

the bonds between benzene and the amide groups, are aggregated in the crystal lattice by making a 3-D hydrogen bond network as shown in Figure 1b. The hydrogen bonds are formed along the *a* and *b* axes, and these mutually perpendicular hydrogen bonds are repeated alternately along the chain axis, forming a jungle-gym-type network. This type of hydrogen bond structure is named the (*a*–*b*) type hereafter in this paper. The 3-D jungle-gym network gives PMIA relatively isotropic mechanical properties, as predicted by a lattice-dynamical calculation.⁵ The combination of a rigid chemical structure with this strong hydrogen bond results in high thermal resistivity, as mentioned above. Clarification of the origins of such a difference in hydrogen bond structure between PPTA and PMIA is important for understanding the essential difference between these two types of polymers and for making a molecular design of novel polymers with excellent physical properties on the basis of the unique combination of a rigid chemical structure with unique hydrogen bonds.

As long as we treat only these polymers, however, we may have some limitations because the crystal regions of polymer materials are in general very small and more or less disordered, making it difficult to obtain precise and detailed information about the crystal structure. To carry out a quantitative discussion about the relationship between the structural and physical properties of these polymers, we need to introduce model compounds that can simulate the essential features of parent polymers and can give us highly qualified single crystals that are useful for X-ray crystal structure analysis. Crystal structures of several model compounds of PPTA were reported and compared with the structure of the parent PPTA,^{6–8} but a detailed discussion has not yet been made. A similar situation can be seen also for PMIA. The reports on the crystal structure of the model compound of PMIA are quite limited^{9,10} and there has been no systematic investigation to reveal the factors controlling the 3-D jungle-gym-type hydrogen bond network of PMIA. Motherwell et al.¹¹ investigated hydrogen bond networks of many amide compounds on the basis of the Cambridge structural database, but no direct information was given for the 3-D jungle-gym-type hydrogen bond network of PMIA. One strategy of our present research is to identify the structural characteristics of a series of model compounds of PMIA and to clarify the factors that produce the unique hydrogen bond networks. Investigation of 3-D hydrogen bond networks is important also in relation to biological systems, where the organized hydrogen bond networks are formed and generate biological functions.

In the present paper, we will describe the crystal structures analyzed for a series of model compounds of PMIA and classify the structural features common to these compounds. This information is considered to be key to the energetic interpretation of the factors controlling the 3-D hydrogen bond network, the details of which will be reported in a separate paper.

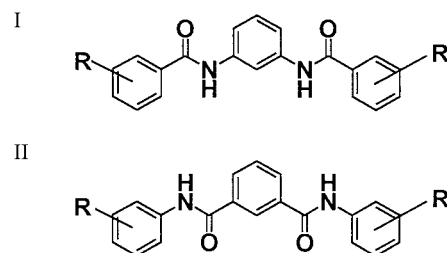
Experimental Section

Samples. The model compounds used in this study are listed in Table 1. These compounds were synthesized from condensation reactions of *m*-phenylene diamine with monosubstituted benzoic acid chloride or of isophthalic acid dichloride with monosubstituted aniline. The single crystals were prepared from the solutions at room temperature by the solvent evaporation method. The morphology of the thus prepared crystals was mostly the squared plate type except for MPBB with needle-shaped crystals.

X-ray Structure Analysis. X-ray diffraction was measured by using a MAC Science DIP 3000 diffractometer system. The

TABLE 1: Model Compounds of Poly(*m*-phenylene isophthalamide)

group	code	R	name
I	MPBB	H	N,N'- <i>m</i> -phenylene bisbenzamide
I	MPPM	<i>p</i> -CH ₃	N,N'- <i>m</i> -phenylene bis- <i>p</i> -methylbenzamide
II	DPIA	H	diphenylene isophthalamide
II	BMMPIA	<i>m</i> -CH ₃	bis- <i>m</i> -methyl-phenyl isophthalamide
II	BPMPIA	<i>p</i> -CH ₃	bis- <i>p</i> -methyl-phenyl isophthalamide



