

Factors Governing the 3-Dimensional Hydrogen-Bond Network Structure of Poly(*m*-phenylene isophthalamide) and a Series of Its Model Compounds (2) Computer Simulation of Crystal Structures of Aromatic Amide Compounds and Comparison with X-ray Analyzed Structures

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Crystal structures have been predicted by using a software Polymorph Predictor and compared with those analyzed by X-ray method for a series of low-molecular-weight aromatic amide compounds as models of poly(*m*-phenylene isophthalamide) and poly(*p*-phenylene terephthalamide). For most of the compounds investigated here, the predicted crystal structure of the lowest or the next lowest packing energy has been found to be in good agreement with the X-ray analyzed structure. However, the energy difference was not very large between these energetically most plausible structures and the other less stable candidates, indicating a difficulty of unique prediction of 3D molecular packing structure and a possibility of existence of various types of crystal modification.

Introduction

In the present paper, we will treat two kinds of polymers, poly(*m*-phenylene isophthalamide) (PMIA) and poly(*p*-phenylene terephthalamide) (PPTA), as typical aromatic polyamides with excellent thermal and mechanical properties. As seen in

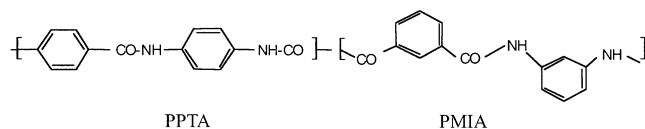


Figure 1, the crystal region of PMIA takes the unit cell structure with 3-dimensionally hydrogen-bonded network between the amide groups of the adjacent chains,¹ whereas PPTA takes the stacking structure of 2-dimensionally hydrogen-bonded sheets.^{2,3} Because these sheets are stacked by relatively weak van der Waals interactions, PPTA shows highly anisotropic mechanical property between the directions parallel and perpendicular to the sheet plane, just like the case of aliphatic nylon.^{4,5} On the other hand, PMIA shows relatively isotropic mechanical properties because of its jungle-gym-type hydrogen-bond network structure.^{5,6}

What is the origin of difference in the crystal structure, in particular the hydrogen bonding mode, between these two polymers? Especially, the complicated 3-D hydrogen bond network of PMIA seems difficult to interpret in a straight manner. To solve this problem, we synthesized a series of model compounds of PMIA and analyzed the crystal structures of these compounds as reported in a previous paper.⁷ By investigating these structures in detail, we found a systematic relation between the hydrogen-bond type and the molecular conformation with meta-substituted amide–benzene structure. As shown in Figure

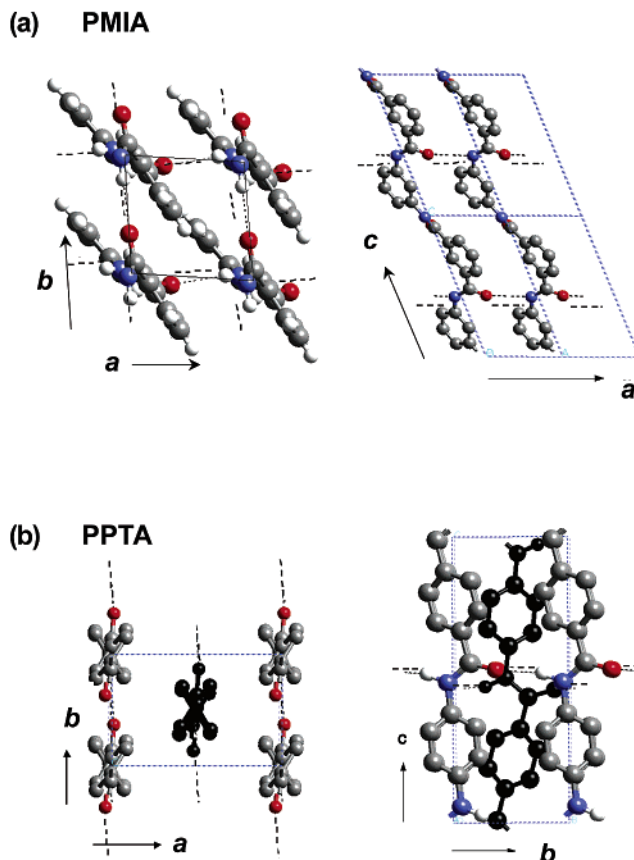


Figure 1. Crystal structures of (a) PMIA¹ and (b) PPTA.^{2,3}

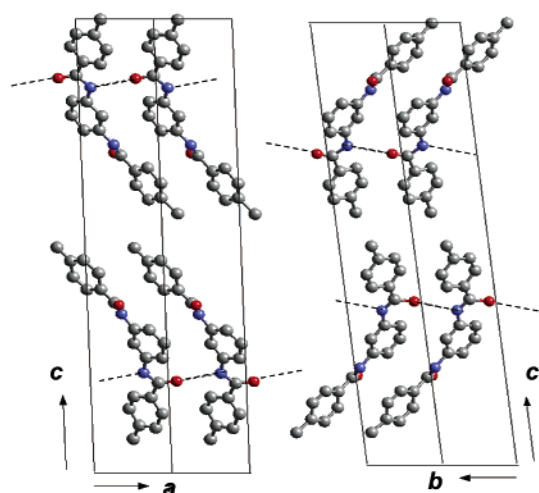
2 and in Table 1, the compounds of cis–trans (CT) conformation, the definition of which is described in a later section, take the jungle-gym-type hydrogen-bond network. That is to say, the hydrogen bonds are made along the *a* and *b* axes alternately

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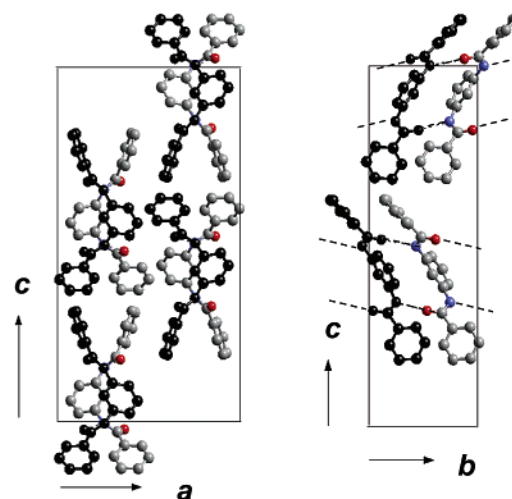
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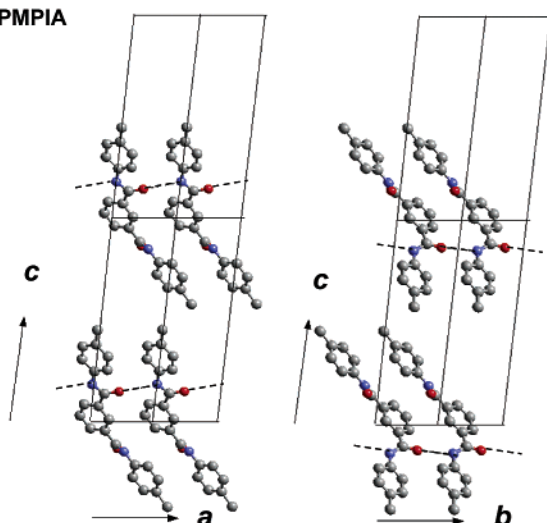
(a) MPPM



(c) MPBB



(b) BPMPA



(d) BMEPIA

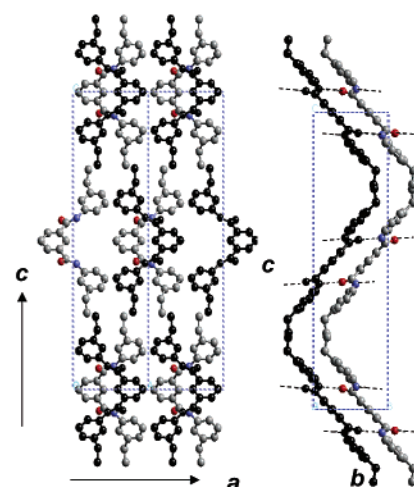
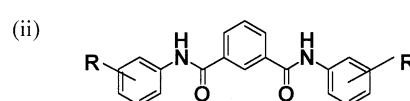
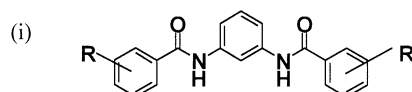


Figure 2. Crystal structures of a series of PMIA model compounds:⁷ (a) MPPM, (b) BPMPA, (c) MPBB, and (d) BMEPIA. The abbreviation of these compound names is referred to in Table 1.

