X-ray Diffraction Study of the Structure of Poly(ethylene 4,4'-biphenyldicarboxylate)

Xiaodong Li and François Brisse*

Département de Chimie, Université de Montréal, C.P. 6128, Succursale A, Montréal, Québec, Canada H3C 3J7

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ABSTRACT: The crystal structure of the mesophase polymer poly(ethylene 4,4'-biphenyldicarboxylate), $[-C_6H_4-COO-CH_2CH_2-OOC-C_6H_4-]_n$ (P2BP), was established using the model compound approach. The model compound, diethyl 4,4'-biphenyldicarboxylate (2BP2), belongs to the triclinic system (a = 6.0625(2), b = 6.7033(3), c = 9.8917(3) Å; α = 97.62(1), β = 99.82(1), γ = 101.30(1)°), space group $P\bar{1}$. The structure of 2BP2 was solved by direct methods and refined by a least-squares procedure to R = 5.60%. The 2BP2 molecule is centrosymmetric with the side chain in the *trans* conformation and a disordered aromatic ring system. The structure of the parent polymer, P2BP, was deduced from its X-ray fiber pattern. P2BP has a triclinic unit cell (a = 5.75, b = 3.82, c = 14.62 Å; α = 90.1, β = 90.3, γ = 78.1°), and the space group is $P\bar{1}$. The geometrical and conformational parameters derived from 2BP2 were used to generate an initial polymer chain which was then packed into its unit cell. The chain position and orientation were then refined. The final R value reached 12.4%. The P2BP polymer adopts a nearly fully extended conformation. The biphenyl moiety is planar, while the carboxylate plane is tilted by 5° with respect to the biphenyl plane. In the packing of both 2BP2 and P2BP, the chains are parallel to one another and the aromatic rings are face-to-face. However, in 2BP2, the molecules are displaced along the main molecular axis, while in P2BP, the chains are shifted sideways. It is suggested that, between 337 and 367 °C, i.e., in the mesophase, P2BP is nematic with a face-to-face disposition of the rings.

Introduction

Many aromatic liquid crystalline polyesters have been studied in the last 10 years. Of these, poly(ethylene 4,4'-biphenyldicarboxylate), P2BP, has been examined by a number of authors.[1-5] However, probably because of its high melting point and its insolubility in most solvents, the structure of P2BP is more difficult to access than that of its analogues.[6-12] Meurisse *et al.*[1] have studied this polyester by differential scanning calorimetry (DSC) and polarized microscopy. They reported a poorly defined texture in the P2BP mesophase which they proposed to be smectic.

The knowledge of the crystal structure of a polymer is important to the understanding of its properties. Furthermore, when the polymer is mesogenic, the structure of the crystalline phase is useful for the understanding of the mesophases. X-ray diffraction[13,14] is the best method for this purpose. We have previously reported on the structure of poly(hexamethylene 4,4'-biphenyldicarboxylate), P6BP.[15] The structure of two monoclinic forms of P6BP was arrived at using the model compound approach. On the basis of the structural information of the low temperature crystalline phases, a description of the smectic mesophase was proposed.

In order to gain some insight into the structure of the present thermotropic polyester P2BP, a model compound, diethyl 4,4'-biphenyldicarboxylate (2BP2) was synthesized and crystallized and its structure was established through the standard X-ray diffraction technique. The structural information thus derived was used to construct a polymer chain and to establish its structure which is reported here.

Experimental Section

Synthesis of 2BP2. 4,4'-Biphenyldicarboxylic acid (Pfaltz and Bauer) reacting with thionyl chloride (Aldrich) in the presence of DMF yielded 4,4'-biphenyldicarboxyl chloride, 1 (mp 177 °C). The latter was purified by recrystallization. The model compound, 2BP2, was then prepared by refluxing 1 for 4 h with an excess of ethanol and under a constant stream of nitrogen.[15] The excess ethanol was distilled out, leaving a white product. A very slow recrystallization from a DMF solution (3 months) yielded fine platelike single crystals. The melting point of 2BP2 was 111.0 °C (lit. 111.5 °C[16]). The density of the single crystal was measured in a $ZnCl_2$ aqueous solution.

Structure Determination of 2BP2. X-ray diffraction was carried out at room temperature with an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu $K\bar{\alpha}$ radiation. The unit-cell dimensions were calculated together with the orientation matrix by accurately centering 25 reflections in the range $20 < \theta < 25°$. The crystal data of interest are given in Table 1. The $\omega/2\theta$ scan technique was used with a scan range calculated by $\Delta\omega = (1.00 + 0.14 \tan \theta)°$ and a scan rate of 4°(2θ)/min. The experimental details of the data collection and the structure refinement are summarized in Table 2. The structure factors were calculated after scaling of the intensity data and the Lorentz and polarization corrections were applied.[17]

The structure was solved in the $P\bar{1}$ space group. The midpoint of the bond C4–C4' coincides with a crystallographic center of symmetry (the atomic numbering is shown in Figure 1). However, the six-membered ring was found to be disordered over two equally important orientations around the pivot axis which passes through the atoms C7–C1···C4–C4'···C1'–C7'. In the refinement of the structure, all C and O atoms were given anisotropic temperature factors, while H atoms were refined isotropically.

