Efficient Synthesis of 2,7-Dibromocarbazoles as Components for Electroactive Materials

Frank Dierschke, Andrew C. Grimsdale, Klaus Müllen*

Max-Planck-Institute for Polymer research, Ackermannweg 10, 55128 Mainz, Germany
Fax +49(6131)379350; E-mail: muellen@mpip-mainz.mpg.de

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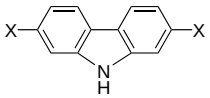
Abstract: An efficient two-step synthesis of 2,7-dibromocarbazole is reported. Nitration and Friedel–Crafts acylation of 2,7-dibromocarbazole proceed readily at the activated 3 and 6 positions to give new multifunctionalised carbazoles, which are of interest as monomers for new electrically active organic materials.

Key words: carbazole, heterocycles, electrophilic aromatic substitution, polymers, conjugation

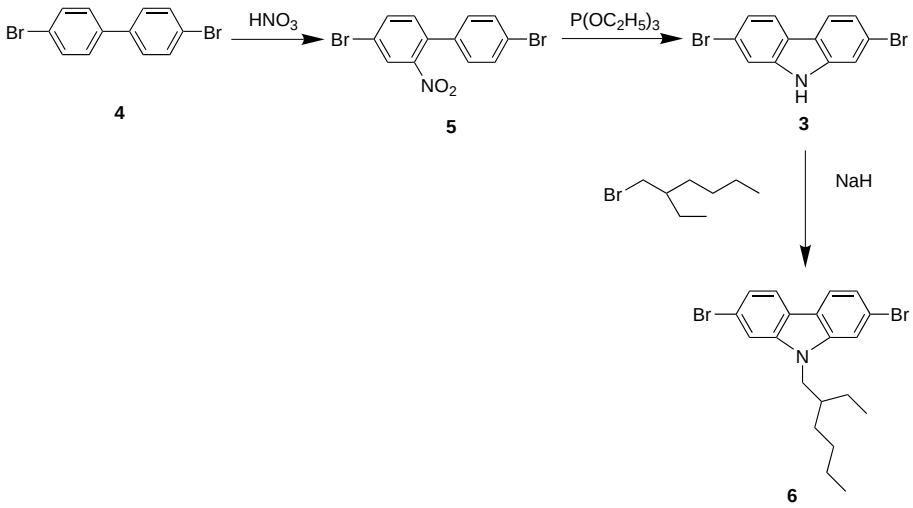
Conjugated organic oligomers and polymers have become the subject of considerable academic and industrial research interest in recent years, due to their applications in electronic devices such as light-emitting diodes,[1] solar cells,[2] and field-effect transistors.[3] One class of material that has recently become of interest are polymers containing 2,7-carbazole units.[4] The preparation of such polymers requires 2,7-dihalocarbazole monomers. Leclerc and coworker[4a] have presented an efficient two-step synthesis of 2,7-dichlorocarbazole (**1**), but the other 2,7-dihalocarbazoles (**2**, **3** in Figure 1)[4,5] are currently available only via inefficient multistep syntheses. As dibromoarenes are generally the preferred monomers for preparation of conjugated polymers and oligomers due to their greater reactivity in organic coupling reactions, an efficient route to 2,7-dibromocarbazole is thus desirable. The ability to readily tune the physical, electronic, and optical properties of polycarbazoles by incorporation of suitable substituents is also an important goal of our research. We now report an efficient two-step synthesis of **3**, and of derivatives containing groups at the 3- and 6-positions, which could be incorporated into conjugated materials in order to optimise their properties.



