dispersion force, due to the lack of an electron correlation correction, the method clearly shows the energetic contribution of long-range electrostatic induction and short-range exchange–repulsion forces, which are dominant in a cooperative hydrogen-bonding stabilization.[37] On the basis of these reports, we considered that the periodic Hartree–Fock LCAO method would be useful for the general understanding of the relative energy of CH/π and hydrogen-bonding interactions in crystals.

In the present study, heavy atoms were placed at positions determined by X-ray crystallographic analyses.[38] The hydrogen atoms were placed to form bonds to the heteroatoms and optimized with RHF using 3-21G* basis sets. Geometry optimizations were carried out for a molecular cluster consisting of eight fixed molecules (four carboxylate molecules and four ammonium molecules). *P*1 symmetry was adopted in a series of the calculations in order to prevent an error, which would arise from the difference in symmetry between crystals of a different space group. In this treatment, two pairs of carboxylate molecules and ammonium molecules were considered as a minimal molecular unit (**MMU**), for which any symmetry operation was avoided to construct a periodic

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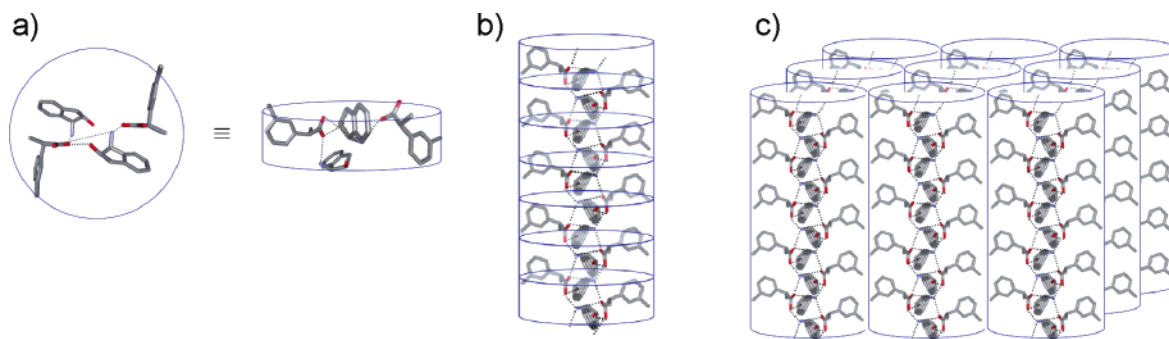
Figure 2. Three cutoff structures for the calculations. (a) Minimal molecular unit consisting of two carboxylate molecules and two ammonium molecules (**MMU**), (b) one-dimensional helical column (**1D**), and (c) three-dimensional crystal (**3D**).

columnar structure. The single point energy calculation for the geometry, mentioned above, was performed with the periodic Hartree–Fock using 6-21G* basis sets. Counterpoise correction is a suitable method for diminishing basis set superposition error (BSSE).[39] However, the BSSE is expected to be small, since we are discussing relative energies. Therefore, we did not apply the counterpoise method in the periodic calculations. The truncation criteria for all of bielectronic, Coulomb overlap, Coulomb penetration, and exchange overlap integrals were 10^{-6}. The charge distribution was evaluated using the Mulliken population analysis.

Calculations were carried out for three kinds of molecular arrangements, which are different in its interaction dimension. A minimal molecular unit (**MMU**), as the smallest isolated molecular cluster; a one-dimensional helical column (**1D**), in which **MMU**s are stacked to be treated as a polymer; and a three-dimensional crystal (**3D**), in which **MMU**s are packed three-dimensionally to be calculated as a bulk crystal. The schematic representations for **MMU**, **1D**, and **3D** are shown in Figure 2. The calculations were performed with CRYSTAL 98,[40] which is an ab initio Hartree–Fock linear combination of atomic orbitals (LCAO) self-consistent field (SCF) program, and with the Gaussian 98 package,[41] for geometry optimization of hydrogen atoms and model calculations.