The refinement was based on F's and the quantity minimized was $\Sigma w\Delta F^2$. The scattering curves were taken from Cromer (C and O)[22] and Stewart *et al.* (H).[23]

Because the molecule is disordered, the $P1$ space group, which does not imply a centrosymmetric molecule, was also considered. However, the disorder remains and, in the refinement, the bond distances became chemically unreasonable. This was consistent with the very high correlation coefficients observed between parameters. Thus, this choice was rejected.

Synthesis of P2BP. Dimethyl 4,4'-biphenyldicarboxylate, 2 (mp 210 °C) was prepared by reacting 1 and methanol. A tube reactor was charged with 2, an excess ethylene glycol, and a small amount of titanium(IV) isopropoxide (Aldrich). The reaction took place at 185 °C with constant stirring and under a stream of Ar. The temperature was then raised gradually to 360 °C. After 1.5 h, the reaction product became viscous. The methanol

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* To whom correspondence may be addressed.

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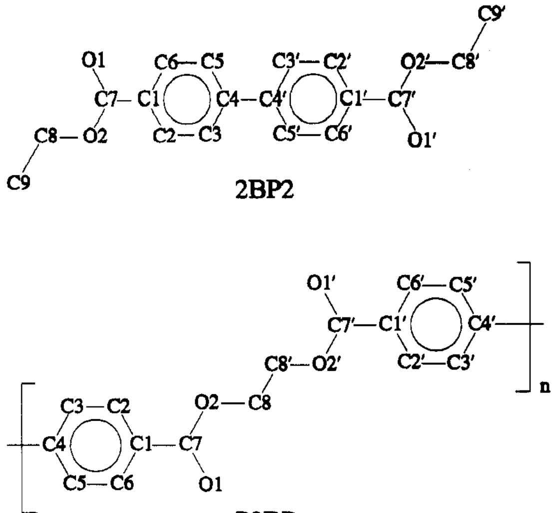


2BP2

P2BP

Figure 1. Atomic numbering adopted for 2BP2 and P2BP. The numbering of the other model compounds, BP2BP, P2P, and ClP2PCl, is similar to that of the P2BP fragment.

Table 1. Crystal Data of Interest for 2BP2 and P2BP

	2BP2	P2BP
mol formula	$C_{18}H_{18}O_4$	$(C_{16}H_{12}O_4)_n$
mol wt	298.34	268.27
$F(000)$	158	140
mp, °C	111.5	337 (M), 367 (I)
unit cell	triclinic	triclinic
a, Å	6.0625(2)	5.73
b, Å	6.7033(3)	3.77
c, Å	9.8917(3)	14.73
α, deg	97.624(3)	89.8
β, deg	99.824(3)	89.8
γ, deg	101.303(3)	79.0
V, Å^3	382.6	312.4
Z	1	1
d_o, g cm^{-3}	1.28	1.32 (amorphous)
d_c, g cm^{-3}	1.295	1.426
space group	$P\bar{1}$	$P\bar{1}$
μ for Cu Kα, cm^{-1}	7.05	8.09
cryst size, mm	0.05 × 0.20 × 0.30	partially crystalline fiber

Table 2. Summary of Intensity Measurements and Structure Refinement

	2BP2	P2BP
λ(Cu K$\bar{\alpha}$), Å	1.541 78	1.541 78
$2\theta_{max}$, deg	140	60
T, K	293	293
h,k,l ranges	$-7 \le h \le 7$ $-8 \le k \le 8$ $-12 \le l \le 12$	$-2 \le h \le 2$ $-1 \le k \le 1$ $-7 \le l \le 7$
max fluctuation of standards, %	0.76	
no. of measd reflns	1445	
no. of obsd reflns when $I \ge k\sigma(I)$	1091	17
k	1.96	
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.056	0.124
$R_w = [\sum w\Delta F^2/\sum wF_o^2]^{1/2}$	0.064	
$S = [\sum w\Delta F^2/(m-n)]^{1/2}$	3.07	
(displacement/σ)$_{max}$	0.04	
(displacement/σ)$_{av}$	0.006	
extreme fluctuations of residual electron density, eÅ^{-3}	−0.15, 0.17	

