Use of helical parameters to generate candidate conformations for crystal packing: illustrative application to a polyimide

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This communication describes the application and extension of a method for calculating the helical parameters with which to describe molecular conformations. The method, which was originally developed by Shimanouchi and others, is applied to a polyimide of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-(4-aminophenoxy)propane (DMDA) which has eight torsional bonds in the chemical repeat unit. Discrete low energy states for these torsions were determined by Ramanchandran energy maps of sequential dihedral pairs or single bond torsional energy diagrams. The total number of possible low energy conformations for these states is 1152 including conformationally related isoenantiomorphs. The method conveniently generates the conformations for subsequent crystal structure packing and refinement. Consideration of these together with the X-ray data of Cheng and co-workers reduces the number to about 15 with about a 2/1 conformation and a *c* axis of approximately 49.2 Å. Of these, about half appear to be good candidates for crystal packing.

(Keywords: polyimide; crystal; X-ray; conformation; BTDA–DMDA; unit cell)

Introduction

High performance polymers for advanced applications generally consist of rigid heterocyclic and/or aromatic moieties exhibiting various torsional degrees of freedom. For the case of a polymer that is capable of crystallizing, multitorsional character in the backbone renders unambiguous identification of the conformational repeat difficult. Even so, the search for candidate structures for subsequent packing determinations can be simplified by selecting helical models with translational periodicities equal or close to the observed fibre identity period, *c*.

Method

In this note, we demonstrate the application and extension of a method for calculating helical parameters originally developed by Shimanouchi and Mizushima[1] and Miyazawa[2]. Application of their methodology allows the helical superstructure to be reduced to three parameters, namely, the translation per monomer along the helical axis (advance per monomer, d_h), the rotation per monomer about the axis (twist, θ_h), and the distance from the helical axis to a reference point (taken as the end of the monomer) in the chain (radius, ρ_h).

As an illustrative example of a polymer with multitorsional character, we consider the polyimide derived from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 2,2-dimethyl-1,3-(4-aminophenoxy)propane (DMDA), hereafter referred to as PI-2. In addition to exhibiting excellent thermal stability and toughness, PI-2 undergoes facile crystallization between 240 and 325°C. Crystallinities calculated from X-ray data have been reported to approach 50%. In addition, the unit cell has been reported[3] to be monoclinic with unit cell dimensions $a = 9.60$ Å, $b = 5.82$ Å, $c = 24.6$ Å and $\gamma = 81.1°$.

For an initial survey, the individual torsions in PI-2 were representative values characteristic of discrete low energy states determined by molecular mechanics methods, discussed below. For example, torsions involving sp^3-hybridized carbons were allowed to adopt only idealized *trans* (180°), *gauche*(+) (+60°) and *gauche*(−) (−60°) conformations. The preferred torsional states for all the rotatable bonds in PI-2 are shown at the top of *Figure 1*. Including conformationally related isoenantiomorphs, a simple combinatorial approach yields 1152 helical conformers. This number is reduced by internal symmetries of the monomer.

In order to calculate the helical parameters for PI-2, a helical model with eight independent internal torsions was constructed. The model appears at the bottom of *Figure 1*. An infinite PI-2 molecule can thus be represented as $-(M_1-M_2-M_3-M_4-M_5-M_6-M_7-M_8)_n-$, where each M_i corresponds to a distinct atomic or pseudoatomic hinge within a given monomer. The calculation was simplified by redefining the torsions denoted as ζ, χ_1, χ_2 and α in *Figure 1* in terms of two virtual torsions denoted τ_{12} and τ_{45}. Comparing the helical model with the real chain, the following equivalencies are noted: $\tau_{12} = \zeta + \chi_1, \tau_{23} = \theta_1, \tau_{34} = \theta_2, \tau_{45} = \chi_2 + \alpha, \tau_{56} = \beta, \tau_{67} = \gamma$, $\tau_{78} = \delta$ and $\tau_{81} = \varepsilon$. Using Miyazawa's notation, ρ_h, d_h, and θ_h were calculated via linear transformation from the helical model internal space defined by dihedrals, τ_{ij}, bond lengths, r_{ij}, and angles, φ_i, as follows:

$$\cos\theta_h = \frac{(a_{11} + a_{22} + a_{33} - 1)}{2}$$

$$d_h^2 = \frac{[b_1(a_{13} + a_{31}) + b_2(a_{23} + a_{32}) + b_3(a_{33} - a_{11} - a_{22} + 1)]^2}{(3 + a_{11} - a_{22} - a_{33})(a_{33} - a_{22} - a_{33} + 1)}$$

$$\rho_h^2 = \frac{(b_1^2 + b_2^2 + b_3^2 + d_h^2)}{(3 - a_{11} - a_{22} - a_{33})}$$