TABLE 1: Structural Data on Poly(*m*-phenylene isophthalamide) and Its Model Compounds^a

formula	code ^b	R	shape	hydrogen bond pattern ^c	space group	Z	Z'	cell parameters					
								<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	α /°	β /°	γ /°
(i)	MPBB	H	CC	(b-b)-(b-b)	<i>Pbca</i>	1	8	14.461	8.374	26.491	90	90	90
(ii)	DPIA	H	CC	(a-a)-(b-b)	<i>P1</i>	4	4	8.363	8.370	23.39	98.897	101.593	90.003
(ii)	BMPPIA	<i>m</i> -CH ₃	CC	(a'-a')-(b'-b')	<i>Cc</i>	2	8	12.076	12.110	24.615	90	99.683	90
(ii)	BMEPIA	<i>m</i> -C ₂ H ₅	CC	(b-b)-(b-b)	<i>P1</i>	2	4	8.540	8.489	27.985	89.985	90.013	90.115
(i)	MPPM	<i>p</i> -CH ₃	TT	(a-b)-(b-a)	<i>P1</i>	1	2	5.146	5.153	33.391	83.560	92.080	86.683
(ii)	BPMPA	<i>p</i> -CH ₃	CT	(a-b)-(a-b)	<i>P1</i>	1	1	5.248	5.127	17.039	83.231	82.773	86.044
	PMIA		CT	...-(a-b)-...	<i>P1</i>	1	1	5.27	5.25	11.3	111.5	111.4	88.0

^a Z: number of molecules in an asymmetric unit, Z': number of molecules in a unit cell. In case of PMIA, Z and Z' are the numbers of monomeric units in a cell. ^b Code: MPBB = *N,N'*-*m*-phenylene bisbenzamide; DPIA = diphenylene isophthalamide; BMPPIA = 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; PMIA = poly(*m*-phenylene isophthalamide). ^c *a'*//[110] direction, *b'*//[10] direction.



when viewed along the *c* axis. This hydrogen bond structure is named (*a-b*)-(*a-b*) type. The compounds of cis-cis (CC) conformation, for example MPBB, exhibit the hydrogen-bond network of different type (*b-b*)-(*b-b*). On the other hand, the

model compounds of PPTA with para-substituted structure show only the 2-D sheet structure, as will be shown in a later section. To interpret this difference in hydrogen bond mode between the chemical compounds with meta- and para-substituted

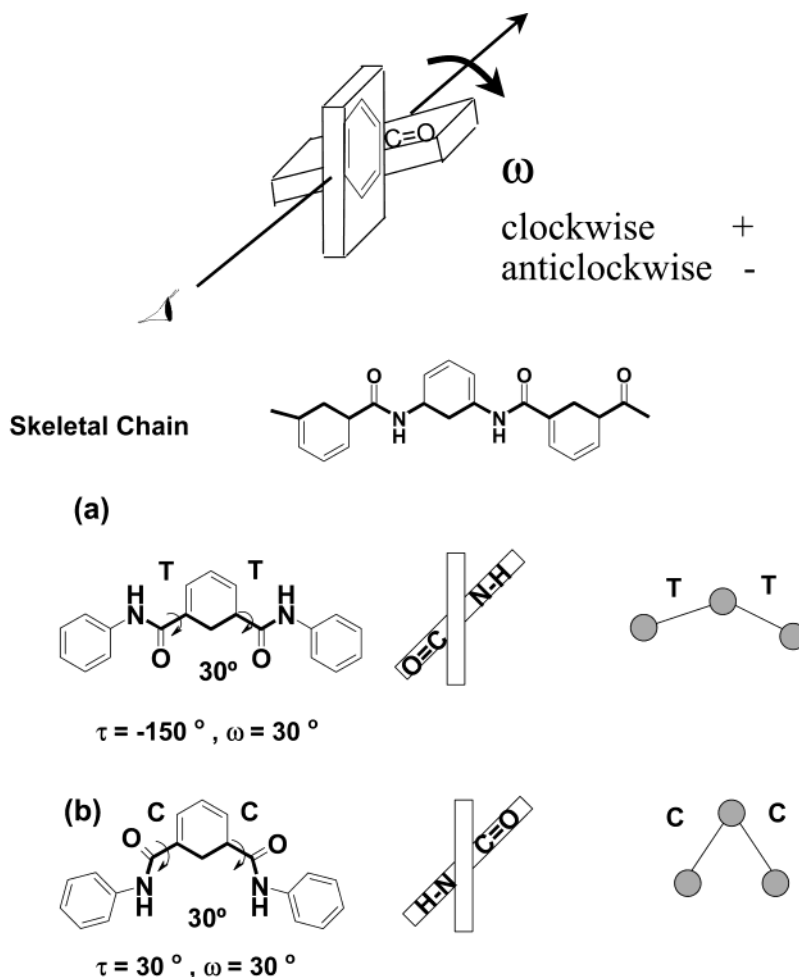


Figure 3. Illustration of skeletal torsional angles. (a) (TT) model and (b) (CC) model. ω is defined as the dihedral angle between benzene and amide group planes. τ is defined as the torsional angle around the bond connecting benzene and amide groups. $\tau = 0^\circ$ corresponds to the cis (C) form. In the examples (a) and (b), $\omega = 30^\circ$ in common but τ is different between the two models. Small triatomic molecules shown in the right-hand sides of the two models illustrate images of the whole molecular shapes.

structures, we have performed the energy calculation and investigated the factors determining the hydrogen bond type. For this purpose, we utilized a software Polymorph Predictor, which has been said useful for the prediction of the packing structure of low-molecular-weight compounds.^{8,9} This software constructs the energetically reasonable crystal structures starting from the chemical formula input into a computer. The reasonableness of this prediction had been checked by several groups through the comparison of the predicted structures with the structures actually analyzed by an X-ray diffraction technique.^{8,9} However, the total number of samples checked by this software is not sufficient for allowing us to predict a crystal structure of an arbitrarily chosen compound in a quantitative (or even qualitative) manner. Besides, no trial has been made for the above-mentioned aromatic amide compounds with various types of hydrogen bond network. This trial should be useful for interpretation of complicated crystal structures of PMIA and PPTA and will give us an opportunity to make a molecular design of novel polymers with more excellent physical properties.

In the present paper, we will describe the results of computer simulation of molecular packing structure for a series of the model compounds of PMIA and PPTA by using a software Polymorph Predictor and will check the usefulness of this software in a quantitative manner through the comparison with the actually analyzed structure data. This test is quite important in the discussion of factors governing the crystal structures

characteristic of aromatic polyamides and their model compounds. In fact, on the basis of the thus characterized software Polymorph Predictor, we have investigated these factors in detail, which will be reported elsewhere in a near future.

Experimental Section

Samples. The aromatic amide compounds of meta structure used here are listed in Table 1. The details of synthesis of these compounds were already described in a previous paper.⁷ Single crystals were prepared from the solutions at room temperature by solvent evaporation method.

X-ray Structure Analysis. The crystal structures of most of the compounds listed in Table 1 were already reported in the previous paper.⁷ However, BMEPIA is a newly synthesized compound, the crystal structure of which was also analyzed by an X-ray diffraction method. The analytical procedure was essentially the same with those made for the other compounds and is skipped here.

Computer Simulation. To find the energetically stable crystal structures, a commercial software Polymorph Predictor was used, a module of Cerius² (version 4.0, Accelrys Inc., USA). Details of this software are referred to in the literature,^{8,9} but the brief outline may be useful for the subsequent discussion.