Table 3. Fractional Atomic Coordinates, Their Esd's, and Equivalent Isotropic Temperature Factors for 2BP2

atom	x	y	z	U_{eq}/U_{iso},[a] Å^2
O1	0.7680(3)	0.2114(3)	0.2448(2)	0.084
O2	0.3907(3)	0.1110(2)	0.1580(2)	0.062
C1	0.5532(3)	−0.0850(3)	0.3108(2)	0.052
C2[b]	0.3488(7)	−0.2285(7)	0.2901(5)	0.056
	0.3414(6)	−0.1809(7)	0.3312(5)	0.052
C3	0.3265(6)	−0.3889(7)	0.3641(5)	0.052
	0.3205(6)	−0.3401(8)	0.4062(6)	0.059
C4	0.5111(3)	−0.4127(3)	0.4595(2)	0.048
C5	0.7157(6)	−0.2660(7)	0.4827(5)	0.062
	0.7218(6)	−0.3203(7)	0.4339(6)	0.059
C6	0.7370(6)	−0.1057(7)	0.4087(5)	0.061
	0.7422(6)	−0.1603(7)	0.3595(6)	0.058
C7	0.5870(4)	0.0952(4)	0.2360(3)	0.057
C8	0.4062(5)	0.2798(4)	0.0783(3)	0.063
C9	0.1703(5)	0.2758(5)	0.0050(3)	0.086
H2	0.214(4)	−0.222(3)	0.231(3)	0.089
	0.228(3)	−0.135(3)	0.293(3)	0.041
H3	0.196(3)	−0.501(3)	0.343(3)	0.070
	0.158(3)	−0.406(3)	0.410(3)	0.041
H5	0.863(3)	−0.280(3)	0.556(3)	0.066
	0.855(3)	−0.370(3)	0.453(3)	0.061
H6	0.878(3)	−0.002(3)	0.437(3)	0.053
	0.883(3)	−0.102(3)	0.342(3)	0.048
H81	0.482(3)	0.409(3)	0.151(2)	0.078
H82	0.513(3)	0.261(3)	0.017(2)	0.085
H91	0.104(3)	0.145(3)	−0.060(2)	0.132
H92	0.062(3)	0.280(3)	0.067(2)	0.118
H93	0.177(3)	0.399(3)	−0.055(2)	0.106

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$; U_{iso} is for H atoms. [b] The atoms of the six-membered ring (see braces) are disordered (50/50).

and the excess diol were removed under 1 mmHg for 1 h. The polymerization yield was 80%. The white product so obtained does not dissolve in ordinary solvents. The density of the amorphous polyester was found to be 1.32 g/cm^3.

By examination under crossed polarizers with a microscope equipped with a hot stage, the polymer was observed to start turning to the liquid crystal state at about 340 °C. The observed texture is very similar to that reported by Meurisse *et al.*[1] DSC shows that P2BP melts at 337 °C (lit. 314 °C,[1] 337 °C,[2] and 335 °C[5]) to form a mesophase and then turns to an isotropic liquid at 367 °C (lit. 350 °C,[1] 339 °C,[2] and 363 °C[5]). At about 390 °C, P2BP decomposes.

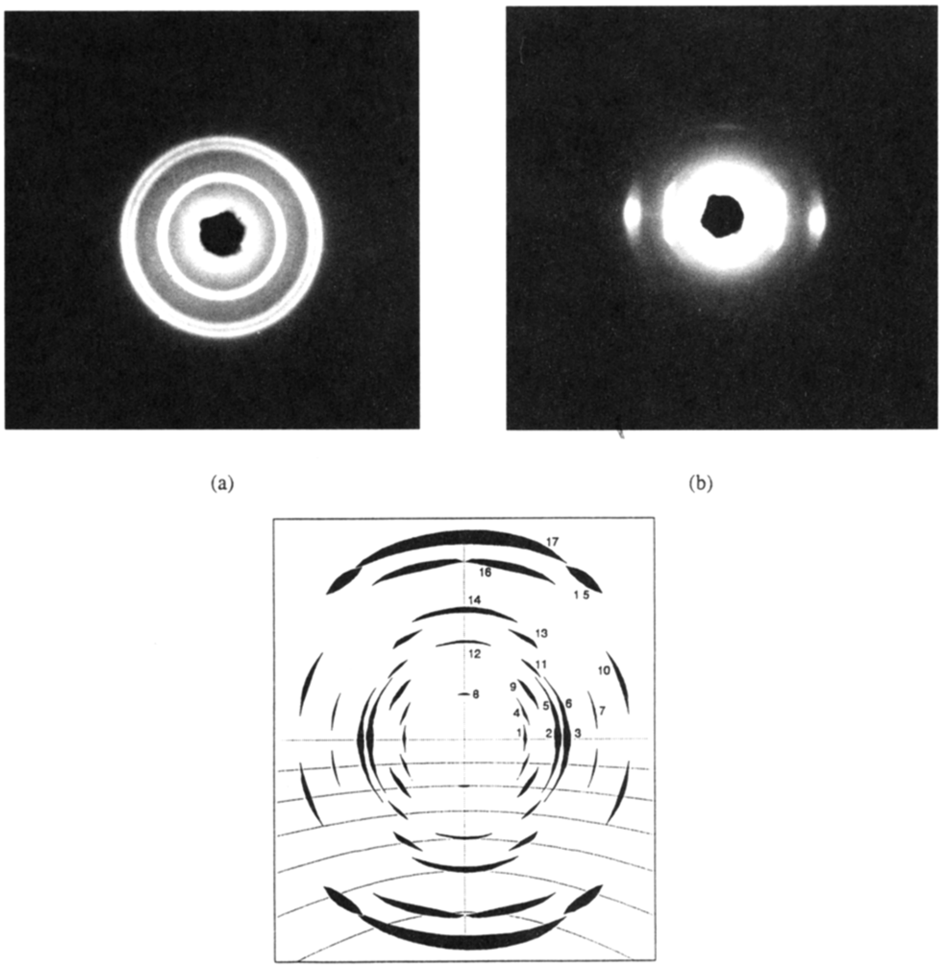
X-ray Diffraction of P2BP. P2BP was drawn into thin fibers (average diameter is 0.05 mm) from the highly viscous isotropic melt. The fibers, which were very fragile, were mounted in a specimen holder and annealed at 250 °C for about 1 month while being progressively stretched. The X-ray fiber diffraction patterns were recorded on a flat film camera (Warhus) using nickel-filtered Cu K$\bar{\alpha}$ radiation. The fiber to film distance, calibrated with NaF standard powder, was about 47 mm. The diffraction patterns are shown in Figure 2.

