Synthesis and Properties of Planar Liquid-Crystalline Bisphenazines

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Received May 17, 2004. Revised Manuscript Received August 19, 2004

A synthetic route to fused bisphenazine compounds has been developed. Thus, 2,7-di-*tert*-butyl-quinoxalino[2′,3′,9,10]phenanthro[4,5-*abc*]phenazine-6,7,15,16-tetraalkoxy compounds have been synthesized in good yields. The structures of these new compounds were ascertained by nuclear magnetic resonance (NMR) and mass spectroscopy. Differential scanning calorimetry (DSC), polarized light microscopy (PLM), and wide-angle X-ray diffraction (WAXD) studies showed that some of these planar molecules display liquid crystalline phases at elevated temperatures. WAXD analysis also indicated that the molecules undergo $\pi-\pi$ stacking in the liquid crystalline phase. Differential pulse voltammetry (DPV) showed that the compounds undergo two reduction processes. Thus, it is speculated that the materials have potential as electron transporting materials in electronic devices such as organic photovoltaic or light-emitting diodes.

Introduction

Considerable research has been carried out aimed at the development of organic materials for use in light-emitting diodes,[1] field-effect transistors,[2] and photovoltaic devices.[3] High charge carrier mobility is essential for high performance in such devices. Discotic columnar liquid crystals possess high hole mobility along the column direction due to the significant π overlap between adjacent disk-shaped molecules.[4] For example, 2,3,6,7,10,11-hexakis (hexylthio) triphenylene (HHTT) has hole mobility on the order of 0.1 $cm^2\ V^{-1}\ s^{-1}$.[5] However, the discotic systems prepared to date for electron transportation do not function as well.[6] High charge mobility has also been displayed by fused-ring, planar molecules that do not exhibit discotic phases but undergo effective $\pi-\pi$ stacking.[7] This paper describes the preparation and characterization of a series of planar, liquid crystalline, fused-ring bisphenazines, which were investigated because of their potential as efficient electron transportation materials.

Experimental Section

Materials. All the solvents were used as received unless noted. All the reagents were purchased from Acros or Aldrich and used without further purification.

Equipment and Methods. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 300 MHz NMR spectrometer. Deuterium chloroform ($CDCl_3$) was used as the solvent unless noted. Mass spectral data were collected on a Bruker Esquire-LC ion trap mass spectrometer. Electrochemistry measurements were performed with a three-electrode setup with the use of a PAR M273A potentiostat. A platinum wire and a silver/silver chloride (Ag/AgCl) reference electrode were employed as the counter electrode and the reference electrode, respectively. The working electrode was a platinum disk with a diameter of 0.5 mm. Before each use, the working electrode was carefully polished using 0.3 μm aluminum oxide polishing compound and cleaned in an ultrasonic bath with acetone. All the measurements were carried out at room temperature. Argon was bubbled through the solutions to remove oxygen, and a slight argon overpressure was maintained during each measurement. The solvent was *o*-dichlorobenzene, and the supporting electrolyte was tetrabutylammonium tetrafluoroborate. The potential values were reported versus the ferrocene/ferrocenium (Fc/Fc^+) couple, as recommended by IUPAC.[8] Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. The temperature

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10.1021/cm0492179 CCC: $27.50
Published on Web 11/03/2004

and heat flow scales were calibrated using standard materials. Transition temperatures were determined using the onset temperatures unless denoted. An onset temperature was defined by the cross-point of the peak slope and the baseline in the DSC trace. In cooling, the onset temperature was determined on the high-temperature side, and upon heating, the onset temperature determined was on the low-temperature side. Polarized light microscopy measurements were conducted on an Olympus (HB-2) polarized light microscope coupled with a Mettler hot stage FP-90. Wide-angle X-ray diffraction (WAXD) experiments were carried out on a Rigaku 18 KW rotating-anode generator (Cu Kα) equipped with an image plate and a hot stage. One-dimensional (1-D) diffraction patterns were generated by integrating the upper half of the 2-D patterns to avoid interference of the beam stopper. X-ray beam was monochromatized using graphite crystals. The diffraction 2θ angles observed on WAXD patterns were calibrated with silicon crystals with known diffraction 2θ angles and crystallite sizes when $2\theta > 15°$ and calibrated with silver behenate when $2\theta < 15°$. The deviation of the measured diffraction angle was $\pm 0.05°$.

