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Model Chemistry Calculations of Thiophene Dimer Interactions: Origin of π-Stacking

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Abstract: The intermolecular interaction energies of thiophene dimers have been calculated by using an aromatic intermolecular interaction (AIMI) model (a model chemistry for the evaluation of intermolecular interactions between aromatic molecules). The CCSD(T) interaction energy at the basis set limit has been estimated from the MP2 interaction energy near the basis set limit and the CCSD(T) correction term obtained by using a medium-size basis set. The calculated interaction energies of the parallel and perpendicular thiophene dimers are −1.71 and −3.12 kcal/mol, respectively. The substantial attractive interaction in the thiophene dimer, even where the molecules are well separated, shows that the major source of attraction is not short-range interactions such as charge transfer but rather long-range interactions such as electrostatic and dispersion. The inclusion of electron correlation increases the attraction significantly. The dispersion interaction is found to be the major source of attraction in the thiophene dimer. The calculated total interaction energy of the thiophene dimer is highly orientation dependent. Although electrostatic interaction is substantially weaker than dispersion interaction, it is highly orientation dependent, and therefore electrostatic interaction play an important role in the orientation dependence of the total interaction energy. The large attractive interaction in the perpendicular dimer is the cause of the preference for the herringbone structure in the crystals of nonsubstituted oligothiophenes (α-terthienyls), and the steric repulsion between the β-substituents is the cause of the π-stacked structure in the crystals of some β-substituted oligothiophenes.

Introduction

During the past two decades, thiophene polymers and oligomers have been studied extensively due to their remarkable electronic and optical properties.[1−3] Various types of electronic devices involving polythiophene have been proposed such as conductors,[4−6] electrode materials,[7,8] and organic semiconductors.[9−12] Polythiophene and its derivatives have a large and very fast nonlinear optical response.[13,14] Recently, the electroluminescence and photoluminescence of thiophene oligomers have also been studied extensively.[15,16] The properties of polythiophene have attracted much interest both from a fundamental point of view and for the many expected applications in the fields of electronics and optoelectronics. The solid-state structure of the polymer defines its band structure and thereby determines its electronic and optical properties.[5,17,18] Therefore, understanding the intermolecular interaction between thiophene rings is essential for the material design strategy.

π-Stacking is observed in the crystals of many oligothiophenes and their derivatives.[19−29] π-Stacking in self-assembled

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polythiophenes is also reported.[18,30−32] The self-assembly of polythiophene and thiophene/phenylene co-oligomers in solution is reported.[33,34] These experimental measurements indicate that the $\pi-\pi$ interaction plays an important role in the control of the solid-state structure and self-assembled structure of thiophene polymer and oligomers. Detailed information on the thiophene dimer interaction is essential for understanding the $\pi-\pi$ interactions of thiophene polymer and oligomers. An accurate potential energy surface for the thiophene dimer is also needed by those who carry out force field simulations of these materials. Although many experimental studies have been reported on the intermolecular interaction of oligothiophenes, it is still difficult to accurately evaluate the potential energy surface of the thiophene dimer by experimental measurements only.

Ab initio molecular orbital calculation is becoming a powerful tool to study intermolecular interactions.[35,36] Ab initio calculation provides sufficiently accurate interaction energy, if a reasonably large basis set is used and electron correlation is properly corrected. The second-order Møller−Plesset perturbation (MP2) method[37,38] has been widely used for the calculations of intermolecular interaction energies of organic molecules. However, the MP2 level electron correlation correction sometimes has serious errors. Recent coupled cluster calculations with single and double substitutions with noniterative triple excitations [CCSD(T)][39] show that the MP2 calculations overestimate the attraction in the benzene and naphthalene dimers significantly.[40−42] Similar overestimation of the attraction was also reported in the calculations of the interactions of some nitrogen-containing aromatic molecules.[43] The MP2 method is not appropriate for studying the intermolecular interaction between aromatic molecules.

The requirement of using the computationally demanding CCSD(T) calculation with a very large basis set is the major obstacle to studying the intermolecular interaction of aromatic molecules by the ab initio method. Due to this difficulty, the intermolecular interactions of only limited aromatic molecules were studied by the high-level ab initio molecular orbital method. Unfortunately, high-level ab initio calculation of the intermolecular interaction in the thiophene dimer has not yet been reported. Therefore, there remain a number of important and fundamental unsettled issues on the interaction in the thiophene dimer: (1) Despite broad interest in the π-stacking of thiophene rings, very little is known about the origin of the attraction in the π-stacking. Although recent ab initio calculations on benzene and naphthalene dimers suggest the importance of dispersion, other interactions such as electrostatic, induction, and charge-transfer interactions may play important roles in the attraction in the thiophene dimer. (2) The size of the interaction energy of the thiophene dimers is also an important issue in understanding the $\pi-\pi$ interaction in the thiophene dimer, but the experimental measurement of the binding energy has not yet been reported. Ab initio calculations with very large basis sets are necessary for the estimation of the dimer interaction energy. (3) The calculations on the benzene dimer show that the dimer interaction energy has a strong orientation dependence. The thiophene dimer interaction energy will also have directionality. However, the magnitude of the orientation dependence and the origin of the directionality in the thiophene dimer interaction are not well understood. (4) Two types of crystal packing (π-stacked and herringbone structures) are observed in the crystals of oligothiophenes. It is significantly important in material design to understand which interaction controls the crystal packing. Unfortunately, however, the reason for the preference in the crystal packing is not well understood.

In this paper, we have calculated the interaction energy of the thiophene dimer by using very large basis sets near saturation and have estimated the MP2 and CCSD(T) level interaction energies at the basis set limit by using model chemistry (aromatic intermolecular interaction (AIMI) model, a model chemistry for obtaining intermolecular interaction energies between aromatic molecules). We discuss the roles of electrostatic, induction, dispersion, and charge-transfer interactions in the attraction and directionality of the thiophene dimer interaction. We also discuss the cause of the preference of the crystal packing of oligothiophenes on the basis of the calculated interaction energies of the thiophene dimers.

Computational Method

The Gaussian 98 program[44] was used for the ab initio molecular orbital calculations. The basis sets implemented in the program and a few modified basis sets were used. Electron correlation was accounted for at the MP2[37,38] and CCSD(T)[39] levels. The geometries of isolated thiophene and 3-methylthiophene molecules were optimized at the MP2/6-311G** level and were used for the calculations on the dimers. The optimized geometries of the monomers are shown in Figure 1. The geometries of 17 thiophene dimers are shown in Figure 2. The C_2 axes of the two thiophene molecules have a parallel or perpendicular orientation in these dimers. X is the middle point of C_2 and C_5 of thiophene, as shown in Figure 1. The intermolecular distance (R) is the distance between the X's of the two thiophenes. The basis set superposition error (BSSE)[45] was corrected for all calculations using

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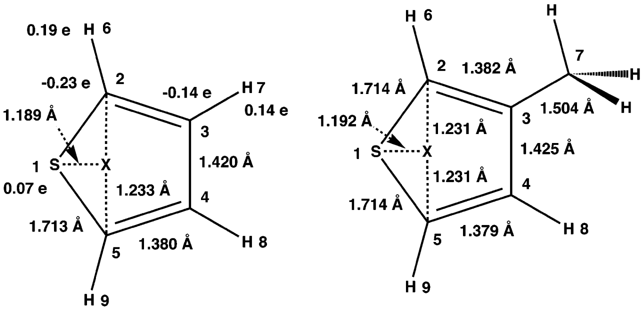

Figure 1. MP2/6-311G** level optimized geometries of thiophene and 3-methylthiophene monomers and atomic charge distributions of thiophene monomer. X is the middle point between C2 and C5 of thiophene. X is close to the mass center of thiophene. The S1−X−C2 and S1−X−C5 angles are 90° in both monomers. The atomic charges were obtained by electrostatic potential fitting using the Merz−Singh−Kollman scheme from the MP2/6-311G** wave functions.

