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# Structure of a Mesomorphic Polymer: Poly(hexamethylene 4,4′-biphenyldicarboxylate). 1. The Model Compounds

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ABSTRACT: In order to establish the structure of the title polymer, P6BP, two model compounds, di-*n*-hexyl 4,4′-biphenyldicarboxylate (6BP6) and hexamethylene di-4-biphenylcarboxylate (BP6BP) were synthesized and their crystal structures were established by X-ray diffraction. The unit cell of 6BP6 is orthorhombic ($a$ = 7.754 (2), $b$ = 11.428 (5), and $c$ = 54.39 (4) Å; space group *Pbca*). The crystal structure of 6BP6 was solved from single crystal diffraction data ($R$ = 0.067). BP6BP is dimorphic: the α-form, whose structure was established ($R$ = 0.043), has a monoclinic unit cell ($a$ = 7.1039 (3), $b$ = 8.1298 (3), $c$ = 22.2308 (4) Å, and $\beta$ = 94.531 (4)°; space group $P2_1/c$); the $\beta$-form, which is obtained upon cooling of the melted α-form, is also monoclinic ($a$ = 13.42, $b$ = 7.59, $c$ = 12.95 Å, and $\beta$ = 95.4°). The aliphatic segments in both 6BP6 and α-BP6BP are in the *all-trans* conformation. The biphenyl dihedral angles are 35.5° and 21.1° for 6BP6 and α-BP6BP, respectively. The equivalent fiber repeats, calculated from both model compounds, are 19.568 (12) and 19.599 (6) Å for 6BP6 and BP6BP, respectively. In the crystal, the 6BP6 molecules adopt a parallel disposition and the aromatic groups are arranged in a face-to-face pattern. The α-BP6BP molecules pack in layers; the chains in the adjacent layers have different orientations, while the biphenyl rings adopt the herringbone pattern.

## Introduction

The thermotropic polyesters whose backbones are composed of both flexible aliphatic sequences and rigid groups, such as 4,4′-biphenyl- or 4,4″-terphenyldicarboxylates, are responsible for some very interesting liquid crystal characteristics.[1] Although, poly(hexamethylene 4,4′-biphenyldicarboxylate) (P6BP) has been investigated for the last 10 years through X-ray diffraction,[2–5] polarized[6,7] and electron microscopies,[8] and DSC,[2–6,9,10] no crystal structure has yet been reported.

Recently, the structure of a related polymer, poly(ethylene 4,4′-biphenyldicarboxylate) (P2BP), was reported using the model compound approach.[11] This approach involves the synthesis and X-ray characterization of a small molecular compound, diethyl 4,4′-biphenyldicarboxylate (2BP2), which is chemically related to P2BP.

The establishment of the structure of P6BP is of interest in order to understand its mesomorphic properties. However, polymers do not form single crystals of a size required by standard X-ray diffraction analysis. Thus, in order to gain some insight into the molecular conformation and the packing mode adopted by P6BP, two compounds modeling P6BP were synthesized and their crystal structures established by standard X-ray diffraction.

The two compounds chosen to model the P6BP polymer are di-*n*-hexyl 4,4′-biphenyldicarboxylate (6BP6) and hexamethylene di-4-biphenylcarboxylate (BP6BP). The former has been studied by Cohen, Duigiud, Poitier, and Swadesh,[12,13] focusing on the thermal analysis and NMR properties. Although there is no information available about BP6BP so far, the structures of its analogues BP2BP (ethylene di-4-biphenylcarboxylate) and BP4BP (tetramethylene di-4-biphenylcarboxylate) have been established by Deguire, Gagné, Dugas, and Brisse.[14]

**Table 1. Unit-Cell Dimensions and Crystal Data of Interest for the Two Model Compounds**

| parameter | 6BP6 | α-BP6BP | $\beta$-BP6BP |
|---|---|---|---|
| mol formula | $C_{26}H_{34}O_4$ | $C_{32}H_{30}O_4$ | $C_{32}H_{30}O_4$ |
| mol wt | 410.55 | 478.59 | 478.59 |
| $F(000)$ | 1776 | 508 | 508 |
| mp, °C | 53.6 | 117.0 | 104.0 |
| unit cell | orthorhombic | monoclinic | monoclinic |
| $a$, Å | 7.754 (2) | 7.1039 (3) | 13.42 |
| $b$, Å | 11.428 (5) | 8.1298 (3) | 7.59 |
| $c$, Å | 54.39 (4) | 22.2308 (14) | 12.95 |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 90 | 94.531 (4) | 95.4 |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 4819.6 | 1279.9 | 1313.2 |
| $Z$ | 8 | 2 | 2 |
| $d_o$, g cm$^{-3}$ | 1.13 | 1.24 | |
| $d_c$, g cm$^{-3}$ | 1.141 | 1.245 | 1.210 |
| space group | *Pbca* | $P2_1/c$ | |
| $\mu$ for Cu Kα, cm$^{-1}$ | 5.66 | 6.08 | 5.92 |
| crystal size, mm | 0.46 × 0.42 × 0.04 | 0.47 × 0.43 × 0.37 | |

The interpretation of the X-ray fiber patterns of the various forms of P6BP, calling upon the model compounds' crystal structures, is reported in the following paper.[15]

## Experimental Section

**Synthesis of 6BP6.** The model compound 6BP6 was prepared in the following way: 4,4′-biphenyldicarboxylic acid (Pfaltz & Bauer) was treated by thionyl chloride (Aldrich) in the presence of DMF. After a 5-h reflux, the excess thionyl chloride was removed and the product, 4,4′-biphenyldicarbonyl chloride (**1**), was purified and recrystallized in xylene. Slightly yellow needlelike crystals of **1** were thus obtained (yield 80%; mp 175 °C). Compound **1** was esterified with 1-hexanol. After the mixture was refluxed for 20 h, 6BP6 was obtained by removing the excess alcohol. The solid 6BP6 was recrystallized twice in hexane, and fine crystalline platelets were obtained (mp 53.6 °C; lit.[12] mp 52 °C). Polarized microscopy and DSC measurements confirmed the absence of liquid crystal phases.