Results and Discussion

I. Model Compound 2BP2. Molecular Structure. The atomic coordinates, the equivalent thermal parameters, and their esd's are presented in Table 3. The molecule of 2BP2 with its two disordered components is displayed in Figure 3, while the packing of the unit cell is illustrated in Figure 4. The final bond distances, bond angles, and torsion angles are listed in the first column of Table 4.

Theoretically, the minimum of the potential energy curve for the biphenyl molecule is at Φ values around 40°, as proposed by various authors.[24-27] This is strongly confirmed by the very high occurrence in the population distribution of more than 100 reported structures containing the biphenyl fragments.[28] It is noted that planar biphenyl fragments, corresponding to a 4 kcal/mol barrier[27] over the minimum, are found much more often than expected. All these planar biphenyl compounds contain two identical R substituents in the 4,4′ positions, where R = H,[29] F,[30] NH_2·HCl,[31] SH,[32] OH,[33] OH (3,3,5,5′-tetranitro),[34] COO-*p*-$C_6H_4COOC_2H_5$ (*β*-form),[35] and CO-OC_2H_5 in this work. Brock[28] suggested that the planar biphenyl groups are likely to be disordered around the pivot axis.

The 50/50 disorder of the biphenyl group may be described in two ways. One may consider two completely



(a) (b)

(c)

Figure 2. X-ray diffraction films of the P2BP fiber: (a) quenched fiber: (b) oriented fiber; (c) schematic representation and indexing of the reflections.

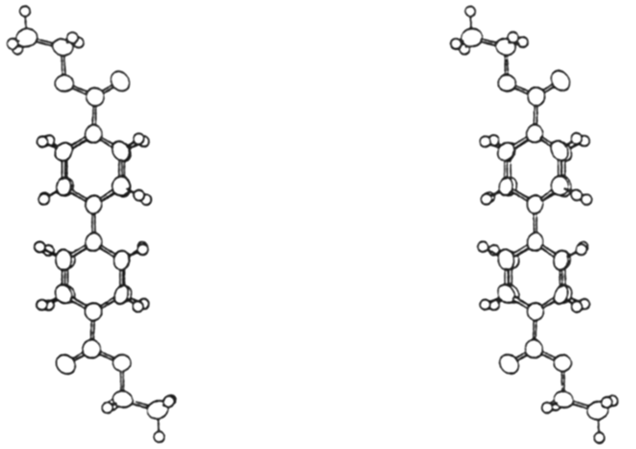


Figure 3. Stereopair showing the 2BP2 molecule with its two disordered orientations.

planar biphenyl groups forming a 26° dihedral angle between them. Each molecule is then centrosymmetric. In the other description, there is a 26° dihedral angle between the two six-membered rings of each biphenyl. The two nonplanar biphenyls are centrosymmetrically related to one another. In this situation, individual molecules do not possess a center of symmetry. However, the pair of molecules is centrosymmetric.

The aliphatic segment of 2BP2 is in the *trans* conformation, the torsion angle $\tau 1$ (C6–C1–C7–O2), $\tau 2$ (C1–C7–O2–C8), and $\tau 3$ (C7–O2–C8–C9) are close to 180°. Hall[36] reported that, in benzoic ester groups, there is an intramolecular affinity between between the nonbonded O and C atoms, more specifically, O1···C6, O1···C8, and O2···C1. As a consequence, $\tau 1$ and $\tau 2$ are always near 180°. In many of the structurs reported for benzoic esters, $\tau 3$ was found to be in the *trans* conformation, as is the case here.

Molecular Packing. The triclinic unit cell of 2BP2 contains only one molecule, so the packing mode is face-to-face (FTF) related to biphenyls and parallel. The interplanar separation, *A*, is 3.57 Å (see Figure 5a). The molecules are displaced along the pivot-axis direction by 5.57 Å. A displacement of 5.64 Å was observed in 6BP6.[15] The shortest O···C intermolecular separation is 3.69 Å, and the shortest C···C is 3.55 Å. Thus, only van der Waals interactions maintain the molecules together.

