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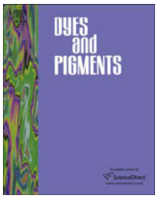

The copper(I) iodide accelerated synthesis of mono- and bisbenzyl substituted 1- and 2-aminoanthraquinones

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ABSTRACT

A series of novel, monobenzyl substituted, 1-aminoanthraquinones, monobenzyl substituted 2-aminoanthraquinones and bisbenzyl substituted 2-aminoanthraquinones were synthesized via the benzylation of 1-/2-aminoanthraquinone, respectively. The benzyl substituted aminoanthraquinone derivatives were characterized by NMR, IR spectroscopy and mass spectrometry; their electrochemical properties were investigated using cyclic voltammogram and their spectrochemical properties were determined using UV–vis spectroscopy in dichloromethane. Copper(I) iodide, in conjunction with 1,10-phenanthroline as ligand, accelerates the reaction rate and enhances reaction yields by ∼30%. The benzyl substituted aminoanthraquinone derivatives are redox active and potentially useful as electrochromic materials as well as for biological and pharmaceutical studies.

1. Introduction

Amino derivatives of anthraquinone have several applications in academic research and industry. Aminoanthraquinones have for a long time been used as dyes, while in recent decades aminoanthraquinones have been widely used in coordination chemistry, since their complexes possess interesting physical properties and have found applications as sensors [1], photo and redox-switchable molecules and multielectron catalysts [2–5], and aminoanthraquinones are known to exhibit quite potent anticancer activities [6]. Aminoanthraquinone derivatives are also efficient and interesting electrochromic materials [7]. Amino-substituted anthraquinones are important in the dye industry, functional materials, biology and pharmaceutical chemistry [6].

2. Experimental

2.1. General

All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. All chemicals and reagents, unless otherwise specified, were purchased from Aldrich, Acros, and TCI Chemical Co. and used as received. All the solvents were further purified before use. All new compounds were characterized by NMR, IR spectroscopy and mass spectrometry. ^{1}H NMR spectra were measured on a Bruker AV300 (300 MHz) spectrometer at the ambient temperature with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded on Bruker AV300 (75 MHz) spectrometer at the ambient temperature and chemical shifts were recorded in parts per million from the solvent resonance employed as the internal standard. Infrared spectroscopic measurements were performed in the range 4000–400 cm^{-1} on a Bruker Tensor 27 FTIR spectrophotometer. Atmospheric pressure chemical ionization mass spectra were obtained on a Bruker HCT Mass Spectrometer. UV spectra were performed on a Unico UV-4802H UV–vis spectrophotometer connected to a computer. Cyclic voltammetry (CV) was carried out on a CHI 650B electrochemical workstation at a scan rate of 100 mV/s with platinum wire and saturated calomel electrodes (SCEs) as the counter and reference electrodes, respectively. A platinum disk (a radius of 4 mm) was used as the working electrode. The solutions were made in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and were degassed with argon prior to electrochemical work.

2.2. General procedure for the synthesis of compounds **3**

To a stirred mixture of **1** (0.22 g, 1.0 mmol), **2** (2.2 mmol), copper(I) iodide (0.019 g, 0.1 mmol), 1,10-phenanthroline (0.04 g, 0.2 mmol) and potassium carbonate (0.27 g, 2.0 mmol) in toluene

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(10 mL) was added a sample of potassium iodide (0.40 g, 2.2 mmol). Argon was bubbled through the ensuing mixture for 15 min after which it was vigorously stirred at 80 °C for 5 h under argon. After the mixture was cooled to room temperature, it was diluted with chloroform and washed with water (3 × 10 mL). The organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified using silica gel column chromatography, eluting with hexane/methylene chloride = 1/1.