incident X-ray beam was a Mo K α line ($\lambda = 0.71073$ Å) from the MAC Science SRA-18X X-ray generator (50 kV and 200 mA). The oscillation amplitude was $\Delta\omega = 4^\circ$ in the full range of $\omega = 0$ – 96° . A total of 24 frames were collected in 48 h, including the reading-out time of the data. This long collection time was needed because of the very small size of the prepared single crystals. The indexing of the observed reflections, estimation of the unit cell parameters, and integration of the reflection intensities were made by using DENZO software, and the scaling of the thus evaluated reflection intensities was made by using SCALEPACK software.^{12,13} DENZO was used to index the observed reflections and refine the lattice parameters and geometrical parameters of the measurement system, such as the rotational axis of the sample, the center position of the oscillation, etcetera, with a limited number of chosen frames. SCALEPACK was used to adjust the intensity scale between the successive frames, from which the exact structure factors were obtained, and refine the lattice parameters further by using the whole data set. The crystal structure was solved by using maXus software (Nonius BV, Delft, The Netherlands), which consisted of a set of programs necessary for the determination of the space group symmetry and the initial models, the least-squares refinement of the structure, etcetera. The direct method was used to find the initial models, where SIR92 software developed by Altmare et al. was used.¹⁴ Least-squares refinement was made on the basis of the full matrix method by using the quantity $\Sigma w(|F_o|^2 - |F_c|^2)^2$ as a minimized function with weight $w = \exp[FA \sin^2 \theta / \lambda^2 / (\sigma^2(F_o) + FBF_o^2)]$, where $\sigma^2(F_o)$ is the square of the standard deviation of the observed structure factor F_o and the coefficients FA and FB were set to the values 0.0 and 0.03, respectively. The reflections satisfying the cutoff condition $|F_o| > 3\sigma(|F_o|)$ were used in the least-squares refinement. Because no detectable effect was found, the absorption correction for the observed intensity was not included in the structural refinement. The reliability of the structural analysis was evaluated by the reliability factors that are defined by the following equations:

$$R = \frac{\sum ||F_o|^2 - |F_c|^2|}{\sum |F_o|^2} \quad \text{and} \quad Rw = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2 / (\sum w|F_o|^2)^2]^{1/2}}$$

Results and Discussion

Crystal Structure of Model Compounds. Figures 2–6 show the crystal structures determined for the model compounds listed in Table 1. The crystallographic data including the cell constants, the space group, and so on are listed in Table 2. The fractional

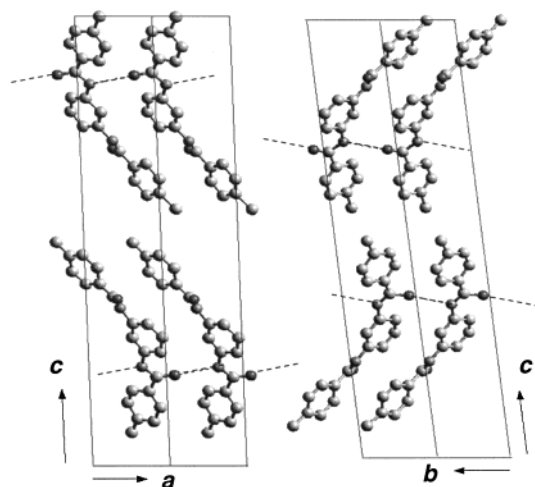


Figure 2. Crystal structure of MPPM.

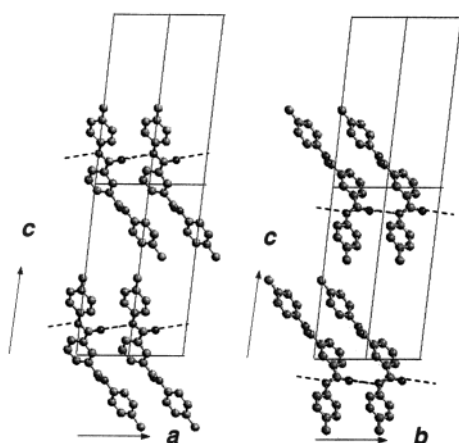


Figure 3. Crystal structure of BPMPA.

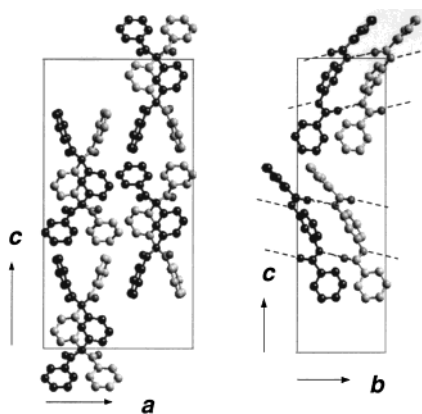


Figure 4. Crystal structure of MPBB.

coordinates of atoms in asymmetric units and geometrical information are given in Supporting Information (Tables A1–A10). In Figures 2–6, the hydrogen bonds are indicated by broken lines. The model compound MPPM (Figure 2) takes the 3-D hydrogen bond network structure. We may describe this structure in the following way: MPPM takes a stacking structure of layers along the c axis. One layer is constructed by two hydrogen bonds between the neighboring molecules along the a and b axes, and the adjacent layer shows the two opposite hydrogen bonds (i.e., along the b and a axes). This hydrogen bond network structure is the $(a-b)-(b-a)$ type, where each pair in parentheses indicates the hydrogen bonds in one layer. More generally, in the notation $(x-y)-(z-w)$, $(x-y)$ indicates

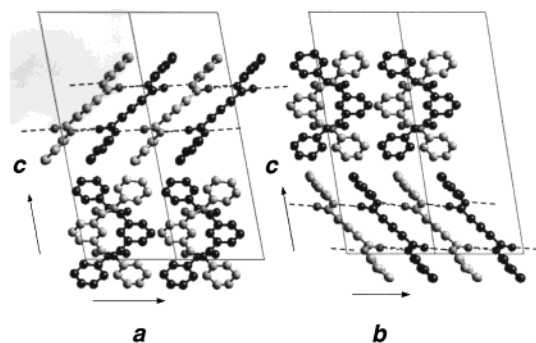


Figure 5. Crystal structure of DPIA.