Synthesis

4,5-Dinitro-veratrole (1). This compound was prepared according to the published procedure.[10] It was obtained as pale yellow crystals (90%). Mp 123.0−124.0 °C (lit.[10] 129.5−130.5 °C). ^{1}H NMR δ: 7.33 (s, 2H), 4.01 (s, 6H).

4,5-Dinitro-catechol (2). A 1-L, one-neck, round-bottom flask was charged with 60 g of 4,5-dinitro-veratrole and 350 mL of hydrobromic acid (48%). The suspension was heated to about 90 °C for 2 days. At the end of the reaction, the reaction became an orange transparent solution. Removal of the water gave a brown crystal (85%). Mp 164.0−166.0 °C. ^{1}H NMR (DMSO-d_6) δ: 6.79 (s, 2H), 3.95 (s, 2H).

2,7-Di-*t*-butyl-pyrene-4,5,9,10-tetraone (5). This compound was prepared using Yamato's route[9] and obtained as bright orange crystals (20%). Mp >300 °C. ^{1}H NMR δ: 8.47 (s, 4H), 1.42 (s, 18H).

General Procedure for the Synthesis of 1,2-Bisalkoxy-4,5-dinitrobenzenes (3a−e). To a one-neck, flat-bottom flask were added 25 mmol of **2**, 55 mmol of alkyl bromide, 12.5 g of anhydrous potassium carbonate, and 70 mL of dried DMF. The mixture was stirred at 70−80 °C overnight. Once the reaction was complete as indicated by TLC, the mixture was poured into 200 mL of cold water and was extracted with 200 mL of methylene dichloride. The organic phase was collected and dried over $MgSO_4$. After removing the solvent, the dark yellow residue was dissolved in hexane containing 5% ethyl acetate and filtered through a Buchner funnel filled with silica gel to give a light yellow solution. After the solution was concentrated on a rotary evaporator, it was placed in a freezer where yellow crystals formed.

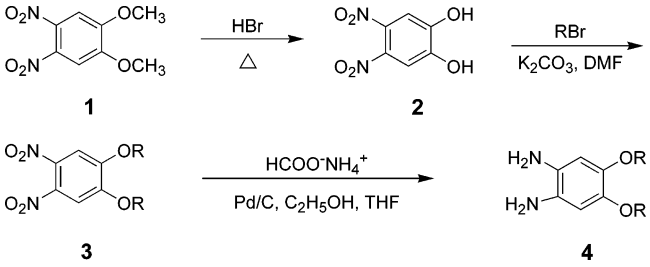
1,2-Bisdecyloxy-4,5-dinitrobenzene (3a). Pale yellow crystals (85%). Mp 76.0−77.0 °C. ^{1}H NMR δ: 7.29 (s, 2H), 4.10 (s, 4H), 1.87 (p, 4H), 1.53−1.28 (m, 28H), 0.89 (t, 6H).

1,2-Bisundecyloxy-4,5-dinitrobenzene (3b). Yellow flakes (82%). Mp 79.0−80.5 °C. ^{1}H NMR δ: 7.29 (s, 2H), 4.10 (s, 4H), 1.87 (t, 8H), 1.53−1.27 (m, 32H), 0.88 (t, 6H).

1,2-Bistetradecyloxy-4,5-dinitrobenzene (3c). Pale yellow powder (83%). Mp 77.5−79.0 °C. ^{1}H NMR δ: 7.30 (s, 2H), 4.08 (s, 4H), 1.85 (p, 4H), 1.47−1.28 (m, 44H), 0.88 (t, 6H).

1,2-Bis(2-ethylhexyloxy)-4,5-dinitrobenzene (3d). Pale yellow oil (73%). Mp 9.0−10.0 °C. ^{1}H NMR δ: 7.29 (s, 2H), 3.98 (d, 4H), 1.80 (m, 2H), 1.50−1.33 (m, 16H), 0.97−0.91 (m, 12H).

