Charge-carrier Transport in 1,4-Bis(phenylethynyl)benzene Derivatives Exhibiting Crystal Mesophases

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1,4-Bis(phenylethynyl)benzene (BPB) derivatives with alkyl or alkoxy terminal chains were synthesized, and the mesomorphic and charge-carrier-transport properties were investigated. The BPB derivatives exhibited high charge-carrier mobilities in the crystal mesophase or crystal phase.

Self-organizing conjugated oligomers have good potential for use as semiconducting materials in organic thin-film transistors.¹⁻⁴ Charge-carrier transport in semiconducting films depends both on the π electrons delocalized over the molecule and on the π - π stacking between the molecules.^{2b,3b} In recent years, there has been increasing interest in arylacetylene oligomers, namely, π systems containing aromatic rings linked by carbon-carbon triple bonds, because they are easy to synthesize and stable in air.⁵⁻¹³ Furthermore, some of these oligomers exhibit charge-carrier mobilities with values exceeding $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. One is a phenylacetylene oligomer with electron donor and acceptor groups, Me₂N(C₆H₄CC)₃SiMe₃.⁵ The others contain fused ring(s) (naphthalene,8 anthracene,^{9,11a,11b} pyrene,^{11c} or benzodithiophene^{12a}) or bithiophene.^{12c} However, due to the existence of such semiconducting oligomers, there have been few studies of charge-carrier transport in oligomers without either thiophene and fused rings or electron donor and acceptor groups.⁶

The phenylacetylene pentamer, $H(C_6H_4CC)_4C_6H_5$, exhibits mobility of 0.045 cm² V⁻¹ s⁻¹ in the vacuum-deposited films.^{6b} It has also been reported that the tetramer, $H(C_6H_4CC)_3C_6H_5$, and its dihexyl derivative exhibit values of 1.3×10^{-3} and 3.5×10^{-5} cm² V⁻¹ s⁻¹, respectively.^{6a} In general, the chargecarrier mobility in a homogeneous series of linear oligomers decreases with decreasing conjugation length.¹⁴ Therefore, the trimer, i.e., 1,4-bis(phenylethynyl)benzene (BPB),^{15–17} and its dialkyl or dialkoxy derivatives would be expected to exhibit mobilities lower than those found for the tetramers.

Nevertheless, a dioctyloxy-terminated derivative of BPB (C₈O-BPB) exhibits mesophases, nematic (N) and two smectic (Sm) phases, and two crystal (Cr) phases.¹⁸ The diheptyloxy derivative (C₇O-BPB, **1**) also exhibits mesophases.¹⁹ Although **1** has been reported to exhibit two or three Cr phases, the thermal behavior is similar to that of C₈O-BPB. Therefore, by utilizing liquid-crystalline (LC) BPB materials, including the above derivatives, i.e., by cooling the materials from the isotropic (I) phase, molecularly ordered thin films would be prepared in the mesophases, including crystal mesophase (CrM phase) such as a CrE phase.^{1,2} Furthermore, although crystallization from a mesophase generally causes cracks to appear in the film, LC BPBs that have two or more Cr phases might provide suitable films with which to investigate mobilities, at least in the highest-temperature Cr phase. Therefore, studies of charge-carrier

transport in LC BPBs have an important role to play in research on self-organizing organic semiconductors, including LC materials.^{1,2,20}

In the present study, we investigated the charge-carrier transport in two LC BPB materials. One is diheptyloxy derivative 1, with a phase sequence of $Cr_1-Cr_2-CrM_1-CrM_2-N-I$, and the other is dioctyl derivative (C_8 -BPB, 2), a new mesogen with a Cr-CrM-N-I phase sequence. We found that C_7O -BPB exhibits mobilities of 0.03 and 0.12 cm² V⁻¹ s⁻¹ in the CrM₁ and Cr₂ phases, respectively. C₈-BPB was found to have a high value of 0.09 cm² V⁻¹ s⁻¹ in the CrM phase. We also investigated the thermal and structural properties of 1 and 2. The CrM₁ phase of 1 and the CrM phase of 2 were both found to be a mesophase in which the molecular long axes are tilted with respect to the layer normal.

BPBs 1 and 2 were synthesized by Sonogashira coupling of 1,4-diiodobenzene with phenylacetylenes 3 and 4, respectively (Scheme 1).²¹ Colorless crystals of 1 and 2, obtained by careful recrystallization, were used to investigate the properties.