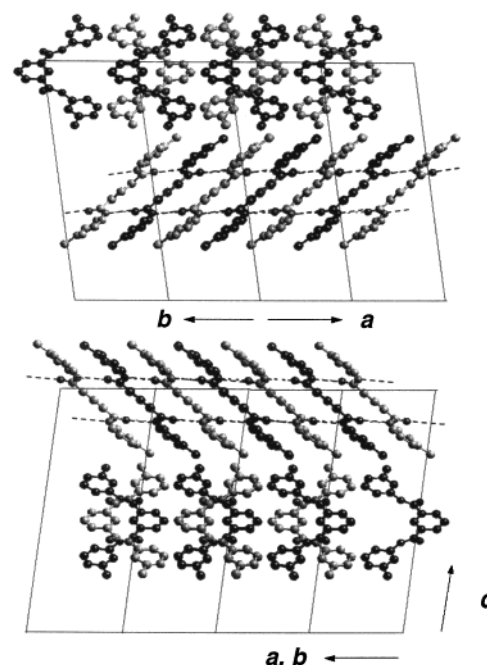


Figure 6. Crystal structure of BMMPIA.

that the hydrogen bonds are formed along the x and y axes (x and $y = a$ or b) for the two amide groups of a molecule. These molecules form a layer structure as illustrated in Figure 7 (layer A). $(z-w)$ indicates the directions of the hydrogen bonds found in the next layer, B. The hydrogen bond structure of the whole crystal lattice can be described by indicating the hydrogen bond directions of successive layers as $(x-y)-(z-w)-\dots$. As seen in Figure 3, the compound BPMPA takes hydrogen bonds of type $(a-b)-(a-b)$, which is the same type as that of the parent polymer shown in Figure 1. In other words, they exhibit jungle-gym-type hydrogen bond networks when viewed along the c axis. In the case of MPBB, the situation is appreciably different, and the hydrogen bonds are formed along the b axis only (i.e., $(b-b)-(b-b)$ type (Figure 4)). Also, in the case of DPIA shown in Figure 5, the hydrogen bonds of one layer are along one direction, the a or b axis only. But these layers are stacked along the c axis in an alternately perpendicular manner, that is to say, the hydrogen bond network of the $(a-a)-(b-b)$ type. The same type of hydrogen bond network is observed also in Figure 6 for the model compound BMMPIA with an $(a'-a')-(b'-b')$ -type structure, where a' and b' are the mutually perpendicular diagonal directions (see Figure 8). (After the structural analysis of DPIA, we noticed that essentially the same structure had been reported in ref 9. In the present discussion, our structural data is used for convenience.)

TABLE 2: Crystallographic Data of Model Compounds of PMIA^a

	MPBB	MPPM	DPIA	BMMPIA	BPMPA
formula	C ₂₀ H ₁₆ N ₂ O ₂	C ₂₂ H ₂₀ N ₂ O ₂	C ₂₀ H ₁₆ N ₂ O ₂	C ₂₂ H ₂₀ N ₂ O ₂	C ₂₂ H ₂₀ N ₂ O ₂
mol wt	316.360	344.414	316.360	344.414	344.414
crystal system	orthorhombic	triclinic	triclinic	monoclinic	triclinic
space group	<i>Pbca</i>	<i>P1</i>	<i>P1</i>	<i>Cc</i>	<i>P1</i>
<i>a</i> /Å	14.4610(10)	5.1460(6)	8.3630(5)	12.0760(5)	5.248(5)
<i>b</i> /Å	8.3740(4)	5.1530(6)	8.3700(4)	12.1100(5)	5.127(5)
<i>c</i> /Å	26.491(3)	33.391(4)	23.387(10)	24.615(10)	17.039(4)
α /deg	90.0	83.560(5)	98.897(2)	90.0	83.231(6)
β /deg	90.0	92.080(6)	101.593(2)	99.683(2)	82.773(5)
γ /deg	90.0	86.683(8)	90.003(5)	90.0	86.044(6)
<i>V</i> /Å ³	3208.0(5)	877.6(2)	1583.50(10)	3548.4(3)	450.9(6)
<i>Z</i> ₁	1	1	4	2	1
<i>Z</i> ₂	8	2	4	8	1
<i>R</i>	0.064	0.058	0.095	0.057	0.068
<i>R</i> _w	0.045	0.056	0.120	0.124	0.092

^a *Z*₁ = number of molecules in an asymmetric unit. *Z*₂ = number of molecules in a unit cell. The expression 26.491(3) indicates 26.491 ± 0.003.