Scheme 1. Synthetic Route to 1,2-Bis-alkoxy-4,5-diaminobenzenes 4



1,2-Bis(3,7-dimethyloctyloxy)-4,5-dinitrobenzene (3e). Pale yellow needles (75%). Mp 79.0−80.0 °C. ^{1}H NMR δ: 7.30 (s, 2H), 4.18 (t, 4H), 1.90−1.18 (m, 20H), 0.97 (d, 6H), 0.89 (d, 12H).

General Procedure for the Synthesis of 1,2-Bisalkoxy-4,5-diaminobenzenes (4a−e). 1,2-Bisalkoxy-4,5-dinitrobenzene (1.0 g) (**3**) was dissolved in 40 mL of ethanol and 20 mL of tetrahydrofuran. To the solution were added 0.2 g of Pd/C (10%) and 10.0 g of ammonium formate. The dark yellow reaction mixture was stirred at room temperature until it became colorless. The reaction mixture was filtered through Celite, and the filtrate was placed in a freezer where slightly pink crystals formed.

General Procedure for the Preparation of the Fused Bisphenazine Compounds (6a−e). To an Erlenmeyer flask were added 0.25 mmol of 2,7-di-*tert*-butyl-pyrene-4,5,9,10-tetraone (**5**), 0.6 mmol of 1,2-the bisalkoxy-4,5-diaminobenzene (**4a−e**), and 50 mL of benzene. The mixture was heated at reflux for 5−6 h. The resulting dark solution was filtered through a Buchner funnel filled with silica gel. The yellow solution was evaporated to dryness on a rotary evaporator, and the residue was recrystallized from benzene/hexanes to afford bright yellow needles:

6a. Yield: 74%. ^{1}H NMR δ: 9.74 (s, 4H), 7.63 (s, 4H), 4.32 (t, 8H), 2.02 (m, 8H), 1.76 (s, 18H), 1.61−1.30 (m, 56H), 0.90 (t, 12H). ^{13}C NMR (75 MHz,$CDCl_3$) δ: 153.49, 150.44, 140.80, 140.09, 129.76, 124.81, 123.03, 107.18, 69.44, 36.11, 32.20, 32.17, 29.89, 29.84, 29.67, 29.60, 29.21, 26.34, 22.92, 14.33. MS *m/z* 1144.0 as a single peak.

6b. Yield: 72%. ^{1}H NMR δ: 9.75 (s, 4H), 7.63 (s, 4H), 4.32 (t, 8H), 2.02 (m, 8H), 1.78 (s, 18H), 1.61−1.30 (m, 64H), 0.90 (t, 12H). ^{13}C NMR (75 MHz,$CDCl_3$) δ: 153.40, 150.18, 140.65, 139.96, 129.74, 124.64, 122.89, 107.03, 69.29, 36.11, 32.29, 32.19, 29.94, 29.77, 29.65, 29.23, 26.36, 22.95, 14.35. MS *m/z* 1200.1 as a single peak.

6c. Yield: 68%. ^{1}H NMR δ: 9.71 (s, 4H), 7.54 (s, 4H), 4.28 (t, 8H), 1.98 (m, 8H), 1.79 (s, 18H), 1.59−1.29 (m, 88H), 0.89 (t, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.40, 150.36, 140.68, 139.99, 129.69, 124.73, 123.02, 107.07, 69.39, 36.12, 32.24, 32.17, 29.98, 29.92, 29.73, 29.61, 29.22, 26.35, 22.92, 14.33. MS *m/z* 1369.2 as a single peak.

6d. Yield: 66%. ^{1}H NMR δ: 9.74 (s, 4H), 7.61 (s, 4H), 4.21 (d, 8H), 1.89 (m, 4H), 1.77 (s, 18H), 1.59−1.42 (m, 32H), 1.04 (t, 12H), 0.96 (t, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.86, 150.38, 140.76, 140.19, 129.85, 124.79, 122.92, 106.90, 71.71, 39.68, 36.12, 32.23, 31.00, 29.43, 24.39, 24.37, 23.31, 14.32, 11.54. MS *m/z* 1031.9 as a single peak.