Results and Discussion

Estimation of the Packing Energy of Columns by Intercolumnar T-Shaped CH(sp²)/π Interaction. The aromatic parts of the ammonium cations in the salt crystals **1** and **2** are different from each other (a phenylene group in **1** and a naphthylene group in **2**). A columnar hydrogen-bonding network, consisting of the ammonium cations, the carboxylate anions, and the hydroxy groups of the ammonium cations, is commonly constructed. This leads to almost identical crystal structures. The distances between the heteroatoms, which form the hydrogen-bonding networks in crystals **1** and **2**, are very close; the N···O distances in **1** and **2** are in range of 2.69–2.87 and 2.69–2.83 Å, and the O···O distances are 2.62 and 2.66

Å, respectively. The distances for the intracolumnar CH(sp³)/π interactions in crystals **1** and **2** are exactly the same (3.96 Å). Moreover, the distances for the intercolumnar CH(sp³)/π interactions in crystal **2** (3.49 and 3.58 Å) are only slightly shorter than that in crystal **1** (3.69 Å). However, the numbers of the intercolumnar T-shaped (formed by perpendicularly located aromatic rings) CH(sp²)/π interactions in crystals **1** and **2** are obviously different: The naphthylene ring of **2** can offer two interaction sites, while the phenylene ring of **1** offers only one site, as shown in Figure 3. The similarity in the crystal structures and the difference in the numbers of the T-shaped CH(sp²)/π interactions strongly suggest that the estimation of the energy of the T-shaped CH(sp²)/π interaction is possible on the basis of the difference between the packing energies of crystals **1** and **2**. The estimated energies of **MMU**s, **1D**s, and **3D**s for **1** and **2** are shown in Table 1. $\Delta E_{\text{1D–MMU}}$ is the stacking energy of **MMU** to form a column. The $\Delta E_{\text{1D–MMU}}$ of **2** is 1.7 kcal/mol higher than that of **1**. On the other hand, $\Delta E_{\text{3D–1D}}$ can be regarded as the packing energy of the columns. The main contribution to the packing energy is the intercolumnar CH(sp²)/π interaction, because the contributions arising from the formation of the hydrogen-bonding networks in **1D** and **3D** would be almost the same, and they are canceled by this treatment. As shown in Table 1, $\Delta E_{\text{3D–1D}}$ is −2.3 kcal/mol for crystal **1** and −5.0 kcal/mol for crystal **2**. The resulting $|\Delta E_{\text{3D–1D}}|$ of **2** is about 2 times larger than that of **1**. This result is in very good agreement with the fact that there are two intercolumnar CH(sp²)/π interactions in **2**, while only one in **1**. The packing energy of the CH(sp²)/π interaction is estimated to be about 2.4 kcal/mol on average. Thus, the present calculations are considered to be appropriate for the estimation of the packing energy caused by the CH(sp²)/π interaction.

Cooperative Effect of T-Shaped Intercolumnar CH(sp²)/π Interaction in a Bulk Crystal. The main force contributing to CH/π interaction has been reported to be a dispersion force, implying that the energy evaluation for CH/π interaction requires the application of a post-Hartree–Fock method, namely, a correlation-corrected method, such as MP2 and CCSD.[14,16,18] To understand the meaning of the energies calculated above, we also carried out calculations for simplified models of the present system. The phenylene groups and the naphthylene groups in the columns of crystals **1** and **2** (**1$_{Ar}$** and **2$_{Ar}$**) were extracted from the X-ray coordinates, respectively, and only the position of the hydrogen atoms were optimized with RHF/3-21G*. Single-point energy calculations were performed with MP2 as well as with RHF using 6-21G* and cc-pVDZ basis