Like its analogues, 2BP2 exhibits no mesomorphism, as has been discussed by Swadesh and his co-workers.[16,37]

II. Polymer P2BP. Unit-Cell Dimensions and Structure Determination. The X-ray fiber pattern of P2BP (Figure 2b) could be indexed with a monoclinic unit cell with *c* as the unique axis. The unit-cell volume and the density measurements indicate the presence of only one chemical unit—C_6H_4–COO–CH_2CH_2–OOC–C_6H_4—per unit cell. However, all the monoclinic space groups require at least two such units in the unit cell. The only situations that would allow for one chemical unit are those where the chemical unit sites on a crystallographic symmetry element such as a 2-fold (rotation or screw) axis parallel to *c* or a

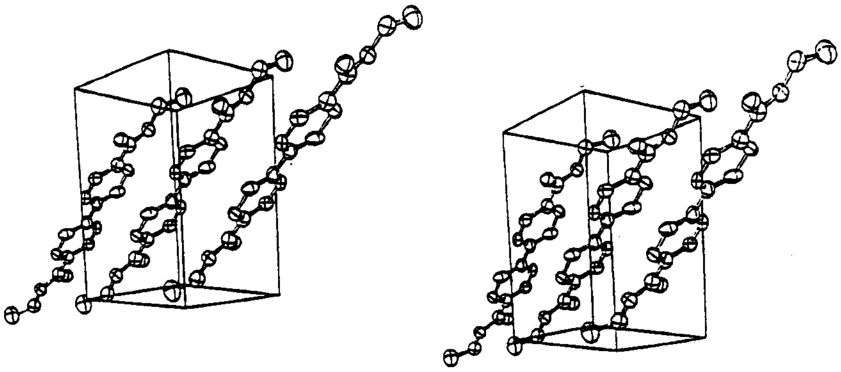


Figure 4. Stereopair showing the unit-cell content of 2BP2.

Table 4. Comparison of the Bond Distances, Angles, and Torsion Angles of 2BP2 to the Corresponding Quantities in Chemically Related Molecules

	2BP2	BP2BP[a]	P2P[a]		ClP2PCl[a]	P2BP
		Bond Distances, Å				
C–C, aromatic	1.382, 1.381	1.389	1.379	1.384	1.384	1.38
O1–C7	1.197(3)	1.202(2)	1.209(2)	1.202(3)	1.204(2)	1.20
O2–C7	1.334(3)	1.366(2)	1.339(2)	1.339(3)	1.344(2)	1.34
O2–C8	1.460(3)	1.444(2)	1.442(2)	1.441(3)	1.452(2)	1.45
C1–C7	1.497(3)	1.487(3)	1.479(2)	1.476(3)	1.482(2)	1.48
C4–C4′	1.502(3)	1.489(3)				1.49
C8–C8′(C9)	1.482(4)	1.493(3)	1.499(3)	1.499(3)	1.493(2)	1.50
		Bond Angles, deg				
C–C–C, aromatic	120.0, 120.0	120.0	120.0	120.0	120.6	120
C7–O2–C8	116.1(2)	116.9(2)	115.9(2)	115.5(2)	115.8(2)	116
C2–C1–C7	123.7(3)	121.8(2)	121.4(2)	122.1(2)	122.8(2)	122
C6–C1–C7	118.0(3)	118.9(2)	119.0(2)	118.1(2)	118.0(2)	118
O1–C7–O2	123.6(2)	123.3(2)	122.3(2)	122.6(2)	123.0(2)	123
O1–C7–C1	124.2(2)	125.1(2)	124.6(2)	124.1(2)	124.5(2)	125
O2–C7–C1	111.8(2)	111.5(2)	113.1(2)	112.8(2)	112.5(2)	112
C3–C4–C4′	121.2(2), 121.1(3)	121.0(2)				120
C5–C4–C4′	120.5(2), 121.1(3)	121.0(2)				120
O2–C8–C8′(C9)	107.5(2)	104.9(2)	104.7(2)	105.2(2)	107.3(2)	107
		Torsion Angles, deg				
C6–C1–C7–O2 (τ1)	−172.3(3), 160.3(2)	178.4(2)	−175.5(2)	−178.4(2)	−172.2(1)	−177
C1–C7–O2–C8 (τ2)	−178.8(2)	−178.2(2)	−176.7(2)	176.4(2)	−176.0(2)	176
C7–O2–C8–C8′(C9) (τ3)	−177.4(2)	177.1(2)	175.6(2)	−176.1(2)	−175.0(2)	−168
O2–C8–C8′–O2′		180	−172.8(2)	−172.8(2)	74.5(2)	180
O1–C7–O2–C8	1.2(4)	0.1(2)	2.5(2)	3.2(2)	4.5(2)	−5
O1–C7–C1–C2	−173.8(3), 161.3(3)	−177.7(2)	−175.8(2)	173.0(3)	−173.0(2)	−176
O1–C7–C1–C6	7.7(4), −19.7(4)	0.2(3)	5.3(3)	−8.4(5)	7.3(2)	5
C2–C1–C7–O2	6.2(4), −18.7(4)	0.6(3)	3.4(3)	3.0(2)	7.5(2)	4