1 X = Cl
2 X = I
3 X = Br

Figure 1 2,7-Dihalocarbazoles **1**–**3**

The starting material for our synthesis was the commercially available 4,4′-dibromobiphenyl (**4**). Nitration with concentrated nitric acid gave the 2-nitro compound **5** in 91% yield (Scheme 1). The melting point is in agreement with the literature,[6] and distinctly different from that of the isomer and other dinitrated products. A reductive Cadogan ring-closure[7] then produced the carbazole **3** in 56% yield. In order to have good solubility for the derived materials, a solubilising group was attached in 96% yield by



4 **5** **3** **6**

Scheme 1

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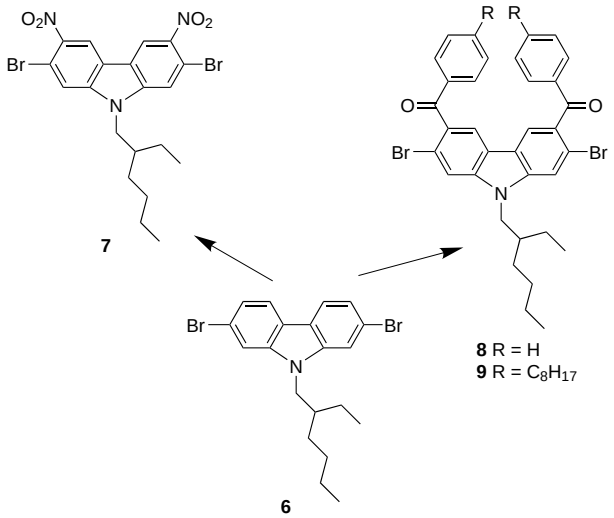
N-alkylation with 2-ethylbromohexane in the presence of sodium hydride to give **6** as a precursor monomer for soluble polymers and oligomers. Our procedures for the last two steps are adapted from the procedures used to make the corresponding dichlorocarbazoles.[4a]

Due to the strong electron-donating effect of the ring nitrogen, the 3- and 6-positions in carbazole are strongly activated towards electrophilic substitution. Provided the bromine groups do not too greatly deactivate the ring, substitution of **6** thus offers a possiblility to incorporate substituents onto 2,7-carbazole polymers which could improve their solubility, phase-forming and/or optical and electronic properties. We accordingly studied the reactivity of **6** towards electrophiles (Scheme 2). Nitration with HNO_3 gave the dinitro compound **7** in 58% yield. Such molecules with electron-accepting groups *para* to electron-donating groups are well known to show second-order nonlinear optical properties, so this may provide a route to polymers with such properties. Friedel–Crafts acylation with benzoyl anhydride and $AlCl_3$ proceeded smoothly to afford the dibenzoylcarbazole **8** in 76% yield. Addition of 4-octylbenzoyl chloride under the similar conditions gave **9** (75%) whose alkyl substituents may be expected to increase the solubility of materials incorporating it. By contrast alkylation with various alkyl halides under the same conditions did not proceed. The preparation of the 3,6-dialkyl materials would therefore require acylation followed by reduction. The synthesis of polymers containing **7**–**9** and investigation of their properties will be reported separately.



Scheme 2

All starting compounds were used as received from commercial sources without further purifications. Column chromatography was carried out on silica gel (grade 60, mesh size 230–400, Merck). ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 or Bruker AMX 300 spectrometer with the use of the solvent proton or carbon signal as internal standard. Melting points were determined on a Büchi hot-stage apparatus and are not corrected. FD Mass spectra were obtained on a VG Instrument ZAB 2-SE-FPD. Elemental analyses were carried out on a Foss Heraeus Vario EL analyser.

4,4′-Dibromo-2-nitrobiphenyl (5)

To a solution of 4,4′-dibromobiphenyl (**4**; 20 g, 0.064 mol) in glacial AcOH (300 mL) at 100 °C was added slowly a mixture of fuming HNO_3 (100%, 92.5 mL) and H_2O (7.5 mL). On heating the reaction mixture for 30 min at 100 °C, the initially formed precipitate redissolved. The solution was cooled down and the resulting yellow paste was collected by filtration. Recrystallisation from EtOH afforded the title compound as a yellow solid (21.52 g, 91%); mp 125–127 °C [Lit.[7] mp 124 °C].