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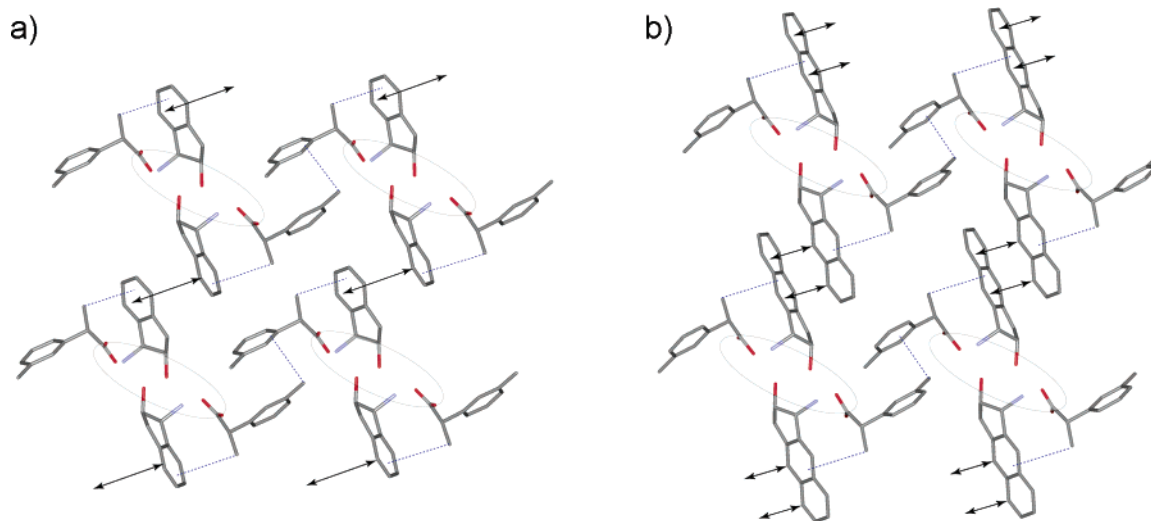
Figure 3. Packing modes of helical columns by CH(sp^2)/π interaction(s) in (a) **1** and (b) **2** crystals.[9,11] The arrows show the CH(sp^2)/π interactions, the blue dotted lines show the CH(sp^3)/π interactions, and the circles indicate the hydrogen-bonding columns.

Table 1. Single-Point Energies of 1 and 2 and the Energy Differences between MMU, 1D, and 3D, Evaluated with Periodic RHF/6-21G*

	1	2
MMU (au)	−1010.963 327	−1163.342 786
1D (au)	−1011.044 040	−1163.426 341
3D (au)	−1011.047 689	−1163.434 363
$\Delta E_{\mathbf{1D-MMU}}$ (kcal/mol)	−50.7	−52.4
$\Delta E_{\mathbf{3D-1D}}$ (kcal/mol)	−2.3	−5.0

sets without/with BSSE correction. The results are summarized in Table 2. The complex formation energies for $\mathbf{1}_{Ar}$ and $\mathbf{2}_{Ar}$, estimated using RHF/6-21G* without BSSE correction, are very small (−0.7 and −0.9 kcal/mol, respectively). Moreover, in the calculation using a larger basis set, i.e., RHF/cc-pVDZ, without BSSE correction, the stabilization energies for $\mathbf{1}_{Ar}$ and $\mathbf{2}_{Ar}$ are again very small or repulsive (−0.1 and 0.5 kcal/mol, respectively). Such tendency is also observed in the formation energies estimated by those with BSSE correction; most of the energies are positive. Furthermore, basis set dependency has been well-examined in the calculations of the formation energies of some benzene dimers by Tsuzuki et al.;[14] they have reported that the formation energies are always positive when the calculations were performed by RHF using any larger basis sets up to the basis set limit. These results lead to the conclusion that RHF is unable to evaluate the weak CH/π interaction in the present dimer models and that the unsuitability of RHF is not caused by the BSSE nor the applied basis set. On the other hand, MP2 calculations with 6-21G* and cc-pVDZ without BSSE correction result in negative values (−2.7 and −3.0 kcal/mol for $\mathbf{1}_{Ar}$ and −6.4 and −7.0 kcal/mol for $\mathbf{2}_{Ar}$, respectively), and even taking BSSE correction into account, the formation energies are still reasonable negative values.[42] These results strongly suggest that MP2 is suitable for the single-point energy calculations of the present dimer models. However, the CH/π interaction energies for crystals **1** and **2**, evaluated with periodic RHF/6-21G*, are both attractive (Table 1), even though the values do not include any correlation contribution. This fact indicates that the attractive
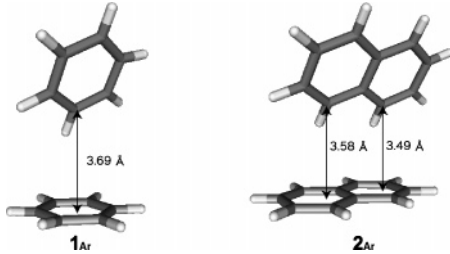
force, which is included in the CH/π interactions, is caused by a cooperative effect originating from surrounding molecules; the effect would mainly arise from so-called static packing, which is a result of the electrostatic contribution of long-range interactions in crystals. Several theoretical approaches for the verification of the cooperative effect of the CH/π interaction have been carried out by using isolated model systems.[43,44] However, BSSE is inevitable in the assumption, so it is very hard to distinguish a cooperative effect from BSSE as far as a limited size of basis sets in a limited computational effort is adopted and individual isolated molecules in finite number are taken into account. The present calculation is the first example to clearly show the cooperative effect of CH/π interaction by a periodic ab initio approach.