[a] BP2BP = ethylene glycol di-*p*-phenylbenzoate (centrosymmetric);[38] P2P = ethylene glycol dibenzoate;[39] ClP2PCl = ethylene glycol di-*p*-chlorobenzoate (centrosymmetric).[40]

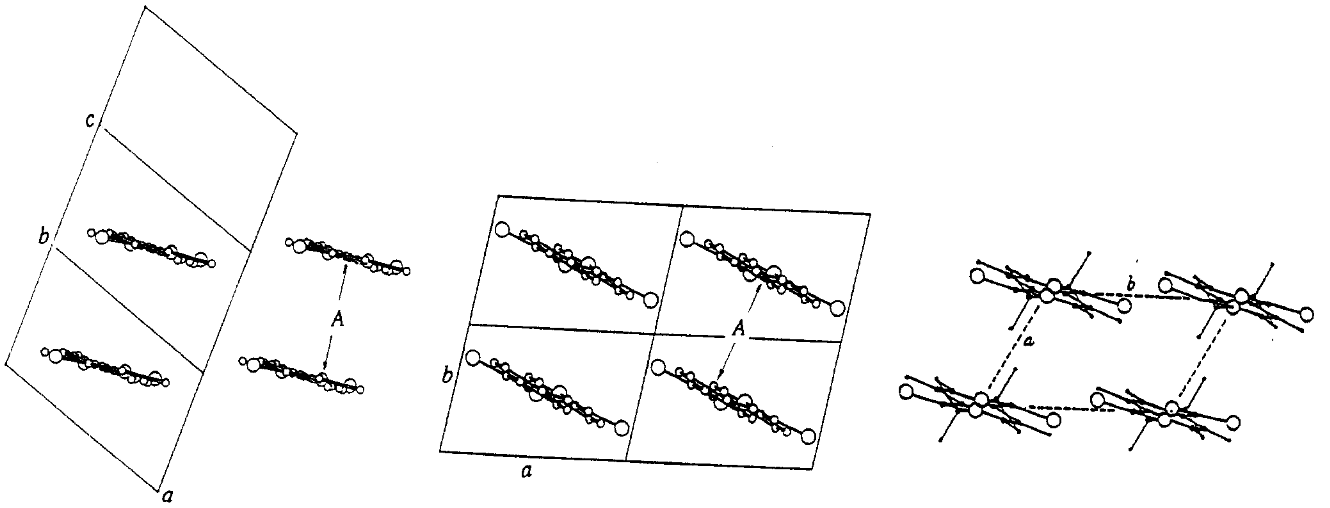
mirror (or glide) plane parallel to *ab* passing through the midpoint of the CH_2–CH_2 bond. Neither of these symmetries are compatible with the polyester chain. Thus, the unit cell has to be triclinic. The unit–cell dimensions, which are given in Table 1, were obtained by a trial and error method. The comparison of the observed and the calculated *d* spacings is given in Table 5. The observed structure factors, $|F_o|$'s, were calculated after Lorentz and polarization corrections were applied to the visually estimated spot intensities.

The structure of the crystalline P2BP was solved in the following way. An initial P2BP chain was built using the structural parameters of the two model compounds 2BP2 and ethylene glycol di-*p*-phenylbenzoate, BP2BP.[38] The value of the observed fiber repeat (or *c*-axis), p_o = 14.7 Å, is close to that calculated from a fully *trans* conformation, p_c = 15.0 Å. Thus, there are only four possible chain conformations of the sequence τ3–τ4–τ3:t-t-t, g-t-t, g^+-t-g^+, and g^+-t-g^-. The chain was aligned with the *c*-axis, and the two possible space groups were tried. The polymer chain was then rotated in order to minimize its interactions with adjacent chains. After some adjustments, the best combination of conformation (t-t-t) and orientation was arrived at with the space group $P\bar{1}$. The comparison of the observed and calculated structure factors is given in Table 5.

Chain Structure. The atomic coordinates of P2BP are listed in Table 6. The bond distances and angles adopted and the torsion angles are shown in the last columns of Table 4. The above parameters are compared with those of the model compounds 2BP2, BP2BP (ethylene glycol di-*p*-phenylbenzoate),[38] P2P (ethylene glycol dibenzoate),[39] and ClP2PCl (ethylene glycol di-*p*-chlorobenzoate).[40] The chains of P2BP in the unit cell are shown as a stereopair in Figure 6.

Chain Packing. The triclinic unit cell of the polymer, P2BP, contains only one monomer. Thus the midpoint of the biphenyl group and that of the central CH_2–CH_2 bond are crystallographic centers of symmetry. The packing mode is face-to-face (FTF) and parallel (Figure 6). The interplanar separation, *A*, is 3.46 Å (see Figure 5b). However, the chains are not displaced along the pivot axis, but in the lateral direction.