6e. Yield: 70%. ^{1}H NMR δ: 9.74 (s, 4H), 7.63 (s, 4H), 4.36 (t, 8H), 2.04 (m, 4H), 1.81 (m, 4H), 1.77 (s, 18H), 1.60−1.23 (m, 32H), 1.07 (d, 12H), 0.91 (d, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.29, 150.27, 140.70, 140.01, 129.77, 124.68, 122.91, 107.00, 67.81, 39.54, 37.67, 36.18, 36.12, 32.28, 30.44, 29.27, 25.04, 22.98, 22.88, 20.12. MS *m/z* 1144.9 as a single peak.

Results and Discussion

The fused bisphenazines were prepared by the route shown in Schemes 1 and 2. Thus, the synthesis of the series of 1,2-bisalkoxy-4,5-diaminobenzenes (**4**)[6b,c] was

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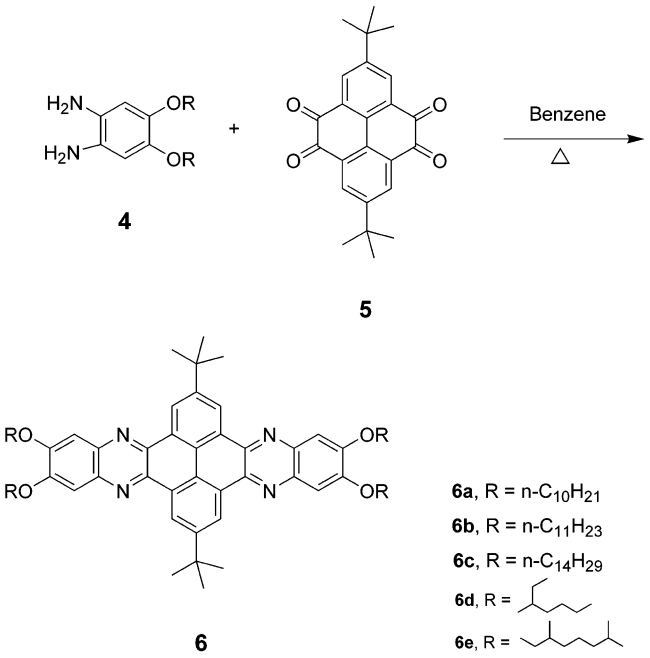
Scheme 2. Synthetic Route to Fused Bisphenazines 6



carried out by a simplified synthetic route (Scheme 1). The starting 1,2-dimethoxy-4,5-dinitrobenzene (**1**) was obtained from the nitration of 1,2-dimethoxybenzene in high yield. Although a route to 1,2-dihydroxy-4,5-dinitrobenzene (**2**) has been described,[12] the reported procedure did not result in complete dealkylation of **1**. Compound **2** was difficult to separate from the mixture obtained. In this work, complete dealkylation was found to proceed in high yield in refluxing 48% hydrobromic acid. Compound **2** was alkylated with the appropriate alkyl bromide to afford 1,2-bisalkoxy-4,5-dinitrobenzenes (**3**). Substitution reactions of this type are generally carried out using acetone as the solvent. However, when acetone was used in this system a mixture of products was obtained, which were difficult to separate. DMF was then used as the solvent, and the reaction temperature was increased to 70−80 °C. Pure products were obtained in good yields. Compounds **3** were reduced with ammonium formate in the presence of Pd/C to afford 1,2-bisalkoxy-4,5-diamionobenzenes (**4**). The diamines quickly changed from white to pink to brown if exposed to air. However, their reactions with 2,7-di-*tert*-butyl-pyrene-4,5,9,10-tetraone (**5**) yielded compounds **6** in 66−74% yield.

