

Factors Governing the Three-Dimensional Hydrogen-Bond Network Structure of Poly(*m*-phenylene isophthalamide) and a Series of Its Model Compounds. 3. Energy Terms Indispensable to the Crystal Structure Prediction

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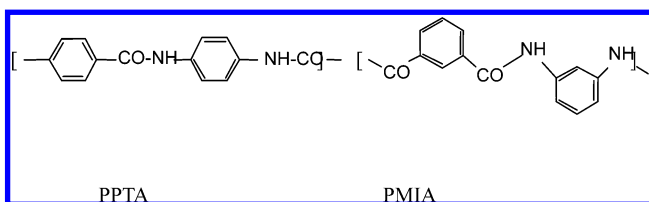
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To clarify the factors that govern the complicated three-dimensional hydrogen-bond network structure of poly(*m*-phenylene isophthalamide) and its model compounds, the packing energy calculations were performed with computer simulation software (Polymorph Predictor) and the important energy terms were extracted successfully. The crystal structures were predicted with and without the various types of interaction terms being taken into consideration and were compared with the X-ray-analyzed structures. Initially, the conformation analysis was made for a single molecule. However, the structure with the lowest energy did not always correspond to the actually observed structure. This finding suggested the importance of intermolecular, as well as intramolecular, interactions. By performing the lattice-energy calculations with and without various types of intermolecular interactions being taken into consideration, and by comparing the results with the observed structures, it has been found that the van der Waals interaction was a primarily important factor in the prediction of the molecular packing structures; however, the electrostatic (and hydrogen-bond) interaction could not be ignored at all. In other words, a good and sensitive balance between these interaction terms was quite important for obtaining a successful reproduction of the observed molecular packing structures of the model compounds.

Introduction

In a series of papers,^{1,2} we have investigated the molecular conformations and packing structures for the various types of model compounds of poly(*m*-phenylene isophthalamide) (PMIA) and poly(*p*-phenylene terephthalamide) (PPTA), by means of



X-ray structure analysis, and compared these structures with the results predicted by a computer software program (Polymorph Predictor).^{3,4} Overall, the agreement between observed and predicted structure was good, which allowed us to recognize the usefulness of this software. The structure prediction is one of the most important themes of the crystallography and a dream of synthesists of chemical compounds. After any excellent technique is established to predict a highly reliable structure, it may be possible to speculate the plausible molecular and packing structures of the complicated chemical compounds and also to make a so-called molecular design of novel materials with more excellent properties. Recently, several types of computer

software have been developed for this purpose.^{5,6} The aforementioned Polymorph Predictor software is one of these programs.

As mentioned previously, we found a good reproduction of the crystal structure for several model compounds of PMIA and PPTA.² The second point to be clarified is the factors that should lead us to a successful reproduction of the crystal structures. For this purpose, we need to investigate the roles of intramolecular and intermolecular interactions in the construction of the three-dimensional (3-D) crystal structures. This trial had been made sometimes but was not very frequently for the so-called aromatic amide compounds, which consist of benzene and amide groups, because of their complicated packing structures. In the present paper, we will clarify the interaction-energy terms that have important roles in the construction of crystal structures of the model compounds of PMIA. In regard to the intramolecular interactions, a conformational analysis is made for isolated molecules, where the conformational energy is calculated by varying the twisting angles about the benzene–amide linkages. The thus-obtained most-stable molecular conformation does not always correspond to that observed in the actual crystal structure. The roles of intermolecular interactions then are investigated, in addition to the intramolecular interactions, through the calculation of the crystal structures with and without various types of interaction terms being taken into consideration, as will be reported in the present paper. The thus-accumulated information will be useful for the application of the Polymorph Predictor program to more-general study of aromatic amide compounds with a complicated 3-D hydrogen-bond network structure.

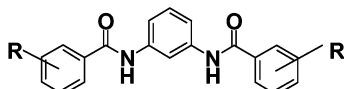
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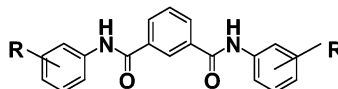
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TABLE 1: Model Compounds of PMIA

formula ^a	code ^b	end group, R	shape ^c	hydrogen-bond pattern ^d	space group	Z ^e
(i)	MPBB	H	CC	(b-b)-(b-b)	Pbca	1
(ii)	DPIA	H	CC	(a-a)-(b-b)	P1	4
(ii)	BMMPIA	<i>m</i> -CH ₃	CC	(a'-a')-(b'-b')	Cc	2
(ii)	BMEPIA	<i>m</i> -C ₂ H ₅	CC	(b-b)-(b-b)	P1	2
(i)	MPPM	<i>p</i> -CH ₃	TT	(a-b)-(b-a)	P1	1
(ii)	BPMPA	<i>p</i> -CH ₃	CT	(a-b)-(a-b)	P1	1
	PMIA		CT	(a-b)-(a-b)	P1	1

^a (i)

(ii)



^b MPBB = *N,N'*-*m*-phenylene bisbenzamide; DPIA = diphenylene isophthalamide; BMMPIA = bis-*m*-methyl-phenyl isophthalamide; BMEPIA = bis-*m*-ethyl-phenyl isophthalamide; MPPM = *N,N'*-*m*-phenylene bis-*p*-methylbenzamide; BPMPA = bis-*p*-methyl-phenyl isophthalamide; and PMIA = poly(*m*-phenylene isophthalamide). ^c Approximate molecular shape expressed by two torsional angles around the benzene–amide linkages of the central part. ^d (a-b)-(b-a), for example, indicates the directions of intermolecular hydrogen bonds. ^{1,2} (a-b) means that the two amide groups in one molecule are linked along the *a*- and *b*-axes by hydrogen bonds with the adjacent molecules in the same layer. The next term, (b-a), refers to the molecules in the next layer. *a'* is parallel to the [110] direction, and *b'* is parallel to the [1 $\bar{1}$ 0] direction. ^e Z is the number of molecules in an asymmetric unit.