Bonding Property of T-Shaped Intercolumnar CH(sp^2)/π Interaction in a Bulk Crystal. To understand the bonding property of the CH(sp^2)/π interactions in crystals **1** and **2** more precisely, we investigated the charge distributions in **1** and **2**. Table 3 shows the Mulliken charges for the aromatic parts, which contribute to the formation of the CH(sp^2)/π interactions, and those for the methyl groups, forming the CH(sp^3)/π interactions, as a comparison. As shown in Table 3, the charges on the atoms in **3D**s are more polarized than those in the corresponding **MMU**s of both crystals. Moreover, the degree of polarization of the aromatic rings in **3D**s is much larger than that of the methyl groups. The differences in charge between **MMU**s and **3D**s for the methyl groups in **1** and **2** are in the range of 0.02−0.05, while those for the aromatic rings are in the range of 0.10−0.16, indicating that the atoms of the aromatic rings are more ionic. This result is in good agreement with reported calculations that show that the CH(sp^2)/π interaction in the gas phase is more electrostatic than the CH(sp^3)/π interaction and that the C−H bond possesses larger bond dipoles.[16] Remarkably, the naphthylene ring in **2** is more charged than the phenylene ring in **1**. This result is consistent with the fact that the aromatic/aromatic distances in crystal **2** is more favorable for the CH(sp^2)/π interaction than those in crystal **1**,
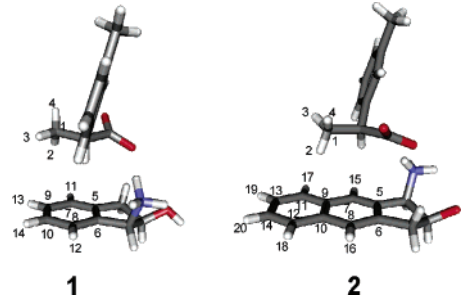
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Table 2. Single-Point Energies of 1_{Ar} and 2_{Ar} and Stabilization Energies of CH(sp^2)/π Interactions, Evaluated Using RHF/6-21G*, RHF/cc-pVDZ, MP2/6-21G*, and MP2/cc-pVDZ without and with BSSE Corrections

	1_{Ar}	2_{Ar}			1_{Ar}	2_{Ar}
RHF/6-21G*				RHF/cc-pVDZ		
two isolated				two isolated		
molecules (au)	−460.979 916	−766.094 621		molecules (au)	−461.275 697	−766.575 965
complex (au)	−460.980 947	−766.096 073		complex (au)	−461.275 853	−766.575 148
ΔE (kcal/mol)	−0.7	−0.9		ΔE (kcal/mol)	−0.1	0.5
$\Delta E_{BSSEcorrected}$	−0.1	1.5		$\Delta E_{BSSEcorrected}$	0.0	1.7
MP2/6-21G*				MP2/cc-pVDZ		
two isolated				two isolated		
molecules (au)	−462.459 443	−768.563 134		molecules (au)	−462.817 249	−769.130 902
complex (au)	−462.463 738	−768.573 405		complex (au)	−462.821 948	−769.141 972
ΔE (kcal/mol)	−2.7	−6.4		ΔE (kcal/mol)	−3.0	−7.0
$\Delta E_{BSSEcorrected}$	−1.5	−3.0		$\Delta E_{BSSEcorrected}$	−1.7	−4.2

Table 3. Charge Distributions (au) of 1 and 2 in MMU and 3D, Evaluated with Periodic RHF/6-21G*