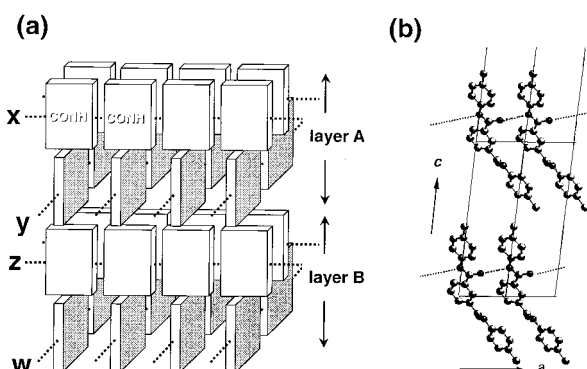


Figure 7. (a) Illustration of the hydrogen bond network (x-y)-(z-w). A pair of rectangular boxes correspond to the two amide groups of a molecule. The direction of the hydrogen bond between amide groups of neighboring molecules is denoted by x, y, z, and w. The first pair of parentheses indicates a set of hydrogen bonds for molecules in layer A, and the second pair, for molecules in layer B. The layers are stacked alternately along the *c* axis. (b) Actual example to show the hydrogen bond network of part (a), where the packing structure of BPMPA is given (see Figure 3).

Figure 8 makes the hydrogen bond network structure clearer, where only the amide groups are extracted from the above-mentioned crystal structures and the hydrogen bonds are drawn between these amide groups. The pictures are the projections along the *c* axes. The thin solid lines indicate the averaged directions of the hydrogen bonds for easier observation of these bonds. As explained above, the four model compounds, MPPM, BPMPA, DPIA, and BMMPIA, have jungle-gym-type hydrogen bond networks, although the combination of hydrogen bonds is not always the same: (*a*-*b*)-(*b*-*a*) for MPPM, (*a*-*b*)-(*a*-*b*) for BPMPA and polymer, and (*a*-*a*)-(*b*-*b*) for DPIA and BMMPIA. Only the case of MPBB shows the hydrogen bonds along one direction, (*b*-*b*)-(*b*-*b*). It should be emphasized here that these model compounds have only slightly different chemical formulas, as seen in Table 1, but they sensitively exhibit different hydrogen bond network structures when, for example, only one hydrogen atom of the terminal benzene ring is exchanged with a methyl group.

Molecular Conformations. In Figure 9, we compare the torsional angles around the bonds between the amide and benzene groups, which were evaluated for the model compounds and the parent polymer. In most cases, the torsional angles are in the range of 24–39°. One exception is seen for the model compound MPBB, where the torsional angles are 38–59°, which are much higher than those for the other cases.

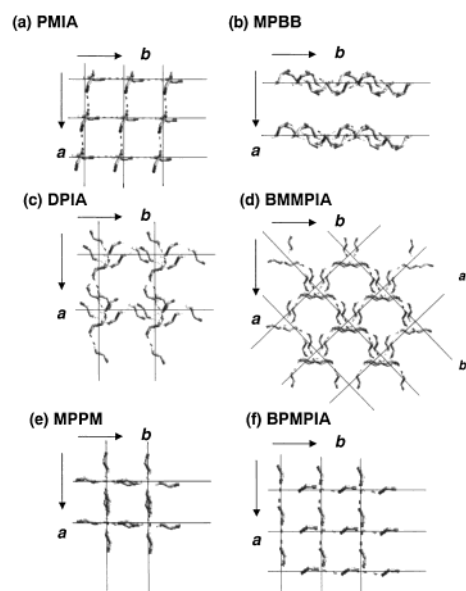


Figure 8. Hydrogen bond networks formed in the model compounds shown in Figures 2–6. Only the amide groups are extracted and are combined by hydrogen bonds indicated by the broken lines. The thin, solid lines are the averaged directions of these hydrogen bonds.