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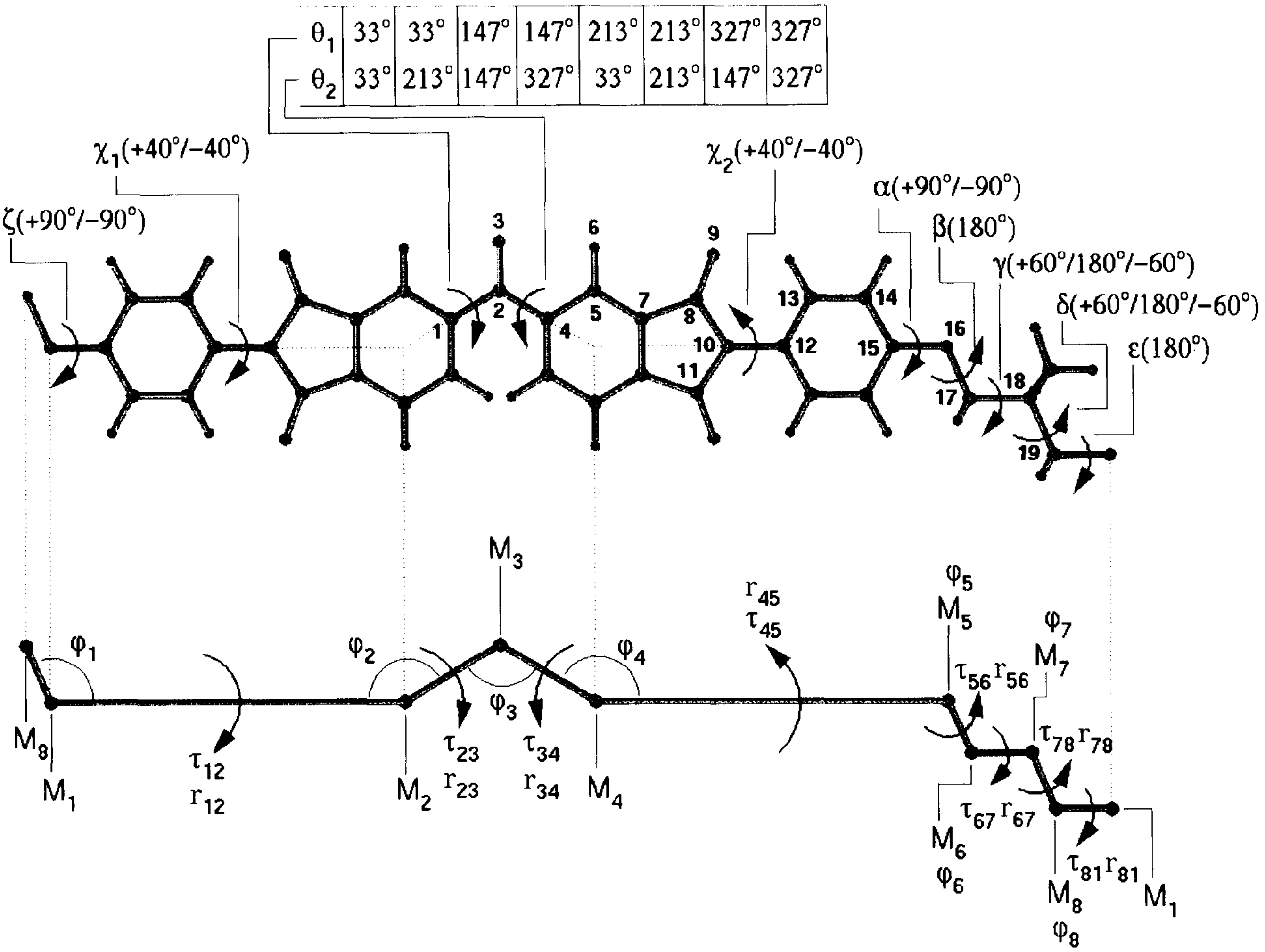