1				2			
		MMU	3D			MMU	3D
methyl				methyl			
	C1	−0.356	−0.388		C1	−0.381	−0.396
	H2	0.150	0.162		H2	0.187	0.161
	H3	0.118	0.166		H3	0.131	0.176
	H4	0.166	0.157		H4	0.135	0.155
	total	0.434	0.485		total	0.453	0.492
phenylene				naphthylene			
	C5	−0.015	−0.038		C5	−0.033	−0.025
	C6	0.000	−0.007		C6	−0.002	−0.035
	C7	−0.159	−0.181		C7	−0.112	−0.137
	C8	−0.175	−0.181		C8	−0.151	−0.139
	C9	−0.146	−0.170		C9	−0.074	−0.065
	C10	−0.151	−0.175		C10	−0.046	−0.091
	total	−0.646	−0.752		C11	−0.087	−0.170
					C12	−0.152	−0.100
					C13	−0.184	−0.150
					C14	−0.129	−0.206
					total	−0.970	−1.118
	H11	0.176	0.190		H15	0.135	0.188
	H12	0.139	0.200		H16	0.175	0.196
	H13	0.175	0.172		H17	0.149	0.192
	H14	0.168	0.197		H18	0.170	0.181
	total	0.658	0.759		H19	0.166	0.173
					H20	0.172	0.200
					total	0.967	1.130

as observed in the X-ray structure. The packing energy of **2**, in which two kinds of CH(sp^2)/π interactions exist, is slightly higher than twice the packing energy of **1**, in which only one kind of CH(sp^2)/π interaction exists (Table 1).

In the next stage, we performed geometry optimizations for the models of 1_{Ar} and 2_{Ar} in gas phase in order to compare the structures of 1_{Ar} and 2_{Ar} in the crystals with those of the models, respectively. As a result, it was found that the distance between the C atom of the C−H bond and the π-plane in the phenylene/phenylene interaction in the crystal **1** is quite shortened, compared with that of the model of 1_{Ar} optimized with MP2/cc-pVDZ in the gas phase (3.69 and 3.83 Å, respectively), while the bond angles and the dihedral angles are almost the same.[45] This means that the optimized structure arises from the relaxation of the static packing.

The present study clearly demonstrated that the CH(sp^2)/ interactions in the crystals of **1** and **2** are close to a conventional hydrogen bond from the viewpoints of the cooperativity, the polarization of the bond, and the shortened interaction distance, even though the character of the model of 1_{Ar} in gas phase is very close to a van der Waals interaction.

Estimation of the Cooperative Enhancement Observed in Intracolumnar Chainlike CH(sp^2)/π Interaction. Because only an intercolumnar CH(sp^2)/π interaction was observed in crystals **1** and **2**, it was impossible to estimate the effect of the cooperative enhancement of the CH/π interaction. In contrast, for crystals **3** and **4**, there exist directly linked intracolumnar CH(sp^2)/π interactions to form a chainlike CH(sp^2)/π interaction network, which is of a different nature from the hydrogen-bonding networks in their columns (Figure 4). This fact indicates that the effect of the cooperative enhancement by the chainlike CH(sp^2)/π interaction network would be clarified upon comparing the stacking energies of **1D**s for **3** and **4**. The schematic representations of the intracolumnar CH(sp^2)/π interaction networks in **3** and **4** are shown in Figure 5. It can be seen that the orientation of the aromatic rings in crystals **3** and **4** are