**Synthesis of BP6BP.** Following the same reaction, 4-biphenylcarboxylic acid (Aldrich) was reacted with thionyl chloride to yield 4-biphenylcarbonyl chloride (**2**), which was then purified by recrystallization. A light yellow powder of **2**

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**Table 2. Summary of Data Collection and Structure Refinement**

| | 6BP6 | α-BP6BP |
|---|---|---|
| $\lambda$ (Cu Kα), Å | 1.54178 | 1.54178 |
| $2\theta_{\max}$, deg | 140 | 140 |
| $T$, K | 293 | 293 |
| $h,k,l$ ranges | $0 \le h \le 9$ | $0 \le h \le 8$ |
| | $0 \le k \le 14$ | $0 \le k \le 9$ |
| | $0 \le l \le 66$ | $-27 \le l \le 27$ |
| max fluctuation of standard reflns, % | 4.5 | 0.6 |
| no. of measd reflns | 4569 | 2425 |
| no. of obsd. reflns | 1431 | 2094 |
| $I \ge k\sigma(I)$, $k =$ | 1.96 | 1.96 |
| $R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ | 0.073 | 0.043 |
| $R_w = [\sum w\Delta F^2/\sum wF_0^2]^{1/2}$ | 0.067 | 0.063 |
| $S = [\sum w\Delta F^2/(m-n)]^{1/2}$ | 1.74 | 3.92 |
| $(\text{displacement}/\sigma)_{\max}$ | 0.05 | 0.17 |
| $(\text{displacement}/\sigma)_{\text{average}}$ | 0.01 | 0.03 |
| extreme fluctuations of the residual electron density, e Å$^{-3}$ | −0.22, 0.16 | −0.35, 0.36 |

**Table 3. Fractional Atomic Coordinates, Their Esd's, and the Equivalent Isotropic Thermal Parameters for 6BP6**

| atom | $X$ | $Y$ | $Z$ | $U_{\text{eq}}$[a] |
|---|---|---|---|---|
| O1 | 0.5959 (7) | 0.3241 (4) | 0.7986 (1) | 0.125 |
| O2 | 0.6363 (6) | 0.1314 (4) | 0.8025 (1) | 0.089 |
| O1′ | 0.6694 (8) | −0.0117 (5) | 0.5990 (1) | 0.141 |
| O2′ | 0.7241 (7) | 0.1757 (4) | 0.5939 (1) | 0.115 |
| C1 | 0.6193 (8) | 0.2067 (6) | 0.7628 (1) | 0.068 |
| C2 | 0.6723 (9) | 0.1009 (6) | 0.7528 (1) | 0.072 |
| C3 | 0.6770 (9) | 0.0870 (7) | 0.7280 (1) | 0.071 |
| C4 | 0.6301 (8) | 0.1736 (6) | 0.7114 (1) | 0.065 |
| C5 | 0.5753 (9) | 0.2796 (7) | 0.7215 (2) | 0.077 |
| C6 | 0.5704 (9) | 0.2957 (7) | 0.7466 (2) | 0.077 |
| C7 | 0.6146 (10) | 0.2302 (8) | 0.7894 (2) | 0.086 |
| C8 | 0.6458 (10) | 0.1450 (7) | 0.8291 (1) | 0.097 |
| C9 | 0.6403 (9) | 0.0237 (7) | 0.8400 (1) | 0.094 |
| C10 | 0.6615 (10) | 0.0291 (8) | 0.8677 (1) | 0.106 |
| C11 | 0.6887 (11) | −0.0926 (8) | 0.8791 (1) | 0.121 |
| C12 | 0.7052 (12) | −0.0905 (9) | 0.9059 (2) | 0.140 |
| C13 | 0.7481 (14) | −0.2065 (9) | 0.9172 (2) | 0.157 |
| C1′ | 0.6655 (8) | 0.1124 (7) | 0.6339 (1) | 0.072 |
| C2′ | 0.6970 (9) | 0.2219 (7) | 0.6438 (1) | 0.076 |
| C3′ | 0.6853 (9) | 0.2432 (7) | 0.6683 (1) | 0.075 |
| C4′ | 0.6376 (8) | 0.1548 (6) | 0.6849 (1) | 0.066 |
| C5′ | 0.6004 (9) | 0.0438 (7) | 0.6749 (1) | 0.072 |
| C6′ | 0.6161 (9) | 0.0243 (7) | 0.6503 (2) | 0.076 |
| C7′ | 0.6862 (10) | 0.0829 (9) | 0.6076 (2) | 0.091 |
| C8′ | 0.7500 (12) | 0.1572 (7) | 0.5675 (1) | 0.133 |
| C9′ | 0.7408 (12) | 0.2725 (7) | 0.5553 (1) | 0.125 |
| C10′ | 0.7778 (12) | 0.2647 (8) | 0.5287 (1) | 0.133 |
| C11′ | 0.7527 (13) | 0.3721 (8) | 0.5143 (1) | 0.139 |
| C12′ | 0.7870 (14) | 0.3676 (9) | 0.4876 (2) | 0.173 |
| C13′ | 0.7585 (16) | 0.4695 (9) | 0.4727 (2) | 0.190 |

[a] $U_{\text{eq}} = {}^1/_3 \sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