Figure 1 A representation of the PI-2 molecule is given at the top and the corresponding helical model with eight independent internal torsions is given at the bottom. The atoms identified as 3, 9 and 16 are oxygen; atom number 10 is nitrogen; atom number 6 is hydrogen; the other numbered atoms are carbon. The unnumbered atoms are identical to equivalent ones which are numbered. The values given for the angles are the low energy values as discussed in the text

where a_{ij} and b_i refer to elements in the matrices **A** and **B**, which in turn were obtained by the matrix operations given below. The various $\mathbf{A}_i$ shown below are defined such that $\tau_i = 180°$ is *trans*:

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} = \mathbf{A}_1\mathbf{A}_2\mathbf{A}_3\mathbf{A}_4\mathbf{A}_5\mathbf{A}_6\mathbf{A}_7\mathbf{A}_8$$

where

$$\mathbf{A}_i = \begin{bmatrix} -\cos\phi_j & -\sin\phi_j & 0 \\ \sin\phi_j\cos\tau_{ij} & -\cos\phi_j\cos\tau_{ij} & -\sin\tau_{ij} \\ \sin\phi_j\sin\tau_{ij} & -\cos\phi_j\sin\tau_{ij} & \cos\tau_{ij} \end{bmatrix}$$

and

$$\mathbf{B} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \mathbf{B}_{12} + \mathbf{A}_1\mathbf{B}_{23} + \mathbf{A}_1\mathbf{A}_2\mathbf{B}_{34} + \ldots$$
$$+ \mathbf{A}_1\mathbf{A}_2\mathbf{A}_3\mathbf{A}_4\mathbf{A}_5\mathbf{A}_6\mathbf{B}_{78} + \mathbf{A}_1\mathbf{A}_2\mathbf{A}_3\mathbf{A}_4\mathbf{A}_5\mathbf{A}_6\mathbf{A}_7\mathbf{B}_{81}$$

where

$$\mathbf{B}_{i,j} = \begin{bmatrix} r_{ij} \\ 0 \\ 0 \end{bmatrix}$$

Molecular mechanics

The intramolecular potential energy profiles for backbone torsions in PI-2 were evaluated using default Tripos force fields available in the SYBYL® modelling software. Polar character was accounted for by incorporating partial electrostatic charges obtained via the Gasteiger–Hückel method. Valence angles and bond lengths were adjusted to be consistent with X-ray structural data obtained for model phthalimide compounds[4,5], and thereafter treated as invariant. A listing of the bond angles and lengths appears in *Table 1*, along with values adopted for ϕ_i and r_{ij}. The preferred states given in *Figure 1* were determined on the basis of Ramanchandran maps of sequential dihedral pairs or single bond torsional energy diagrams. (An example for which all torsions were fixed except α, ζ, τ_{56} and τ_{81} is shown in *Figure 2*. The diagram suggests that the molecule will adopt a 2/1 conformation with a repeat close to 49.2 Å for this case. It is clear, however, that this is not a convenient method for generating all 1152 conformations.) Single bond torsional energy diagrams were used in the case of the isolated C_{10}(phthalimide)–C_{12}(phenyl) torsion. The effect of next-nearest neighbour rotations on the location of the potentials wells was found not to be important within the DMDA segment of PI-2.

Table 1 Geometrical parameters of the molecular and helical model repeats[a]

PI-2 bond	Bond length (Å)	PI-2 angle	Bond angle (deg)	Helical bond	r_{ij} (Å)	Helical angle	ϕ_i (deg)
C_1–C_2	1.42	C_1–C_2–O_3	117.0	M_1–M_2	9.04	M_1–M_2–M_3	150.0
C_2–O_3	1.23	C_1–C_2–C_4	124.0	M_2–M_3	2.82	M_2–M_3–M_4	124.0
C_4–C_5	1.40	C_2–C_4–C_5	120.0	M_3–M_4	2.82	M_3–M_4–M_5	150.0
C_5–H_6	1.08	C_4–C_5–H_6	120.0	M_4–M_5	9.04	M_4–M_5–M_6	114.0
C_7–C_8	1.48	C_5–C_7–C_8	131.5	M_5–M_6	1.43	M_5–M_6–M_7	109.5
C_8–O_9	1.20	C_7–C_8–O_9	129.8	M_6–M_7	1.53	M_6–M_7–M_8	109.0
C_8–N_{10}	1.42	C_7–C_8–N_{10}	105.9	M_7–M_8	1.53	M_7–M_8–M_1	109.5
N_{10}–C_{12}	1.43	C_8–N_{10}–C_{11}	111.2	M_8–M_1	1.43	M_8–M_1–M_2	114.0
C_{12}–C_{13}	1.40	C_8–N_{10}–C_{12}	124.4				
C_{15}–O_{16}	1.39	C_{12}–C_{13}–C_{14}	120.0				
O_{16}–C_{17}	1.43	C_{15}–O_{16}–C_{17}	114.0				
C_{17}–C_{18}	1.53	O_{16}–C_{17}–C_{18}	109.5				
		C_{17}–C_{18}–C_{19}	109.0				