At first, a chemical formula of the molecule in question was input into a computer. This chemical structure was energetically minimized, and the thus constructed 3-D molecular model was

TABLE 2: Crystal Structures Predicted for MPBB^a

	space group	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	α /°	β /°	γ /°	density/ g cm ⁻³	total energy/ kcal mol ⁻¹	hydrogen bond	molec shape	twisting angle/°			
												τ_1	τ_2	τ_3	τ_4
obsd	<i>Pbca</i>	14.46	8.37	26.49	90	90	90	1.310		(b-b)-(b-b)	CC	-41.2	58.9	39.5	37.5
calcd	<i>Pbca</i>	14.29	8.26	26.24	90	90	90	1.357	-80.323	(b-b)-(b-b)	CC	-46.0	57.9	41.0	41.7
calcd	<i>P2₁/c</i>	7.07	7.31	30.7	111.05	90	90	1.419	-81.974	(a'-b')-(a'-b')	CC	-32.6	36.3	36.3	-32.6
	<i>P1</i>	7.57	15.21	7.04	90.00	90.00	112.14	1.398	-80.546	(b-b)-(b-b)	CC	-37.4	36.8	36.8	-37.4
	<i>P2₁2₁2₁</i>	6.80	12.22	18.25	90	90	90	1.386	-78.380	(b'-b')-(b'-b')	CT	-23.5	33.2	-42.6	-21.3
	<i>P2₁</i>	7.31	7.08	15.72	90	111.49	90	1.393	-81.156	(a'-b')-(a'-b')	CC	-32.6	36.3	36.3	-32.6
	<i>C2/c</i>	7.03	14.89	29.20	80.58	90	90	1.394	-81.256	(b-b)-(b-b)	CC	-35.4	46.9	27.0	-33.7
	<i>P1</i>	5.22	5.05	16.69	77.00	84.98	85.89	1.400	-79.824	(a-b)-(a-b)	CC	-35.3	40.6	39.4	26.3

^a Definition of torsional angles is as follows:

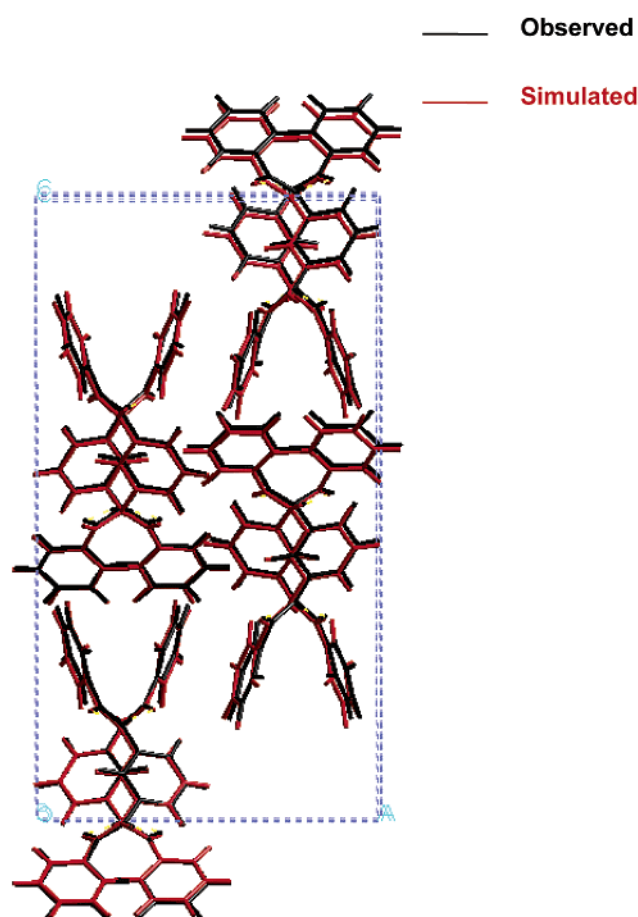
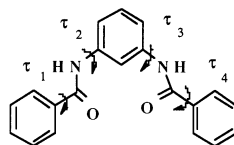


Figure 4. Comparison in molecular packing mode of MPBB between the observed and predicted structures, where the predicted structure was obtained by assuming the space group *Pbca* from the starting.

used as a starting structure for the packing structure prediction. The potential force field used in the minimization process might be chosen arbitrarily, but a COMPASS force field was used in the present study.¹⁰ Before starting the software, we needed to make several assumptions. One was about the number of molecules included in a crystallographically asymmetric unit. The second assumption was a possible space group symmetry. The space groups employed were those encountered frequently in the X-ray structure analysis of general organic compounds; for example, *P1*, *P1*, *P2₁*, *P2₁/c*, *Pbca*, and so on. The position and orientation of molecules packed in the unit cell were given

at random. The unit cell parameters (*a*, *b*, *c*, α , β , and γ) were also given a random. About 4000 crystal structure models were generated in average and their energies were minimized, where the molecules were treated as rigid bodies. The annealing process in the temperature range of 60 000–300 K was applied to erase the unreasonable strains in the packing structures as much as possible. The thus generated structural models were classified into groups by investigating the similarity of structures (clustering process), and one model of each cluster was picked up as the representative. For these structures, the full energy minimization was carried out with taking away the assumption of rigid body, and then the most stable structures were picked up as energetically possible candidates. Normally, the top 10 structures were listed up and compared with the actually analyzed structure.

Results and Discussion

Classification of Crystal Structures of PMIA Model Compounds. Figure 2a–d shows some examples of the crystal structures determined by the X-ray method for the compounds listed in Table 1. In this table are listed also the molecular conformation and intermolecular hydrogen bonding modes. The detailed information such as fractional coordinates, molecular parameters, etc. were already presented in the previous paper.⁷ One exception is about BMEPIA, the crystal structure of which was analyzed in the present study as given in the Supporting Information. Before comparing these actually analyzed structures with the computer-predicted ones, we pick up some characteristic points of these structures.

(1) *Molecular Conformation.* Molecular conformations of these compounds can be described by using two kinds of parameters shown in Figure 3. At first, we assume a flat molecule. The τ is a torsional angle around a bond of skeletal chain as given by a bold line. Because the molecule is assumed to be flat, the τ can take only two angles: $\tau = 0^\circ$ corresponding to the cis (C) form and $\tau = 180^\circ$ to the trans (T) form. Example (a) in Figure 3 shows the (TT) form concerning the two central skeletal bonds τ_1 and τ_2 . Example (b) is the case of the (CC) form. The actual molecule is not flat but is twisted more or less around the bonds between the benzene and amide groups. This torsional angle ω is almost common to all of the model compounds treated here, 25–30°, except for the case of MPBB with $\omega = 40$ –59°. It must be known here that a set of (τ_1 , τ_2) determines a conformation of the central part of the molecule or a rough shape of the whole molecule and is useful for description of the difference in molecular form among the