Similar torsional angles are observed for many compounds containing benzene–amide bonds,^{6–10,15,16} suggesting that these benzene–amide torsional angles are mainly determined by intramolecular interactions between the benzene and amide groups. As pointed out by Tashiro et al.,² the torsional angles are primarily determined by the energetic balance between the two kinds of interactions. One is the repulsive force between the nonbonded atoms (i.e., the hydrogen atom extending from the benzene ring and the H or O atom of the amide group). Another is an overlap of the π orbitals of benzene and amide planes: the coplanar structure is the most preferable because of electronic conjugation. The balance between these two kinds of interaction energy gives the torsional angles at 25–31° as the energetically stable structure. Essentially the same results could be obtained by carrying out the classical mechanics calculation as shown in Figure 10. By taking the nonbonded van der Waals and electrostatic interactions into consideration, the energetically minimal positions were found at 25–30°, where the conformational energies were calculated for the chemical structures of NH₂–CO– ϕ –CO–NH₂ and CH₃–CO–NH– ϕ –NH–CO–CH₃ (ϕ is a benzene ring) by using Cerius² software (version 4.0, Accelrys Inc., USA) with a COM-

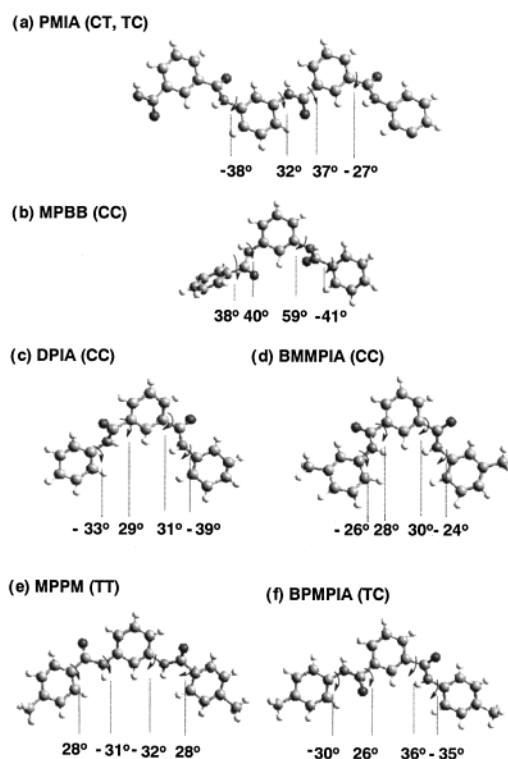


Figure 9. Molecular conformations (TT, CC, and CT) and internal torsional angles ω between benzene and the amide groups of PMIA and its model compounds.

PASS force field.¹⁷ The results are consistent with the observed values listed in Figure 9.

Although the torsional angles are relatively close to each other, as mentioned above, we notice that the molecular shape is appreciably different depending on the model compound when we see the whole molecular shape of these compounds as well as that of the parent polymer. To clarify the situation, we denote

the molecular shape by using a set of torsional angles. As seen in Figure 11a, the fully extended chain conformation of PMIA may be described as an all-trans conformation when the skeletal chain indicated by the bold line is traced. The conformations of the flat molecules shown in Figure 11b, c, and d are expressed, respectively, as TT, CC, and CT, where only the central parts consisting of benzene and two amide groups are shown. As seen there, the conformations TT, CC, and CT show the entire molecular shapes. When the molecule is assumed to be an anchor made by two bonds connecting the benzene rings, the angle of anchor is remarkably different depending on the conformation of these flat molecules. The TT form takes the anchor of larger angle, whereas the CC form shows an acute anchor angle. When we see the molecular shape of the model compounds in Figure 9, we can express the conformation as listed in Table 3. When the molecules are assumed to take the flat plane by twisting the benzene or amide groups by minimal rotational angles, the molecules of MPBB, DPIA, and BMMPIA take the CC form, those of BPMPA and polymer (PMIA) take the CT form, and that of MPPM takes the TT form. Of course, the actual molecules do not take such planar conformations but are twisted by ca. 30° around the benzene–amide bonds. The notations CC, CT, and TT are used here for convenience to indicate the rough shapes of these molecules. In addition to such a conformational description, we need to use the twisting angle between benzene and the amide groups, which is now denoted by ω as defined in Figure 12. ω is a dihedral angle between the two planes of benzene and the amide groups. The + and – signs correspond to the two types of structures shown in Figure 12. Therefore, the actual molecular shape of the model compounds can be described by using a set of flat forms (TT, TC, and CC) and the twisting angles ω . The expressions for the model compounds are given in Figure 9.