Computer Simulation Method

In the present paper, the prediction of possible crystal structures was made by means of a commercial software package (Polymorph Predictor, from Accelrys, Inc.).^{3,4} Brief explanation of this software was already made in the previous paper.² Generally speaking, this program generates crystal structures randomly by starting from one molecule, under the assumption of a proper space group symmetry, and it finds the energetically stable structures after energy minimization by changing various parameters, such as the molecular geometry, the molecular orientation, and the lattice constants. In the actual calculation of the packing energy, the proper potential functions must be adopted. In the present calculations, the COMPASS⁸ and the Dreiding II⁹ methodologies with atomic charges calculated by an ab initio molecular orbital method were employed, because they gave relatively good reproductions of the X-ray-analyzed structures. These force fields are the sets of various interaction terms that concern covalent bonding, bond-angle deformation, torsion, and such nonbonded interatomic interactions as van der Waals interaction, electrostatic interaction, and hydrogen bonding. To clarify which energy term is significant for the reproduction of the observed crystal structure, the energy calculation was made with and without some of these various interaction terms being taken into consideration.

Intramolecular Interaction

Conformation analysis was made for the molecules listed in Table 1. Initially, the energetically most-stable torsional angle was sought for benzene–amide bonds. The models used were quite simple: benzene–CONH₂ and benzene–NHCOH. These molecules were energetically minimized by changing all the molecular parameters of bond lengths, bond angles, and torsional angles, where the COMPASS force field was employed. The thus-obtained structures were deformed by changing the torsional angle between the benzene and amide groups, and the corresponding total energy and its components were calculated. Figure 1 shows the result. In the case of the benzene–CONH linkage, the minimal energy was obtained at a torsional angle of ca. 25°, which corresponds well with the observed values.¹ By increasing the torsional angle from 0° to 90°, the torsional potential energy was increased remarkably and the nonbonded interatomic interaction energies or the van der Waals and electrostatic interaction energies decreased in parallel. The opposite behaviors of these different energy terms, i.e., the

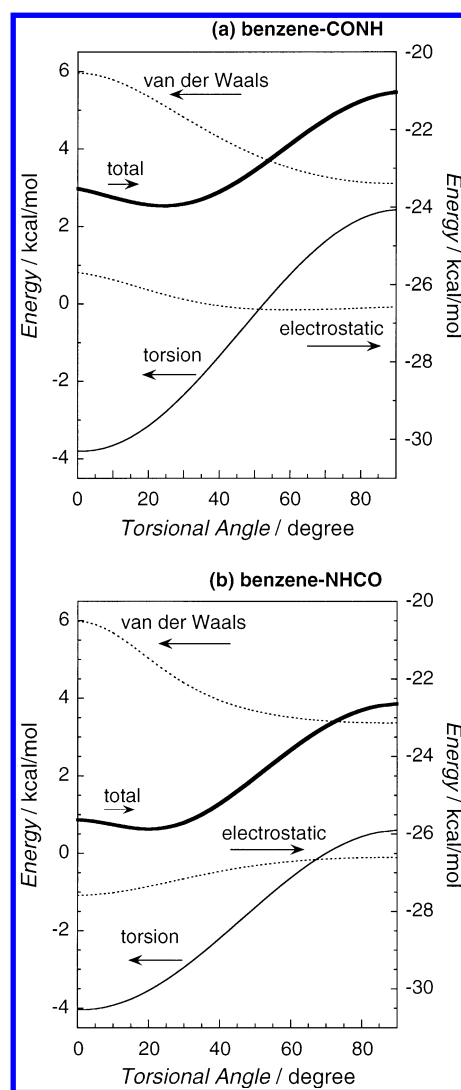


Figure 1. Potential energy curves calculated for the compounds of (a) benzene–CONH₂ and (b) benzene–NHCOH, as a function of the torsional angle around the benzene–amide linkage. The balance between the van der Waals (dotted line associated with the scale on left-hand side), electrostatic (dotted line associated with the scale on the right-hand side), and torsional (thin solid line) energy terms gives the total energy curve (thick solid line) with optimal torsional angles of ~20°–30°. The calculation was made by utilizing a COMPASS force field.

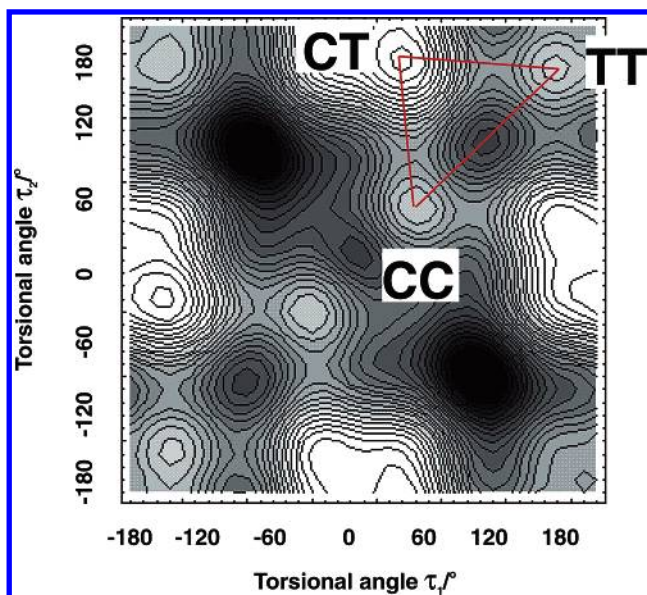


Figure 2. Two-dimensional contour map as a function of the two torsional angles τ_1 and τ_2 , the definition of which is given as benzene-CONH-(τ_1)-benzene-(τ_2)-NHCO-benzene. Three minimal points are named the CC, CT, and TT forms, where C (cis) and T (trans) are deviated from the exact definitions (0° and 180° , respectively) by $\sim 30^\circ$.

valence energy (torsion) and the nonbonded interatomic energy (van der Waals and electrostatic interactions), give the minimal point at a torsional angle of ca. 25° . In other words, a good balance between the electronic conjugation to give a coplanar structure of a benzene ring and an amide group and the H \cdots H repulsive force working between the H atoms of benzene and the NH group gave the energetically most-preferable torsional angle.¹⁰ The same situation also is observed in the case of the benzene-NHCO linkage shown in Figure 1b: the torsional angle of ca. 20° gave the most-stable structure.