2.2.1. *N-Benzyl-1-aminoanthraquinone (**3a**)*

Yield: (0.26 g) 83%. Red powder. M.p.: 197–198 °C (reported [10] 194–195 °C). δ_H (300 MHz, $CDCl_3$): 10.1 (s, NH), 8.24–8.30 (m, 2Ar-H), 7.70–7.80 (m, 2Ar-H), 7.63 (d, $J = 7.3$, Ar-H), 7.50 (m, Ar-H), 7.34–7.39 (m, 4Ar-H), 7.28–7.32 (m, Ar-H), 7.03 (d, $J = 8.3$, Ar-H), 4.61 (s, CH_2). δ_C (75 MHz, $CDCl_3$): 185.3, 183.7, 151.5, 138.0, 135.3, 135.0, 134.7, 133.9, 133.0, 128.9, 127.5, 127.1, 126.8, 118.2, 116.1, 113.5, 47.0. FT-IR (KBr, cm^{-1}): 3281(m), 3066(w), 3026(w), 2932(w), 2861(w), 1667(s), 1629(s), 1591(m), 1565(m), 1498(m), 1459(m), 1292(s), 1266(s), 708(s). MS (m/z): 313.1 (M^+).

2.2.2. *N-(4-Methylbenzyl)-1-aminoanthraquinone (**3b**)*

Yield: (0.28 g) 86%. Red powder. M.p.: 183–184 °C. δ_H (300 MHz, $CDCl_3$): 10.1 (s, NH), 8.20–8.30 (m, 2Ar-H), 7.65–7.78 (m, 2Ar-H), 7.62 (d, $J = 7.3$, Ar-H), 7.49 (m, Ar-H), 7.21 (dd, $J = 7.7$, 4Ar-H), 6.97 (d, $J = 8.2$, Ar-H), 4.50 (s, CH_2), 2.33 (s, CH_3). δ_C (75 MHz, $CDCl_3$): 185.2, 183.8, 151.6, 137.2, 135.4, 135.0, 134.9, 134.7, 134.2, 134.0, 133.0, 129.6, 129.2, 128.2, 127.3, 127.1, 126.8, 118.4, 116.1, 113.4, 46.8, 21.2. FT-IR (KBr, cm^{-1}): 3284(m), 3049(w), 2917(w), 2844(w), 1666(s), 1629(s), 1590(m), 1563(m), 1498(m), 1458(m), 1289(s), 1266(s), 705(s). MS (m/z): 327.1 (M^+).

2.2.3. *N-(4-Bromobenzyl)-1-aminoanthraquinone (**3c**)*

Yield: (0.27 g) 69%. Red powder. M.p.: 216–217 °C. δ_H (300 MHz, $CDCl_3$): 10.1 (s, NH), 8.24–8.30 (m, 2Ar-H), 7.70–7.82 (m, 2Ar-H), 7.63 (d, $J = 7.3$, Ar-H), 7.47–7.52 (m, 3Ar-H), 7.25–7.27 (m, 2Ar-H), 6.94 (d, $J = 8.5$, Ar-H), 4.56 (s, CH_2). δ_C (75 MHz, $CDCl_3$): 185.5, 183.6, 151.3, 137.1, 135.4, 134.9, 134.7, 134.1, 134.0, 133.5, 133.2, 133.0, 132.0, 128.7, 127.2, 126.8, 121.3, 118.1, 116.3, 113.7, 46.4. FT-IR (KBr, cm^{-1}): 3283(m), 2919(w), 2849(w), 1671(s), 1629(s), 1589(m), 1565(m), 1501(m), 1459(m), 1295(s), 1267(s), 703(s). MS (m/z): 391.0 (M^+).