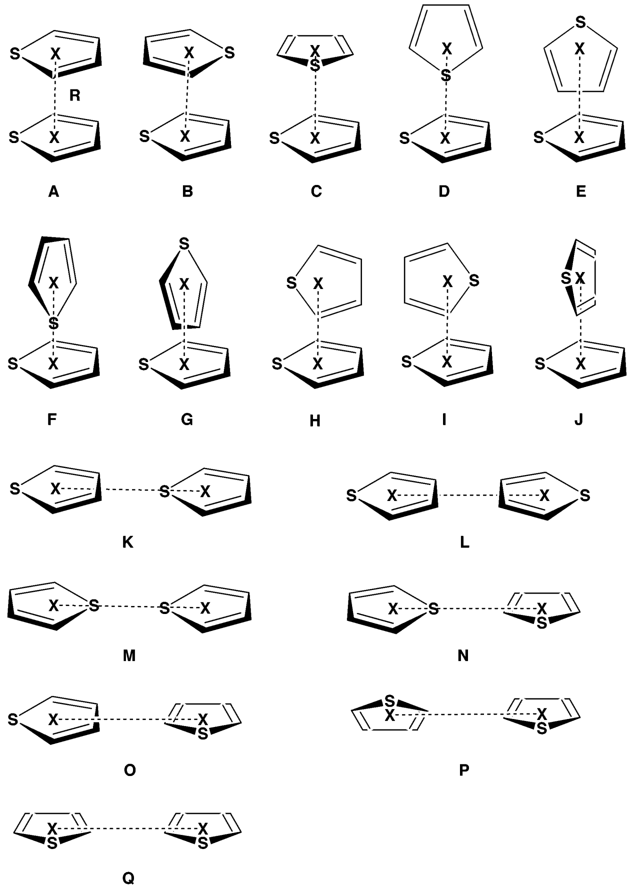

Figure 2. Geometries of the thiophene dimers. The C_2 axes of thiophenes have a parallel or perpendicular orientation in the dimers.

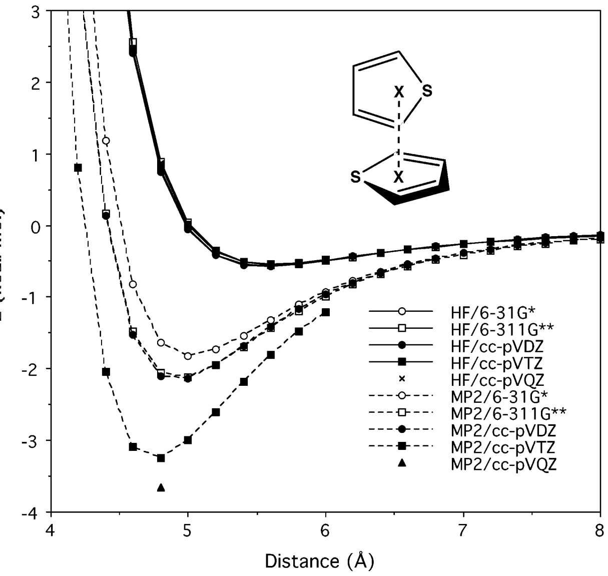

Figure 3. HF and MP2 interaction energy potentials of thiophene dimer I calculated by using several basis sets.

the counterpoise method.[46] The MP2 interaction energies at the basis set limit were estimated by using the method proposed by Feller[47] from the interaction energies calculated with Dunning correlation-consistent basis sets (cc-pVXZ, X = D, T, and Q).[48,49] The CCSD(T) level intermolecular interaction energies of the dimers were estimated with the AIMI model.[41,42] The aug(d)-6-311G* basis set is the 6-311G* basis set augmented with diffuse d functions on carbon and sulfur atoms (α_d(C) = 0.1565 and α_d(S) = 0.1625). The aug(d,p)-6-311G** basis set is the 6-311G** basis set augmented with the diffuse d functions on carbon and sulfur atoms and diffuse p functions on hydrogen atoms (α_p(H) = 0.1875).[41,50] Distributed multipoles[51,52] up to a hexadecapole on all atoms were obtained from the MP2/6-311G** wave functions of an isolated thiophene using CADPAC version 6.[53] The electrostatic and induction energies of the dimers were calculated by using Orient version 3.2.[54] The electrostatic energies of the dimers were calculated as interactions between distributed multipoles of monomers. The induction energies were calculated as interactions of polarizable sites with electric field produced by the multipoles of monomers.[55] The atomic polarizabilities of carbon (α = 10 au) and sulfur (α = 20 au) were used for the calculations.[56] Distributed multipoles and polarizabilities were used only for the estimation of the electrostatic and induction energies.

Results and Discussion

Aromatic Intermolecular Interaction (AIMI) Model. The intermolecular interaction energies of thiophene dimer I were calculated by using the Hartree−Fock (HF) and MP2 methods with several basis sets, as shown in Figure 3. The basis set dependence of the HF interaction energies is not large. On the other hand, the MP2 interaction energies depend strongly on the basis set, as in the case of benzene and naphthalene dimers.[40−42,57−59] Small basis sets underestimate the molecular polarizability and thereby the dispersion interaction consider-

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ably.[60] The strong basis set dependence shows that a large basis set is necessary for the accurate evaluation of the intermolecular interaction energy of the thiophene dimer.

Recent CCSD(T) calculations show that the MP2 calculations greatly overestimate the attraction in the benzene and naphthalene dimers.[40−42] The MP2 calculation also overestimates the attraction in the thiophene dimer, as we will show later. This means that the MP2 method is not appropriate for studying the thiophene dimer interaction. However, it is not an easy task for today's computers to obtain the intermolecular interaction energy between aromatic molecules at the CCSD(T) level with the use of a very large basis set near saturation. Therefore, we have used the AIMI model[41,42] to study the intermolecular interaction in the thiophene dimer.

The MP2 and CCSD(T) interaction energies (E_{MP2} and $E_{\mathrm{CCSD(T)}}$) of the benzene and naphthalene dimers depend strongly on the basis set, while the basis set dependence of the CCSD(T) correction terms ($\Delta\mathrm{CCSD(T)} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$) is not large.[41,42] The weak basis set dependence of ΔCCSD(T) suggests that the CCSD(T) interaction energy at the basis set limit ($E_{\mathrm{CCSD(T)(limit)}}$) can be estimated sufficiently accurately from E_{MP2} calculated with a large basis set near saturation and ΔCCSD(T) obtained by using a medium-size basis set, according to the equation

$$E_{\mathrm{CCSD(T)(limit)}} = E_{\mathrm{MP2}} + \Delta\mathrm{CCSD(T)}$$

In the AIMI model, $E_{\mathrm{CCSD(T)(limit)}}$ is estimated by using this equation. Three levels of AIMI models, I, II, and III, have been proposed.[41] In model I, the aug(d)-6-311G* basis set was used for the calculation of E_{MP2}. The 6-31G* basis set was used for the calculation of ΔCCSD(T). In model II, the aug(d,p)-6-311G** basis set was used for the calculation of E_{MP2}. The 6-311G* basis set was used for the calculation of ΔCCSD(T). In model III, the estimated E_{MP2} and ΔCCSD(T) values at the basis set limit were used to obtain $E_{\mathrm{CCSD(T)(limit)}}$. In the calculations of the benzene dimer interaction energy, the three models have provided nearly identical interaction energies.[41] Although E_{MP2} and $E_{\mathrm{CCSD(T)}}$ of the thiophene dimers depend on the basis set strongly, the basis set dependence of ΔCCSD(T) is weak, as in the case of the benzene dimer (we show the details of the basis set dependence later). The weak basis set dependence of ΔCCSD(T) suggests that the AIMI models can estimate the CCSD(T) interaction energies of the thiophene dimers sufficiently accurately. We have used AIMI model I for the calculations of the interaction energy potentials of the 17 differently oriented thiophene dimers. In addition, we have used computationally more demanding AIMI models II and III for the calculations on selected dimers to evaluate the performance of the models.