Strictly speaking, the two models described in Figure 1 were too simple to assume them to be good models for PMIA. In the actual model compounds, the situation is more complicated: the central benzene and amide groups are connected to the other benzene and amide groups (see Table 1). Therefore, in the second step, the potential energy was calculated as a function of two twisting angles (τ_1 and τ_2) or the two dihedral angles between two amide planes and a central benzene ring. For example, Figure 2 shows a two-dimensional (2-D) contour map of the conformational energy plotted against τ_1 and τ_2 , which was calculated for a molecule of *N,N'*-*m*-phenylene bisbenzamide (MPBB; see Table 1). Three types of conformation were found as the stable molecular forms: cis-trans (CT), cis-cis (CC), and trans-trans (TT) types, where C and T were originally 0° and 180° , respectively; however, the actual C angle was $\sim 30^\circ$ and the actual T angle was $\sim 150^\circ$, because of 30° twisting around the benzene-amide bond. Figure 3 shows the potential energy curves estimated along the three paths that connect the minimal points of these conformations (see Figure 2). The CT form is more stable than the TT and CC forms. Table 2 lists the energy values that have been calculated for the three energetically stable conformations for all the compounds used in the present paper. The CT conformation is the most stable for all the compounds. However, the CT form is not always realized in the actual crystal lattice, as seen in Table 2. As shown in Figure 3, the energy difference and energy barrier height between these conformations are only 1–2 kcal/mol. Therefore, the introduction of intermolecular interactions seems to cover the energy gap and stabilize the CC and TT molecular forms, in some cases.

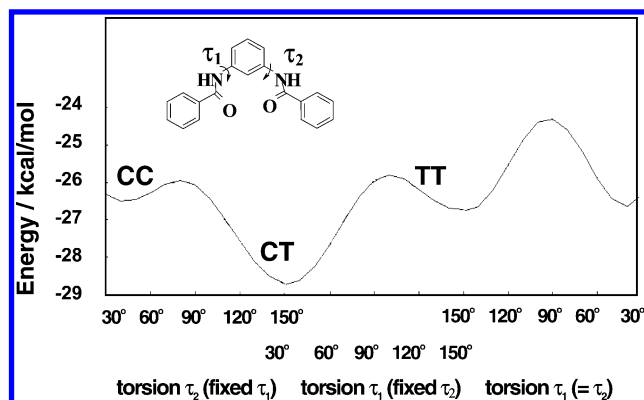


Figure 3. Potential energy curves obtained along the routes drawn by straight solid lines in the contour map of Figure 2.

TABLE 2: Relative Stability of Isolated Molecules of PMIA Model Compounds

model compounds	Energy/kcal mol ⁻¹			relative stability ^a	form observed ^b
	CC	CT	TT		
MPBB	-26.6	-28.2	-26.4	TT ~ CC < CT	CC
DPBA	-21.0	-22.5	-20.8	TT ~ CC < CT	CC
BMPPIA	-43.6	-46.1	-44.6	TT < CC < CT	CC
BMEPIA	-43.0	-44.9	-43.6	TT < CC < CT	CC
MPPM	-42.7	-44.8	-42.7	TT ~ CC < CT	TT
BPMPPIA	-37.5	-38.8	-37.4	TT ~ CC < CT	CT
PMIA	-29.8	-34.7	-31.8	TT < CC < CT	CT

^a Torsional angles: T $\approx 150^\circ$ and C $\approx 30^\circ$ (refer to Figures 1 and 2). ^b Molecular conformation revealed by X-ray structure analyses.¹

Role of Various Energy Terms in Building Up the Packing Structure

As described in the previous paper,² the Polymorph Predictor program is useful for the reproduction of the crystal structures of PMIA model compounds. Here, we will investigate the role of individual energy terms in the process of building up the crystal structures. Before discussing the calculated results, we need to check the suitability of the set of potential energy functions COMPASS⁸ or Dreiding II.⁹ As already reported in the previous paper,² the COMPASS and Dreiding II functions with atomic charges transferred from an ab initio molecular orbital calculation give relatively good reproductions of the observed crystal structure. The Dreiding II force field with the atomic charges calculated by the Gasteiger method¹¹ did not give any good results: the molecules were not bonded together by hydrogen bondings. Therefore, COMPASS and Dreiding II methodologies with ab initio charges will be used in the present paper. It should be noticed that the intermolecular interactions are classified mainly into two types (van der Waals interaction and electrostatic interaction), in the case of the COMPASS force field, whereas they are classified into three types (van der Waals interaction, electrostatic interaction, and hydrogen bonding) in the case of Dreiding II methodology. The hydrogen-bond energy term is included in the combination form of the van der Waals interaction energy and the electrostatic interaction energy in the COMPASS force field. To estimate the role of the individual energy term in the reproduction of the observed crystal structure, we calculated the packing structures using the Polymorph Predictor program with and without these energy terms being taken into account, where the three types of energy terms employed in the Dreiding II force field were used for this purpose.