The phase-transition behavior of **1** and **2** was investigated using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC, Figure S1).²¹ The thermotropic data are summarized in Table 1. C₇O-BPB formed N and two CrM phases and two Cr phases enantiotropically. On cooling from the isotropic phase, a nematic Schlieren texture appeared,²² which changed to a mosaic texture (Figure 1a). On further cooling, striped patterns were observed in the CrM₁ phase, and very small scratch-like cracks were found in some domains of the Cr₂ phase (Figures 1b and 1c). Finally, enlarged cracks and defect lines



Scheme 1. Synthesis of BPB derivatives 1 and 2.

Table 1. Phase-transition temperatures (°C) and transition enthalpies (in square brackets, $kJ\,mol^{-1})$ of BPBs 1 and 2

Compound	Phase transition ^a	
1	h: Cr ₁ 72 [16.4] Cr ₂ 131 [13.0] CrM ₁ 177 [2.8	
	CrM ₂ 179 [20.3] N 223 [1.7] I	
	c: I 223 [1.7] N 179 [20.5] CrM ₂ 175 [2.9]	
	CrM ₁ 127 [13.0] Cr ₂ 70 [16.4] Cr ₁	
2	h: Cr 49 [8.2] CrM 155 [19.9] N 171 [1.0] I	
	c: I 170 [1.0] N 155 [19.3] CrM 49 [1.4] Cr	

^ah: on heating; c: on cooling; Cr: crystal phase; CrM: crystal mesophase; N: nematic phase; I: isotropic phase.



Figure 1. Photomicrographs of the CrM_2 (a), CrM_1 (b), Cr_2 (c), Cr_1 (d) phases for C₇O-BPB and the CrM (e) and Cr (f) phases for C₈-BPB.

were observed in the Cr_1 phase (Figure 1d). On the other hand, C_8 -BPB formed N, one CrM, and one Cr phases. On cooling from the isotropic liquid, after the appearance of the nematic Schlieren texture, a mosaic texture was observed in the CrM phase (Figure 1e). Crystallization occurred with the formation of large grain boundaries (Figure 1f).

The POM observations showed that all the mesophases except the N phase were a CrM phase (i.e., soft crystal phase), which exhibits a long-range positional order of the molecules.^{22,23} In such a mesophase, BPBs **1** and **2** might exhibit high mobilities.^{1,2} It was also observed that the Cr₂ phase of **1** hardly contained any crystal grain boundaries. We, therefore, expected that BPB **1** might provide a thin film with which to investigate mobilities in the crystal phase.

X-ray diffraction (XRD) measurements were carried out to investigate the structural properties of the CrM and Cr phases of **1** and **2** (Figure S2).²¹ The main *d* spacings are listed in Table 2. The XRD results indicate that the CrM₁ phase of **1** is a tilted mesophase such as a CrH phase. Two sharp peaks (*d* spacings = 27.5 and 13.7 Å) corresponding to the first- and second-order reflections of the layer were observed. The layer spacing is much shorter than the length (38 Å) of an extended C₇O-BPB molecule determined by MM2 calculations, indicating that the molecules are tilted at an angle within the layer. The tilt angle of the molecular long axis with respect to the layer normal is estimated to be 43°. Three strong peaks and a weak halo were observed in the wide angle region, indicating that the CrM₁ phase is a tiled mesophase of the H or K type (i.e., a CrM phase with herringbone packing of the tilted molecules).^{22,23}

Unlike the CrM₁ phase, the XRD profiles of the Cr₁ and Cr₂ phases showed a number of strong peaks and no halos in the wide angle region. In the Cr₂ phase, the layer spacing was 33.4 Å and the tilt angle was estimated to be 28°. This spacing is

Table 2. Layer spacings $(d_{001}, \text{ Å})$ and d spacings (d, Å) of $2\theta = 18-25^{\circ}$ in the CrM and Cr phases at a temperature $(T, ^{\circ}\text{C})$ for BPBs **1** and **2**

Compound	Phase $[T]^a$	d_{001}	d
1	CrM ₁ [150]	27.5	4.44, 4.17, 4.02
	Cr ₂ [100]	33.4	4.64, 4.45, 4.22, 3.88
	Cr ₁ [50]	32.8	4.60, 4.38, 4.15, 3.89, 3.71
2	CrM [100]	31.1	4.64, 4.42, 4.31, 4.20, 3.96
	Cr [30]	35.2, 24.4 ^b	4.63, 4.48, 4.27, 4.07, 3.89

^aMeasured on cooling. ^bThe height ratio of the peaks = 10:0.6.

significantly longer than that in the CrM_1 phase and almost the same as that in the Cr_1 phase.