(45) The model of 2_{Ar} having a naphthylene/naphthylene interaction in the gas phase gave no local minimum close to the X-ray structure upon optimizing with MP2/cc-pVDZ, although some local minima, stabilized by a π/π interaction stronger than a CH/π interaction, were found.
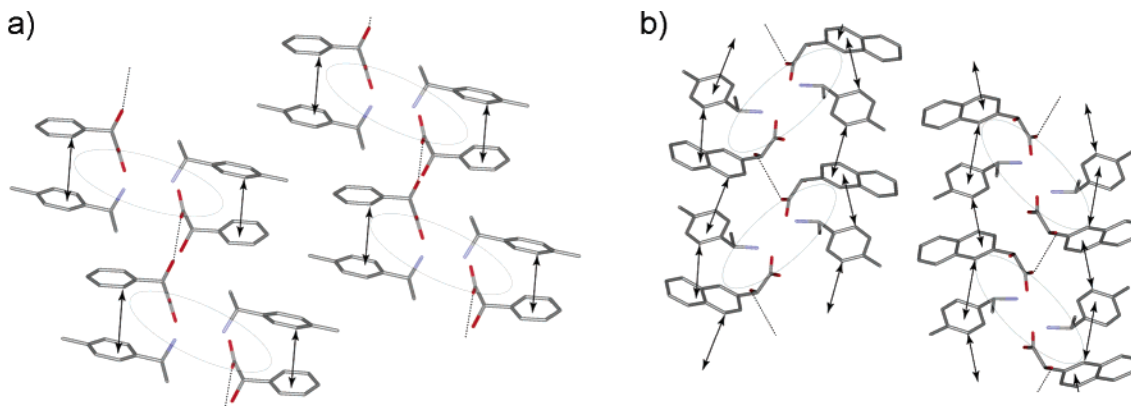
Figure 4. Packing modes of helical columns by hydrogen bonds and CH(sp^2)/π interactions in (a) **3** and (b) **4** crystals.[30,31] The dotted lines show the hydrogen bonds, the arrows show the CH(sp^2)/π interactions, and the circles indicate the hydrogen-bonding columns.
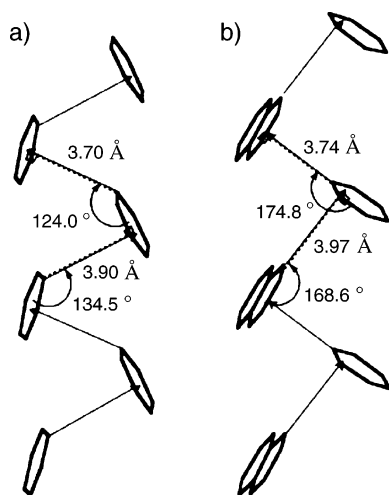
Figure 5. Schematic representations of the intracolumnar CH(sp^2)/π interaction networks observed in (a) **3** and (b) **4** crystals. The arrows show the direction of the C−H bond participating in the CH(sp^2)/π interaction.

Table 4. Single-Point Energies of 3 and 4 and the Energy Differences between MMU, 1D and 3D, Evaluated with Periodic RHF/6-21G*

	3	**4**
MMU (au)	−934.006 340	−1086.845 387
1D (au)	−934.063 266	−1086.922 564
3D (au)	−934.086 882	−1086.933 317
ΔE_{1D-MMU} (kcal/mol)	−35.7	−48.4
ΔE_{3D-1D} (kcal/mol)	−14.8	−6.8

largely different. In crystal **3**, the aromatic groups participating in the CH(sp^2)/π interaction are arranged in such an orientation that the extension of the C−H bond in one of the aromatic groups crosses the π-plane of the other aromatic group at 124.0° and 134.5°, although the distance between the C atom and the π-plane is short. On the other hand, in crystal **4**, the aromatic groups are vertically oriented and they are acting as a proton donor as well as an acceptor. Obviously the T-shaped CH(sp^2)/π interaction observed in crystal **4** is preferred to that in **3**. The preference in orientation is supported by a study on dimer models in the gas phase, reported by Tsuzuki et al.[16] Table 4 shows that the stacking energies ΔE_{1D-MMU} of **MMU**s for crystals **3** and **4**, evaluated with periodic RHF/6-21G*, are −35.7 and −48.4 kcal/mol, respectively. The large energy difference of 12.7 kcal/mol includes not only the CH(sp^2)/π interactions but also the hydrogen-bonding networks. However,

the distances of the hydrogen bond are 2.74, 2.77, and 2.86 Å for **3** and 2.81, 2.88, and 2.90 Å for **4**. This means that the hydrogen-bonding network in **4** is energetically less favorable compared to that in **3**. Thus, most of the energetic advantage of **4** is considered to originate from the cooperative enhancement of the effective T-shaped CH(sp^2)/π interaction. It is noteworthy that the stacking energy of **MMU** for **4** (−48.4 kcal/mol) is comparable to that of **1** (−50.7 kcal/mol), although **1** includes an additional intracolumnar hydrogen bond. This result clearly indicates that the cooperative enhancement of the T-shaped CH(sp^2)/π interaction is very large and that its energetic contribution is almost in the range of a conventional hydrogen bond.