As an example, Figure 4 shows the packing structures predicted for *N,N'*-*m*-phenylene bis-*p*-methylbenzamide (MPPM) (see Table 1) by employing the Dreiding II force field with and

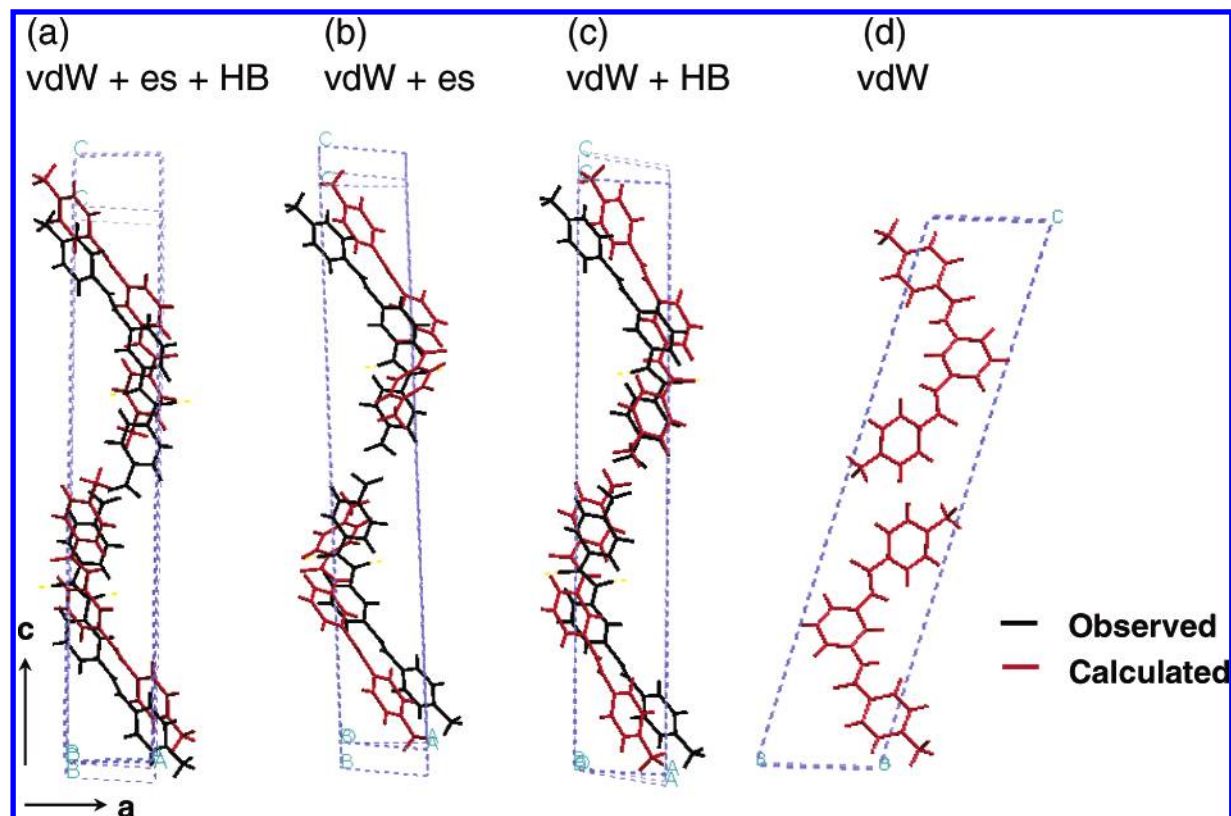
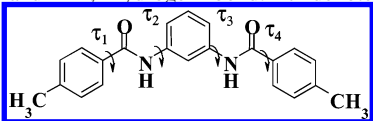


Figure 4. Comparison of the crystal structure of *N,N'*-*m*-phenylene bis-*p*-methylbenzamide (MPPM) between the X-ray analysis and the prediction, where the space-group symmetry was $P\bar{1}$ (vdW, van der Waals interaction; es, electrostatic interaction; and HB, hydrogen bonding). The potential function used here was the Dreiding II methodology with ab initio atomic charges.

TABLE 3: Cell Parameters and Molecular Conformation of MPPM Obtained by Energy Calculations^a

parameter ^b	observed ^c	vdW + es + HB	vdW + es	vdW + HB	vdW
<i>a</i> (Å)	5.15	5.03	4.98	5.14	4.07
<i>b</i> (Å)	5.15	5.03	5.16	5.15	7.00
<i>c</i> (Å)	33.39	36.35	35.80	34.76	32.65
α (°)	83.56	87.08	97.07	80.60	105.27
β (°)	92.08	72.58	101.61	80.88	92.82
γ (°)	86.68	91.42	87.36	89.29	94.84
τ_1 (°)	28	34	-34	30	11
τ_2 (°)	-31	-32	-32	-30	-1.1
τ_3 (°)	-32	-32	-27	-30	27
τ_4 (°)	28	34	31	31	22
HB ^d	-(<i>a</i> - <i>b</i>)-(<i>b</i> - <i>a</i>)-	-(<i>a</i> - <i>b</i>)-(<i>b</i> - <i>a</i>)-	-(<i>a</i> - <i>b</i>)-(<i>b</i> - <i>a</i>)-	-(<i>a</i> - <i>b</i>)-(<i>b</i> - <i>a</i>)-	no

^a Calculation was made by taking some limited types of interaction into account. vdW, van der Waals interaction; es, electrostatic interaction; and HB, hydrogen bond. ^b τ denotes torsional angles around the benzene and amide groups (refer to the picture shown below).



^c X-ray analyzed values. ^d Hydrogen bonds are formed in the direction of the *a*- or *b*-axis alternately along the *c*-axis (refer to refs 1 and 2).

without particular energy terms being taken into account, where the starting molecular model was the TT form, which was similar to the X-ray-analyzed structure. Table 3 lists the cell parameters of these packing structures. The van der Waals interaction term alone could not reproduce the molecular conformation, the packing structure, and the hydrogen-bond pattern that were detected for the actual crystal structure. Introduction of only the electrostatic interaction caused collisions among the molecules and the energy diverged to infinity. The combination of the van der Waals interaction term with the electrostatic interaction term produced essentially the same crystal structure as that predicted by taking all three energy terms together: the cell parameters and the torsional angles (τ_1 – τ_4) were reproduced relatively well, except for the torsional angle

τ_1 . The combination of the van der Waals interaction and the hydrogen-bonding term produced essentially the same result.

