A Direct Synthesis of Indolocarbazoles *via* New Dinitroterphenyl Precursors

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The two indolocarbazoles **2** and **4** were synthesized *via* the reductive ring closure of dinitrodiphenylbenzenes with triethylphosphite as reducing agent in a high boiling solvent. The electrochemical behaviour of the title systems is discussed.

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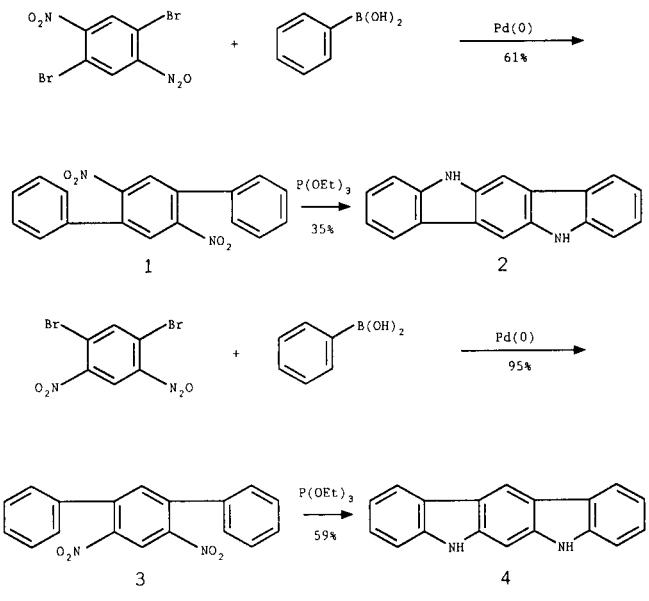
Although the syntheses of all five possible isomeric indolocarbazoles have already been published, up to now the procedures used are quite tedious and often give only low yields [1-4]. As part of our continuing efforts toward the design of new donors for electrically conducting charge-transfer complexes [5-7] we have worked out a straightforward two-step synthesis for two of these isomers, namely the 5,11-dihydroindolo[3,2-*b*]carbazole **2** and the 5,7-dihydroindolo[2,3-*b*]carbazole **4**. 2',5'-Dinitro-1,1':4',1''-terphenyl **1** [8] is readily available by Pd(0)-catalyzed coupling of phenylboronic acid with 1,4-dibromo-2,5-dinitrobenzene [9] in a toluene-water mixture. Reaction of boronic acid with 1,3-dibromo-4,6-dinitrobenzene [10] gives the corresponding 2',4'-dinitro-1,1':5',1''-terphenyl **3** [8] in nearly quantitative yield. It appears that Cadogans carbazol synthesis *via* reductive ring closure of 2-nitrobiphenyls [11] can also be applied to the terphenyl derivatives **1** and **3** described above. Thus, reaction of 2',5'-dinitro-1,1':4',1''-terphenyl **1** with triethylphosphite in *tert*-butylbenzene provides a 35% yield of 5,11-dihydroindolo[3,2-*b*]carbazole **2** in a two-fold ring closure, while the analogous reaction of 2',4'-dinitro-1,1':5',1''-terphenyl with triethylphosphite gives 5,7-dihydroindolo[2,3-*b*]carbazole **4** in 59% yield.

Scheme 1



The electrochemical behaviour of compounds **1**, **3** and **4** is studied by cyclic voltammetry [12]. The first reduction potential for the dinitro compound **1** is shifted by 1.6 V to more positive values as compared to the terphenyl **5** [13]. This significant shift is due to the strong inductive and mesomeric effect of the nitro substituents stabilizing the anionic species. As is demonstrated in Figure 1, the reduction behaviour of the two isoelectronic compounds **1** and **3** differs markedly; in particular the potential difference between the first and second reduction step for compound **3** (400 mV) is much larger than for **1** (120 mV). The dianion is easily stabilized by the *para*-nitro substituted system **1** as can be verified by invoking the resonance structure **6**. No such stabilization is possible for the *meta*-substituted compound **3**. Unfortunately the electrochemical oxidation of 5,7-dihydroindolo[2,3-*b*]carbazole in dichloromethane is accompanied by the product adsorption on the gold working electrode. This leads to peak broadening, which renders an exact determination of oxidation potential difficult. The approximated values are given in Table 1.