In many respects, the crystal structure of P2BP is very reminiscent of that of polyethylene terphthalate, PET.[41] Both unit cells are triclinic. In both cases the polymer



(a) (b) (c)

Figure 5. Comparison of the 2BP2, P2BP, and PET structures, in projection onto the plane normal to the chain.

Table 5. Observed and Calculated Structural Data for the P2BP Reflections

spot no.	*hkl*	d_{obs}, Å	d_{cal}, Å	$\lvert F_o \rvert$	$\lvert F_c \rvert^a$
1	1 0 0	5.62	5.628	3.14	3.308
2	0 1 0	3.71	3.699	4.32	4.488
3	1 1 0	3.44	3.404	4.90	4.885
4	$\bar{1}$ 0 1 1 0 1	5.26	5.252 5.263	4.44	4.132
5	0 1 1 0 $\bar{1}$ 1	3.59	3.589 3.586	3.25	2.243
6	1 1 1 1 1 $\bar{1}$	3.30	3.319 3.314	3.55	2.778
7	2 0 1	2.78	2.766	1.12	1.156
8	0 0 2	7.27	7.364	1.79	0.721
9	$\bar{1}$ 0 2	4.43	4.465	1.47	1.684
10	2 1 $\bar{2}$ 2 1 2	2.34	2.347 2.353	1.07	0.585
	2 1 2		2.353		
11	$\bar{1}$ 0 3	3.69	3.694	1.49	1.622
12	0 0 4^b	3.65	3.682	1.90	1.726
13	$\bar{1}$ 0 4 1 0 4	3.08	3.077 3.086	1.49	1.262
14	0 0 5^b	2.90	2.946	1.01	0.118
15	1 $\bar{1}$ 5	2.04	2.049	0.96	1.496
16	$\bar{1}$ 0 6 1 0 6	2.25	2.247 2.253	1.57	1.441
17	0 0 7^b	2.06	2.104	1.89	1.851

[a] For overlapped spots, $F_c = (\sum_i F_{c,i}^2)^{1/2}$. [b] Meridional reflections not included in the refinement.

chains are in a nearly all-*trans* conformation with very similar types of packing. Both structures are compared to Figure 5b,c through a projection of the chain onto a plane normal to the *c*-axis.

There are, however, some more specific differences. For example, the tilt of the nearly planar polymer chain with respect to the *a*-axis is 30° for P2BP, while in PET, the polyester plane is 16° away from the *b*-axis. Furthermore, the tilt of the carboxylate group with respect to the aromatic plane is 5° for P2BP and 12° for PET. In P2BP, the O–CH_2–CH_2–O squence of atoms is nearly coplanar with the carboxylate group, while there is a clear departure from planarity in PET where a torsion angle of 20° about the O–CH_2 bond is reported.

It has long been found that most of the roughly planar aromatic hydrocarbons, such as benzene, naphthalene, anthracene, and biphenyl, adopt a herringbone (HB) packing.[42,43] This was even considered to be a *sine qua non* condition.[44] For most of the 4,4′-disubstituted biphenyls, a similar situation is observed, but there are exceptions. The unusual FTF packing is often found in biphenyldicarboxylates, such as 2BP2, P2BP, as well as 6BP6 and α-P6BP,[15] and 10BP10.[45]

The FTF packing can be explained by the following factors: (i) the pivot axis is somewhat parallel for all the

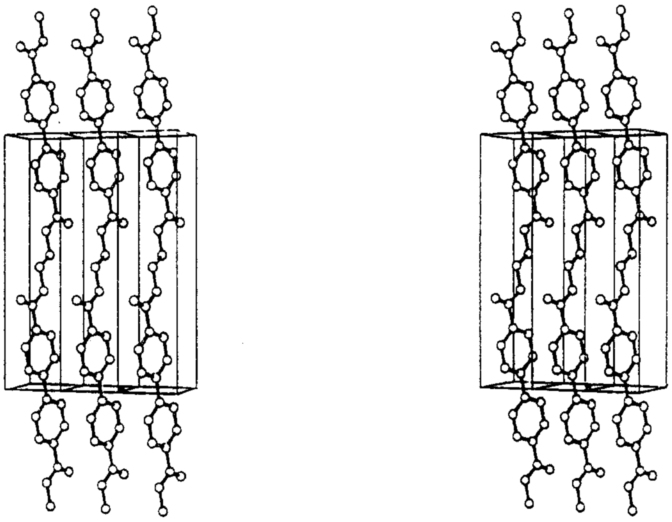


Figure 6. Stereopair showing the unit-cell content of P2BP.