Orientation Dependence of Interaction Energy. The values of E_{MP2}, ΔCCSD(T), and $E_{\mathrm{CCSD(T)(limit)}}$ for the 17 dimers (Figure 2) calculated with AIMI model I are summarized in Table 1. The electrostatic (E_{es}), induction (E_{ind}), repulsion (E_{rep}), and correlation interaction energies (E_{corr}) for the 17 dimers at the potential minima are summarized in Table 2. E_{corr} is the contribution of electron correlation to the calculated interaction energy, which is the difference between $E_{\mathrm{CCSD(T)(limit)}}$ obtained by AIMI model I (E_{total}) and the HF/aug(d)-6-311G* level interaction energy (E_{HF}). A major part of E_{corr} is dispersion energy. E_{rep} ($=E_{\mathrm{HF}} - E_{\mathrm{es}} - E_{\mathrm{ind}}$) is mainly exchange-repulsion energy, but it also includes other terms.

The calculated total interaction energy (E_{total}) depends strongly on the orientation of the dimer, as shown in Table 2. The calculated interaction energies of the parallel dimers A−C are between −1.32 and −1.59 kcal/mol. The perpendicular dimers D−J have larger (more negative) interaction energies (−1.67 to −2.60 kcal/mol) than the parallel dimers. The calculated interaction energies of the coplanar dimers K−Q (−0.06 to −0.73 kcal/mol) are considerably smaller than those of the parallel and perpendicular dimers.

In all the dimers, the absolute value of E_{corr} is substantially larger than that of E_{es}. This shows that dispersion interaction is mainly responsible for the attraction in the thiophene dimer. The E_{corr} values of the parallel dimers A−C (−4.25 to −4.41 kcal/mol) are considerably larger (more negative) than those of the perpendicular dimers D−J (−2.58 to −3.38 kcal/mol) and coplanar dimers K−Q (−0.46 to −1.41 kcal/mol). This shows that dispersion interaction significantly stabilizes the parallel dimers. Apparently, the short intermolecular distance in the parallel dimers at the potential minimum ($R = 4.0$ Å) is the cause of the large dispersion interaction. The intermolecular distances in the perpendicular and coplanar dimers are 4.8−5.2 and 6.4−7.4 Å, respectively.

The electrostatic interaction is highly orientation dependent. The parallel dimers A−C have substantial repulsive E_{es} (0.72−0.78 kcal/mol). The perpendicular dimers D and F have small repulsive E_{es} (0.16 and 0.30 kcal/mol, respectively). The other perpendicular dimers E and G−J have attractive E_{es} (−0.31 to −0.73 kcal/mol); the perpendicular dimers H−J have especially large attractive E_{es} (−0.62 to −0.73 kcal/mol). Although the E_{corr} values of the parallel dimers A−C (−4.25 to −4.41 kcal/mol) are larger (more negative) than those of the perpendicular dimers H−J (−2.58 to −2.64 kcal/mol), the perpendicular dimers H−J have larger E_{total}. Apparently, the large attractive E_{es} in the perpendicular dimers H−J is the cause of E_{total} (−2.28 to −2.60 kcal/mol) being larger than that for dimers A−C (−1.32 to −1.59 kcal/mol). Although the absolute value of E_{es} is always substantially smaller than that of E_{corr}, E_{es} is highly orientation dependent, and therefore electrostatic interaction is important for the orientation dependence of E_{total}. The absolute values of E_{ind} for the 17 dimers are smaller than 0.2 kcal/mol, as shown in Table 2. The absolute value of E_{ind} is always substantially smaller than that of E_{es}.

Intermolecular Interaction Potentials of Dimers B and I. The $E_{\mathrm{CCSD(T)(limit)}}$ values of dimers B and I were calculated with varying intermolecular distance by using AIMI model I. The calculated $E_{\mathrm{CCSD(T)(limit)}}$ values were compared with E_{HF} and E_{MP2} values calculated by using the aug(d)-6-311G* basis set, as shown in Figures 4 and 5. The MP2 method substantially overestimates the attraction in the thiophene dimer, as in the cases of the benzene and naphthalene dimers.[40−42]

The calculated interaction energy potentials of dimers B and I are very shallow near the potential minima. Substantial attraction still exists even where molecules are well separated. This shows that short-range interactions such as charge transfer are not the major source of the attraction, but long-range interactions such as electrostatic and dispersion interactions are

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Table 1. Interaction Energies of the 17 Differently Oriented Thiophene Dimers Calculated by Using AIMI Model I[a]