[a] See *Figure 1* for an identification of the symbols. The dimensions and

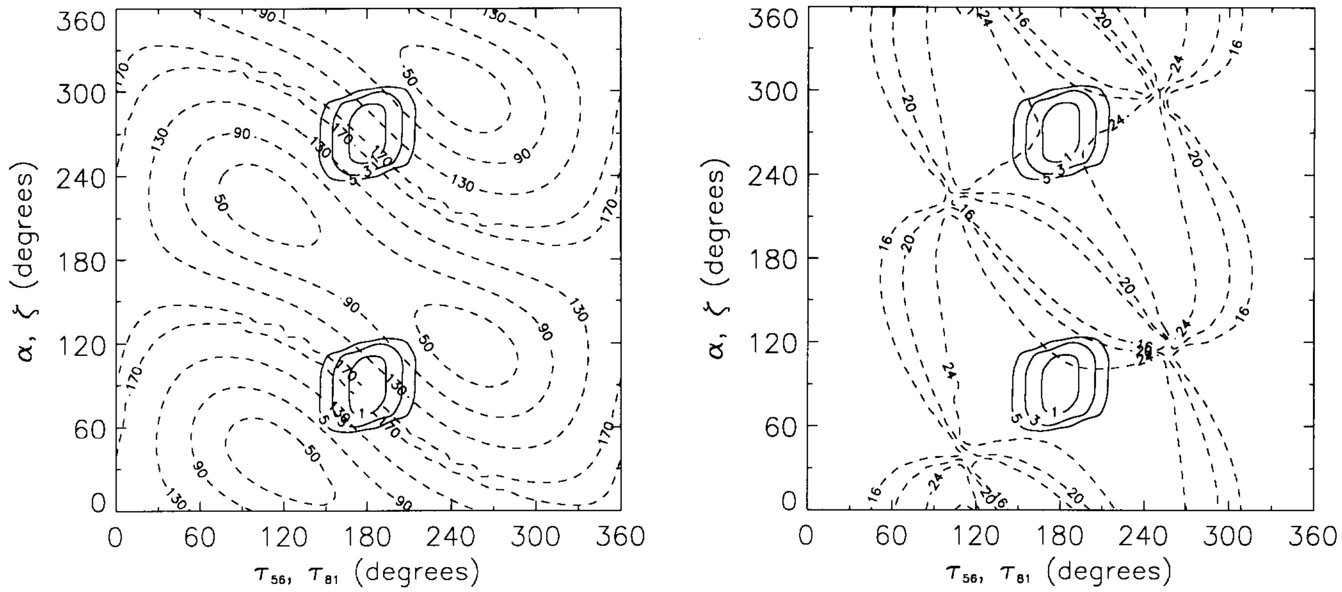

Figure 2 Ramanchandran energy plots overlaid (dashed lines of constant value) with the twist of the repeat unit in degrees on the left and the advance per repeat unit in Ångström on the right. The solid lines are lines of constant energy in kcal mol^{-1}. The results were obtained as a function of rotation about α, ζ and τ_{36}, τ_{81}. The angles τ_{67} and τ_{78} were held at 180°, τ_{23} and τ_{34} at 147° with χ_1 and χ_2 at 40°

Results

The number of monomer units, u, and the number of turns, t, per helical repeat were not found to be exact integers for either the reported value of 24.6 Å or its double 49.2 Å. (Given the X-ray data, a doubling of c cannot be ruled out.) Therefore, fibre repeats, c', were calculated for the resulting conformations by rounding either u or t to the nearest integer:

$$c' = d_h u, \quad \text{where } u = 1, 2, 3, \ldots$$

or

$$c' = \frac{360 d_h t}{\theta_h}, \quad \text{where } t = 1, 2, 3, \ldots$$

Assuming coincidence of the c axis with the molecular axis, a direct comparison of c and c' was made. (Small departures from coincidence of the fibre and molecular axes might be expected, but large ones would not. The c axis is along the fibre axis for the annealed and drawn PI-2 films[3].) No conformations were found for which a single monomer could be the crystallographic motif of the molecule in the c direction. A rather large number of nearly commensurate helices having values of c' within 10% of both 24.6 Å and 49.2 Å were found and retained initially for further consideration.