In a similar way, the packing structure of bis-*p*-methyl-phenyl isophthalamide (BPMPA; see Table 1) with the space group $P1$ was calculated using the Dreiding II force field with ab initio atomic charges where the CT conformation was used as a starting model. The results are shown in Figure 5 and Table 4. The van der Waals interaction alone gave a structure that was similar to the actual structure but was not good enough. The hydrogen-bonding term could not give any good results. The electrostatic interaction alone resulted in the collision of atoms. A combination of the van der Waals interaction with electrostatic force or with hydrogen-bonding force produced a relatively good reproduction of the observed crystal structure, a result that was

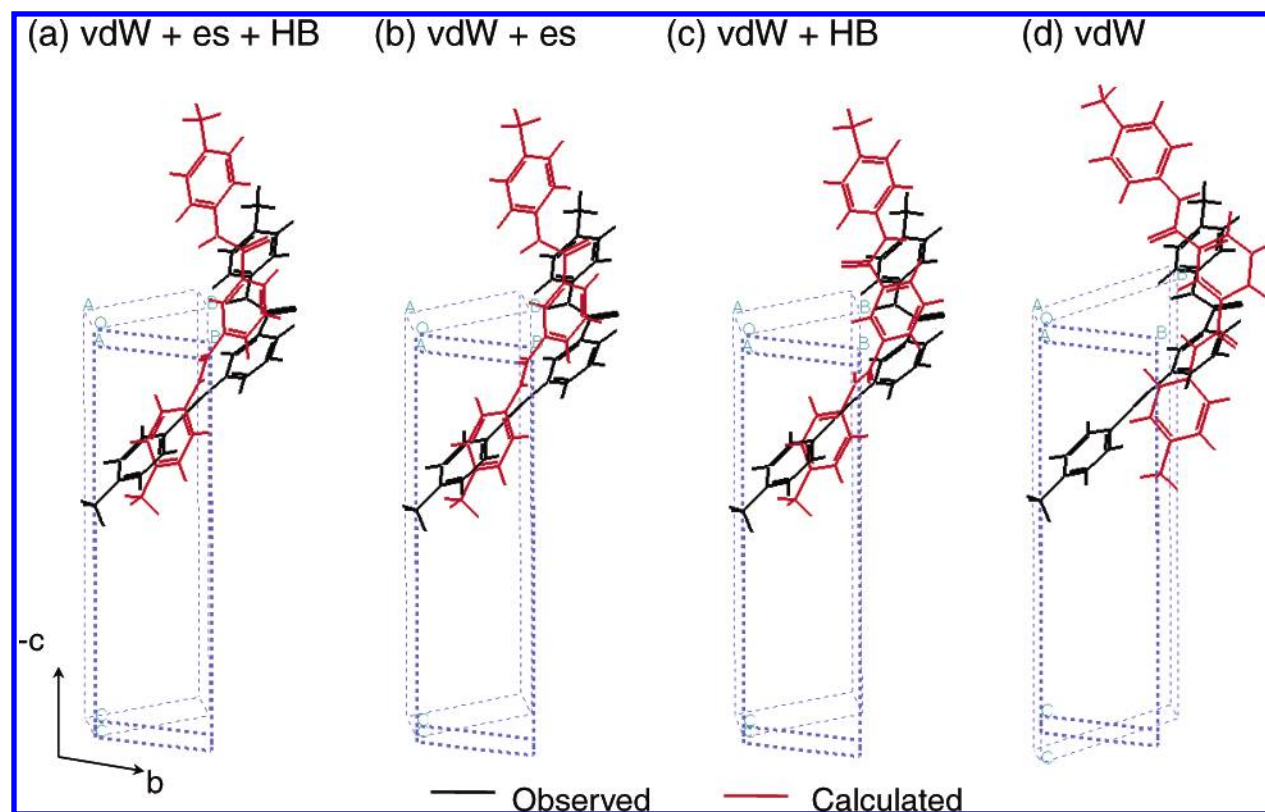
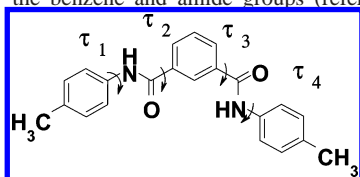


Figure 5. Comparison of crystal structure of bis-*p*-methyl-phenyl isophthalamide (BPMPA) between the X-ray analysis and the prediction, where the space-group symmetry was *P1* (vdW, van der Waals interaction; es, electrostatic interaction; and HB, hydrogen bonding). The potential function used here was the Dreiding II methodology with ab initio atomic charges.

TABLE 4: Cell Parameters and Molecular Conformation of BPMPA Obtained by Energy Calculations^a

parameter ^b	observed ^c	vdW + es + HB	vdW + es	vdW + HB	vdW
<i>a</i> (Å)	5.25	5.11	5.20	5.15	4.00
<i>b</i> (Å)	5.13	5.06	5.10	5.26	6.27
<i>c</i> (Å)	17.04	17.74	17.55	17.49	19.08
α (°)	83.23	100.32	101.23	100.71	107.91
β (°)	82.77	99.90	100.59	101.56	99.19
γ (°)	86.04	90.12	90.03	89.11	88.66
τ_1 (°)	-35	-34	-30	-31	-15
τ_2 (°)	37	39	35	36	15
τ_3 (°)	27	29	25	26	19
τ_4 (°)	-31	-33	-28	-29	-16

^a Calculation was made by taking some limited types of interaction into account. vdW, van der Waals interaction; es, electrostatic interaction; and HB, hydrogen bonding. ^b τ denotes torsional angles around the benzene and amide groups (refer to the picture shown below).