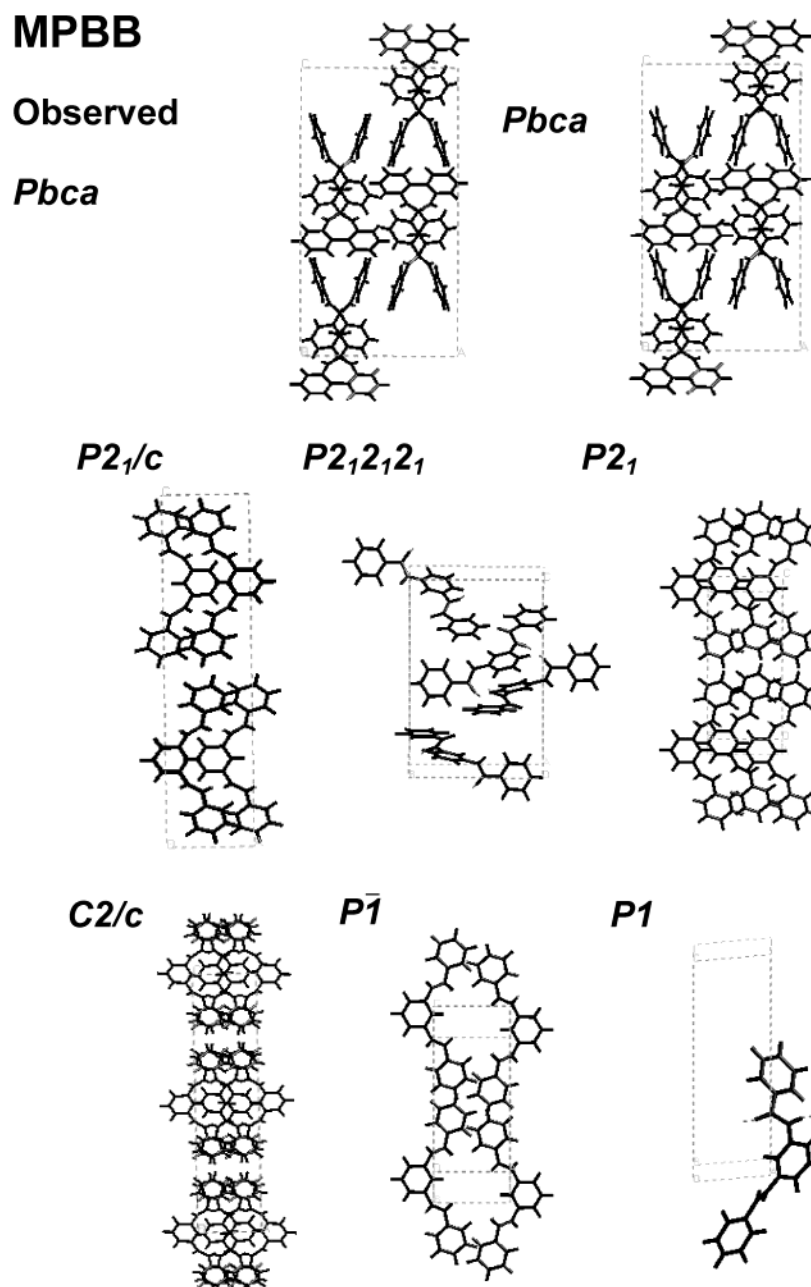


Figure 5. Comparison in molecular packing mode of MPBB between the observed structure and the predicted structures of the lowest energy obtained under the assumption of various space groups.

compounds, whereas the torsional angle ω represents the local twisting angle between the benzene and amide groups. Therefore, in the subsequent discussion, we will describe the molecular shape roughly by using a set of (τ_1, τ_2) and ignoring the torsional angles ω . Table 1 shows the thus classified molecular conformations for all of the compounds treated here. They are classified into three types: (TT), (TC), and (CC) forms. The parent polymer PMIA is included in the group of (CT).

(2) *Packing Mode of Molecules.* As seen in Figure 2, the molecules are packed with layer structure. A molecule in a layer is connected with the neighboring molecules by the two hydrogen bonds. Therefore, the molecular packing mode can be expressed in terms of the directions of hydrogen bonds in each layer and the stacking mode of these layers. For example, as shown in Figure 2a, the model compound MPPM takes the hydrogen bond of ... $-(a-b)-(b-a)-(a-b)-(b-a)-$..., where the term $(a-b)$ indicates that the two amide groups of a molecule

are connected with the neighboring molecules through the two hydrogen bonds along the a and b directions approximately. Similarly, the second term $(b-a)$ is for the next layer. In Table 1 are shown the thus classified hydrogen bonding modes for all of the compounds treated here. PMIA takes the hydrogen bonds of $(a-b)-(a-b)-$ type.

(3) *Relation between Molecular Conformation and Packing Mode.* When we see Table 1, we notice a good relation between the molecular shape and the packing mode of these molecules. For example, the compounds of (CC) conformation take the hydrogen bond network of the $(b-b)-(b-b)$ or $(b-b)-(a-a)$ type. That is, the molecules of the (CC) form can take the hydrogen bonds along the same directions in one layer, and these layers are stacked so that the hydrogen bonds of each layer are in the parallel direction or in the perpendicular direction. The compound of (TT) form shows the structure of $(a-b)-(b-a)$ type. The compounds of the (CT) form take the packing

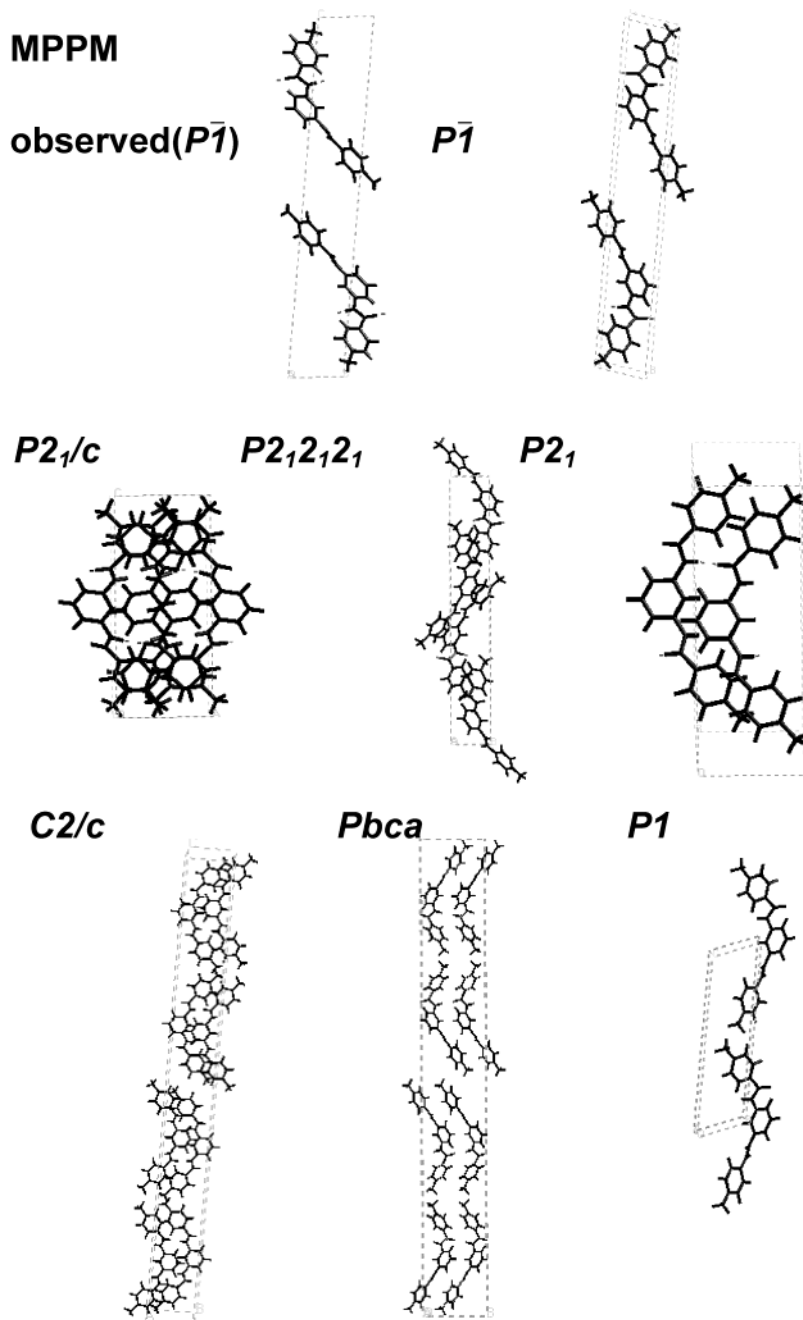


Figure 6. Comparison in molecular packing mode of MPPM between the observed structure and the predicted structures of the lowest energy obtained under the assumption of various space groups.

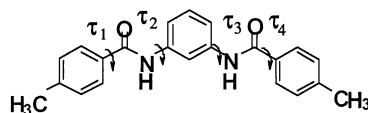
mode of $(a-b)-(a-b)$ type. Although the total number of compounds treated here might be too small to generalize such a relationship to all of the compounds with meta benzene–amide structure, this relationship will be useful as the first step for the systematic investigation of factors governing the packing structure observed for a series of aromatic amide compounds and also for the prediction of packing structure of a new compound with similar chemical formula.