**Table 4. Fractional Atomic Coordinates, Their Esd's, and the Equivalent Isotropic Thermal Parameters for α-BP6BP**

| atom | $X$ | $Y$ | $Z$ | $U_{\text{eq}a}$ |
|---|---|---|---|---|
| O1 | 0.6958 (2) | −0.3752 (2) | 0.00883 (5) | 0.078 |
| O2 | 0.5324 (1) | −0.2103 (1) | 0.06696 (5) | 0.070 |
| C1 | 0.8324 (2) | −0.2950 (2) | 0.10595 (6) | 0.058 |
| C2 | 0.8249 (2) | −0.1838 (2) | 0.15349 (7) | 0.067 |
| C3 | 0.9686 (2) | −0.1791 (2) | 0.19914 (7) | 0.068 |
| C4 | 1.1220 (2) | −0.2867 (2) | 0.19992 (6) | 0.059 |
| C5 | 1.1275 (2) | −0.3962 (2) | 0.15180 (7) | 0.066 |
| C6 | 0.9860 (2) | −0.3999 (2) | 0.10546 (7) | 0.064 |
| C7 | 0.6829 (2) | −0.3001 (2) | 0.05546 (7) | 0.061 |
| C8 | 0.3759 (2) | −0.2074 (2) | 0.02066 (7) | 0.067 |
| C9 | 0.2399 (2) | −0.0788 (2) | 0.03798 (7) | 0.060 |
| C10 | 0.0695 (2) | −0.0637 (2) | −0.00797 (6) | 0.060 |
| C21 | 1.5557 (3) | −0.2723 (2) | 0.34554 (8) | 0.088 |
| C22 | 1.5908 (3) | −0.3413 (3) | 0.29075 (9) | 0.093 |
| C23 | 1.4524 (2) | −0.3437 (2) | 0.24302 (8) | 0.082 |
| C24 | 1.2727 (2) | −0.2824 (2) | 0.25030 (6) | 0.063 |
| C25 | 1.2397 (3) | −0.2164 (2) | 0.30575 (7) | 0.083 |
| C26 | 1.3798 (3) | −0.2090 (3) | 0.35273 (8) | 0.095 |

[a] $U_{\text{eq}} = {}^1/_3 \sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

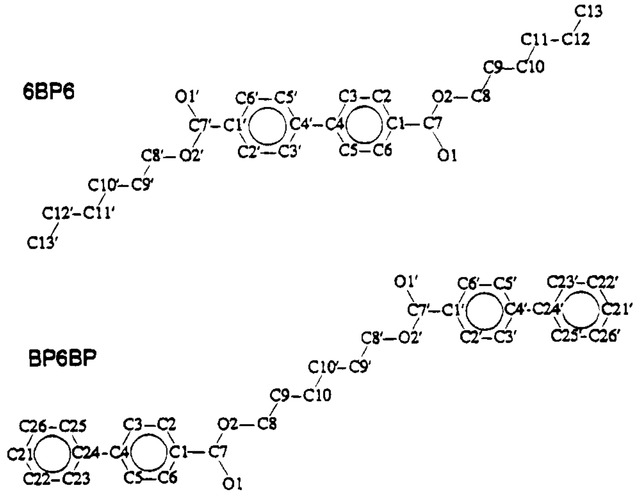

**Figure 1.** Atomic numbering adopted for 6BP6 and BP6BP.

(mp 110 °C) was obtained. In turn, **2** was reacted with a stoichiometric amount of 1,6-hexanediol and an excess of pyridine (3 times, w/w of reactants). The reactants were stirred at room temperature for 1 h.[16] The produce was purified and recrystallized in THF, and single crystals (α-phase) were obtained (mp 117.0 °C). No liquid crystal phase was observed. However, another solid crystalline phase (β-phase) emerged after BP6BP was recrystallized from the melt.

**X-ray Diffraction.** Well-developed single crystals were mounted on a glass fiber and transferred to a goniometer head and onto an Enraf-Nonius CAD-4 single crystal diffractometer. The unit-cell dimensions (see Table 1) and the orientation matrix were computed by a least-squares refinement of the angular settings of 25 well-centered reflections in the range $40 \le 2\theta \le 50°$. The data collections were performed using the $\omega/2\theta$ scan technique with a scan width $\Delta\omega = (1.00 + 0.14 \tan \theta)°$ and a scan rate of 4° min$^{-1}$. The stability of the crystal was monitored using standard reflections whose intensities were measured every hour, and the orientation was checked every 100 measurements. The largest fluctuations of the intensities of the reference reflections were 4.5% (6BP6) and 0.6% (BP6BP). After the data were reduced to a unique set of measurement, the diffracted intensities were corrected for Lorentz and polarization effects. An absorption correction was applied to BP6BP data. The extreme values of the transmission factor were 0.74 and 0.82.[17]

The crystal structures of the model compounds were solved by direct methods, using the MULTAN[18] program and refined by block-diagonal least squares.[19] The coordinates of the nonhydrogen atoms of 6BP6 were refined with anisotropic temperature factors. However, the coordinates and the isotropic temperature factors of only the aromatic H atoms were refined. The positions of the other H atoms were recalculated after each refinement cycle, $d(\text{C–H}) = 1.0$ Å, $\theta(\text{C–C–H}) = 110°$ and the methyl H's kept in the staggered disposition.

In the case of BP6BP, all the non-hydrogen atoms in the asymmetric unit, or half of the molecule, were found. The midpoint of the central bond coincides with the crystallographic center of symmetry at (0,0,0). The refinement proceeded smoothly with isotropic and then anisotropic temperature factors. All the hydrogen atoms were located on difference Fourier syntheses.

Both refinements were weighted, based on $F$'s, and the quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The weights were derived from the counting statistics of the intensities. The scattering factors for C and O atoms were taken from Cromer and Mann[20] and for H atoms from Stewart, Davidson, and Simpson.[21] The data collection and structure refinement are outlined in Table 2.