Relation between the Conformation and Packing Mode of Molecules. When the molecular structure in Figure 9 is compared with the hydrogen bond network in Figure 8, we notice that the molecules of the CC form take the intermolecular

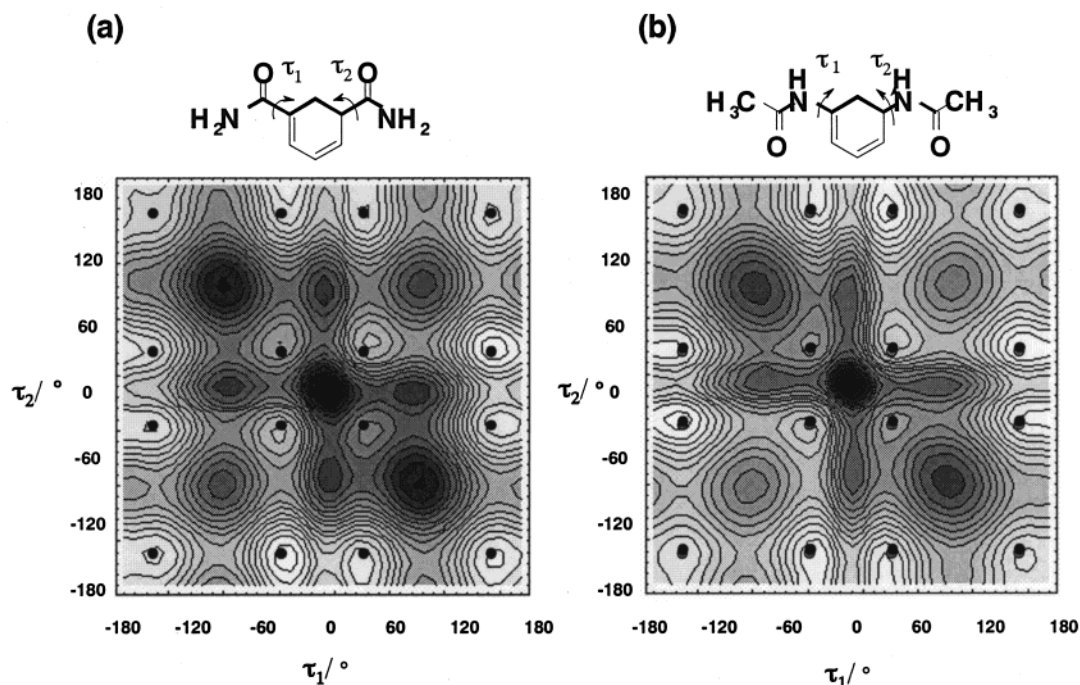


Figure 10. Energy contour maps calculated for model compounds of (a) $\text{NH}_2\text{--CO--}\phi\text{--CO--NH}_2$ and (b) $\text{CH}_3\text{--CO--NH--}\phi\text{--NH--CO--CH}_3$ (ϕ = benzene ring). The solid circles show the torsional angles that were observed for the various model compounds (see Figure 9). These observed values are found to correspond well to the energetically minimal positions.

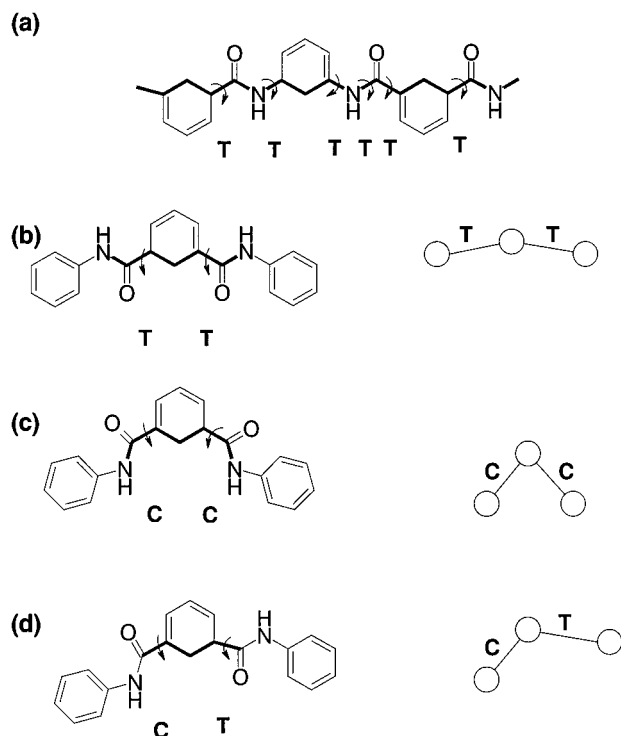


Figure 11. Definition of molecular conformations of PMIA and the model compounds. (a) The bold line indicates a skeletal chain extracted from PMIA chains. The skeletal chain conformation shown here is expressed as ...TTTT... (b)–(d) Molecular conformations of planar forms of model compounds. The torsional angles indicated here are for the skeletal bonds: (b) TT, (c) CC, and (d) CT. The anchors shown at the right sides are the whole images of the molecules, where the virtual bonds are assumed to pass through the neighboring two benzene rings.