With 2, the XRD results indicate that the CrM phase is a tilted mesophase, which has a more crystal-like 3D structure than the CrM₁ phase of **1** does. Two peaks $(d_{001} = 31.1 \text{ Å} \text{ and}$ $d_{002} = 15.5$ Å) were observed in the low angle region. d_{001} was shorter than the length (38 Å) of an extended C_8 -BPB molecule, and the tilt angle was estimated to be 35°. In the wide angle region, five strong peaks and a very weak halo were observed, indicating that the molecular arrangement is more highly ordered than that in the CrM₁ phase is. The XRD profile of the Cr phase, as those of the Cr₁ and Cr₂ phases, showed a number of strong peaks in the wide angle region. Interestingly, only in the Cr phase of 2, three peaks were observed in the low angle region. These are attributable to two layer spacings ($d_{001} = 35.2$ Å, $d_{002} = 17.6$ Å, and $d'_{001} = 24.4$ Å). Although the peak intensity of d'_{001} is much smaller than that of d_{001} , this structure in the Cr phase is a major factor in causing the large grain boundaries.

The charge-carrier-transport properties of BPBs 1 and 2 were investigated with a conventional time-of-flight (TOF) method.^{3a} The thin films for the TOF measurements were prepared by a melt process; the isotropic liquid was placed in a sandwich cell composed of indium-tin-oxide (ITO)-coated substrates, with a cell gap of 10 μ m, and carefully cooled. A suitable film of 2 was formed in the CrM phase. With 1, a suitable film was obtained in the CrM₁ and Cr₂ phases. The POM observations of the above films showed that the films had a number of domains where most of the molecules were homogeneously aligned (Figure S3).²¹

Typical transient photocurrents of **1** and **2** for holes are shown in Figure 2. The shape of the photocurrent curve was characteristic of nondispersive transport, and the mobility (μ) was calculated according to the equation: $\mu = d^2/V\tau$, where *d*, *V*, and τ are the sample thickness, applied voltage, and transit time, respectively. The mobilities in **1** and **2** were almost independent of the temperatures in the mesophase and in the crystal phase. For **1**, the values in the CrM₁ and Cr₂ phases were 0.03 and 0.12 cm² V⁻¹ s⁻¹, respectively. The value in the CrM phase of **2** was 0.09 cm² V⁻¹ s⁻¹.

The TOF results showed that the mobilities were dependent on the molecular order and motion (rotational diffusion), which would affect the π -orbital overlap between adjacent molecules. In the CrM₁ phase of **1**, the CrM phase of **2**, and the Cr₂ phase of **1**, in that order, the mobility increased significantly both with increasing molecular order and with decreasing molecular motion. Interestingly, the mobilities in the BPB derivatives were much higher than those in the tetramers mentioned in the



Figure 2. Transient photocurrents for holes of **1** at 145 (a) and 90 °C (b) (applied field: $2.0 \times 10^3 \text{ V cm}^{-1}$; sample thickness: 10 µm) and **2** at 100 °C (c) (applied field: $2.5 \times 10^3 \text{ V cm}^{-1}$; sample thickness: 10 µm).

introduction, although the tetramer values were determined by field-effect transistor (FET) method. This difference in mobility can be attributed to the degree of molecular order. The BPB mesogens self-organize to form a molecularly well-ordered structure in the crystal mesophase and crystal phase.

In conclusion, two LC BPB derivatives with alkyl or alkoxy terminal chains were synthesized, and the mesomorphic and charge-carrier-transport properties were investigated. The BPBs exhibited high mobilities of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the crystal mesophase or crystal phase. Our results indicate that BPB derivatives, which are short oligomers containing neither a thiophene nor a fused ring, have good potential for use as semiconducting materials. Further studies are in progress with the aim of preparing molecularly ordered thin films of BPBs by the solution process.

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