The phase behaviors of compounds **6** were investigated using DSC, PLM, and WAXD. The phase transition temperatures and phase types are summarized in Table 1. All three *n*-alkyl substituted compounds (**6a**−**c**) displayed complicated polymorphous crystalline phases. Compounds **6a** and **6b** displayed liquid crystalline phases above 200 °C. DSC thermograms of **6a** obtained with a scan rate of 10 °C/min are shown in Figure 1. During cooling, three major exothermic transition processes occurred at 267.0, 190.9, and 149.7 °C (peak). The heats of transitions were 12.1, 10.9, and 18.8 kJ/mol, respectively. During heating, only two major endothermic thermal events were observed at 213.2 °C (the heat of transition of 36.2 kJ/mol) and at 267.6 °C (heat of transition of 12.5 kJ/mol). Clearly, the endothermic peak at 267.6 °C during heating corresponds to the exothermic peak at 267.0 °C. PLM observations revealed that an isotropic liquid to ordered phase transition occurred at 267.0 °C during cooling. Figure 2 shows the texture of the ordered phase that developed upon cooling from the isotropic phase. To probe the structure of this phase, a WAXD pattern was obtained at 252 °C (Figure 3). Although it was not possible to determine the exact structure of the phase based on this 1-D pattern alone, its liquid crystalline nature is strongly suggested by the sharp reflections in the small-angle region and the diffuse halos in the wide-angle region. The halo with the maximum at about 24.6° 2θ-angle (d spacing ~0.36 nm) also indicates the existence of effective $\pi-\pi$ stacking. The effective π stacking along with the electron-deficient nature of **6a** suggests that it should function as an effective electron-transport material. Two additional phases developed during further cooling (190.9 °C, K1; 149.7 °C, K2). A third phase (213.2 °C, K3) formed during heating. All three phases showed a large number of sharp reflections in both the small- and wide-angle regions of their WAXD patterns, indicating their crystalline nature.

In the *n*-alkyl substituted series of compounds, both the melting points and the isotropization temperatures decreased as the length of the alkyl group increased. The isotropization temperatures decreased more than the melting temperatures; thus, the liquid crystalline phase temperature range became narrower. No liquid crystalline phase was observed for **6c** upon heating. To further decrease the melting point and broaden the temperature range of the liquid crystalline phases, the linear alkyl chains were replaced with branched alkyl groups. Surprisingly, the two branched alkyl-substituted homologues **6d** and **6e** displayed even higher melting points, and no liquid crystalline phases were observed.

Table 1. Phase Behavior of the Fused Bisphenazines 6

compd	R	phase transition[a]
6a	*n*-$C_{10}H_{21}$	K $\xrightarrow{213}$ LC $\xrightarrow{268}$ I
6b	*n*-$C_{11}H_{23}$	K $\xrightarrow{210}$ LC $\xrightarrow{234}$ I
6c	*n*-$C_{14}H_{29}$	K $\xrightarrow{202}$ I
6d	2-methylhexyl	K $\xrightarrow{>350}$ I
6e	3,7-dimethyloctyl	K $\xrightarrow{316}$ I

[a] The transition temperatures (°C) were determined with DSC with a heating rate of 10 °C/min. The phases were determined with PLM and WAXD.

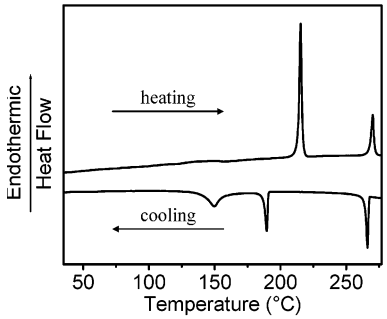


Figure 1. DSC thermograms of **6a** obtained with a scan rate of 10 °C/min.

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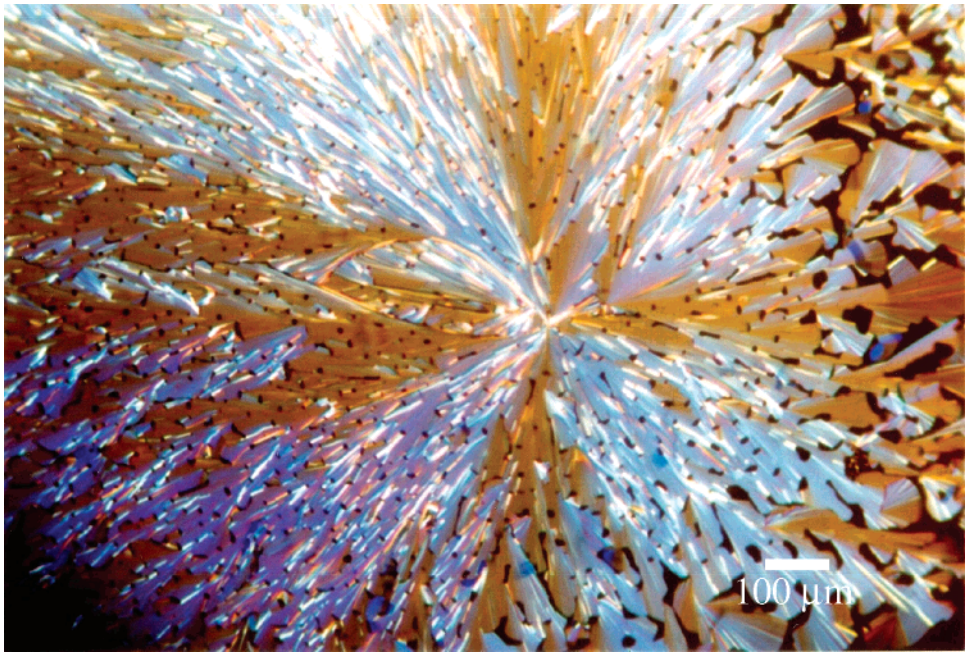