Computer Simulation of Packing Structure. As mentioned in the introductory section, the purpose of this study is to check to what extent the software Polymorph Predictor can reproduce the actually analyzed structures of aromatic amide compounds. A brief explanation of this software was already given in the Experimental Section. As the representative compounds of the three groups classified in Table 1, the compounds MPBB, MPPM, and BPMPA are investigated here.

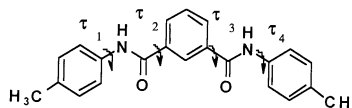
At first, we need to assume a flat molecular conformation of each compound, (CC), (CT), or (TT) and then twist this molecule around the bonds between benzene and amide groups to get an energetically stable molecular form. Even when we start from these three types of molecular structure, the molecule might change its conformation to other form, from the (CT) to (CC) form for example, at the final stage of simulation if the potential energy barrier between these two conformations is relatively low. The situation is a little complicated, and therefore, the details of this problem will be reported in a separate paper. Rather, as the first trial, the molecular conformation revealed by the X-ray structure analysis was directly used here as the starting model. Then the structures of the lowest packing energy were investigated under the assumption of various space group symmetries.

TABLE 3: Crystal Structures Predicted for MPPM^a

	space group	a/Å	b/Å	c/Å	α°	β°	γ°	density /g cm ⁻³	total energy /kcal mol ⁻¹	hydrogen bond	molec shape	twisting angle/ $^\circ$			
												τ_1	τ_2	τ_3	τ_4
obsd	<i>P</i> 1	5.15	5.15	33.39	83.56	92.08	86.68	1.311	-	(a-b)-(b-a)	TT	28.0	-31.4	-31.8	27.9
calcd	<i>P</i> 1	5.02	5.02	33.72	98.77	98.77	90.82	1.380	-102.83	(a-b)-(b-a)	TT	32.3	-31.9	-31.9	32.3
calcd	<i>P</i> 2 ₁ /c	6.91	15.08	16.08	84.49	90	90	1.373	-100.36	(a'-b')-(a'-b')	TT	30.5	-26.6	-32.0	19.2
	<i>P</i> 2 ₁ 2 ₁ 2 ₁	9.93	4.96	34.09	90	90	90	1.363	-97.427	(a-b)-(b-a)	TT	4.5	-23.0	-35.3	39.4
	<i>P</i> 2 ₁	7.06	7.20	19.08	61.03	90	90	1.350	-101.60	(a'-b')-(a'-b')	TT	33.4	-32.8	-32.8	33.4
	<i>C</i> 2/c	7.12	7.10	68.87	90	105.59	90	1.364	-102.17	(a'-b') ² -(b'-a') ²	TT	31.9	-32.4	-32.3	33.8
	<i>P</i> 1	5.04	5.04	17.97	68.79	85.02	88.87	1.350	-101.61	(a-b)-(a-b)	TT	33.3	-32.8	-32.8	33.3
	<i>P</i> bca	4.94	9.88	72.74	90	90	90	1.288	-97.199	(a-b)-(b-a)	TT	87.3	41.5	36.2	-35.0

^a Definition of torsional angles is as follows:TABLE 4: Crystal Structures Predicted for BPMPA^a

	space group	a/Å	b/Å	c/Å	α°	β°	γ°	densit /g cm ⁻³	total energy /kcal mol ⁻¹	hydrogen bond	molec shape	twisting angle/ $^\circ$			
												τ_1	τ_2	τ_3	τ_4
obsd	<i>P</i> 1	5.25	5.13	17.04	83.23	83.77	86.04	1.268	-	(a-b)-(a-b)	CT	-34.7	36.5	26.5	-30.5
calcd	<i>P</i> 1	5.19	5.00	16.77	93.15	102.9	91.22	1.351	-94.633	(a-b)-(a-b)	CT	31.8	-40.4	-26.5	29.4
calcd	<i>P</i> 2 ₁ /c	5.03	5.20	64.92	90	90	88.61	1.346	-94.544	(a-b)-(b-a)	CT	-31.4	40.2	27.0	-29.2
	<i>P</i> 1	5.07	5.20	38.84	109.89	116.76	91.46	1.361	-94.991	(a-b)-(b-a)	CT	-31.2	40.1	27.3	-28.6
	<i>P</i> 2 ₁ 2 ₁ 2 ₁	5.01	10.84	32.06	90	90	90	1.314	-91.273	(a-b)-(b-a)	CT	-30.6	43.7	15.8	29.3
	<i>P</i> 2 ₁	4.37	5.01	38.79	90	90	85.03	1.351	-95.468	(b-b)-(b-b)	TT	-31.8	38.8	-36.6	-39.6
	<i>C</i> 2/c	7.29	7.18	70.69	90	113.87	90	1.353	-94.008	(a'-b') ² -(b'-a') ²	CT	30.5	-39.3	-27.9	30.4
	<i>P</i> bca	9.05	9.98	38.57	90	90	90	1.309	-91.008	(b-b)-(b-b)	TT	-50.9	-46.4	37.2	-25.9

^a Definition of torsional angles is as follows:

(1) *MPBB*. As an example, we will see at first the simulation result obtained for *MPBB* under the assumption of the space group *Pbca*, the same with that determined by the X-ray structure analysis. Following the process mentioned in the Experimental Section, many possible packing structures were generated randomly, and the energetically stable structures were picked up under the assumption of rigid body. A total of 1597 models were extracted by this stage. After clustering these structures, energy minimization was carried out by taking away the assumption of rigid body molecule, and 83 structures were obtained as accepted models at the final stage. Table 2 shows the cell constants of the *Pbca* model with the lowest energy. Figure 4 shows the packing structure of this model in comparison with the X-ray analyzed structure. The cell constants, the torsional angles of the benzene-amide bonds, and the hydrogen bonding mode in the unit cell [(b-b)-(b-b)] are reproduced quite well when compared with the observed data. The structure of the second lowest energy did not match the actual structure.

The other space group *P*2₁/c was tried as the second case. The structure of the lowest packing energy is shown in Figure 5 and Table 2. This structure does not match the observed data. Similarly, the other kinds of space groups were also tried but did not give any good correspondence with the observed structure as seen in Figure 5. In Table 2 are given the unit cell parameters and the internal rotation angles of these structures of the lowest energies. As mentioned above, the structure predicted for the space group *Pbca* is in good agreement with the observed one, but this is not necessarily the most stable structure. As seen in Table 2, the structure of space group *P*2₁/c is in the lowest energy state. However, the energy difference among the various structures is 1–4 kcal/mol at most. This suggests the two important points. The first point is that the

Polymorph Predictor has a limitation in energy resolution and can predict the energetically stable structure within an error of several kcal/mol. The second point is a possibility of crystal modifications. That is to say, another packing structure with lower (higher) energy than *Pbca* might be existent as a possible crystal modification, although the structure of *Pbca* happened to be obtained under the crystallization condition adopted in the present experiment. In other words, by changing the crystallization condition, other type of packing structure might be realized for the same compound.

(2) *MPPM*. Among the results shown in Figure 6 and Table 3, the *MPPM* model with the lowest energy is found for *P*1. The cell constants correspond relatively well to the observed values. The same situation can be seen also for the torsional angles. The simulated hydrogen bonding mode is (a-b)-(b-a), which corresponds to the observation. The structure of comparable energy value was found for *C*2/c, suggesting an existence of another crystal modification.

(3) *BPMPA*. The simulation results for *BPMPA* are listed in Table 4 and Figure 7. The space group *P*2₁ gives the structure of the lowest energy. However, the space groups of *P*1, *P*1, *P*2₁/c, and *C*2/c also give the structures with only slightly different energies from that of *P*2₁. The actual single crystal takes the space group *P*1. The cell constants predicted for *P*1 are close to the observed values. The observed hydrogen bonding mode is -(a-b)-(a-b)-..., which is reproduced well in the simulation.

