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Synthesis and Electrochemistry of a Liquid Crystalline Pyrrole and a Structurally Related Thiophene

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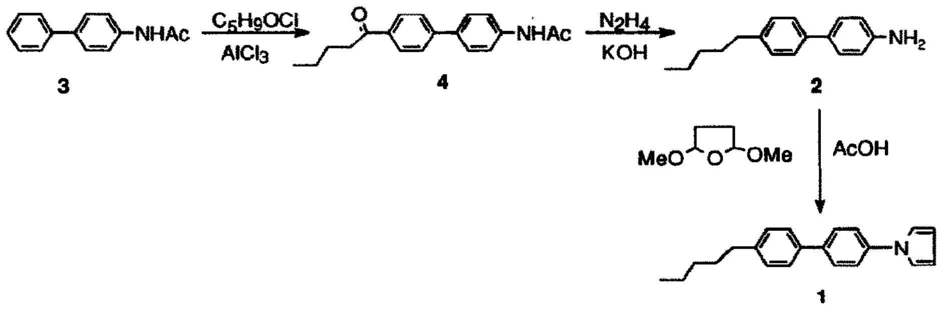
Abstract: A pyrrolic analog (4-pyrrole-4'-pentylbiphenyl) of the liquid crystal 4-pentyl-4'-cyanobiphenyl (K-15) exists as a liquid crystal between 200°C and 213°C. Attempts to electropolymerize this liquid crystalline pyrrole failed. A structurally related thiophene (3-(4-pentylphenyl)thiophene) has no stable liquid crystalline phase but can be electropolymerized to an isotropic conducting polymer.

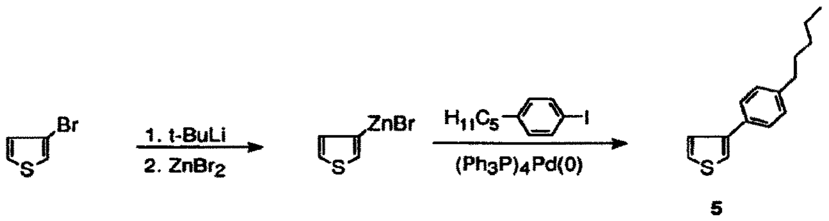
Conducting polymers show great promise as technologically important materials.[1] It has been proposed that higher conductivity may be attained by alignment of the conjugated polymer chains in the solid state.[2] Previous work in this laboratory seeking to achieve such alignment by electropolymerization of a disordered monomer (pyrrole) in an ordered solvent (i.e., in the nematic phase of 4-cyano-4'-pentylbiphenyl, K15) produced modest anisotropic conductivity but no detectable crystallinity.[3] The observed anisotropy is probably restricted by spatial disruption during oligomer deposition.[4] Therefore, a means to enhance local order during electropolymerization might yield a conducting polymer with greater crystallinity and highly anisotropic conductivity. We describe herein the synthesis of a liquid crystalline pyrrole which we hoped might polymerize, like its unsubstituted parent, to a conducting polymer, but with improved long-range order.

The synthesis of the 4-pentyl-4'-biphenylpyrrole **1** takes place by the acid-catalyzed ring annulation of the amino-4'-pentylbiphenyl **2**[5] with 2,5-dimethoxytetrahydrofuran, eqn 1.[6] Aniline **2** is prepared by Friedel-Crafts acylation of N-acetyl-1-aminobiphenyl **3**, followed by Wolff-Kishner reduction and hydrolysis of the resulting 4-acetanilido-4'-pentanoylbiphenyl **4**. The analogous thiophene **5** is synthesized by a Pd(0) catalyzed coupling of 4-iodopentylbenzene[7] with 3-thiophenyl zinc bromide, eqn 2.[8]



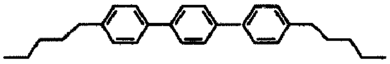
(1)

Differential scanning calorimetry of **1** reveals two phase transitions: one at 200°C (crystalline to liquid crystalline transition) with a measured enthalpy of 17.1 kJ/mol and a second at 213°C (liquid crystal to isotropic melt) with 0.1 kJ/mol. The structurally related thiophene **5** shows no intermediate phases between the solid and the isotropic melt.