Figure 2. PLM micrograph of **6a** taken at 261 °C during cooling from the isotropic phase.

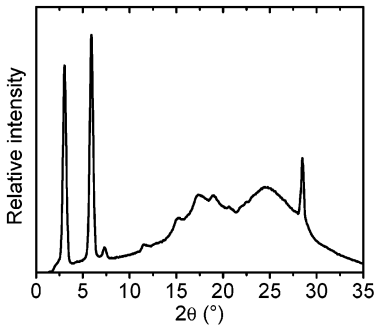

Figure 3. WAXD pattern of **6a** taken at 252 °C. (The sharp diffraction peak at 28.46° (2θ-angle) is due to the silicon internal calibration standard.)

Table 2. Reduction Potentials of the Fused Bisphenazines 6

compd	R	reduction potential[a] (V)
6a	n-$C_{10}H_{21}$	−1.94/−2.12
6b	n-$C_{11}H_{23}$	−1.95/−2.13
6c	n-$C_{14}H_{29}$	−1.93/−2.13
6d	2-methylhexyl	−1.94/−2.13
6e	3,7-dimethyloctyl	−1.94/−2.13

[a] Potential values were determined vs the ferrocene/ferrocenium (Fc/Fc^+) couple.

To ascertain the electron-deficient nature of **6a**−**f**, differential pulse voltammetry (DPV) experiments were carried out (Table 2). Two reduction processes were observed with all the compounds. The alkyl chain pendent did not significant influence the reduction processes, as all of the compounds displayed similar reduction potentials. The DPV curve of **6a** is shown in Figure 4. Two reduction processes were observed at −1.94 and −2.12 V, respectively. The first reduction potential value suggests that **6a** has a similar electron affinity as compared to 2,4,6-tris(3,4,5-tridodecyloxyphenylethynyl)triazine (−1.49 V vs SCE or −2.05 V vs Fc/Fc^+ [8b]),[11] but is not as electron deficient as hexaazatriphenylenehexacarboxyltriimide (−0.35 V vs SCE).[6a] These discotic compounds are currently being evaluated as electron transport materials. The first reduction potential is lower than that of polypyridine, which has been used as an electron transport material.[13]

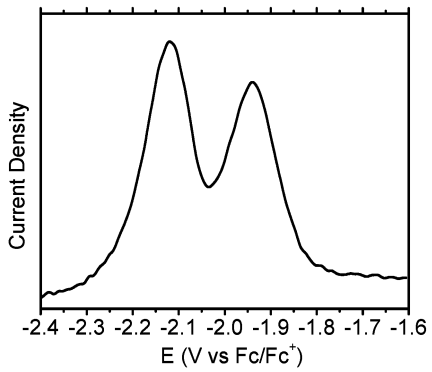

Figure 4. DPV curve of **6a**. (Potential range, 0 → −2.6 V; pulse height, 25 mV; pulse width, 50 mV; scan rate, 20 mV/s.)

In summary, a new series of planar fused bisphenazines has been prepared. The heterocyclics undergo two reduction processes. Some of the compounds display liquid crystalline behavior with $\pi-\pi$ overlap in their liquid crystalline phases. It is speculated that the compounds may function as electron transport materials. Further structural modifications are currently being explored.

Acknowledgment. The support of this work by the Air Force/UA Collaborative Center in Polymer Photonics is gratefully acknowledged. The center is funded by the Air Force Office of Scientific Research, the Air Force Material Laboratory, and the University of Akron.

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