^1H NMR (250 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 1.9 Hz, 2 H), 8.29 (d, *J* = 8.53 Hz, 2 H), 8.18 (dd, *J* = 8.83, 1.88 Hz, 2 H).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 149.24, 135.54, 135.27, 134.10, 133.00, 132.01, 129.38, 127.24, 123.04, 121.81.

MS: *m*/*z* = 356.9 [M^+] (calcd 357.00).

2,7-Dibromocarbazole (3)

A mixture of compound **5** (20.77 g, 58.2 mmol) and triethyl phosphite (75 mL) was heated under reflux for 18 h in an inert atmosphere. The excess of triethyl phosphite was distilled off and the product was purified by column chromatography (5–20% EtOAc in hexane) to provide 10.6 g of the title compound as a white solid (56%);

mp 236–238 °C [Lit.[5] mp 233–234 °C].

^1H NMR (250 MHz, acetone-d_6): δ = 10.59 (br s, 1 H, NH), 8.07 (d, *J* = 8.53 Hz, 2 H), 7.72 (d, *J* = 1.58 Hz, 2 H), 7.35 (dd, *J* = 1.58, 8.53 Hz, 2 H).

^{13}C NMR (75.46 MHz, acetone-d_6): δ = 141.97, 123.28, 122.58, 122.46, 119.93, 114.87.

MS: *m*/*z* = 325.1 [M^+] (calcd 324.02).

2,7-Dibromo-*N*-(2-ethylhexyl)carbazole (6)

To a mixture of compound **3** (10 g, 31 mmol) and anyd DMF (100 mL) was added slowly NaH (1.73 g, 60% w/w dispersion in mineral oil, 43 mmol). After 30 min, 2-ethylhexyl bromide (7.13 mL, 40 mmol) was added and the solution was stirred for 18 h under argon. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The organic fractions were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The product was purified by column chromatography (10% EtOAc in hexane) to give the title compound as a white solid (12.9 g, 96%); mp 105–108 °C.

^1H NMR (250 MHz, CD_2Cl_2): δ = 7.93 (d, *J* = 8.53 Hz, 2 H), 7.55 (d, *J* = 1.58 Hz, 2 H), 7.35 (dd, *J* = 1.58, 8.22 Hz, 2 H), 4.09 (m, 2 H, NCH_2), 2.02 (m, 1 H, CH), 1.31(br m, 8 H, alkyl), 0.90 (m, 6 H, 2 CH_3).

^{13}C NMR (62.89 MHz, CD_2Cl_2): δ = 142.29, 122.77, 121.79, 121.59, 119.91, 112.76, 48.09, 39.49, 31.10, 28.92, 24.67, 23.39, 14.12, 11.01.

MS: *m*/*z* = 437.4 [M^+] (calcd 437.22).

Anal. Calcd for $C_{20}H_{23}Br_2N$: C, 54.94; H, 5.30; N, 3.20. Found: C, 54.82; H, 5.42; N, 3.13.

2,7-Dibromo-*N*-(2-ethylhexyl)-3,6-dinitrocarbazole (7)

Compound **6** (1.5 g, 3.43 mmol) was taken in glacial AcOH (7 mL) and heated to 80 °C. Then HNO_3 (1.3 mL, 92.5%) was added and the temperature was raised to 100 °C. After ca.1 h, the crude reaction mixture was poured into H_2O and extracted with CH_2Cl_2. The combined organic fractions were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was first subjected to column chromatography (10% EtOAc in hexane) and then fur-

ther purified by recrystallisation from EtOH to give the title compound as a yellow solid (0.9 g, 58%); mp 188–191 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.72 (s, 2 H), 7.71 (s, 2 H), 4.17 (m, 2 H, NCH_2), 1.99 (m, 1 H, CH), 1.30 (br m, 8 H, alkyl), 0.93 (m, 6 H, 2 CH_3).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 143.72, 143.14, 120.92, 119.49, 115.92, 113.84, 48.45, 39.28, 30.65, 28.42, 24.26, 22.91, 13.95, 10.79.