Table 6. Fractional Atomic Coordinates of P2BP

atom	*x*	*y*	*z*
O1	0.0601	0.7437	0.3483
O2	0.4371	0.4944	0.3808
C1	0.3370	0.5813	0.2279
C2	0.5595	0.4182	0.2038
C3	0.6215	0.3808	0.1140
C4	0.4653	0.5173	0.0486
C5	0.2437	0.6846	0.0728
C6	0.1791	0.7145	0.1624
C7	0.2588	0.6201	0.3240
C8	0.3838	0.5417	0.4768
H2	0.6742	0.3284	0.2498
H3	0.7778	0.2561	0.0974
H5	0.1311	0.7829	0.0269
H6	0.0208	0.8307	0.1789
H81	0.3031	0.7961	0.4895
H82	0.2795	0.3722	0.4973

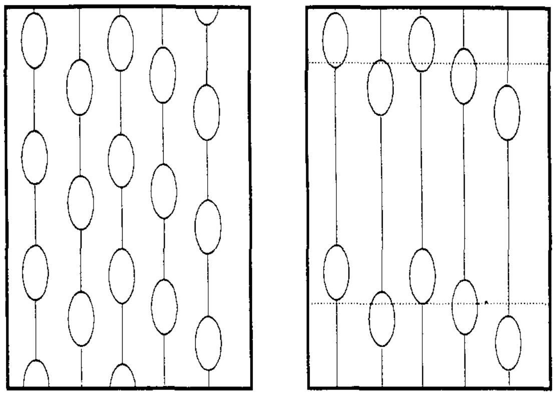

short spacer long spacer

Figure 7. Spacer length and mesophase layers (with the same displacement along the chain).

molecules, (ii) the stiff carboxylic groups are almost coplanar with the biphenyl and adopt and *E* conformation, (iii) the aliphatic sequences are *all-trans*, and, thus, the whole molecule takes a planar "S-shape", and (iv) the displacement of the aromatic groups along the pivot axis is small, or the aromatic groups are nearly at the same height. Thus, only if there were no spatial interference, the aromatic groups would pack in the HB pattern with intermolecular distances (from center to center) of 4.8–5.1 Å.[13] However, in the case of the compounds studied here, if the molecules were packed in the HB mode, the aliphatic chains would keep the two aromatic groups too far for significant interactions.

Possible Structure of the Mesophase. Since there are only a small number of structural variables for the rigid P2BP chain, it is reasonable to expect that the polymer chain in the mesophase will similarly be in an *all-trans* conformation.

Comparing the diffraction patterns of P2BP in Figure 2a, and b, one may find that the 002 spot is strong in (b) but does not show in (a) even after a much longer exposure time. This reflection will emerge and the intensity will be stronger as the fiber orientation increases. Therefore, considering the high melting point, it is believed that the diffraction pattern of Figure 2a contains a significant contribution from the "frozen" mesophase for which the 002 reflection is absent.

Since, in both patterns, the strongest reflections occur with the same *d* values, the polymer chains in the mesophase should therefore be arranged in the FTF pattern. In fact, as previously mentioned, the stiff planar structure tends to adopt this type of packing. If the packing of the crystalline P2BP can be kept with perfect layers in the mesophase, then a smectic type would be expected. However, as shown in Figure 2a, the disappearance of the 002 reflection may indicate that the chains are not packed in layers. Thus, in the mesophase, P2BP should pack like 2BP2, that is, in the FTF mode with a displacement of about 5.5 Å along the pivot axis.

Generally, in spite of the pivot-axis displacement, if the aliphatic spacer is long enough, the layers will still exist; however, in the case of short spacers, the layers will vanish (see Figure 7). This agrees with many observations that smectic properties are more marked when the spacer is lengthened. Shorter spacers are more likely encountered in nematic mesophases.[14,46] The mesophases of PnBP, where *n* is 3–10 and 12, were reported to be smectic.[1,2,6,7] For P2BP, however, it is believed that the shortest spacer leads to a nematic mesophase. As illustrated in Figure 7, when there is a 5.5-Å displacement along the chain related to a 14-Å monomer length, there should be no smectic layers at all.

Conclusion

The model compound 2BP2 has a triclinic unit cell. Its structure was determined by single-crystal X-ray diffraction. The molecule possesses a crystallographic center of symmetry. The planar biphenyl group is disordered around the pivot axis, probably due to the high potential barrier. The aliphatic sequence is in a *trans* conformation, and thus the molecule is planar. The parent polymer P2BP melts at about 337 °C to form a mesophase and turns to an isotropic liquid at 367 °C. Its crystal structure was investigated by X-ray fiber diffraction. The unit cell of P2BP was found to be triclinic with $a = 5.73$, $b = 3.77$, and $c = 14.73$ Å and $\alpha = 89.9$, $\beta = 89.9$, and $\gamma = 79.0°$. The structural information about 2BP2 was used to generate an initial chain of P2BP. The polyester has a nearly *all-trans* conformation. The P2BP biphenyl group was found to be planar. The packing of 2BP2 and P2BP are of the FTF type relative to the aromatic rings. However, in 2BP2, the molecules are displaced along the pivot axis with respect to one another, while the P2BP chains are displaced in a lateral direction. The chain packing and the diffraction films of the quenched P2BP fiber indicate that the mesophase is very possibly nematic. The packing of the chains is suggested to be FTF, with a displacement along the chain axis.

Supplementary Material Available: A table of anisotropic temperature factors (1 page); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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