R^b	E_{HF}^c	$E_{MP2(L)}^d$	$E_{MP2(M)}^e$	$E_{CCSD(T)(M)}^f$	ΔCCSD(T)^g	$E_{CCSD(T)}^h$
Dimer A						
3.8	4.75	−2.06	0.46	1.49	1.04	−1.02
4.0	3.09	−2.10	−0.15	0.63	0.78	−1.32
4.2	2.10	−1.87	−0.37	0.22	0.59	−1.28
4.4	1.50	−1.56	−0.42	0.04	0.46	−1.10
Dimer B						
3.8	4.09	−2.41	0.08	1.02	0.94	−1.47
4.0	2.66	−2.31	−0.36	0.36	0.72	−1.59
4.2	1.82	−2.00	−0.49	0.06	0.55	−1.45
4.4	1.31	−1.63	−0.48	−0.06	0.42	−1.21
Dimer C						
3.6	6.79	−1.89	1.28	2.56	1.28	−0.61
3.8	4.26	−2.36	0.15	1.11	0.96	−1.40
4.0	2.77	−2.28	−0.33	0.40	0.73	−1.56
4.2	1.88	−1.99	−0.49	0.07	0.56	−1.43
Dimer D						
4.4	4.58	−2.23	0.51	1.61	1.10	−1.13
4.6	2.59	−2.58	−0.43	0.36	0.79	−1.78
4.8	1.49	−2.45	−0.78	−0.20	0.58	−1.87
5.0	0.88	−2.14	−0.84	−0.41	0.44	−1.70
Dimer E						
5.0	1.69	−2.30	−0.88	−0.38	0.50	−1.80
5.2	0.57	−2.42	−1.33	−0.97	0.36	−2.06
5.4	0.02	−2.23	−1.39	−1.12	0.27	−1.96
5.6	−0.24	−1.94	−1.29	−1.08	0.21	−1.73
Dimer F						
4.4	4.94	−1.94	0.82	1.98	1.16	−0.79
4.6	2.87	−2.36	−0.19	0.65	0.84	−1.53
4.8	1.71	−2.29	−0.57	0.04	0.61	−1.67
5.0	1.06	−2.01	−0.67	−0.21	0.46	−1.55
Dimer G						
4.8	3.38	−1.94	−0.16	0.57	0.72	−1.22
5.0	1.52	−2.47	−1.06	−0.54	0.52	−1.94
5.2	0.55	−2.44	−1.34	−0.95	0.39	−2.05
5.4	0.07	−2.19	−1.32	−1.02	0.29	−1.89
Dimer H						
4.8	1.39	−2.64	−0.96	−0.40	0.56	−2.08
5.0	0.37	−2.68	−1.40	−0.99	0.41	−2.28
5.2	−0.14	−2.45	−1.46	−1.16	0.30	−2.15
5.4	−0.36	−2.12	−1.37	−1.14	0.23	−1.89
Dimer I						
4.6	2.47	−2.81	−0.83	−0.02	0.81	−2.00
4.8	0.80	−3.18	−1.63	−1.05	0.58	−2.59
5.0	−0.03	−3.03	−1.82	−1.39	0.43	−2.60
5.2	−0.40	−2.68	−1.73	−1.41	0.32	−2.36
Dimer J						
4.6	3.08	−2.24	−0.17	0.64	0.81	−1.43
4.8	1.25	−2.77	−1.16	−0.58	0.58	−2.19
5.0	0.31	−2.73	−1.48	−1.05	0.43	−2.31
5.2	−0.15	−2.46	−1.48	−1.16	0.32	−2.14
Dimer K						
6.2	1.23	−0.81	−0.15	0.04	0.19	−0.62
6.4	0.68	−0.87	−0.38	−0.25	0.14	−0.73
6.6	0.37	−0.81	−0.45	−0.35	0.10	−0.71
6.8	0.20	−0.71	−0.44	−0.36	0.08	−0.63
Dimer L						
6.8	1.07	−0.39	−0.14	−0.06	0.07	−0.32
7.0	0.70	−0.43	−0.25	−0.19	0.06	−0.37
7.2	0.49	−0.40	−0.26	−0.21	0.06	−0.35
7.4	0.37	−0.34	−0.24	−0.18	0.05	−0.29
Dimer M						
6.2	1.28	−0.48	0.16	0.37	0.21	−0.28
6.4	0.79	−0.57	−0.08	0.08	0.16	−0.41
6.6	0.51	−0.54	−0.18	−0.05	0.13	−0.41
6.8	0.35	−0.48	−0.20	−0.09	0.11	−0.37
Dimer N						
6.4	0.62	−0.67	−0.28	−0.18	0.09	−0.57
6.6	0.26	−0.71	−0.43	−0.36	0.07	−0.64
6.8	0.09	−0.66	−0.45	−0.40	0.05	− 0.61
7.0	0.00	−0.58	−0.42	−0.38	0.04	−0.54
Dimer O						
6.4	1.49	−0.42	0.05	0.19	0.14	−0.28
6.6	0.95	−0.53	−0.19	−0.09	0.10	−0.42
6.8	0.65	−0.50	−0.26	−0.18	0.08	−0.42
7.0	0.47	−0.44	−0.25	−0.19	0.07	−0.37
Dimer P						
6.8	0.80	−0.12	0.05	0.09	0.04	−0.08
7.0	0.56	−0.16	−0.04	−0.01	0.03	−0.14
7.2	0.41	−0.16	−0.07	−0.04	0.02	−0.13
7.4	0.32	−0.14	−0.06	−0.04	0.02	−0.12
Dimer Q						
7.2	0.53	−0.07	−0.00	0.02	0.02	−0.05
7.4	0.41	−0.07	−0.02	−0.00	0.02	−0.06
7.6	0.32	−0.06	−0.02	−0.00	0.02	−0.05
7.8	0.27	−0.05	−0.01	0.00	0.02	−0.03

[a] Energies in kilocalories per mole. BSSE-corrected interaction energies. The geometries of the dimers are shown in Figure 2. [b] Intermolecular distance. See Figure 2. [c] HF interaction energies calculated with the aug(d)-6-311G* basis set. See the text. [d] MP2 interaction energies calculated with the aug(d)-6-311G* basis set. See the text. [e] MP2 interaction energies calculated with the 6-31G* basis set. [f] CCSD(T) interaction energies calculated with the 6-31G* basis set. [g] CCSD(T) correction terms: the difference between $E_{CCSD(T)(M)}$ and $E_{MP2(M)}$. [h] Estimated CCSD(T) interaction energy [$E_{CCSD(T)(limit)}$]: the sum of $E_{MP2(L)}$ and ΔCCSD(T). See the text.

mainly responsible for the attraction.[52,61] Electron correlation increases the attraction considerably. This shows that dispersion interaction is significant for the attraction in the thiophene dimers.

Geometry Optimization of Dimers B and I. Intermolecular geometrical parameters of dimers B and I were fully optimized at the MP2/6-311G** level while keeping the geometry of monomers. The C_{2h} and C_s symmetry constraints were imposed in the geometry optimization of dimers B and I, respectively. The optimized geometries are shown in Figure 6. The horizontal and vertical displacements (R_1 and R_2) in the optimized geometry of dimer B are 1.928 and 3.326 Å, respectively. The geometry optimization increases the R_1 considerably to reduce the steric repulsion of sulfur atoms, which have a large atomic radius, and thereby decreases the R_2 substantially. A C−H bond of a thiophene has close contact with another thiophene ring in the optimized geometry of dimer I.

Effects of Electron Correlation and Accuracy of AIMI Models. The intermolecular interaction energies of dimers B and I (the optimized geometries) were calculated at the MP2 and CCSD(T) levels by using several basis sets for the evaluation of the effects of electron correlation. The calculated interaction energies are summarized in Table 3. The MP2

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(61) Nonbonding interactions can be separated into two main types. One is long-range interactions, such as electrostatic and dispersion interactions, where the energy of interaction behaves as some inverse power of R. Another is short-range interactions, such as exchange-repulsion and charge-transfer interactions. Short-range interactions arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.

Table 2. Electrostatic, Induction, and Dispersion Energies in the Thiophene Dimers[a]

dimer	R^b	$E_{total}{}^c$	$E_{es}{}^d$	$E_{ind}{}^e$	$E_{rep}{}^f$	$E_{corr}{}^g$
parallel						
A	4.0	−1.32	0.78	−0.15	2.47	−4.41
B	4.0	−1.59	0.73	−0.15	2.08	−4.25
C	4.0	−1.56	0.72	−0.15	2.20	−4.32
perpendicular						
D	4.8	−1.87	0.16	−0.09	1.41	−3.36
E	5.2	−2.06	−0.42	−0.08	1.07	−2.63
F	4.8	−1.67	0.30	−0.08	1.49	−3.38
G	5.2	−2.05	−0.31	−0.08	0.94	−2.60
H	5.0	−2.28	−0.62	−0.13	1.12	−2.64
I	5.0	−2.60	−0.73	−0.13	0.83	−2.58
J	5.0	−2.31	−0.64	−0.18	1.12	−2.61
coplanar						
K	6.4	−0.73	0.25	−0.01	0.43	−1.41
L	7.0	−0.37	0.31	−0.00	0.40	−1.07
M	6.6	−0.41	0.29	−0.00	0.22	−0.92
N	6.6	−0.64	−0.04	−0.02	0.33	−0.91
O	6.8	−0.42	0.32	−0.02	0.34	−1.07
P	7.0	−0.14	0.37	−0.02	0.20	−0.69
Q	7.4	−0.06	0.30	−0.00	0.12	−0.46

[a] Energies in kilocalories per mole. BSSE-corrected interaction energies. The geometries of the dimers are shown in Figure 2. [b] Intermolecular distances at the potential minima. See the text. [c] CCSD(T) interaction energy [$E_{CCSD(T)(limit)}$] estimated by using AIMI model I. See the text. [d] The electrostatic energy. [e] The induction energy. [f] Difference between the HF/aug(d)-6-311G* interaction energy (E_{HF}) and $E_{es} + E_{ind}$. [g] Difference between E_{total} and E_{HF}.