^c X-ray-analyzed values.¹

comparable to that obtained by taking all the interactions into consideration.

In this way, the van der Waals interaction is principally important for the reproduction of the packing structure of PMIA model compounds but is not always perfect. Rather, the combination of the van der Waals interaction with the hydrogen bonding or the electrostatic interaction gives a much better result. In other words, a good balance between these three energy terms is very important in building a reasonable molecular packing structure. This conclusion is not new and has been well-known, at least qualitatively. However, an actual check with the various

interaction terms being taken into account has not been reported at all for the aromatic amide compounds. Sometimes, prediction of the crystal structure was made by assuming a simplified van der Waals potential curve only;¹² the result was not bad when it was compared with that from the X-ray structure analysis. However, we do not have any guarantee to be able to apply this type of potential function to the complicated crystal structure of PMIA model compounds. The knowledge obtained here is important in the quantitative (or even qualitative) prediction of crystal structure of novel compounds or the molecular design: we need to employ a combination set of refined potential function parameters of the van der Waals and electrostatic interactions. As noted in the previous paper,² we need to check the reproducibility of vibrational spectra as well as the reproducibility of the crystal structure to obtain the really reliable force-field parameters.

In the packing energy calculation that has been described in the previous paragraphs, the starting molecular shape was originally similar to that observed in the actual crystal structure. It is more general to start from the unknown structure, as seen typically in the molecular design of new compounds. As a trial, the prediction of packing structures was started from the aforementioned three possible forms of CC, TT, and CT (see Table 2). For example, Figure 6 shows the case of MPBB. The space group was assumed to be the same as that of the X-ray-analyzed structure, *Pbca*. The COMPASS force field was used in the calculation. When we started from the energetically minimized CC form, which was similar to the X-ray-analyzed molecular shape, the finally obtained packing structure was similar to the actually observed structure. When the molecular shape of the TT form was used as a starting conformation, the structure of the lowest energy was different and the energy value was slightly higher than that of the CC case. At the same time,

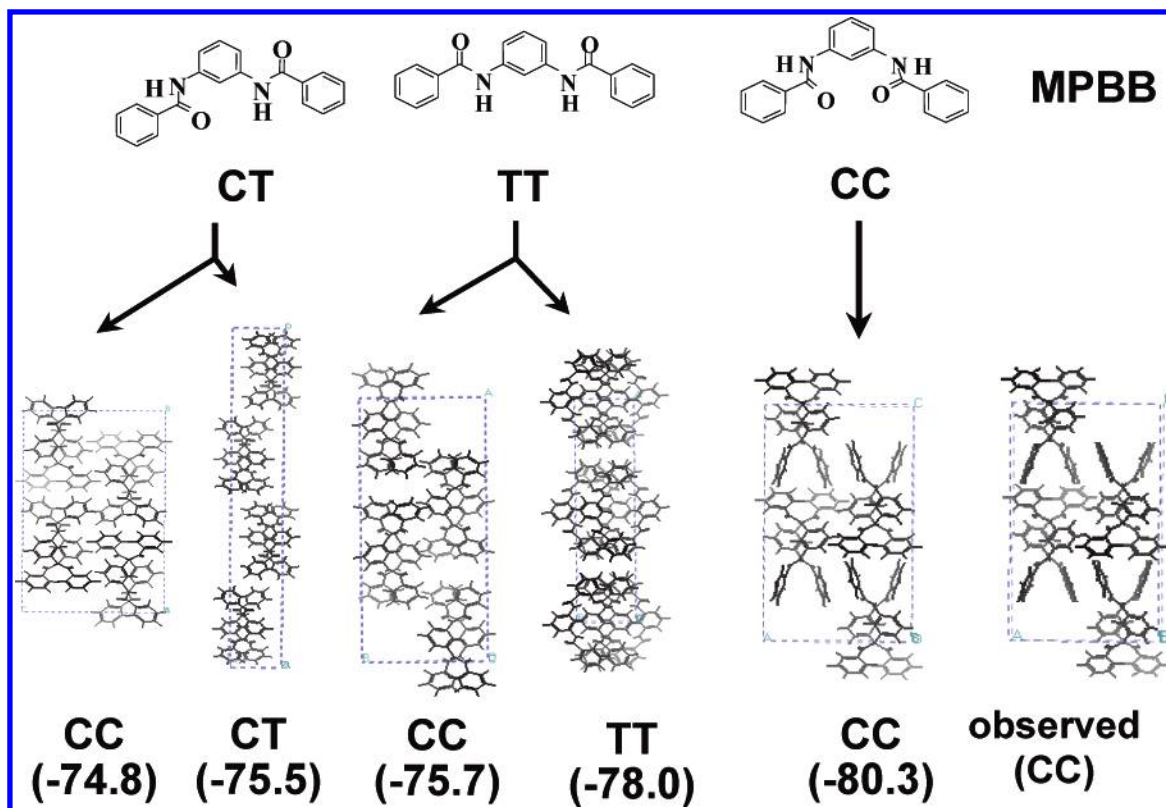


Figure 6. Comparison of packing structure of *N,N'*-*m*-phenylene bisbenzamide (MPBB) between the X-ray analysis and the prediction, where the space-group symmetry was *Pbca*. The potential function used here was the COMPASS methodology. Numerical values given in parentheses are the lattice energies, given in units of kcal/mol. The molecular conformations at the starting points of calculation were CT, TT, or CC (refer to Figure 2). In some cases, the molecular shape changed during the calculation. The structure model predicted for the CC form was in good agreement with the X-ray-analyzed structure.²