The crystalline β-BP6BP phase was investigated by X-ray powder diffraction using a Debye Scherrer camera of radius

**Table 5. Comparison of the Bond Distances and Bond Angles in 6BP6 and α-BP6BP**

| | 6BP6 | | |
|---|---|---|---|
| | unprimed | primed | α-BP6BP |
| | Bond Distance (Å) | | |
| O1−C7 | 1.194 (11) | 1.185 (11) | 1.214 (2) |
| O2−O7 | 1.347 (10) | 1.330 (11) | 1.336 (2) |
| O2−C8 | 1.455 (8) | 1.466 (9) | 1.454 (2) |
| C1−C7 | 1.470 (12) | 1.481 (11) | 1.482 (2) |
| C4−C4′(C24) | 1.456 (10) | | 1.488 (2) |
| C8−C9 | 1.508 (11) | 1.477 (11) | 1.494 (2) |
| C9−C10 | 1.518 (9) | 1.478 (10) | 1.525 (2) |
| C10−C11(C10′) | 1.537 (12) | 1.469 (12) | 1.516 (2) |
| C11−C12 | 1.468 (11) | 1.477 (12) | |
| C12−C13 | 1.497 (14) | 1.445 (14) | |
| | Bond Angle (deg) | | |
| C7−O2−C8 | 116.4 (6) | 117.7 (6) | 117.0 (1) |
| C2−C1−C6 | 117.9 (7) | 117.1 (7) | 118.7 (1) |
| C2−C1−C7 | 123.5 (7) | 124.1 (7) | 121.5 (1) |
| C6−C1−C7 | 118.6 (7) | 118.7 (7) | 119.7 (1) |
| C3−C4−C5 | 116.1 (7) | 116.9 (6) | 117.3 (1) |
| O1−C7−O2 | 123.0 (8) | 122.1 (8) | 123.6 (1) |
| O1−C7−C1 | 125.6 (8) | 125.2 (8) | 124.2 (1) |
| O2−C7−C1 | 111.4 (7) | 112.7 (7) | 112.2 (1) |
| O2−C8−C9 | 106.9 (6) | 107.8 (6) | 107.7 (1) |
| C8−C9−C10 | 110.4 (6) | 112.2 (7) | 111.8 (1) |
| C9−C10−C11(C10′) | 112.2 (6) | 116.5 (7) | 112.9 (1) |
| C10−C11−C12 | 113.4 (7) | 118.1 (8) | |
| C11−C12−C13 | 114.3 (8) | 119.9 (9) | |
| C22−C21−C26 | | | 119.0 (2) |
| C23−C24−C25 | | | 117.2 (2) |

**Table 6. Torsion and Dihedral Angles of 6BP6 and α-BP6BP**

| | | 6BP6 | | |
|---|---|---|---|---|
| | | unprimed | primed | α-BP6BP |
| | | Torsion Angles (deg) | | |
| C6−C1−C7−O2 | $\tau 1$ | 169.4 (7) | 176.5 (7) | 170.5 (1) |
| C1−C7−O2−C8 | $\tau 2$ | 176.0 (6) | 179.2 (6) | 179.5 (1) |
| C7−O2−C8−C9 | $\tau 3$ | 170.8 (6) | 164.2 (7) | 170.4 (1) |
| O2−C8−C9−C10 | $\tau 4$ | 176.3 (5) | 175.9 (6) | 179.9 (1) |
| C8−C9−C10−C11(C10′) | $\tau 5$ | −169.9 (6) | 173.2 (7) | −179.2 (1) |
| C9−C10−C11(C10′)−C12(C9′) | $\tau 6$ | −178.5 (7) | −179.5 (8) | 180.0 |
| C10−C11−C12−C13 | $\tau 7$ | −174.6 (7) | 177.9 (9) | |
| O1−C7−O2−C8 | | −3.3 (10) | −1.7 (11) | 1.4 (2) |
| O1−C7−C1−C2 | | 167.9 (8) | 175.5 (8) | 168.1 (2) |
| O1−C7−C1−C6 | | −11.3 (12) | −2.6 (12) | −10.3 (2) |
| O2−C7−C1−C2 | | −11.5 (10) | −5.5 (11) | −11.0 (2) |
| C3−C2−C1−C7 | | −178.4 (7) | −176.3 (7) | −178.4 (1) |
| C5−C6−C1−C7 | | 178.7 (7) | 177.7 (7) | 179.5 (1) |
| | | Dihedral Angles [Plane−Plane] (deg) | | |
| [C1−C2−‥−C6]−[C1′(C21)−C2′(C22)−‥−C6′(C26)] | $\Phi$ | −35.1 | | +21.1 |
| [C1−C2−‥−C6]−[C1−C7(−O1)−O2] | $\epsilon$ | +11.4 | +4.9 | +10.9 |
| [C1−C7(−O1)−O2]−[O2−C8−C9−C10‥] | $\psi$ | +3.3 | +22.5 | +10.2 |

180/π mm and nickel-filtered Cu $K\bar{\alpha}$ radiation. After a 3-h exposure, 35 diffracted lines were recorded on the cylindrical film.

**DSC Characterization.** The DSC measurements were carried out on 6BP6 and the two forms of BP6BP using a Perkin-Elmer DSC-1B apparatus. Indium was used for calibration, and a scan rate of 10 °C/min was used for both heating and cooling.

## Results and Discussion

The coordinates and the equivalent thermal parameters of 6BP6 and α-BP6BP are presented in Tables 3 and 4, respectively. The atomic numbering is shown in Figure 1. The molecular structure and the packing in the unit cell for 6BP6 and α-B6BP are shown as stereopairs[22] in Figures 2 and 4, respectively. The bond distances and angles of the two model compounds are listed in Table 5, while the torsion angles and the dihedral angles are given in Table 6.

**I. 6BP6. Molecular Structure.** The molecule does not possess any symmetry element as was the case with 2BP2.[11] The two planar aromatic rings of the biphenyl group form a dihedral angle, Φ, of 35.1°. This value falls within the range of observations reported in the Cambridge Data File[23,24] and is consistent with the lowest potential barrier obtained by theoretical calculations.[25−27]

There is an interaction[28−31] between the atoms of the carboxylic group and those of the aromatic group of the benzoate moiety. The plane of the carboxylic group [C1−C7(O1)−O2] is only approximately coplanar with the adjacent aromatic ring. In 6BP6, the dihedral angle, ϵ, between the above two planes was found to be 11.4 and 4.9° at the unprimed and primed ends of the molecule, respectively. The two carboxylic groups are in the *E* conformation, the most commonly observed conformation.[32−34] Since all the observed torsion angles in the aliphatic sequences take values very close to 180° (Table 6), the molecule is in the *all-trans* conformation. The equivalent fiber repeat calculated from the midpoint of the C10−C11 bond to that of C10′−C11′ is 19.568 (12) Å.