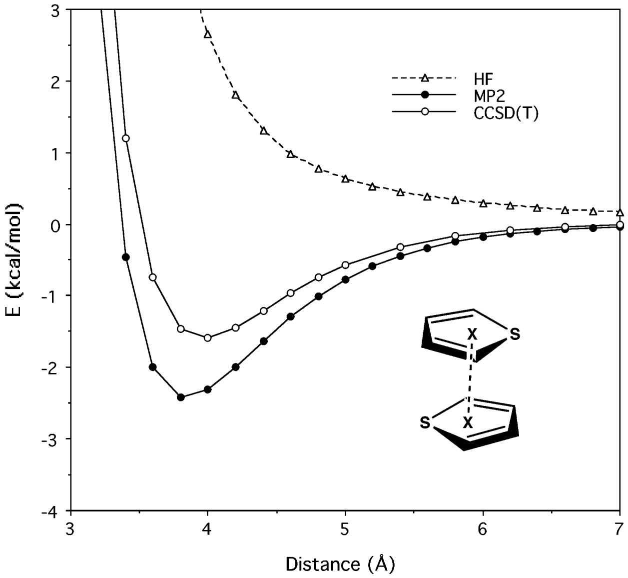

Figure 4. HF, MP2, and CCSD(T) interaction energies of thiophene dimer B. The HF and MP2 interaction energies were calculated with the aug(d)-6-311G* basis set. The CCSD(T) interaction energy was calculated by using AIMI model I. See the text.

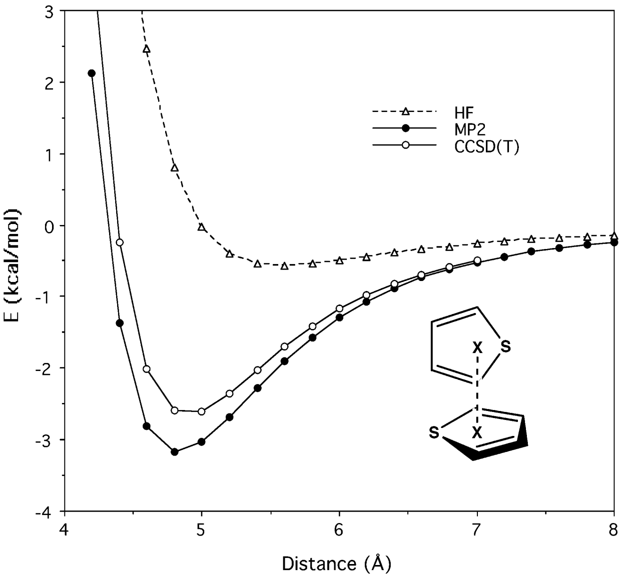

Figure 5. HF, MP2, and CCSD(T) interaction energies of thiophene dimer I. The HF and MP2 interaction energies were calculated with the aug(d)-6-311G* basis set. The CCSD(T) interaction energy was calculated by using AIMI model I. See the text.

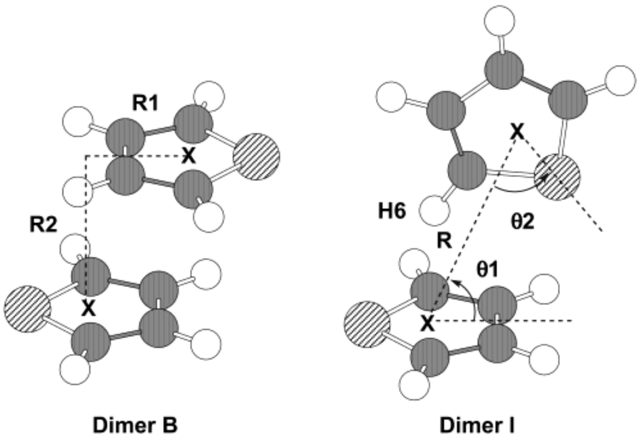

Figure 6. MP2/6-311G** level optimized geometries of thiophene dimers B and I. R_1 and R_2 for dimer B are 1.928 and 3.326 Å, respectively. R, θ_1, and θ_2 for dimer I are 4.498 Å, 68.2°, and 60.8°, respectively. See the text.

calculations overestimate the attraction in the thiophene dimers compared to the more reliable CCSD(T) calculations, as in the cases of the benzene and naphthalene dimers. Although the MP2 and CCSD(T) interaction energies depend strongly on the basis set, the basis set dependence of ΔCCSD(T) ($=E_{CCSD(T)} - E_{MP2}$) is weak. The weak basis set dependence of ΔCCSD(T) suggests that we can estimate $E_{CCSD(T)(limit)}$ of the thiophene dimer sufficiently accurately by the AIMI models.

The $E_{CCSD(T)(limit)}$ values of the optimized geometries of dimers B and I were estimated with AIMI models I, II, and III, as summarized in Table 4. The values of $E_{CCSD(T)(limit)}$ for dimers B and I estimated with model III are −1.71 and −3.12 kcal/mol, respectively. The values of $E_{CCSD(T)(limit)}$ estimated with models I and II are not largely different from those obtained with model III. The good agreement indicates that sufficiently accurate interaction energies are obtained with models I and II.

The E_{MP2} and ΔCCSD(T) values estimated at the basis set limit were used for the model III calculations. The MP2 interaction energies were calculated with the Dunning's correlation-consistent basis sets (cc-pVXZ, X = D, T, Q), as summarized in Table 5. The MP2 interaction energy at the basis set limit was estimated by using the method proposed by Feller.[47] By Feller's method, the calculated interaction energies were fitted to the form $a + b\exp(-cX)$ (where $X = 2$ for cc-pVDZ, 3 for cc-pVTZ, etc). The MP2 energy at the basis limit ($E_{MP2(limit)}$) was then estimated by extrapolation. The estimated values of $E_{MP2(limit)}$ for dimers B and I are −4.26 and −4.73 kcal/mol, respectively. These values are not largely different from the interaction energies obtained by using the cc-pVQZ basis set.

The ΔCCSD(T) at the basis set limit was estimated from the value of ΔCCSD(T) (2.14 and 1.29 kcal/mol, respectively)

Table 3. Calculated HF, MP2, and CCSD(T) Interaction Energies of the Thiophene Dimers[a]

basis set	E_{HF}[b]	E_{MP2}[b]	$E_{CCSD(T)}$[b]	$E_{corr(MP2)}$[c]	$E_{corr(CCSD(T))}$[d]	ΔCCSD(T)[e]	ΔCCSD(T)/$E_{corr(MP2)}$
dimer B (optimized)							
6-31G	6.42	2.09	2.69	−4.33	−3.73	0.60	−0.14
6-31G*	6.52	0.70	2.02	−5.82	−4.50	1.33	−0.23
6-311G*	6.20	−0.57	1.04	−6.77	−5.16	1.61	−0.24
6-311G**	6.22	−0.87	0.81	−7.09	−5.42	1.67	−0.24
cc-pVDZ	6.18	−0.62	1.10	−6.80	−5.09	1.71	−0.25
cc-pVTZ(-f,d)[f]	6.29	−2.53	−0.38	−8.82	−6.67	2.14	−0.24
basis set limit[g]	6.18[h]	−4.26[i]		−10.45[j]		2.55[k]	
dimer I (optimized)							
6-31G	2.27	−0.07	0.31	−2.34	−1.96	0.38	−0.16
6-31G*	2.00	−1.47	−0.61	−3.47	−2.61	0.86	−0.25
6-311G*	2.05	−2.01	−1.02	−4.05	−3.06	0.99	−0.24
6-311G**	2.11	−2.13	−1.12	−4.24	−3.23	1.01	−0.24
cc-pVDZ	1.91	−2.21	−1.12	−4.12	−3.03	1.09	−0.26
cc-pVTZ(-f,d)[f]	1.97	−3.61	−2.32	−5.58	−4.29	1.29	−0.23
basis set limit[g]	2.12[h]	−4.73[i]		−6.85[j]		1.61[k]	