TABLE 3: Molecular Conformation and Hydrogen-Bond Network in Poly(*m*-phenylene isophthalamide) (PMIA) and Its Model Compounds

model compounds	molecular shape ^a	hydrogen bond in a layer ^b	stacking mode of layers ^c
MPBB	CC	(<i>b</i> – <i>b</i>)	...–(<i>b</i> – <i>b</i>)–(<i>b</i> – <i>b</i>)–...
DPIA	CC	(<i>a</i> – <i>a</i>), (<i>b</i> – <i>b</i>)	...(<i>a</i> – <i>a</i>)–(<i>b</i> – <i>b</i>)–...
BMMPIA	CC	(<i>a'</i> – <i>a'</i>), (<i>b'</i> – <i>b'</i>)	...(<i>a'</i> – <i>a'</i>)–(<i>b'</i> – <i>b'</i>)–...
MPPM	TT	(<i>a</i> – <i>b</i>)	...(<i>a</i> – <i>b</i>)–(<i>b</i> – <i>a</i>)–...
BPMPPIA	TC	(<i>a</i> – <i>b</i>)	...(<i>a</i> – <i>b</i>)–(<i>a</i> – <i>b</i>)–...
PMIA	TC	(<i>a</i> – <i>b</i>)	...(<i>a</i> – <i>b</i>)–(<i>a</i> – <i>b</i>)–...

^a C, cis and T, trans (refer to Figure 11). ^b The notation of (*b*–*b*) and so on indicates the direction of the hydrogen bonds in a layer (refer to Figure 7). ^c The notation of (*a*–*a*)–(*b*–*b*) and so on indicates the directions of the hydrogen bonds in the successively stacked layers (refer to Figure 7).

hydrogen bonds of the (*a*–*a*) or (*b*–*b*) type in a layer, as listed in Table 3. The molecules of the CT and TT forms take hydrogen bonds of the (*a*–*b*) type, that is to say, the molecular shape and the hydrogen bond pattern in a layer are intimately related to each other, although the total number of examples might be too small to use in establishing an empirical rule. When the thus created layers are stacked together, the direction of the intermolecular hydrogen bonds of the adjacent two layers (A and B in Figure 7) can be classified as perpendicular or parallel. In the cases of MPBB, DPIA, and BMMPIA, which commonly take the molecular shape of the CC form and the (*a*–*a*) or (*b*–*b*) hydrogen bonds in a layer, the successive layers are stacked in parallel ((*b*–*b*)–(*b*–*b*) for MPBB) or perpendicularly ((*a*–*a*)–(*b*–*b*) for DPIA and BMMPIA) concerning the direction of hydrogen bonds. Similarly, BPMPPIA and MPPM, which can take the CT and TT forms, respectively, and the (*a*–*b*)–type

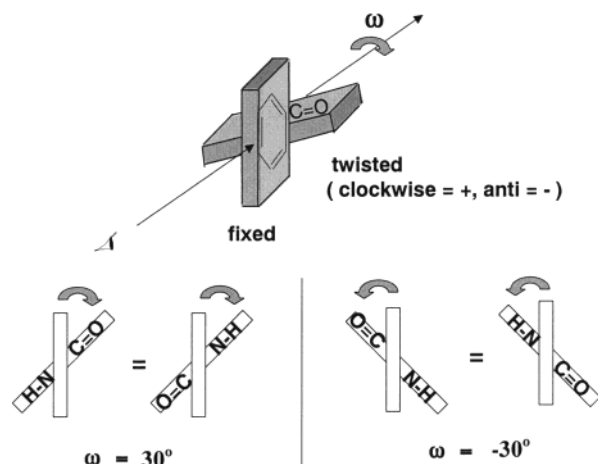


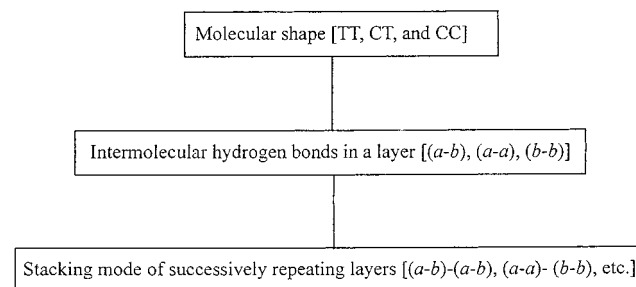
Figure 12. Definition of the dihedral angle ω around the bond connecting benzene and the amide groups. Benzene and the amide groups are assumed to be simple, flat, and planar, without any distinction between the front and the back.