Estimation of the Packing Energy of Columns with Intercolumnar Hydrogen-Bonding Interaction. We estimated the packing energy of columns, in which both hydrogen-bonding and CH(sp^2)/π interactions play a role for the linkage of columns. In crystals **3** and **4**, the corresponding carboxylate has a hydroxy group at the α-carbon. In the crystals the hydroxy group links hydrogen-bonded helical columns, consisting of the ammonium cations and the carboxylate, by forming another hydrogen bond with the vacant site of the carboxylate in the neighboring column, although in crystals **1** and **2** the columns are linked only by CH(sp^2)/π interactions. Table 4 shows the energies of **3D**s for crystals **3** and **4** and their packing energies (ΔE_{3D-1D}) of 14.8 and 6.8 kcal/mol, respectively. The energy difference between **3** and **4** originates from the pattern of the intercolumnar interactions. The hydroxy group in **3** offers one hydrogen-donating site, which forms a hydrogen bond with the facing carboxylate. The upper and lower carboxylates in the neighboring column leads to a three-point hydrogen bond with a short distance (2.82 Å) and two long distances (3.05 Å). This chainlike network is linking the oxygen atoms directly.[31] The hydroxy group in **4** forms only one simple hydrogen bond (2.89 Å) with the facing carboxylate in the neighboring column, which results in an additional intercolumnar CH(sp^2)/π interaction.[30] The schematic representations of the intercolumnar hydrogen-bonding interactions are depicted in Figure 6. The large advantage of the packing energy (ΔE_{3D-1D}) of 8.0 kcal/mol for **3** originated from the cooperative enhancement of the hydrogen-bonding network. This enhancement effect is sufficiently large, even though the bond distance is comparable to that of a conventional hydrogen bond.

Relative Energetic Contribution of CH(sp^2)/π and Hydrogen-Bonding Interactions in a Bulk Crystal. Since the

a) b)
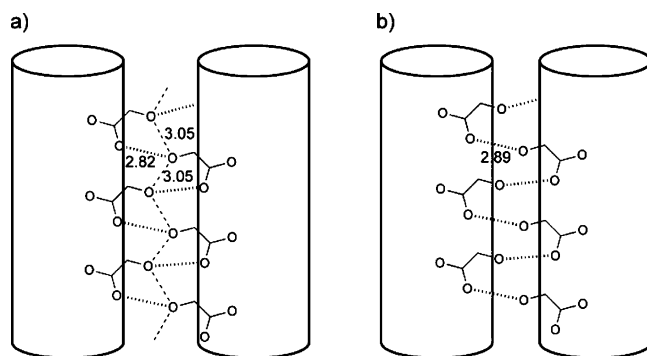
Figure 6. Schematic representations of intercolumnar hydrogen-bonding interactions in (a) **3** (three-point interaction) and (b) **4** (one-point interaction) crystals. The bond distances are in angstrom.

packing energies (ΔE_{3D-1D}) for **1**−**4** are calculated (see Tables 1 and 4), the relative energetic contribution of CH(sp^2)/π and hydrogen-bonding interactions can be deduced. The difference in ΔE_{3D-1D} between **1** and **4** shows that the energetic contribution of the CH(sp^2)/π interaction is roughly a half of that of a conventional hydrogen bond. Furthermore, it can be seen that two simultaneous CH(sp^2)/π interactions, observed in the naphthylene−naphthylene groups in **2**, show a higher energetic contribution than that of the hydrogen bond, observed in **4**. The reason for the larger energy in the CH(sp^2)/π interaction energy, compared to a gas-phase model system, is owing to the cooperative effect, which is of electrostatic nature.

Conclusion

The total energies of four kinds of self-assembled organic crystals, **1**−**4**, with almost identical hydrogen-bonding network, were estimated with a periodic ab initio method in three modes with different dimension (**MMU**, **1D**, and **3D**). The results revealed that the CH/π interactions were always attractive in the crystals. In the solid state, we obtained a cooperative effect in the CH(sp^2)/π interaction, which could not be determined using gas-phase calculations. Moreover, the atoms participating in the CH(sp^2)/π interaction were found to be largely polarized in the crystals. The present results reveal for the first time that the characteristics of the CH(sp^2)/π interaction in bulk crystals does resemble a conventional hydrogen bond from the viewpoints of the cooperativity, the polarization of the bond, and the shortened interaction distance. The good agreement of our results with the predictions made on the basis of crystallographic data demonstrates the great potential of the relative energy calculations in the solid state. In the future, the method may be applied to estimate, predict, and design supramolecules.