[a] Energies in kilocalories per mole. The geometries of the dimers are shown in Figure 6. [b] BSSE-corrected interaction energies. [c] MP2 correlation interaction energies: the difference between E_{MP2} and E_{HF}. [d] CCSD(T) correlation interaction energies: the difference between $E_{CCSD(T)}$ and E_{HF}. [e] CCSD(T) correction terms: the difference between $E_{CCSD(T)}$ and E_{MP2}. [f] Modified cc-pVTZ basis set. The f functions on heavy atoms and d functions on hydrogen atoms were removed. [g] Values estimated at the basis set limit. [h] HF/cc-pVQZ level interaction energies. [i] MP2 interaction energies estimated at the basis set limit ($E_{MP2(limit)}$). See the text. [j] MP2 correlation interaction energy estimated at the basis set limit ($E_{corr(MP2,\ limit)}$): the difference between $E_{MP2(limit)}$ and the HF/aug(d,p)-6-311G** level interaction energies. [k] CCSD(T) correction term (ΔCCSD(T)) estimated at the basis set limit. See the text.

Table 4. Calculated MP2 and CCSD(T) Interaction Energies of the Thiophene Dimers[a]

AIMI model	E_{MP2}	ΔCCSD(T)[b]	$E_{CCSD(T)(limit)}$[c]
dimer B			
I[d]	−2.96	1.33	−1.63
II[e]	−3.24	1.61	−1.63
III[f]	−4.26	2.55	−1.71
dimer I			
I[d]	−3.65	0.86	−2.80
II[e]	−3.95	0.99	−2.96
III[f]	−4.73	1.61	−3.12

[a] Energies in kilocalories per mole. The geometries of the dimers are shown in Figure 6. BSSE-corrected interaction energies. [b] CCSD(T) correction terms. See the text. [c] Estimated CCSD(T) interaction energies: the sum of E_{MP2} and ΔCCSD(T). [d] E_{MP2} was calculated by using the aug(d)-6-311G* basis set. ΔCCSD(T) was calculated by using the 6-31G* basis set. [e] E_{MP2} was calculated by using the aug(d,p)-6-311G** basis set. ΔCCSD(T) was calculated by using the 6-311G* basis set. [f] E_{MP2} was the MP2 interaction energy at the basis set limit ($E_{MP2(limit)}$) estimated by using the method proposed by Feller. ΔCCSD(T) at the basis set limit was estimated from the calculated ΔCCSD(T) by using a modified cc-pVTZ basis set. See the text.

Table 5. Calculated HF and MP2 Interaction Energies of the Thiophene Dimers[a]

basis set	bf[b]	E_{HF}[c]	E_{MP2}[c]	$E_{corr(MP2)}$[d]
dimer B (optimized)				
cc-pVDZ	188	6.18	−0.62	−6.80
cc-pVTZ	420	6.21	−2.87	−9.07
cc-pVQZ	798	6.18	−3.73	−9.91
aug(d)-6-311G*	270	6.31	−2.96	−9.27
aug(d,p)-6-311G**	318	6.28	−3.24	−9.52
basis set limit		6.18[e]	−4.26[f]	−10.45
dimer I (optimized)				
cc-pVDZ	188	1.91	−2.21	−4.12
cc-pVTZ	420	2.09	−3.77	−5.86
cc-pVQZ	798	2.12	−4.36	−6.48
aug(d)-6-311G*	270	2.09	−3.65	−5.74
aug(d,p)-6-311G**	318	2.05	−3.95	−6.00
basis set limit		2.12[e]	−4.73[f]	−6.85

[a] Energies in kilocalories per mole. BSSE-corrected interaction energies. The geometries of the dimers are shown in Figure 6. [b] Number of basis functions used for the calculations on thiophene dimers. [c] BSSE-corrected interaction energies. [d] Difference between E_{MP2} and E_{HF}. [e] HF/cc-pVQZ level interaction energies. [f] MP2 interaction energies estimated at the basis set limit ($E_{MP2(limit)}$). See the text.

calculated by using a modified cc-pVTZ basis set (cc-pVTZ(-f,d)). The cc-pVTZ(-f,d) basis set is the cc-pVTZ basis set excluding the f functions on carbon and sulfur atoms and d functions on hydrogen atoms. The ΔCCSD(T) values of dimers B and I calculated with several basis sets are summarized in Table 3. While ΔCCSD(T) depends on the basis set, ΔCCSD(T) is always 23−26% of the absolute value of the MP2 level correlation interaction energy ($E_{corr(MP2)} = E_{MP2} - E_{HF}$) if basis sets larger than the 6-31G* basis set are used, as summarized in Table 3. A similar ΔCCSD(T)/$E_{corr(MP2)}$ ratio has been reported from the calculations on the benzene dimers.[41,42] The $E_{corr(MP2)}$ values of dimers B and I calculated with the cc-pVTZ(-f,d) basis set are −8.82 and −5.58 kcal/mol, respectively. The estimated $E_{corr(MP2)}$ values of the dimers at the basis set limit are −10.45 and −6.85 kcal/mol, respectively, as shown in Table 3. The cc-pVTZ(-f,d) basis set underestimates the absolute value of $E_{corr(MP2)}$ for dimers B and I by as much as 1.63 and 1.27 kcal/mol, respectively. We can expect that the cc-pVTZ(-f,d) basis set underestimated ΔCCSD(T) for dimers B and I by as much as 0.41 and 0.32 kcal/mol (25% of the underestimation of $E_{corr(MP2)}$), respectively, if we assume that ΔCCSD(T) is 25% of $E_{corr(MP2)}$. According to this assumption, we can estimate that the ΔCCSD(T) values for dimers B and I at the basis set limit are 2.55 and 1.61 kcal/mol, respectively.

In models I and II, E_{MP2} was calculated by using the aug(d)-6-311G* and aug(d,p)-6-311G** basis sets, respectively. Although these basis sets employ small numbers of basis functions, the E_{MP2} values calculated by using these basis sets are close to those obtained by using large cc-pVTZ and cc-pVQ basis sets, as shown in Table 5.