The average values of C(O)−O and C═O bond distances are 1.339 and 1.190 Å, while the O−C═O, C−C═O, and C−C(O)−O bond angles have averages of 122.6°, 125.4°, and 112.1°, respectively. In the biphenyl rings, the average C−C bond length and C−C−C angle are 1.388 Å and 120.0°, respectively. The aromatic bond angles at the junction of the rings, C3−C4−C5 and C2−C1−C6, are 116.1 (7) and 119.9 (7)° (116.9 (6) and 117.1 (6)° at the primed end, respectively). According to Domenicano *et al.*,[35] this slight ring angle departure from 120° is induced by the substitutions at C4 and C1. The two hexyl chains of 6BP6 are geometrically different from each other. The average C−C bond distance and C−C−C angle in the unprimed-side hexyl sequence are 1.506 Å and 112.6°, while in the primed chain, these are 1.469 Å and 116.7°, respectively. However, when one considers the average $C_i$‥$C_{i+2}$ distances in the unprimed and primed regions, one observes very similar values: 2.518 and 2.499 Å, respectively. It seems that the primed hexyl chain is subjected to more strain than the unprimed chain.

**Molecular Packing.** The shape of the 6BP6 molecule is that of the letter "S" and it is approximately in a plane containing the C4−C4 bond and the *all-trans* aliphatic chains. This plane is parallel to the *bc* face of the unit cell. As Figure 2b shows, the molecules pack in such a way that the planes of the aromatic groups in different molecules are arranged in a "face-to-face" pattern. In view of potential facial interactions, each molecule is displaced from its neighbors in a direction parallel to the *c* axis.

The *ac* projection of the unit cell (Figure 3) gives a sideview of the 6BP6 molecules. This reveals that they are curved unsymmetrically and that the two molecules resemble a sewing needle. The two unprimed hexyl sequences constitute the "eye of the needle", while the two primed hexyl chains form the "needle point". The

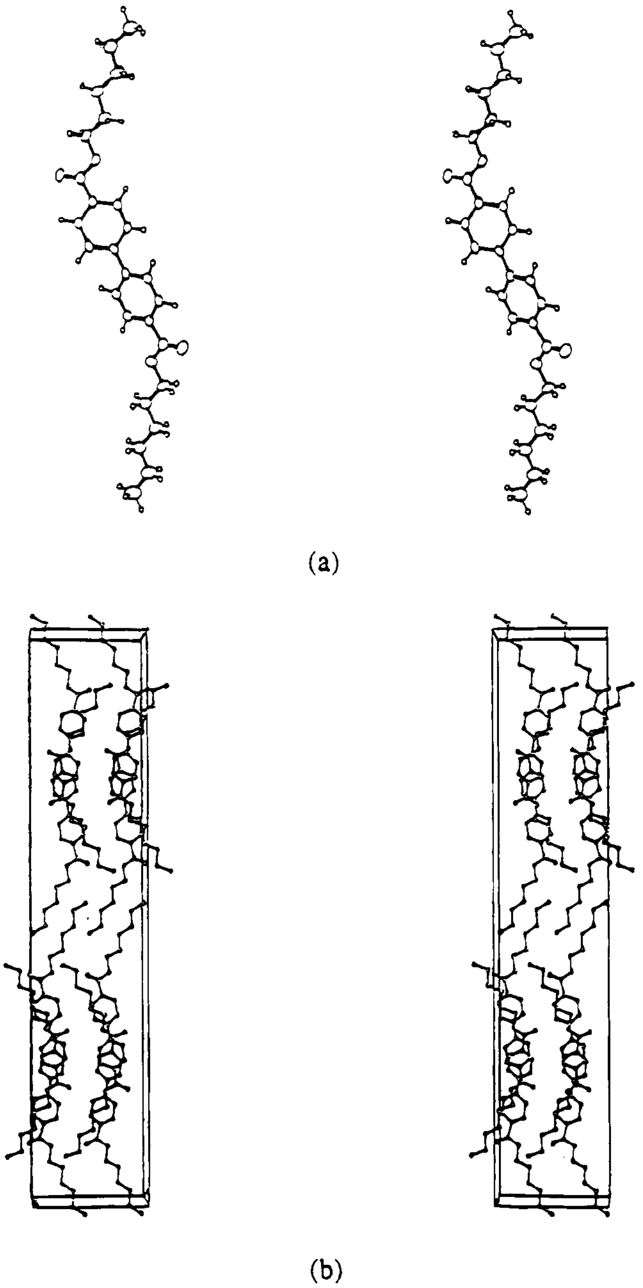

**Figure 2.** Stereopairs showing the molecule (a) and the unit-cell content (b) of 6BP6.

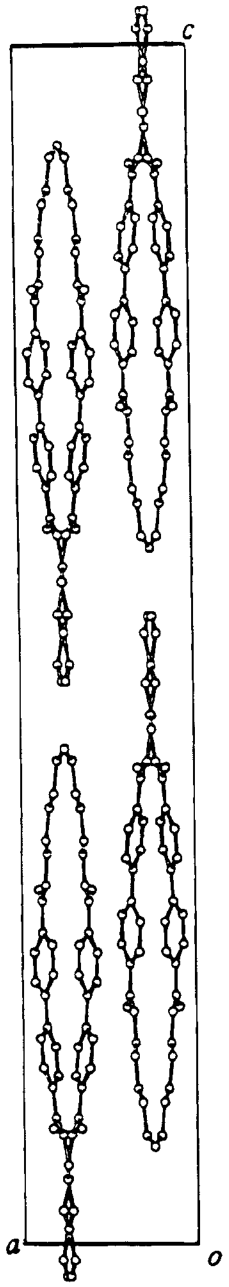

**Figure 3.** *ac* projection of the unit cell of 6BP6 displaying the "sewing needle" arrangement.

nonbonded interatomic distances in the needle point are closer than those in the eye of the needle. The differences are of about 0.2–0.3 Å. For example, the nearest H9⋯O1 distances are 2.77 (4) and 2.53 (6) Å in the unprimed and primed sides, respectively. The dihedral angles between the carboxylic group and the planar alkyl segment $\psi$ are 3.3° and 22.5° for unprimed and primed sides, respectively. The larger $\psi$ angle measures the primed-side chain's deformation to reduce its interactions with its neighbor. Since the shortest nonbonded intermolecular C⋯O contact is 3.269 (9) Å, and the shortest C⋯C contact is 3.658 (10) Å, the molecules are held in the crystal by van der Waals forces only.