(2)

Although **1** was designed to be a pyrrolic analog of K-15, its phase behavior is markedly different. First, the temperature for the solid-to-mesophase transition is higher by 170°C than in K-15. Second, the optical texture of **1**, viewed through a cross-polarized microscope, lacked the irregular, multicolor textures as seen in K-15[3] and instead resembled a smectic phase.[9] In short, **1** resembles triphenyl **6**, which displays a smectic phase between 192 °C and 213 °C.[10]



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Although other N-substituted pyrroles have previously been electropolymerized,[4,11] **1** failed to polymerize upon oxidation in either butyronitrile or dichloromethane containing 0.1 M tetrabutylammonium perchlorate. A cyclic voltammogram of a 0.05 M solution of **1** (not shown) failed to show any polymer growth upon repeated anodic cycling from 0 to +1.5 V (in dichloromethane) or from 0 to +1.7 V (in butyronitrile) (both vs. SSCE).

In contrast, a cyclic voltammogram of a 0.05 M solution of **5** containing 0.1M tetrabutylammonium perchlorate in acetonitrile showed smooth polymer growth upon repeated anodic cycling from 0 to +1.0 V (vs. SSCE), Figure 1. Thiophenes substituted with aryl groups at the 3-position electropolymerize into conducting polymer films.[12] No evidence for anisotropy was evident, however, in the resulting film when viewed through a cross-polarized microscope at temperatures up to 300 °C.

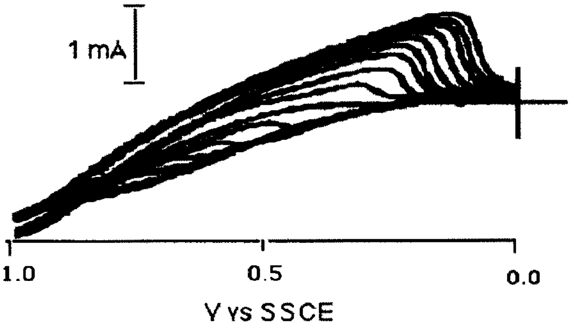

Figure 1. Superimposed successive cyclic voltametric scans of **5** on platinum foil as a 0.05 M solution in acetonitrile containing 0.1 M tetrabutylammonium perchlorate at room temperature. Scan rate: 100 mV / sec. Successive scans are shown as increasing oxidation and reduction currents.

EXPERIMENTAL SECTION

4-pyrrole-4'-pentylbiphenyl 1: 2,5-dimethoxytetrahydrofuran (0.55 mL, 4.0 mmol), 4-amino-4'-pentylbiphenyl 2[5] (1.0 g, 4 mmol), and 10 mL glacial acetic acid were placed in a 25 mL flask fitted with a reflux condenser and placed under dry nitrogen. The mixture was heated to reflux for 6 h. The mixture, having been cooled, was poured into 50 mL water, extracted with benzene, separated, and dried over anhyd. $MgSO_4$. The solvent was removed under reduced pressure and the crude solution was recrystallyzed from hexane to yield a cream colored powder of **1**, 0.75 g, 52%.

4-acetanilido-4'-pentanoylbiphenyl 4. m.p. 204-207 °C. ^{1}H NMR ($CDCl_3$): δ 8.00 (d, J= 8.3 Hz, 2H), 7.60 (m, 6H), 7.38 (s, 1H), 3.00 (t, J = 7.4 Hz, 2H), 2.20 (s, 3H), 1.70 (m, 2H), 1.40 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 200.2, 168.3, 144.8, 138.0, 135.7, 135.6, 128.7, 127.8, 126.79, 120.1, 35.4, 26.6, 24.7, 22.5, 13.9. IR (cm^{-1}): 3200 (s), 2955-2750 (s), 1680 (vs), 1600, 1510-1480, 809 (vs). HRMS, m/e calc. for $C_{19}H_{22}NO_2$: 296.165719; found: 296.165054. Elemental Analysis, calc. for $C_{19}H_{22}NO_2$: C 77.26% H 7.17% N 4.74%, found: C 76.76% H 7.16% N 4.72%.

4-amino-4'-pentylbiphenyl 2. ^{1}H NMR ($CDCl_3$) δ 7.31 (m, 4H), 7.12 (dd, J= 3.0 Hz, J'= 8.8 Hz, 2H), 6.65 (dd, J= 1.0 Hz, J'= 5.0 Hz, 2H), 3.60 (br s, 2H), 2.52 (t, 2H), 1.51 (m, 2H), 1.22 (m, 4H), 0.81 (t, J= 4.4 Hz, 3H). ^{13}C ($CDCl_3$): δ 145.5, 141.0, 138.5, 131.7, 128.7, 127.8, 126.2, 115.4, 35.5, 31.6, 31.2, 22.6, 14.0.