Roles of Electrostatic, Induction, and Dispersion Interactions. The calculated E_{total}, E_{es}, E_{ind}, E_{rep}, and E_{corr} values of dimers B and I (optimized geometry) are summarized in Table 6. E_{total} is the same as $E_{CCSD(T)(limit)}$ obtained by using AIMI model III. E_{rep} is the difference between the HF/cc-pVQZ level interaction energy (E_{HF}) and the sum of E_{es} and E_{ind}. The absolute values of E_{corr} (=$E_{total} - E_{HF}$) of the two dimers are substantially larger than those of E_{es}, which indicates that dispersion interaction is the major source of the attraction in

Table 6. Electrostatic, Induction, and Dispersion Energies of the Thiophene and Benzene Dimers[a]

dimer	E_{total}[b]	E_{es}[c]	E_{ind}[d]	E_{rep}[e]	E_{corr}[f]
thiophene[g]					
B (parallel)	−1.71	1.46	−0.30	5.02	−7.89
I (perpendicular)	−3.12	−1.14	−0.29	3.55	−5.24
benzene[h]					
slipped-parallel	−2.48	0.90	−0.25	3.01	−6.14
T-shape	−2.46	−0.55	−0.17	1.74	−3.48

[a] Energies in kilocalories per mole. BSSE-corrected interaction energies. The geometries of the dimers are shown in Figures 6 and 7. [b] CCSD(T) interaction energy [$E_{CCSD(T)(limit)}$] estimated by using AIMI model III. See the text. [c] Electrostatic energy. [d] Induction energy. [e] Difference between the HF/cc-pVQZ interaction energy (E_{HF}) and $E_{es} + E_{ind}$. [f] Difference between E_{total} and E_{HF}. [g] MP2/6-311G** level optimized geometries (Figure 6) were used. [h] Reference 41.

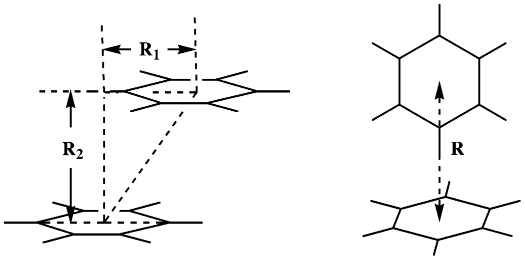

Figure 7. Structures of parallel-displaced and T-shaped benzene dimers. R_1, R_2, and R are 1.8, 3.5, and 5.0 Å, respectively.

the dimers. E_{total} of dimer I (−3.12 kcal/mol) is substantially larger (more negative) than that of dimer B (−1.71 kcal/mol). The large attractive E_{es} (−1.14 kcal/mol) is the cause of the larger E_{total} of dimer I. The atomic charges of thiophene monomer obtained by the electrostatic potential fitting using the Merz−Singh−Kollman scheme[62,63] from the MP2/6-311G** level wave functions are shown in Figure 1. H_6 has a large positive charge (0.19 e, $1e = 1.602 \times 10^{-19}$ C). The Coulombic interaction between H_6 (Figure 6) and the negatively charged carbon atoms of anther thiophene explains the attractive electrostatic interaction. Cooke et al. reported that a thiophene acts as a π-base in the thiophene···HCl complex.[64] Although thiophene has a sulfur atom, the induction energies are not large. The E_{ind} values for the two dimers are about −0.3 kcal/mol.

Comparison with Benzene Dimer. The interaction energy of dimer I calculated by using AIMI model III (−3.12 kcal/mol) is substantially larger than that of dimer B (−1.71 kcal/mol), as shown in Table 6. On the other hand, the interaction energies of the parallel-displaced and T-shaped benzene dimers (Figure 7) calculated by using AIMI model III are nearly identical (−2.46 and −2.48 kcal/mol, respectively).[41]

E_{corr} of thiophene dimer B (−7.89 kcal/mol) is larger (more negative) than that of the parallel-displaced benzene dimer (−6.14 kcal/mol). The large atomic polarizability of sulfur explains the large dispersion interaction in the thiophene dimer. E_{total} of dimer B is smaller than that of the parallel-displaced benzene dimer. E_{es} of dimer B (1.46 kcal/mol) is larger than that of the slipped-parallel benzene dimer (0.90 kcal/mol). The larger repulsive electrostatic energy in thiophene dimer B is the cause of the smaller E_{total}.

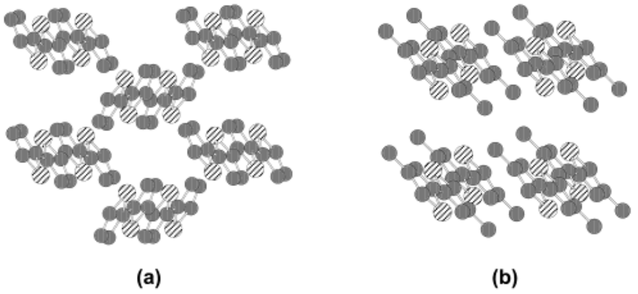

Figure 8. Crystal structures of α-quaterthiophene (a) and its β-methyl derivative (b).

The interaction energy of thiophene dimer I is considerably larger than that of the T-shaped benzene dimer. The E_{es} values of thiophene dimer I and the T-shaped benzene dimers are −1.14 and −0.55 kcal/mol, respectively. In addition, E_{corr} of thiophene dimer I (−5.24 kcal/mol) is considerably larger than that of the T-shaped benzene dimer (−3.48 kcal/mol). The larger electrostatic and dispersion interactions are the cause of the lager E_{total} of thiophene dimer I.

Crystal Packing of Oligothiophenes. In most cases, the long axes of oligothiophene molecules (α-terthienyls) are parallel in the crystal. The thiophene rings of two neighboring oligothiophenes cannot take the orientations of dimers C−E, H−J, and N−Q if the long axes of the two oligothiophenes are parallel. The orientations of the other seven dimers (A, B, F, G, and K−M) are close to the possible orientations of the thiophene rings of two neighboring oligothiophenes. Our calculations show that the perpendicular dimers F and G have the largest interaction energies among the seven dimers. The interaction energies of dimers F and G (−1.67 and −2.05 kcal/mol) are larger (more negative) than those of the parallel dimers A and B (−1.32 and −1.59 kcal/mol) and coplanar dimers K−M (−0.73, −0.37, and −0.41 kcal/mol).

The thiophene rings of the nearest neighboring oligothiophenes take nearly perpendicular orientation (herringbone structure) in many oligothiophene crystals. Nonsubstituted oligothiophenes have the herringbone structure in the crystals.[65−70] The crystal structure of α-quaterthiophene is shown in Figure 8a as an example.[68] The orientations of the thiophene rings in the nearest neighboring oligothiophenes are close to those in the thiophene rings in the perpendicular thiophene dimers F and G. Apparently, the large attractive interaction between the thiophene rings in the perpendicular orientation is the cause of the preference for the herringbone structure in the crystal.

The thiophene rings of the nearest neighboring oligothiophenes take slipped-parallel orientation (π-stacked structure) in some β-substituted oligothiophenes.[25−29] The crystal structure of α-quater(β-methylthiophene) is shown in Figure 8b as an example. [25] In the π-stacked structure, the orientations of the thiophene rings in the nearest neighboring oligothiophenes are

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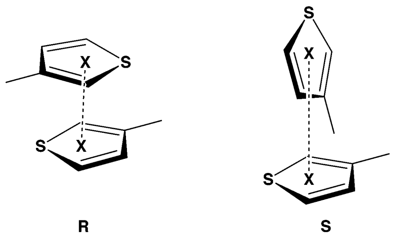

Figure 9. Geometries of the 3-methylthiophene dimers. The S1−X axes of 3-methylthiophenes have a parallel or perpendicular orientation in the dimers.