**II. α-BP6BP. Molecular Structure.** The center of the α-BP6BP molecule (Figure 4a) coincides with a crystallographic inversion center. The aliphatic sequence is also in the *all-trans* conformation, and the molecule is fully extended. The equivalent fiber repeat, the distance between the midpoint of the C4–C24 bond to that of C4′–C24′, is 19.599 (6) Å, which is very close to that observed in 6BP6.

With a value of 10.9 Å, the dihedral angle $\epsilon$ compares well with that at the unprimed end of 6BP6. In the aromatic group, the average C–C bond distance is 1.386 Å and the average C–C–C angle is 120.0°. The junction angles clearly deviate from 120°; their values are 117.3 (1)° (C3–C4–C5), 118.7 (1)° (C2–C1–C6), 117.7 (2)° (C23–C24–C25), and 119.0 (2)° (C22–C21–C26). The average aliphatic C–C bond distance and C–C–C bond angle with values of 1.512 Å and 112.4°, respectively, are similar to those reported for the unprimed hexyl chain of 6BP6. The dihedral angle $\Phi$ between the two rings of the biphenyl group is 21.1°. In a crystal, $\Phi$ is governed not only by the intramolecular potential energy but also by the packing energy which is contributed by all of the intermolecular nonbonded interactions. In order to quantify the effect of the molecular packing on the $\Phi$ angle, the following calculation was carried out. In this calculation, only the two terminal aromatic rings are rotated around the C21⋯C24 and C21′⋯C24′ axes. The other atoms are kept at their crystallographic positions. The packing energy is cal-

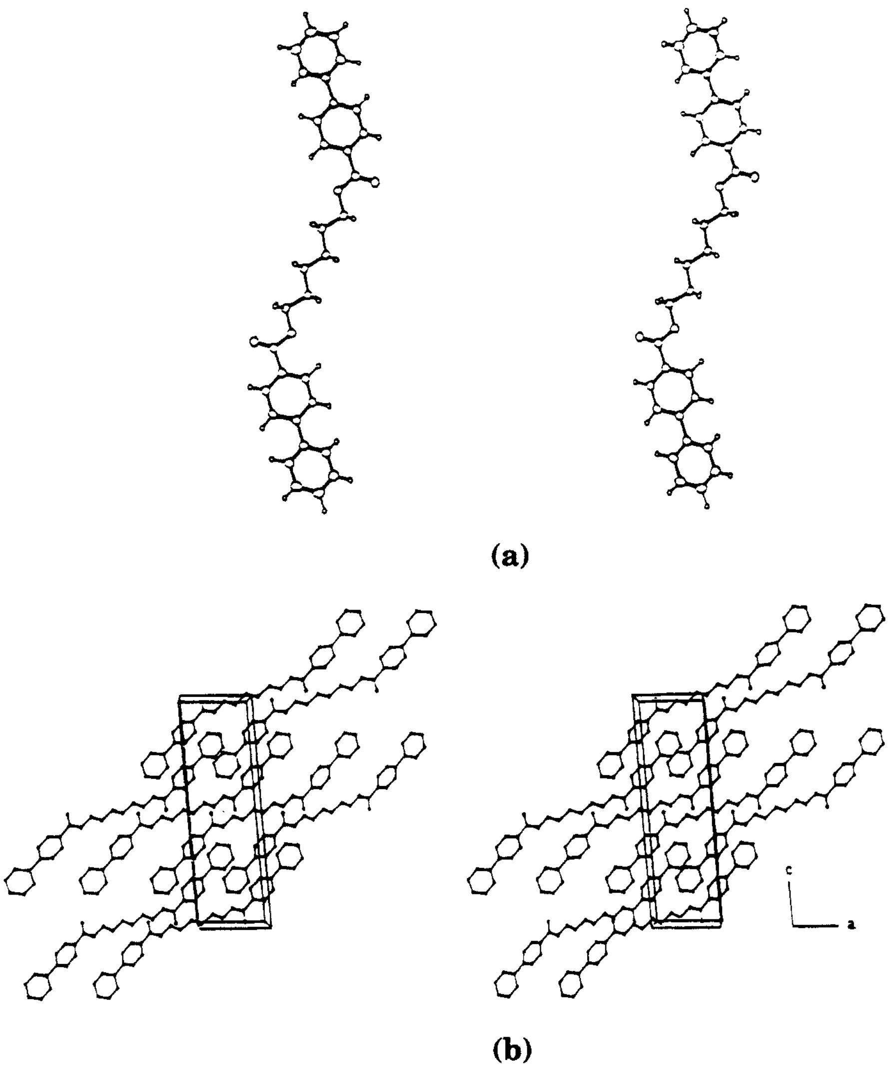

**Figure 4.** Stereopairs showing the molecule (a) and the unit-cell content (b) of α-BP6BP.

culated using the relationship given by Pertsin and Kitaïgorodski[36]

$$\mathrm{PE} = \sum \mathrm{E}_{ij} = \sum [B_{ij} \exp(-C_{ij} r_{ij}) - A_{ij} r_{ij}^{-6}]$$

where $A_{ij}$, $B_{ij}$, and $C_{ij}$ are Williams' constants,[37] $r_{ij}$ is the intermolecular nonbonded distance. Only the shortest contacts for all the Φ angles, C–C (<4.2 Å), C–H (<3.5 Å), and H–H (<3.0 Å) were considered. These shortest interactions contribute about 99.8% of the packing energy change, Δ(PE). The graph shown in Figure 5 is that of the difference between the calculated packing energy and that calculated for the observed value of Φ in α-BP6BP:

$$\Delta(\mathrm{PE}) = (\mathrm{PE})_{\Phi} - (\mathrm{PE})_{\Phi=21.1°}$$

The minimum Δ(PE) is calculated to be at 24°, very close to the observed quantity. This calculation shows that the Φ angle, in a certain range, is dependent on the molecular packing.