In this way, all of these three cases were found to reproduce the actually observed structural data relatively well. However, as seen in Tables 2–4, the energy difference is small among many possible structural models, only 1–4 kcal/mol. Such a small energy difference might lead us to the wrong prediction

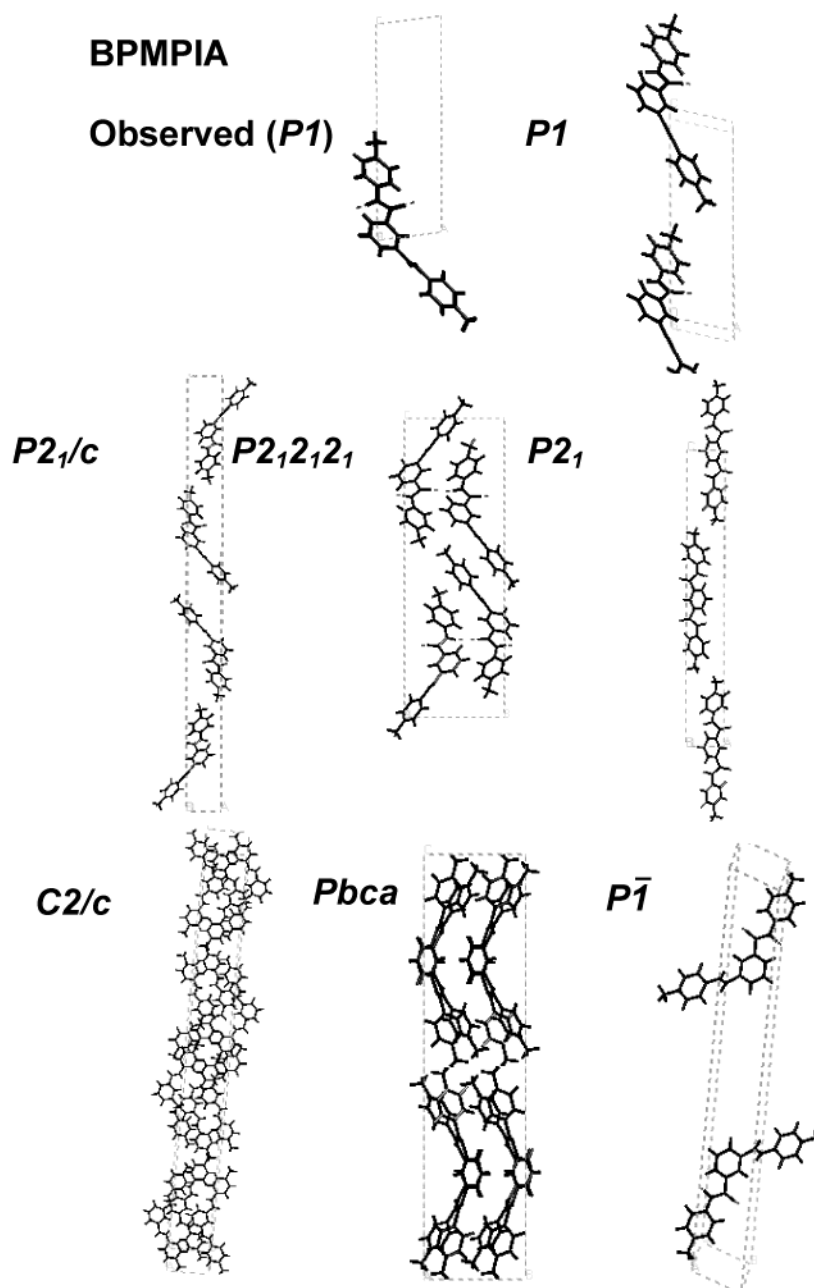


Figure 7. Comparison in molecular packing mode of BPMPA between the observed structure and the predicted structures of the lowest energy obtained under the assumption of various space groups.

of the actually observable crystal modification. In other words, it is still difficult at the present stage to get a unique answer without any experimental information about the space group and so on. At the same time, however, we have a possibility of crystal modifications or the existence of several plausible models with the similar packing energy.

Another important point associated with the above-mentioned problem is about the choice of potential force field. In the present calculation, we employed the COMPASS force field,¹⁰ which has been said to simulate the structure with high reproducibility. Even this force field, however, could not always simulate the X-ray analyzed structure as the model with the lowest packing energy. As a trial, we applied another force field, Dreiding II¹¹ with the atomic charges given by ab initio molecular orbital calculation. The result obtained for the compound MPPM with the space group *P1* is given in Figure 8b. The agreement with the observed data is in almost the same

order with the case of COMPASS force field [Figure 8a]. When we applied the Dreiding II force field with the atomic charges calculated by a classical Gastiger method,¹² the result was much worse, as shown in Figure 8c.

Which is better between the COMPASS and the Dreiding II with ab initio charges for the prediction of the crystal structure of aromatic amide compounds? As long as the structural parameters were investigated for a series of model compounds discussed here, the predicted parameters were in almost the same order of agreement with the observed data for both the force fields. Another judgment is to compare the calculated vibrational spectra with the observed data. For example, we calculated the normal-mode frequencies of MPPM crystal by using these two kinds of potential force field. As shown in Figure 9, the calculated vibrational frequencies were found to fit the observed data better for COMPASS force field than Dreiding II with ab

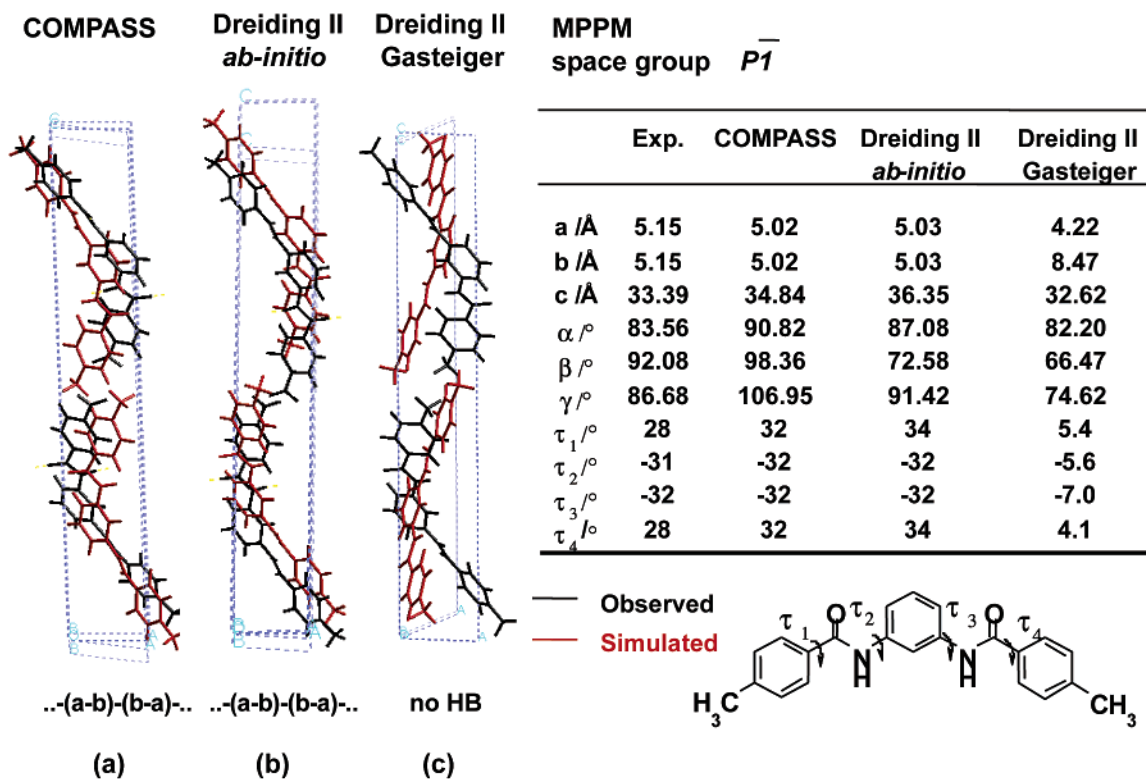


Figure 8. Comparison in molecular packing mode of MPPM between the observed structure and the simulated structures obtained by using various potential force fields under the assumption of $P\bar{1}$ space group. It is noted that model (c) does not show any hydrogen bondings.