4-pyrrole-4'-pentylbiphenyl 1. mp 213-215 °C. ^{1}H NMR (CD_2Cl_2): δ 7.61 (d, J= 8.6 Hz, 2H), 7.48 (d, J= 8.1 Hz, 2H), 7.42 (d, J= 8.6 Hz, 2H), 7.22 (d, J= 8.1 Hz, 2H), 7.10 (t, J=2.1 Hz, 2H), 6.29 (t, J=2.1 Hz, 2H), 1.64 (m, 2H), 2.63 (t, J= 7.5 Hz, 2H), 1.33 (m, 4H), 0.89 (t, J= 4.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 142.3, 139.7, 138.5, 137.5, 128.9, 128.0, 126.7, 120.7, 119.3, 110.4, 35.6, 31.6, 31.2, 22.6, 14.0. IR (cm^{-1}): 3141-3029 (w), 2955-2859 (s), 1688, 1503 (m), 1458(m), 1406(m), 809 (vs). HRMS (m/e): calc. for $C_{21}H_{23}N$, 289.183050; found: 289.182919.

3-(4-pentylphenyl)thiophene 5: In a dry 250 mL three-neck flask fitted with a gas line, thermometer, and a rubber septum, 3-bromothiophene (2.4 mL, 0.026 mol) was dissolved in 30 mL of anhydrous ether. The solution was cooled to -78 °C and t-butyllithium (1.7 M, 46.2 mL) was added slowly via syringe. The mixture is stirred at -78°C for 90 min. The solution having been warmed to rt, $ZnBr_2$ in ether (1.0 M, 26.0 mL) was added via syringe and the resulting solution was stirred for 30 min. In a dry 250 mL round bottom flask, 4-iodopentylbenzene,[7] 100 mL dry THF, and 100 mg tetrakis(triphenylphoshine)palladium(0) were mixed. The contents of this flask were added to the thiophene mixture by cannula. The resulting mixture was stirred for 48 h at rt under Ar. The reaction mixture was then poured over a mixture of cold diethyl ether (100 mL) and 3N HCl (150 mL). The aqueous layer was separated and extracted twice with ether. The combined organic extracts were washed with sat. $NaHCO_3$ and dried over anhyd. $MgSO_4$. The ethereal solution was then passed through a plug of silica gel and the solvent was removed under reduced pressure. The crude product was taken up in hexane and passed through a plug of silica gel. The solvent was removed under reduced pressure. The crude product was recrystallized from methanol/H_2O to yield 2.3g (39%) of a waxy solid.

3-(4-pentylphenyl) thiophene 5. mp 51.0-55.0 °C. ^{1}H NMR ($CDCl_3$): δ 7.49 (m, 3H), 7.36 (m, 2H), 7.19 (d, J= 8.0 Hz, 2H), 2.59 (t, 2H, J= 7.6 Hz), 1.54 (m, 2H), 1.31 (m, 4H), 0.88 (t, 3H, J= 6.7 Hz). ^{13}C

NMR ($CDCl_3$): δ 142.3, 142.1, 142.0, 133.3, 128.8, 126.3, 120.3, 126.0, 35.6, 31.5, 31.1, 22.6, 14.0. IR (cm^{-1}): 3102 (w), 2954-2856 (s), 1466(m), 1201(m), 1087 (m), 841 (m). HRMS (m/e): calc. for $C_{15}H_{18}S$: 230.112923; found: 230.113515.

The temperature and enthalpy of phase transitions of the compounds and mixtures used in this study were measured on a Perkin-Elmer DSC-2 differential scanning calorimeter. Optical textures were observed with a Leitz Laborlux D cross-polarized optical microscope equipped with a hot stage and a thermocouple.

All electrochemical measurements were performed with a PAR 173 potentiostat with a Model 179 coulometer. Cyclic voltammograms were recorded on a Houston Instruments 2000 x-y recorder. Electrochemistry was performed at a doped indium-tin oxide (ITO) electrode (Delta Technologies) in a standard three electrode arrangement verses a saturated sodium chloride reference electrode. Electrolytic quality tetrabutylammonium perchlorate (Fluka) and spectroscopic grade dichloromethane (Baker), butyronitrile (Aldrich) and acetonitrile (Burdock and Jackson) were used as received.

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