2.2.4. *N-(4-Vinylbenzyl)-1-aminoanthraquinone (**3d**)*

Yield: (0.31 g) 91%. Red powder. M.p.: 198–199 °C. δ_H (300 MHz, $CDCl_3$): 10.1 (s, NH), 8.24–8.30 (m, 2Ar-H), 7.69–7.80 (m, 2Ar-H), 7.62 (d, $J = 7.5$, Ar-H), 7.49 (m, Ar-H), 7.38 (dd, $J_1 = 7.9$, $J_2 = 7.8$, 4Ar-H), 7.00 (d, $J = 8.2$, Ar-H), 6.71 (dd, $J_1 = 17.6$, $J_2 = 10.9$, $=CH$), 5.74 (d, $J = 17.6$, 1H, $=CH_2$), 5.25 (d, $J = 10.9$, 1H, $=CH_2$), 4.59 (s, CH_2). δ_C (75 MHz, $CDCl_3$): 185.3, 183.7, 151.5, 137.5, 136.9, 136.4, 135.3, 134.9, 134.7, 134.1, 133.9, 133.0, 127.2, 126.8, 126.7, 118.2, 116.1, 113.9, 113.5, 46.8. FT-IR (KBr, cm^{-1}): 3264(m), 3065(w), 3004(w), 2924(w), 2850(w), 1663(s), 1628(s), 1590(m), 1565(m), 1499(m), 1461(m), 1294(s), 1268(s), 706(s). MS (m/z): 339.1 (M^+).

2.3. *General procedure for the synthesis of compounds **5***

Argon was bubbled through a stirred mixture comprising **4** (0.65 g, 3.0 mmol), potassium iodide (0.17 g, 1.0 mmol), copper(I) iodide (0.019 g, 0.1 mmol), 1,10-phenanthroline (0.04 g, 0.2 mmol) and potassium carbonate (0.27 g, 2.0 mmol) in dioxane (10 mL) for 15 min. The mixture was maintained at 90 °C for 5 min, after which a degassed solution of **2** (1.0 mmol) in dioxane (5 mL) was added dropwise. The mixture was vigorously stirred at 90 °C for 10 h under argon; after the mixture had cooled to room temperature, it was diluted with chloroform and washed with water (3 × 10 mL). The organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by silica gel column chromatography, eluting with hexane/methylene chloride = 1/2.

2.3.1. *N-Benzyl-2-aminoanthraquinone (**5a**)*

Yield: (0.23 g) 73%. Orange powder. M.p.: 224–225 °C. δ_H (300 MHz, $CDCl_3$): 8.23–8.29 (m, 2Ar-H), 8.14 (d, $J = 8.5$, Ar-H), 7.69–7.78 (m, 2Ar-H), 7.43 (d, $J = 2.1$, Ar-H), 7.32–7.44 (m, 5Ar-H), 6.90 (dd, $J_1 = 8.5$, $J_2 = 2.1$, Ar-H), 4.89 (s, NH), 4.51 (s, CH_2). δ_C (75 MHz, $CDCl_3$): 183.9, 181.6, 152.5, 137.6, 135.4, 134.2, 134.0, 133.7, 133.1, 129.9, 128.9, 127.8, 127.5, 127.0, 126.9, 123.8, 117.2, 109.0, 47.7. FT-IR (KBr, cm^{-1}): 3052(w), 3026(w), 2922(w), 2853(w), 1669(s), 1647(s), 1589(m), 1571(m), 1494(m), 1450(m), 1328(s), 1290(s), 718(s). MS (m/z): 313.1 (M^+).

2.3.2. *N-(4-Methylbenzyl)-2-aminoanthraquinone (**5b**)*

Yield: (0.25 g) 76%. Orange powder. M.p.: 205–206 °C. δ_H (300 MHz, $CDCl_3$): 8.21–8.25 (m, 2Ar-H), 8.13 (d, $J = 8.6$, Ar-H), 7.70–7.74 (m, 2Ar-H), 7.42 (d, $J = 2.1$, Ar-H), 7.25 (d, $J = 7.6$, 2Ar-H), 7.17 (d, $J = 7.6$, 2Ar-H), 6.89 (dd, $J_1 = 8.6$, $J_2 = 2.1$, Ar-H), 4.83 (s, NH), 4.45 (s, CH_2), 2.34 (s, CH_3). δ_C (75 MHz, d_6-DMSO): 183.3, 180.1, 153.6, 136.1, 135.6, 134.7, 134.4, 133.7, 133.4, 133.0, 129.4, 129.1, 127.1, 126.4, 126.3, 121.3, 116.8, 108.4, 45.6, 20.6. FT-IR (KBr, cm^{-1}): 3068(w), 3021(w), 2917(w), 2856(w), 1668(s), 1629(s), 1590(m), 1512(m), 1441(m), 1332(s), 1291(s), 716(s). MS (m/z): 327.1 (M^+).