**Molecular Packing.** In the unit cell of α-BP6BP, the shortest nonbonded intermolecular C–O distance is 3.486 (2) Å and the shortest C–C distance is 3.570 (2) Å.

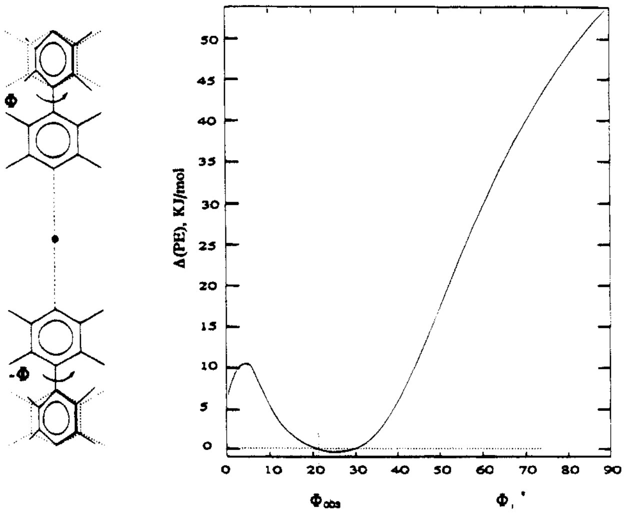

**Figure 5.** Relationship between the α-BP6BP's dihedral angle Φ and the corresponding packing energy difference.

The packing of the α-BP6BP molecules is shown by the stereopair in Figure 4b. Although the α-BP6BP molecules form layers parallel to the *ab* plane, their orientations differ in adjacent layers. However, the pivot axes, the C1–C21 direction, of all the molecules are parallel and are tilted by 49° with respect to the *ab* plane. The most significant packing difference between α-BP6BP and 6BP6 is that the aromatic groups in the α-BP6BP crystals adopt a herringbone pattern (Figure 6a).

It is interesting to note that BP2BP,[14] which is chemically related to α-BP6BP, belongs to the same space group and has a very similar unit cell. Only the

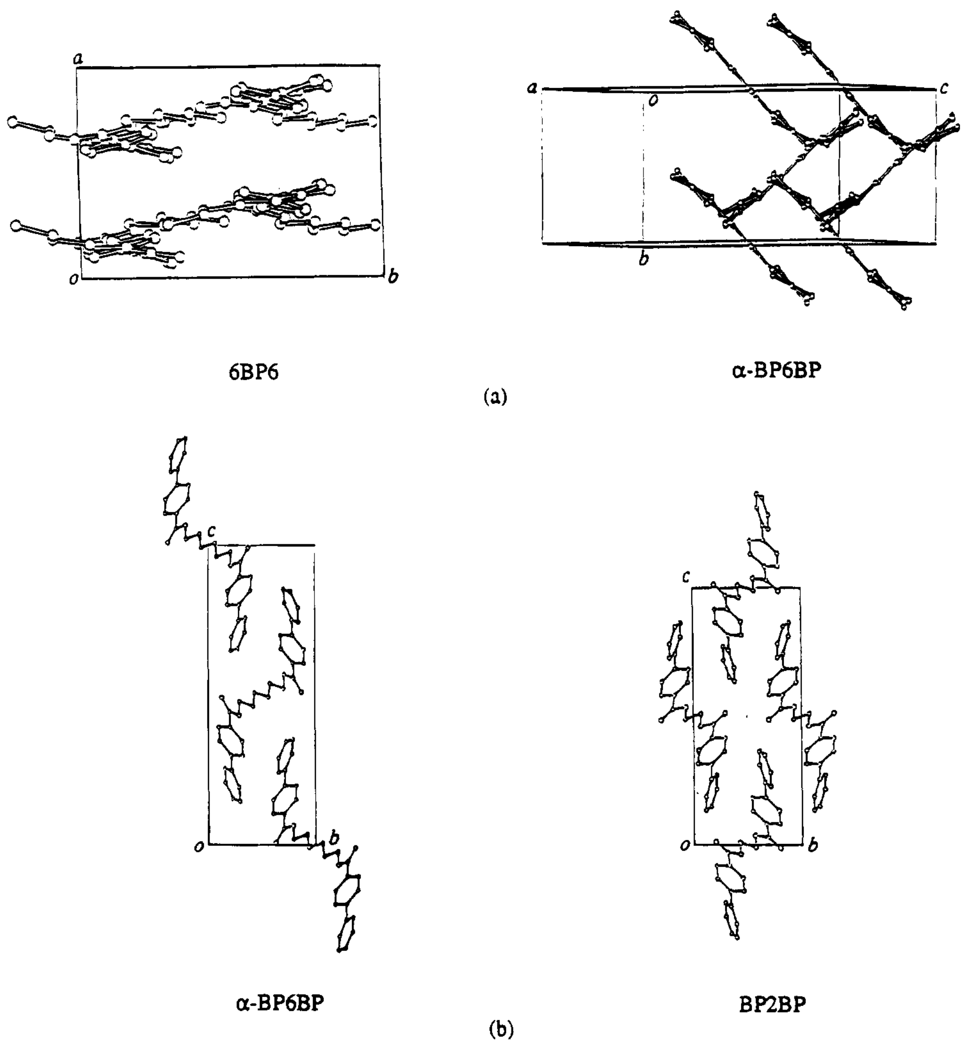

**Figure 6.** Comparison of the molecular packing of (a) 6BP6 (*ab* projection, at left) and α-BP6BP (as seen down the pivot axis, at right) and of (b) α-BP6BP (left) and BP2BP (right), both in the *bc* projection.