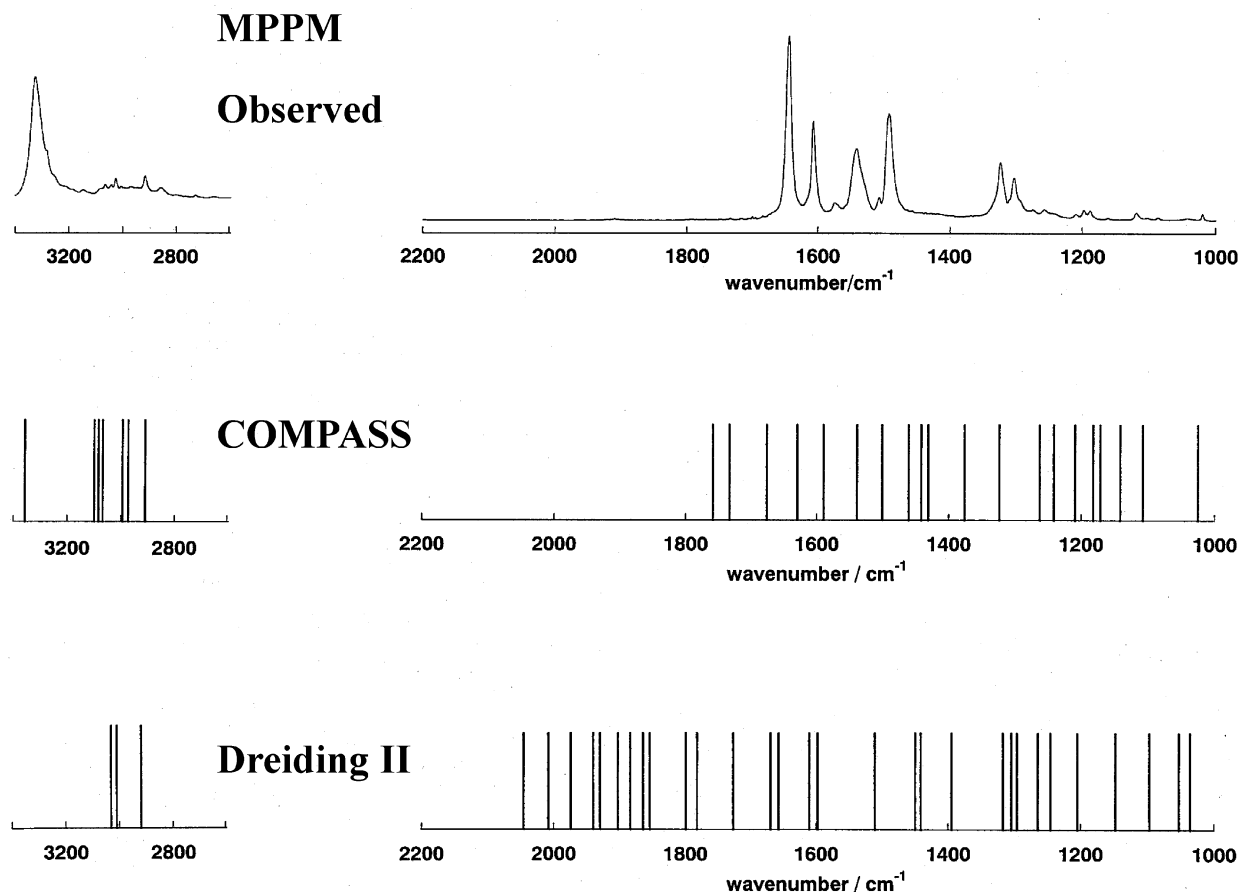


Figure 9. Comparison in infrared spectra of MPPM between the observed data and the simulations made by using COMPASS or Dreiding II force field.

initio charges. This example is suggestive. The calculation of packing structure is not much sensitive to a choice of potential

force field parameters compared with the calculation of vibrational spectra. In other words, the force field parameters must

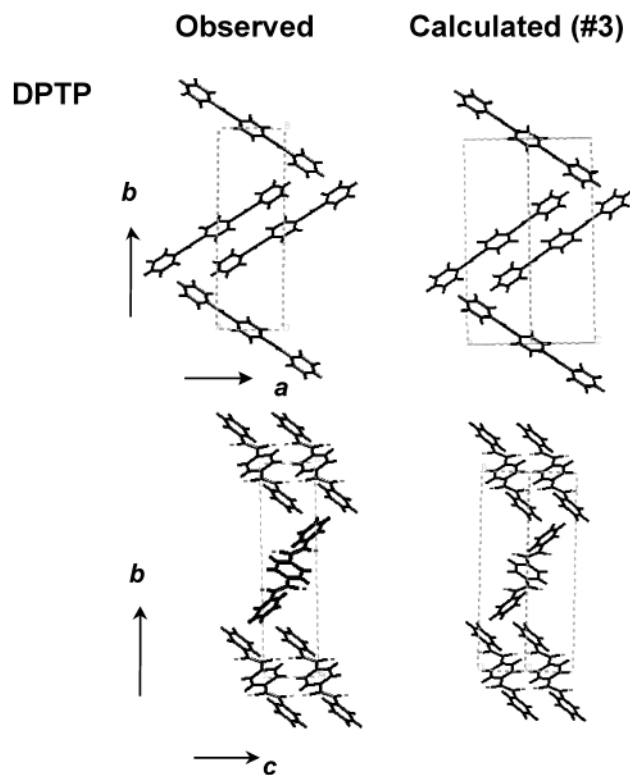
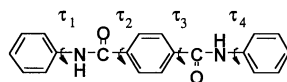


Figure 10. Comparison in molecular packing mode of DPTP between the observed structure and the simulated structures of the lowest energy obtained under the assumption of $P2_1/c$ space group.

TABLE 5: Structure Parameters Predicted for DPTP with the Space Group Symmetry of $P2_1/n$

	total energy (kcal/mol)	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	$\tau_1/^\circ$	$\tau_2/^\circ$	$\tau_3/^\circ$	$\tau_4/^\circ$
Observed											
		6.91	21.46	5.32	90	107.20	90	32.1 ^a	32.2	-32.2	-32.1
Calculated											
#1	-77.886	8.22	5.12	34.78	90	86.35	90	-31.1	31.5	-31.5	31.1
#2	-77.754	8.12	5.12	35.24	90	94.36	90	33.4	30.8	-30.8	-33.4
#3	-77.250	9.74	22.12	7.09	90	105.85	90	29.5	33.6	-33.6	-29.5

^a Definition of torsional angles is as follows:



be selected so that they can predict both the packing structure and the vibrational spectra as reasonably as possible.

Prediction of Crystal Structure of PPTA Model Compounds. A similar type of simulation was made for the model compounds of PPTA where the COMPASS force field was applied.

(1) **DPTP.** The chemical formula of diphenyl-*p*-terephthalamide (DPTP) is shown in Figure 10 and Table 5 with the observed crystallographic data.¹³ The simulation was made by assuming a space group $P2_1/n$ which was actually found by the X-ray analysis. The unit cell parameters and torsional angles are compared with the observed values in Table 5. Figure 10 shows a comparison of simulated crystal structure with the observed one, where the structure of the 3rd lowest energy is shown. The calculated cell constants a and c are much longer than the observed data. The two-dimensional hydrogen-bond sheet structure is well reproduced. It should be noticed that the structure models with the lowest (#1 in Table 5) and the next lowest (#2 in Table 5) energy could not reproduce the observed

data at all, but the relatively good agreement could be obtained for the structure model with the 3rd lowest energy.

(2) **PPDB.** *N,N'*-(*p*-phenylene)dibenzamide (PPDB) was reported to show two kinds of crystal modifications, $P2_1/c$ ¹⁴ and $Pbca$.¹⁵ The simulation was made for these two space group symmetries. As seen in Figure 11, the crystal structure with the lowest energy gave a good agreement with the observed structure for the case of $P2_1/c$. In the case of $Pbca$ (Figure 12), the relatively good correspondency was found for the model with the 15th lowest energy. Besides, this model includes two molecules in an asymmetric unit, different from the observed structure. The packing energy difference between the structures of $P2_1/c$ and $Pbca$ is calculated to be ca. 6 kcal/mol. The crystal modification of $P2_1/c$ is energetically more stable than the $Pbca$ structure. However, we do not know whether the $P2_1/c$ structure is really more stable and can be observed more frequently in the crystallization process or not.