MS: *m*/*z* = 526.2 [M^+] (calcd 527.22).

Anal. Calcd for $C_{20}H_{21}Br_2N_3O_4$: C, 45.56; H, 4.01; N, 7.97. Found: C, 45.66; H, 3.96; N, 7.89.

3,6-Dibenzoyl-2,7-dibromo-*N*-(2-ethylhexyl)carbazole (8)

To a mixture of compound **6** (1 g, 2.28 mmol) and $AlCl_3$ (3.4 g, 25.5 mmol) in nitrobenzene (14 mL) was added benzoic anhydride (1.54 g, 6.8 mmol) at 0 °C. The reaction mixture was stirred for 8 h and then quenched with ice. The inorganic precipitate was dissolved in 2 M HCl and the product was extracted with Et_2O (3 × 50 mL). The combined organic fractions were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The product was first purified by column chromatography (20% EtOAc in hexane) and then recrystallisation from EtOAc to afford the title compound as a white solid (1.1 g, 76%); mp 201–203 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.99 (s, 2 H), 7.83 (d, *J* = 7.26 Hz, 4 H), 7.67 (s, 2 H), 7.57 (m, 2 H), 7.54 (t, *J* = 7.26 Hz, 4 H), 4.15 (m, 2 H, NCH_2), 2.06 (m, 1 H, CH), 1.35 (br m, 8 H, alkyl), 0.92 (m, 6 H, 2 CH_3).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 195.92, 142.77, 137.12, 133.38, 131.94, 130.34, 128.52, 122.14, 120.95, 118.18, 114.38, 48.05, 39.26, 30.75, 28.53, 24.33, 23.00, 13.99, 10.88.

MS: *m*/*z* = 645.1 [M^+] (calcd 645.44).

Anal. Calcd for $C_{34}H_{31}Br_2NO_2$: C, 63.27; H, 4.89; N, 2.17. Found: C, 63.28; H, 4.73; N, 2.19.

2,7-Dibromo-*N*-(2-ethylhexyl)-3,6-bis(4-octylbenzoyl)carbazole (9)

To a mixture of compound **6** (1 g, 2.28 mmol) and $AlCl_3$ (0.73 g, 5.5 mmol) in 1,2-dichloroethane (3 mL) was added slowly, 4-octylbenzoyl chloride (1.35 g, 4.8 mmol) at r.t. The mixture was stirred for 4 h at 50 °C and then quenched with ice. The inorganic precipitate was dissolved in 2 M HCl (2 M) and the product was extracted with CH_2Cl_2. The organic fractions were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The product was purified by column chromatography (10% EtOAc in hexane) to provide **9** as a yellowish solid (1.6 g, 75%); mp 90–93 °C.

^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.00 (s, 2 H), 7.75 (d, *J* = 7.58 Hz, 6 H), 7.29 (d, *J* = 8.21 Hz, 4 H), 4.23 (m, 2 H, NCH_2), 2.68 (t, *J* = 7.7 Hz, 4 H, ArCH_2), 2.13 (m, 1 H, CH), 1.66–1.27(br m, 42 H, alkyl), 0.92 (m, 12 H, 4 CH_3).

^{13}C NMR (75.47 MHz, CD_2Cl_2): δ = 196.05, 150.26, 143.51, 135.61, 132.95, 131.18, 129.40, 122.57, 121.77, 118.60, 115.18, 48.86, 40.05, 36.84, 32.72, 31.92, 31.51, 30.41, 30.37, 30.25, 30.13, 29.36, 25.14, 23.85, 23.49, 14.71, 14.62, 11.49.

MS: *m*/*z* = 925.00 [M^+] (calcd 925.98).

Anal. Calcd for $C_{54}H_{71}Br_2NO_2$: C, 70.04; H, 7.73; N, 1.51. Found: C, 69.96; H, 7.71; N, 1.45.

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