Table 1

Cyclic Voltammetric Data for Reduction and Oxidation

Compound	$E^1_{1/2}$/V	$E^2_{1/2}$/V
Reduction (in THF, with $TBAPF_6$)		
1	-1.04	-1.16
3	-1.18	-1.58
5	-2.65	-2.85
Oxidation (in dichloromethane, with $TBAPF_6$)		
4	+0.75	+1.3

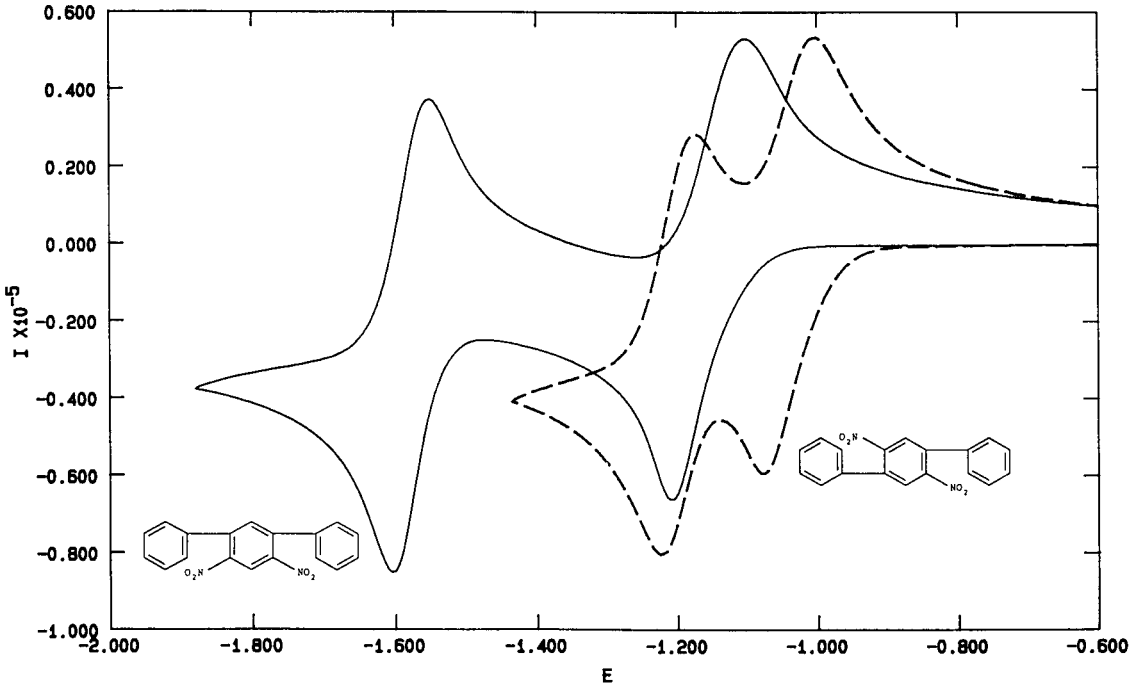
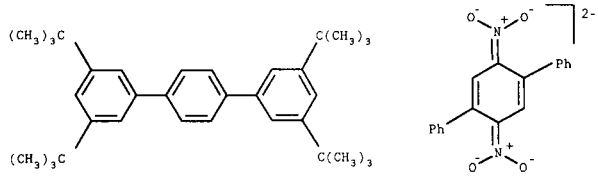


Figure 1. Cyclovoltammetric reduction (THF, $TBAPF_6$) of **1** (dashed line) and **3** (solid line).



5

6

EXPERIMENTAL

The ^{1}H- and ^{13}C-nmr spectral data were obtained on a Varian Gemini 200 spectrometer. The molecular weights were obtained using a VG Trio-2000 mass spectrometer.

2',5'-Dinitro-1,1':4',1''-terphenyl (**1**).