the molecular conformation changed from the original TT form to the CC form during energy minimization. The packing structure of the thus-obtained CC form was different from that of the original CC form and the packing energy was ca. 5 kcal/mol higher. Annealing this new crystal form at a high temperature through the molecular dynamics calculation might cause it to convert to the more-stable original structure. Nevertheless, it is interesting to note that the molecular shape can be changed during energy minimization. This change is considered to originate from the low-energy barrier between the TT and CC forms (~ 2 kcal/mol, as shown in Figure 3). A similar situation also was observed when the calculation was started from the CT form. The two types of structures were obtained as the energetically stable structures; one consisted of the CT molecules and the other consisted of the CC molecules. The CT-type molecule transformed to the CC form by crossing the energy barrier (see Figure 3). This new packing structure of the CC molecules was energetically higher than the aforementioned two types of structures that were composed of the similar CC-type molecules. Annealing at high temperature might cause the transformation of this less-stable packing structure to the most-stable structure.

The result shown in Figure 6 is important in such a sense that the molecular shape is not necessarily fixed but can be converted to another possible form, because of the combination effect of intramolecular and intermolecular interactions. Therefore, it may be possible to predict the molecular packing structure, starting from an arbitrarily designed molecular shape. In other words, however, it is necessary to check the predicted crystal structures by changing the starting molecular shape in various ways when we want to get as reasonable a crystal structure as possible. Figure 6 tells us that the MPBB compound

has many plausible packing structures, all of which have similar energy values (within a difference of only several kilocalories per mole). That is to say, we have a possibility of polymorphism and may obtain a different type of crystal structure by changing the crystallization conditions only slightly. Similar possibility was found also for BPMPA. This compound was found to exhibit other types of X-ray diffraction (XRD) patterns when the original crystal was heated to a high-temperature region. We are now investigating which of the predicted crystal structures gives the best fit to the observed XRD pattern.

Crystal Structure of PMIA

The Polymer Predictor software cannot predict the crystal structure of a polymer with infinite length. The energetically stable structure was searched for PMIA, and the effect of various energy terms on the structure was investigated. The monomeric units of PMIA assumed three types of molecular conformations: CC, CT, and TT forms, which are similar to the aforementioned model compounds. The energetically minimized crystal structures obtained for these chain conformations are shown in Figure 7, where the Dreiding II methodology with ab initio charges was used. In the cases of the CT and TT forms, the amide groups were found to orient toward the alternately perpendicular directions to form the 3-D hydrogen-bond networks. This is because the amide groups that are attached to the meta positions of the benzene ring are oriented at directions that are 60° different, when the benzene–amide bonds are twisted by $\sim 30^\circ$. In the case of the CC form, on the other hand, the hydrogen bonds in the *a*-axis direction are long and weak, so the hydrogen bonds are formed only along the *b*-axis; that

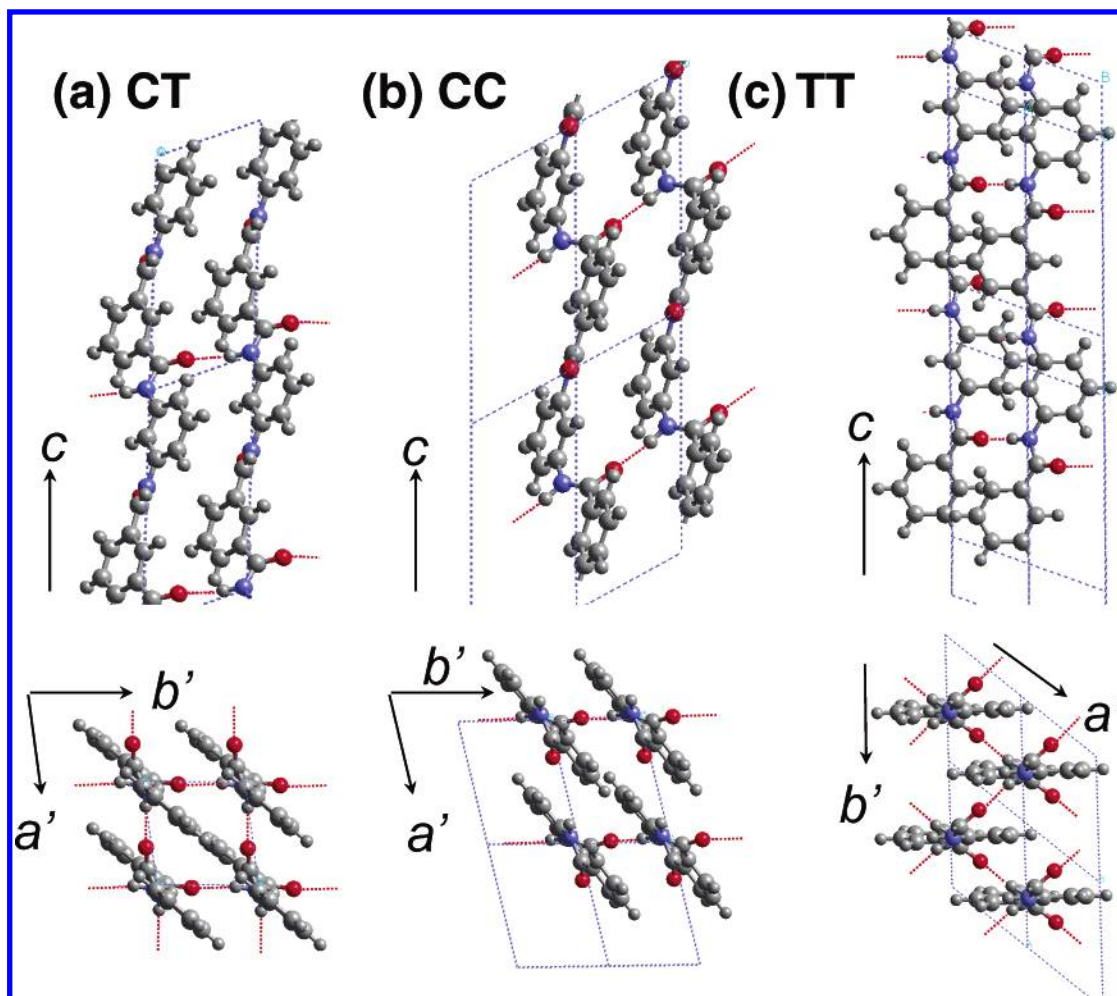
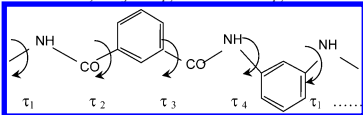


Figure 7. Energetically minimized crystal structure models obtained for the three possible conformations of PMIA. The space group was *P1*. The potential function used here was the Dreiding II methodology with ab initio atomic charges.