The total number of candidate helices was further reduced by eliminating those that corresponded to conformations exhibiting either higher energies or inconsistencies with the observed density and X-ray pattern[3]. Those eliminated included helices with values of u and t inconsistent with the observed pattern. For example, a 2/1 helix with a c of 24.6 Å is inconsistent with the X-ray data[3]. The first observed meridional reflection[3] corresponds to a spacing of 24.6 Å. For the 2/1 helix, the first meridional reflection is the 002 rather than the 001. Thus, it would correspond to a c of 49.2 Å. By an equivalent argument, helices with more than two units

Table 2 Candidate conformation approximating a 2/1 helix and a c of 49.2 Å

Advance/ monomer, d_h (Å)	Twist monomer θ_h (deg)	Radius ρ_h (Å)	Torsional angles (deg) τ_{12}	τ_{23}	τ_{34}	τ_{45}	τ_{56}	τ_{67}	τ_{78}	τ_{81}	'Exact values' Units, u	Turns, t	Energy/ monomer (kcal mol^{-1})
23.32	178.1	5.19	130	−147	−147	−130	180	180	−60	180	2.11	1.04	151.11
22.96	176.7	5.70	50	−147	−147	−50	180	180	−60	180	2.14	1.05	151.19
22.30	174.9	5.90	130	−147	−147	−130	180	−60	180	180	2.21	1.07	151.19
21.93	173.5	6.33	50	−147	−147	−50	180	−60	180	180	2.24	1.08	151.11
22.00	164.5	7.75	130	−147	−147	130	180	60	180	180	2.24	1.02	151.11
22.89	162.3	7.20	−50	−147	−147	−50	180	60	180	180	2.15	0.97	151.11
24.94	163.0	5.55	−130	−147	−147	−130	180	180	180	180	1.97	0.89	152.54
23.68	158.6	6.64	50	−147	−147	50	180	180	180	180	2.08	0.92	152.54

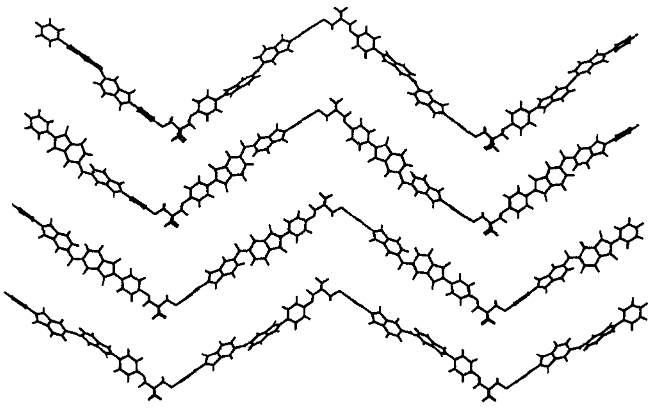

Figure 3 The first four conformations of *Table 2*. For simplicity, the DMDA moiety has been omitted at one end of the four-monomer sequence. The central two monomers exhibit a helical repeat of $2d_h$

in a 24.6 Å repeat (and hence all others with that repeat) can also be eliminated. In the case of the helices with a 49.2 Å repeat, a 2/1 conformation would present no consistency problems and is a possibility. However, those with more than two units in a 49.2 Å repeat can again be eliminated. For a 73.8 Å repeat, a 3/1 conformation would present no consistency problems, etc.

After elimination of conformations that do not satisfy reasonable criteria, a list of 2/1 candidates was generated (*Table 2*). Some of the listed possibilities are shown in 'side' projection in *Figure 3*. It is apparent that a number of these could pack efficiently in a crystal structure. The 'end' projections (not shown) agree with this. It is possible that some of the structures might require a doubling of a and/or b but this appears unlikely on the basis of present X-ray data. Final selection must rest with consideration of the cylindrically averaged Fourier transform of the molecule, packing energetics, and the deviation of the computed structure factors from the experimentally determined ones.

Conclusion

While the number of possible conformations adopted by the multitorsional crystalline polymer, PI-2, is quite large, the method described above provides a useful tool for generating candidate structures for subsequent crystal structure packing and refinement. It also provides data leading to the conclusion that there are no conformations consistent with a c value of 24.6 Å and that there are a number of 2/1 conformations consistent with a repeat of 49.2 Å.

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