A mixture of 1,4-dibromo-2,5-dinitrobenzene (3 g, 9.20 mmoles), phenylboronic acid (4.5 g, 36.6 mmoles), sodium carbonate (9 g, 84.9 mmoles), water (50 ml) and toluene (50 ml) is refluxed under an argon atmosphere and a solution of tetrakis(triphenylphosphino)palladium(0) (130 mg, 0.112 mmole) in toluene (50 ml) is added rapidly *via* syringe. After refluxing for 1 day, the organic layer is separated while hot and dried over magnesium sulfate. The solvent is evaporated and the crude product is recrystallized from dimethyl sulfoxide to give **1** as slightly yellow crystals (1.8 g, 61%), mp 215°; ^{1}H-nmr (deuteriochloroform): δ 7.91 (s, 2H), 7.49 (m, 6H), 7.40 (m, 4H); ^{13}C-nmr (DMSO-d_6): δ 150.31, 135.34, 134.71, 129.49, 129.30, 128.16, 127.36; ms: (EI, 70 eV) m/z 320 (M^+).

Anal. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.74. Found: C, 67.72; H, 3.66; N, 8.93.

2',4'-Dinitro-1,1':5',1''-Terphenyl (**3**).

2',4'-Dinitro-1,1':5',1''-terphenyl (**3**) was prepared similarly as (**1**) using 1,3-dibromo-4,6-dinitrobenzene (3 g, 9.20 mmoles) as dibromo component. Recrystallisation from ethanol yielded yellow needles (2.8 g, 95%), mp 149°; ^{1}H-nmr (deuteriochloroform): δ 8.45 (s, 1H), 7.58 (s, 1H), 7.49 (m, 6H), 7.40 (m, 4H); ^{13}C-nmr (DMSO-d_6): δ 147.49, 139.08, 135.52, 135.35, 129.45, 129.13, 128.22, 121.06; ms: (EI, 70 eV) m/z 320 (M^+).

Anal. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.74. Found: C, 67.44; H, 3.49; N, 9.02.

5,11-Dihydroindolo[3,2-*b*]carbazole (**2**).

A solution of **1** (1 g, 3.12 mmoles) and triethylphosphite (2.1 g, 12.6 mmoles) in 20 ml *tert*-butylbenzene is refluxed for 2 days under a continous stream of argon. The solvent is distilled off at reduced pressure (2 mbar, 180° oil bath). Ethanol (5 ml) and *n*-hexane (5 ml) are added to the dark residue, causing the precipitation of a white solid. The flask is then stored in a refrigerator for several days and the precipitated solid is recovered by filtration. Refluxing with ethanol followed by filtration yields a yellow, amorphous powder (280 mg, 35%), mp >300°; ^{1}H-nmr (DMSO-d_6): δ 10.98 (s, 2H), 8.20 (d, 2H), 8.12 (s, 2H), 7.41 (m, 4H), 7.14 (t, 2H); ^{13}C-nmr (DMSO-d_6): δ 141.11, 135.39, 125.69, 122.94, 122.90, 120.43, 117.90, 110.75, 100.73; ms: (EI, 70 eV) m/z 256 (M^+).

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 84.71; H, 4.39; N, 10.82.

5,7-Dihydroindolo[2,3-*b*]carbazole (**4**).

Using the procedure described for **2**, 5,7-dihydroindolo[2,3-*b*]-carbazole (**4**) is prepared from 2',4'-dinitro-1,1':5',1''-terphenyl (**3**) (1 g, 3.12 mmoles). An amorphous white solid precipitates (470

mg, 59%), mp > 300°; ^{1}H-nmr (DMSO-d_6): δ 11.06 (s, 2H), 8.82 (s, 1H), 8.17 (d, 2H), 7.39 (m, 5H), 7.19 (m, 2H); ^{13}C-nmr (DMSO-d_6): δ 140.67, 140.54, 124.63, 123.58, 119.52, 118.47, 117.55, 111.37, 110.50, 107.38; ms: (EI, 70 eV) m/z 256 (M^+).

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 84.81; H, 4.45; N, 11.22.

The cyclic voltammograms were obtained as described elsewhere [13]. The half-wave potentials of Table 1 are given *vs.* standard calomel electrode (SCE) at a scan rate of 100 mV/s and a temperature of 0°. Gold and platinum working electrodes were used. A silver wire was employed as a quasi-reference, and for calibration Cp_2Fe/Cp_2Fe^+ (Cp: η-cyclopentadienyl) as an internal standard (310 mV *vs.* SCE) was used.

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