TABLE 5: Cell Parameters and Molecular Conformation of PMIA Obtained by Energy Calculation^a

parameter ^b	CT					CC,		TT,
	observed ^c	vdW + es + HB	vdW + es	vdW + HB	vdW	vdW + es + HB	vdW + es + HB	vdW + es + HB
<i>a</i> (Å)	5.27	5.16	5.21	5.25	3.82	6.44		4.95
<i>b</i> (Å)	5.25	5.05	5.10	5.26	6.58	4.98		6.79
<i>c</i> (Å)	11.3	11.34	11.33	11.31	11.33	10.48		11.95
α (°)	111.5	109.1	109.5	110.5	97.6	64.1		113.9
β (°)	111.4	109.5	109.7	111.8	105.7	73.7		105.4
γ (°)	88.0	90.9	91.1	89.6	86.2	93.7		47.2
τ_1 (°)	-145.5	-150.7	-154.4	-154.7	-162.8	-39.6		-147.7
τ_2 (°)	153.2	152.9	156.5	156.9	164.0	45.8		138.1
τ_3 (°)	-37.8	-35.5	-32.1	-32.2	-15.5	17.9		138.4
τ_4 (°)	31.5	36.4	32.0	32.7	15.9	-22.6		-147.2
HB	<i>abab</i>	<i>abab</i>	<i>abab</i>	<i>abab</i>	no	- <i>b-b-</i>		<i>a'b'a'b''</i>
energy (kcal/mol monomeric unit)		-2.33				5.62		0.87

^a Calculation was made by taking some limited types of interaction into account. vdW, van der Waals interaction; es, electrostatic interaction; and HB, hydrogen bonding. ^b τ denotes torsional angles around the benzene and amide groups (refer to the picture shown below).



^c X-ray analyzed values.¹

is, the crystal is composed of the stacking structure of 2-D sheets. These structural features of PMIA are quite similar to the observation that was made for the series of model compounds shown in Table 1: only the CT and TT forms exhibit the 3-D hydrogen-bond networks of the (*a-b*) type and the CC form makes a sheet structure of type (*a-a*) or (*b-b*). The packing energy of PMIA was -2.3 kcal/mol for the CT chain,

5.6 kcal/mol for the CC chain, and 0.9 kcal/mol for the TT chain. The structure that was actually analyzed is the CT form,⁷ which is the most-stable structure among them. From these considerations, we may say that PMIA and its model compounds can take the 3-D network structure of (*a-b*) type, because of a combination effect between the stable CT (and TT) conformation and the 30° twisting around the benzene-amide linkages.

The energy minimization was made also by considering the limited types of interaction. Table 5 shows those results. The three cases of vdW + es + HB, vdW + es, and vdW + HB (in which vdW represents van der Waals interaction, es represents electrostatic interaction, and HB represents hydrogen bonding) produced essentially the same results. When only the van der Waals interaction term was considered in the calculation, the structure was quite different from the observed interaction.

Conclusions

An energetically stable packing structure was sought for the several model compounds of poly(*m*-phenylene isophthalamide) (PMIA), using a computer software package (Polymorph Predictor), and the factors that govern the crystal structure were extracted. The summary is as follows.

(1) Conformation analysis was made for the benzene–amide linkage, and a torsional angle of $\sim 20^\circ$ – 30° was found to be the most preferable. This angle was found to originate from a balance between the electronic conjugation between the benzene and the amide group and the nonbonded interatomic repulsive force between these two groups. For the model compounds listed in Table 1, the three stable conformations were possible: the trans–trans (TT), cis–trans (CT), and cis–cis (CC) forms. However, the most-stable conformation did not necessarily correspond to the actually observed form when only the intramolecular interactions were taken into account, indicating the importance of a combination of intramolecular and intermolecular interactions for the prediction of crystal structure.

(2) The Polymorph Predictor software was used to reproduce the crystal structures of model compounds on the basis of potential function parameter sets of the COMPASS or Dreiding II methodologies with ab initio atomic charges. The calculation was made by taking the various types of interaction terms into consideration, and a combination of the van der Waals interaction with the electrostatic interaction or hydrogen bonding was needed for relatively reasonable reproduction of the crystal structure.

(3) When the Polymorph Predictor calculation was started from an arbitrarily chosen molecular shape, under an assumption of a suitable space group symmetry, the molecular conformation changed sometimes during energy minimization. This observation suggests a possibility of stable crystal modifications with the similar energy values. However, at the same time, this finding warns us to perform a structure prediction by starting

from as many different types of molecular conformations as possible, to find the energetically most-stable and most-plausible structure.

(4) The stable packing structure of PMIA was investigated, starting from the conformationally stable three forms of TT, CT, and CC type. The CT chain conformation gave the most-stable structure, and the cell parameters and the hydrogen-bonding mode were in good agreement with the X-ray-analyzed values. This stable CT conformation is considered to be important as a basic structure to form the three-dimensional hydrogen-bond network when the benzene–amide torsional angles are $\sim 30^\circ$.

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