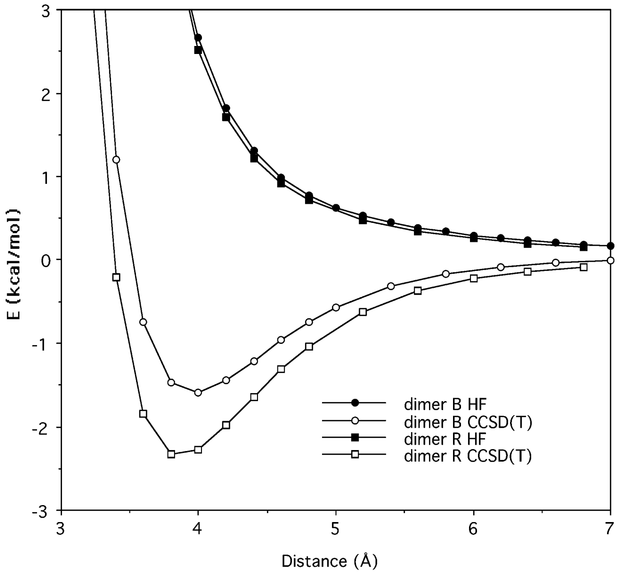

Figure 10. HF and CCSD(T) interaction energies of the parallel thiophene dimer B and 3-methylthiophene dimer R. The HF interaction energies were calculated with the aug(d)-6-311G* basis set. The CCSD(T) interaction energy was calculated by using AIMI model I. See the text.

close to those of the the thiophene rings in the parallel thiophene dimers A and B. Our calculations show that perpendicular orientation (herringbone structure) is more stable than parallel orientation (π-stacked structure). However, the thiophene rings of the nearest neighboring β-substituted oligothiophenes cannot take perpendicular orientations in the crystal, due to the steric repulsion of the β-substituents. The steric repulsion of the β-substituents explains the observed π-stacked structure of the β-substituted oligothiophenes.

The intermolecular interaction energies of the parallel and perpendicular 3-methylthiophene dimers (Figure 9) were calculated with AIMI model I to confirm the effects of methyl substituents on the intermolecular interaction. The calculated interaction energy potentials of the 3-methylthiophene dimers R and S are compared with the potentials of the parallel and perpendicular thiophene dimers B and G, respectively, as shown in Figures 10 and 11. The interaction energy of the parallel 3-methylthiophene dimer R calculated at the potential minimum ($R = 3.8$ Å) is −2.27 kcal/mol. The calculated interaction energy of the parallel thiophene dimer B ($R = 4.0$ Å) is −1.59 kcal/mol. The methyl groups increase the attraction in the dimer in the parallel orientation. The HF potentials of the two parallel dimers are nearly identical, as shown in Figure 10. This indicates that the methyl groups increase the dispersion interaction, and therefore the 3-methylthiophene dimer has a larger (more negative) interaction energy.

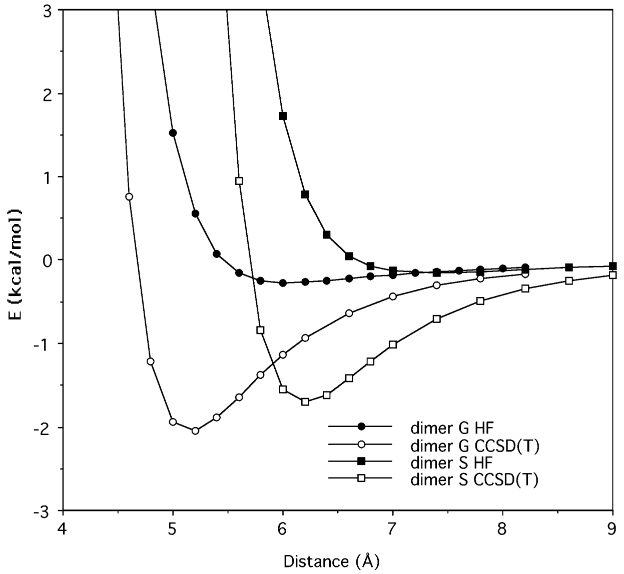

Figure 11. HF and CCSD(T) interaction energies of the perpendicular thiophene dimer G and 3-methylthiophene dimer S. The HF interaction energies were calculated with the aug(d)-6-311G* basis set. The CCSD(T) interaction energy was calculated by using AIMI model I. See the text.

The interaction energy of the perpendicular 3-methylthiophene dimer S calculated at the potential minimum is −1.70 kcal/mol, which is substantially smaller than that of the perpendicular thiophene dimer G (−2.05 kcal/mol). The intermolecular distance of the perpendicular 3-methylthiophene dimer S at the potential minimum ($R = 6.2$ Å) is considerably larger than that of the perpendicular thiophene dimer G ($R = 5.2$ Å). The large steric repulsion due to the methyl groups is the cause of the larger intermolecular separation, and the large separation decreases the attraction.

The methyl groups stabilize the parallel dimer but destabilize the perpendicular dimer. The parallel 3-methylthiophene dimer is more stable (-2.27 kcal/mol) than the perpendicular dimer S (−1.70 kcal/mol), in contrast to the parallel and perpendicular thiophene dimers B and G (−1.59 and −2.05 kcal/mol, respectively). The dimer orientation preference of 3-methylthiophene is completely different from that of nonsubstituted thiophene. This difference explains the difference between the crystal packing of nonsubstituted oligothiophenes (herringbone structure) and that of substituted oligothiophenes (π-stacked structure).

Conclusions

The interaction energies of the thiophene dimers were calculated at the MP2 and CCSD(T) levels by using several basis sets. Small basis sets underestimate the attraction considerably, and the MP2 method overestimates the attraction greatly compared to the CCSD(T) method, as in the cases of the benzene and naphthalene dimers. Although the MP2 and CCSD(T) interaction energies (E_{MP2} and $E_{\mathrm{CCSD(T)}}$) are strongly basis set dependent, the basis set dependence of the CCSD(T) correction term ($\Delta\mathrm{CCSD(T)} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$) is weak. This suggests that AIMI models provide sufficiently accurate interaction energies of the thiophene dimers.

The CCSD(T) interaction energies ($E_{\mathrm{CCSD(T)(limit)}}$) of the parallel and perpendicular thiophene dimers estimated by using the most accurate AIMI model III are −1.71 and −3.12 kcal/

mol, respectively. The $E_{\mathrm{CCSD(T)(limit)}}$ values of the dimers estimated by using the computationally less demanding AIMI models I and II are not largely different from those estimated by using model III. The good performance of the AIMI models for the evaluation of the thiophene dimer interaction energy suggests that the AIMI models are also useful for studying the interaction energy of the thiophene dimer.

Our calculations show that dispersion interaction is the major source of the attraction in the thiophene dimers. Especially parallel (stacked) dimers are considerably stabilized by dispersion interaction. Electrostatic interaction is repulsive in the parallel dimers, which shows that dispersion interaction is the major source of the attraction in the π-stacking of oligothiophenes. The parallel and perpendicular thiophene dimers have larger dispersion energies than the slipped-parallel and T-shaped benzene dimers. The large atomic polarizability of the sulfur atom explains the large dispersion energy.

Electrostatic interaction is highly orientation dependent. Electrostatic interaction stabilizes the perpendicular thiophene dimers considerably. Although the electrostatic interaction is substantially smaller than the dispersion interaction, electrostatic interaction is important for the orientation dependence of the total interaction energy. Electrostatic interaction is mainly responsible for the total interaction energy of the perpendicular thiophene dimer being larger than that for the parallel dimer.

The perpendicular thiophene dimers have larger attractive interaction energies than the parallel dimers. The large interaction energy is the cause of the preference for the herringbone structures in the crystals of nonsubstituted oligothiophenes. Some β-substituted oligothiophenes have π-stacked structures in the crystals. The parallel 3-methylthiophene dimer is more stable than the perpendicular dimer, in contrast to the case with the thiophene dimer. The β-substituent destabilizes the perpendicular dimer. This explains the observed π-stacked structures of the β-substituted oligothiophenes in the crystal.

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Supporting Information Available: Geometry coordinates and calculated energies for the dimers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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