TABLE 4: Conformational Energy of Isolated Molecules

compounds	starting models ^a			relative stability	observed
	CC	TC	TT		
MPBB	–26.6 ^b	–28.2	–26.4	TT \approx CC < TC	CC
DPIA	–21.0	–22.5	–20.8	TT \approx CC < TC	CC
BMMPIA	–43.6	–46.1	–44.6	CC < TT < TC	CC
MPPM	–42.7	–44.8	–42.7	TT \approx CC < TC	TT
BPMPPIA	–37.5	–38.8	–37.4	TT \approx CC < TC	TC
PMIA	–29.8 ^c	–34.7	–31.8	CC < TT < TC	TC

^a Planar models used for energy minimization. ^b Unit kcal/mol of molecule. ^c Energy for one repeating unit in a fiber period.

hydrogen bonds in a layer, show the stacking structure of parallel hydrogen bonds ((*a*–*b*)–(*a*–*b*) for BPMPPIA) or perpendicular hydrogen bonds ((*a*–*b*)–(*b*–*a*) for MPPM). The parent polymer PMIA of the CT conformation shows a similar structure to that of BPMPPIA with the CT conformation. In this way, we can systematically classify a series of model compounds in terms of the molecular shape, the hydrogen bonds in one layer, and the stacking mode of the layers, as shown in Table 3.



One significant question at this point is the reason that these model compounds and polymer take such a systematic relation between the molecular conformation and the various types of intermolecular hydrogen bonds. Before discussing this question, however, we need to find some reason that the starting conformations or the whole shapes of the molecules must take the either the TT, CT, or CC form. As a trial, the energetic stability of these three conformations was compared by carrying out the calculation of the conformational energy for an isolated molecule. The calculation was made by using Cerius² software with a COMPASS force field.¹⁷ Table 4 shows the thus obtained results. The energy stability is different depending on the molecule, but the CT form is the most stable for every case.

This result is different from the observed results except for those for BPMPA and PMIA, meaning that not even the molecular conformation is determined by the intramolecular interactions only. Rather, the complicated coupling between the intra- and intermolecular interactions is considered to govern the molecular shape as well as the packing structure. Therefore, we need to calculate the lattice energy to clarify the factors governing the packing mode of these model compounds. The details will be reported elsewhere.

Summary

In this paper, the molecular and crystal structures of a series of model compounds of poly(*m*-phenylene isophthalamide) or PMIA were analyzed by the X-ray diffraction method. Although the number of model compounds used here is limited, a systematic consideration could be made about the relationship between the molecular conformation and the packing structure of molecules in association with the type of intermolecular hydrogen bonds. The main results are summarized below.

(1) Almost all of the model compounds studied here have benzene–amide torsional angles in the range of 24–39°. This is the same situation that was found for poly(*p*-phenylene terephthalamide) and its model compounds. The reason for this common feature could be determined by carrying out the energy calculation about the twisting angles of the bonds between benzene and the amide groups. As already reported, the torsional angle can be approximately determined by the intramolecular nonbonded interatomic interactions between benzene and amide groups or by the balance between the tendency to take the coplanar, electronically resonant structure through the π -conjugation and the tendency to avoid the repulsion between the hydrogen (and oxygen) atoms of benzene and amide groups.

(2) The whole shape of a molecule taken in a crystal lattice is classified as TT, CT, or CC when the molecule is assumed to be flat without any twisting around the benzene–amide bonds. The two amide groups of the CC form tend to take the intermolecular hydrogen bonds of the (*a*–*a*) or (*b*–*b*) type in one layer. Similarly, the TT and CT forms take the (*a*–*b*)–type intermolecular hydrogen bonds in a layer. The stacking structure of the successive layers can also be classified systematically in good correlation with the above-mentioned molecular shapes and intermolecular hydrogen bond types, as summarized in Table 3. For example, the model compounds of the CC conformation take the (*a*–*a*) or (*b*–*b*) type of intermolecular hydrogen bonds in a layer and show the stacked layer structures of parallel type ((*b*–*b*)–(*b*–*b*)) or perpendicular type ((*a*–*a*)–(*b*–*b*)). The model compounds of the CT or TT conformation, which take the (*a*–*b*)–type hydrogen bonds in a layer, show the stacked layer structure of the parallel ((*a*–*b*)–(*a*–*b*)–...) or perpendicular type ((*a*–*b*)–(*b*–*a*)–...), respectively. The plausible reasons for this classification need to be extracted by carrying out the energy calculation of the crystal lattice.

We notice that the model compounds studied here are not as long as the parent polymer but possess only three benzene rings

and two amide groups per molecule. Despite such a short sequence of monomeric units, however, they already show the essential features of the molecular conformation and the 3-D hydrogen bond network observed for the polymer, although the change of end groups leads to a modification of the stacking mode of successive layers. The next job is to extend the molecular length of these model compounds further and to investigate the similarity in packing structures between the model compounds and the parent polymer.

It must be also mentioned that poly(*p*-phenylene terephthalamide) (PPTA) and its model compounds almost always show the 2-D sheet structure (Figure 1a). The meta arrangement of benzene and the amide groups in PMIA and its model compounds gives a very complicated but systematic 3-D hydrogen bond network structure. The energetic consideration will be helpful in understanding this high contrast between meta and para compounds.

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Supporting Information Available: CIF data of the model compounds. Fractional coordinates of atoms in asymmetric units and geometrical information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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