**Table 7. Observed and Calculated *d*-Spacings of *β*-BP6BP**

| arc no. | *hkl* | $d_{cal}$ (Å) | $d_{obs}$ (Å) | intensity | arc no. | *hkl* | $d_{cal}$ (Å) | $d_{obs}$ (Å) | intensity |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 001 | 12.794 | 12.81 | m | 23 | 410 | 3.058 | 3.05 | w |
| 2 | $\bar{1}01$ | 9.708 | 9.70 | w |  | 104 | 3.047 |  |  |
| 3 | 010 | 7.586 | 7.61 | w | 24 | 320 | 2.888 | 2.88 | vw |
| 4 | 200 | 6.862 | 6.73 | w |  | 222 | 2.878 |  |  |
| 5 | 110 | 6.597 | 6.57 | m | 25 | $\bar{5}10$ | 2.673 | 2.64 | vw |
| 6 | 002 | 6.397 | 6.37 | vw |  | 214 | 2.614 |  |  |
| 7 | $\bar{1}11$ | 5.978 | 5.96 | vw | 26 | 032 | 2.352 | 2.35 | vw |
| 8 | 111 | 5.756 | 5.78 | vw |  | $\bar{2}24$ | 2.351 |  |  |
| 9 | 102 | 5.570 | 5.57 | m | 27 | 512 | 2.278 | 2.27 | vw |
| 10 | 210 | 5.014 | 5.01 | w | 28 | 404 | 2.209 | 2.20 | vw |
| 11 | 012 | 4.890 | 4.93 | m |  | 330 | 2.199 |  |  |
| 12 | $\bar{1}12$ | 4.703 | 4.68 | vs | 29 | $\bar{5}04$ | 2.153 | 2.15 | vw |
| 13 | 300 | 4.445 | 4.46 | w |  | 331 | 2.151 |  |  |
| 14 | 003 | 4.265 | 4.26 | vs | 30 | $\bar{5}22$ | 2.118 | 2.11 | w |
| 15 | 301 | 4.089 | 4.09 | w |  | $\bar{3}32$ | 2.110 |  |  |
|  | $\bar{2}12$ | 4.089 |  |  | 31 | $\bar{4}24$ | 2.044 | 2.04 | vw |
| 16 | 103 | 3.957 | 3.98 | s |  | 233 | 2.040 |  |  |
| 17 | 310 | 3.841 | 3.87 | w | 32 | 430 | 2.016 | 2.00 | vw |
|  | 020 | 3.793 |  |  |  | $\bar{4}31$ | 2.009 |  |  |
| 18 | $\bar{3}31$ | 3.764 | 3.76 | s | 33 | 620 | 1.921 | 1.92 | vw |
|  | $\bar{2}03$ | 3.759 |  |  |  | $\bar{1}41$ | 1.861 |  |  |
| 19 | $\bar{1}21$ | 3.533 | 3.53 | w | 34 | 325 | 1.860 | 1.86 | vw |
| 20 | $\bar{3}12$ | 3.418 | 3.42 | vw |  | 026 | 1.859 |  |  |
| 21 | 022 | 3.263 | 3.26 | s | 35 | 720 | 1.705 | 1.70 | vw |
| 22 | 004 | 3.199 | 3.19 | m |  | $\bar{3}42$ | 1.699 |  |  |

*c* dimension of BP2BP is clearly smaller because of the shorter aliphatic chain. As Figure 6b shows, the two compounds have the same packing mode and molecular conformation.

**Polymorphism of BP6BP.** The two different crystal forms of BP6BP were studied by polarized microscopy and DSC. The α-form, which originated from the THF solution, melts into an isotropic liquid at 117.0 °C. After cooling, in a second heating run, the solid now melts at 104 °C. This solid is another crystalline form ($\beta$-BP6BP). It has been characterized by its powder diffraction pattern from which a monoclinic unit cell has been calculated (Table 1). The comparison of the observed and calculated $d$-spacings is listed in Table 7. The density of $\beta$ is larger than that of the $\alpha$-form. The DSC measurements indicate that the melting of $\beta$-BP6BP at 104 °C requires a smaller fusion enthalpy than that of the $\alpha$-form. The phase relationship between the $\alpha$- and $\beta$-forms is illustrated below.

$$\alpha\text{-BP6BP} \xrightarrow[117\ ^\circ\text{C}]{23.0\ \text{kcal/mol}} \begin{array}{c}\text{isotropic}\\ \text{melt}\end{array} \xrightleftharpoons[104\ ^\circ\text{C}]{15.7\ \text{kcal/mol}} \beta\text{-BP6BP}$$

## Conclusions

Two model compounds 6BP6 and BP6BP, which are chemically related to the mesogenic polyester P6BP, were prepared, and their structures were established by X-ray diffraction. The aliphatic chains of both molecules adopt the *all-trans* conformation. The 6BP6 molecule is characterized by a biphenyl dihedral angle, $\Phi$, of 35.1°. The $\alpha$-form of BP6BP is centrosymmetric, and thus the two aromatic rings of the biphenyl groups have the same $\Phi$ angle of 21.1°. The $\Phi$ angle of $\alpha$-BP6BP was examined, and the observed $\Phi$ value corresponds to the longest nonbonded distance of $(\text{atom}\cdots\text{atom})_{\min}$ and the lowest packing energy. This implies that the $\Phi$ angle is mostly dependent on the packing pattern adopted. The equivalent fiber repeats in 6BP6 and $\alpha$-BP6BP are very close: 19.568 (12) Å and 19.599 (6) Å, respectively. They compare well with the actual fiber repeat of $\alpha$-P6BP, the parent polyester: $p$ = 19.62 Å.

The 6BP6 molecules pack in a parallel manner, and the biphenyl groups are in a face-to-face arrangement. The $\alpha$-BP6BP molecules pack in layers, and the molecules in successive layers have different orientations. The biphenyl groups of $\alpha$-BP6BP are arranged in a herringbone mode. Another crystalline form of BP6BP ($\beta$-phase) was also found and characterized by powder diffraction.

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**Supplementary Material Available:** Tables listing hydrogen atom coordinates and anisotropic temperature factors with their esd's (4 pages); two tables of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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