In this way, the software Polymorph Predictor has been found to give a good prediction of the crystal structures of aromatic amide compounds, although they are not always the structures of the lowest energies. The torsional angles around the benzene–amide bonds are about 30° for most of the compounds treated here, which give a variety of molecular shapes for the meta structure but do not affect the whole molecular shape of the para structure. This difference in molecular shape results in the difference between the 3D and 2D hydrogen bonding modes of meta- and para-substituted aromatic compounds through the combination with the intermolecular interactions. The detailed discussion on this point will be reported in a separate paper.

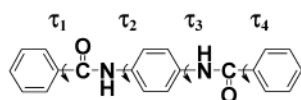
Through the research described in this paper, it has been confirmed that the Polymorph Predictor seems very useful for the discussion of the packing structure in a systematic manner and gives us a chance to design a new material with a unique packing structure. However, we need to notice that the best answer given by this software is not necessarily the real practical structure, being an alert to use this type of software in a quantitative manner. It is also needed to know that the Polymorph Predictor calculates the lattice energy only. A better way to predict the crystal structure more exactly might be a comparison of free energy including the contribution of vibrational entropy S_{vib} . For example, for constant temperature T and pressure P , a Gibbs free energy G is given by $G = E + PV - TS_{\text{vib}}$, where V is a volume and E is an internal energy. Even when the packing energy E is lower for a structural model, the contribution of S_{vib} might inverse the structural stability at a nonzero temperature. This type of stability inversion was actually reported for the polyethylene crystal: the orthorhombic-type packing structure is by about 0.2 kJ/mol CH_2 unit less stable than the triclinic-type structure as for the packing energy but the former structure is lower by 0.3 kJ/mol CH_2 unit than the latter when the contribution of S_{vib} is taken into account at 300 K.¹⁶ The calculation of S_{vib} requires the frequency distribution function estimated from the frequency-phase angle dispersion curves along all of the possible directions of phonon propagation in the crystal lattice. This calculation is a tedious work and has not yet been tried to the model compounds treated in the present study.

Conclusions

In this paper, we performed the computer simulation of the crystal structures of a series of model compounds of PMIA and PPTA by using software Polymorph Predictor. The molecular conformation and molecular packing structure, in particular, the hydrogen-bonding mode could be reproduced relatively well.

PPDB (form I): COMPASS
Space Group: $P2_1/c$

	Experiment	Calculation
a /Å	18.06	35.12
b /Å	5.25	5.12
c /Å	8.03	8.23
$\alpha /^\circ$	90	90
$\beta /^\circ$	93.99	94.83
$\gamma /^\circ$	90	90
$\tau_1 /^\circ$	31.4	31.9
$\tau_2 /^\circ$	36.5	33.7
$\tau_3 /^\circ$	-36.5	-33.7
$\tau_4 /^\circ$	-31.4	-31.9



Observed **Calculated (#1)**

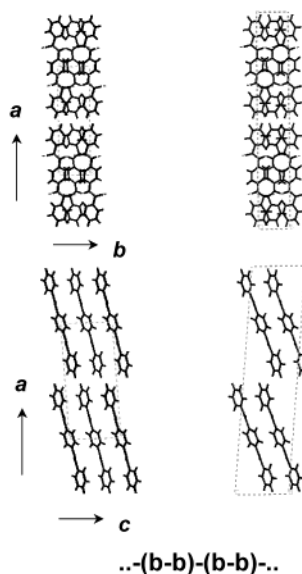
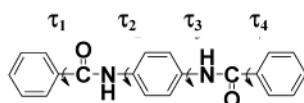


Figure 11. Comparison in molecular packing mode of PPDB form I between the observed structure and the simulated structures of the 3rd lowest energy obtained under the assumption of $P2_1/c$ space group.

PPDB (form II): COMPASS
Space Group: $Pbca$

	Experiment	Calculation
a /Å	9.54	9.84
b /Å	18.27	32.55
c /Å	9.39	9.85
$\alpha /^\circ$	90	90
$\beta /^\circ$	90	90
$\gamma /^\circ$	90	90
$\tau_1 /^\circ$	24.7	18.3
$\tau_2 /^\circ$	56.3	49.3
$\tau_3 /^\circ$	-56.3	-49.0
$\tau_4 /^\circ$	-24.7	-24.4



Observed **Calculated (#15)**

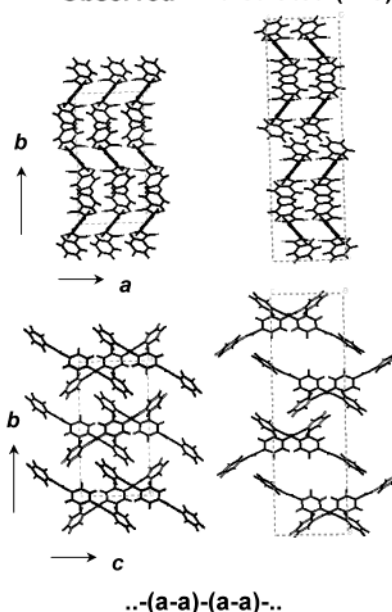


Figure 12. Comparison in molecular packing mode of PPDB form II between the observed structure and the simulated structures of the 15th-lowest energy obtained under the assumption of $Pbca$ space group.

However, the structure obtained in this way was not always of the lowest energy among the many possible candidates. Here, we see a limitation of computer prediction of packing structure and/or a possibility of other kinds of crystal modification. Of course, the probability of perfect prediction is dependent on various parameters including potential function parameters, and so on. Anyway, however, this software could give us relatively good reproduction of the hydrogen-bond network structure of the PMIA model compounds and 2-D hydrogen-bond sheet structure of the PPTA model compounds. The question arising from this result may be about the reasons why we could get comparatively good reproduction of packing structure. In other words, what kind of factors govern the molecular packing mode of these compounds? In the next paper, we will clarify the details of the contribution of various interaction parameters such as

van der Waals interaction, Coulombic interaction, hydrogen bonding, etc. in the determination of molecular packing modes of aromatic amide compounds.

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Supporting Information Available: Fractional atomic coordinates and equivalent isotropic temperature factors of BMEPIA (Table A-1). Selected geometry parameters for BMEPIA (Table A-2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Kakida, H.; Chatani, Y.; Tadokoro, H. *J. Polym. Sci.* **1976**, *14*, 427.
- (2) Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1977**, *10*, 413.
- (3) Northolt, M. G. *Eur. Polym. J.* **1974**, *10*, 799.
- (4) Tashiro, K.; Tadokoro, H. *Macromolecules* **1981**, *14*, 781.
- (5) Tashiro, K. *Prog. Polym. Sci.* **1993**, *18*, 377.
- (6) Tashiro, K.; Kobayashi, M. *Polymer* **1991**, *32*, 1516.
- (7) Nimmanpipug, P.; Tashiro, K.; Rangsiman, O. *J. Phys. Chem.* in press.
- (8) Luesen, F. J. *J. Cryst. Growth* **1996**, *166*, 900.
- (9) Lommerse, J. P. M.; Motherwell, W. D. S.; Ammon, H. L.; Dunitz, J. D.; Gavezzotti, A.; Hofmann, D. W. M.; Luesen, F. J. J.; Mooij, W. T. M.; Orice, S. L.; Schweizer, B.; Schmidt, M. U.; van Eijck, B. P.; Verwer, P.; Williams, D. E. *Acta Cryst* **2000**, *B56*, 697.
- (10) Sun, H. *J. Phys. Chem.* **1998**, *B102*, 7338.
- (11) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III. *J. Phys. Chem* **1990**, *94*, 8897.
- (12) Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219.
- (13) Harkema, S.; Gaymans, R. J.; Hummel, G. J. Z. *Acta Crystallogr.* **1979**, *B35*, 506.
- (14) Adam, W. W. *Acta Crystallogr.* **1978**, *B34*, 954.
- (15) Harkema, S.; Gaymans, R. J. *Acta Crystallogr.* **1977**, *B33*, 3609.
- (16) Kobayashi, M.; Tadokoro, H. *Macromolecules* **1975**, *8*, 897.