2.3.3. *N-(4-Bromobenzyl)-2-aminoanthraquinone (**5c**)*

Yield: (0.24 g) 61%. Orange powder. M.p.: 242–244 °C. δ_H (300 MHz, $CDCl_3$): 8.23–8.29 (m, 2Ar-H), 8.14 (d, $J = 8.5$, Ar-H), 7.72–7.78 (m, 2Ar-H), 7.49 (d, $J = 8.2$, 2Ar-H), 7.41 (d, $J = 2.2$, Ar-H), 7.25 (d, $J = 8.2$, 2Ar-H), 6.88 (dd, $J_1 = 8.5$, $J_2 = 2.2$, Ar-H), 4.86 (s, NH), 4.48 (s, CH_2). δ_C (75 MHz, d_6-DMSO): 183.2, 180.2, 153.4, 138.3, 134.7, 134.4, 133.7, 133.5, 133.0, 131.4, 129.4, 126.5, 126.4, 121.6, 120.1, 116.8, 108.5, 45.2. FT-IR (KBr, cm^{-1}): 3046(w), 2921(w), 1670(s), 1652(s), 1592(m), 1573(m), 1485(m), 1440(m), 1328(s), 1292(s), 714(s). MS (m/z): 391.0 (M^+).

2.3.4. *N-(4-Vinylbenzyl)-2-aminoanthraquinone (**5d**)*

Yield: (0.27 g) 80%. Orange powder. M.p.: 212–213 °C. δ_H (300 MHz, $CDCl_3$): 8.23–8.29 (m, 2Ar-H), 8.14 (d, $J = 8.5$, Ar-H), 7.69–7.77 (m, 2Ar-H), 7.41 (m, 3Ar-H), 7.33 (d, $J = 7.7$, 2Ar-H), 6.89 (dd, $J_1 = 8.5$, $J_2 = 2.3$, Ar-H), 6.71 (dd, $J_1 = 17.6$, $J_2 = 10.9$, $=CH$), 5.75 (d, $J = 17.6$, 1H, $=CH_2$), 5.26 (d, $J = 10.9$, 1H, $=CH_2$), 4.80 (s, NH), 4.50 (s, CH_2). δ_C (75 MHz, $CDCl_3$): 183.9, 181.6, 152.5, 137.3, 137.1, 136.2, 135.4, 134.2, 133.9, 133.6, 133.1, 129.9, 127.7, 126.9, 126.8, 126.7, 123.8, 117.2, 114.2, 109.1, 47.4. FT-IR (KBr, cm^{-1}): 3084(w), 3022(w), 3004(w), 2920(w), 2851(w), 1669(s), 1628(s), 1589(m), 1573(m), 1510(m), 1459(m), 1329(s), 1291(s), 715(s). MS (m/z): 339.1 (M^+).

2.4. *General procedure for the synthesis of compounds **6***

To a stirred mixture of **4** (0.22 g, 1.0 mmol), **2** (6.0 mmol), copper(I) iodide (0.019 g, 0.1 mmol), 1,10-phenanthroline (0.04 g, 0.2 mmol) and potassium carbonate (0.55 g, 4.0 mmol) in DMF (10 mL) was added a sample of potassium iodide (0.90 g, 6.0 mmol). Argon was bubbled through the ensuing mixture for 15 min after which it was vigorously stirred at 120 °C for 8 h under argon. After the mixture was cooled to room temperature, it was poured into water (50 mL). The precipitate was passed through a glass filter and dried in a vacuum desiccator. The crude product was purified by silica gel column chromatography, eluting with hexane/methylene chloride = 1/1.

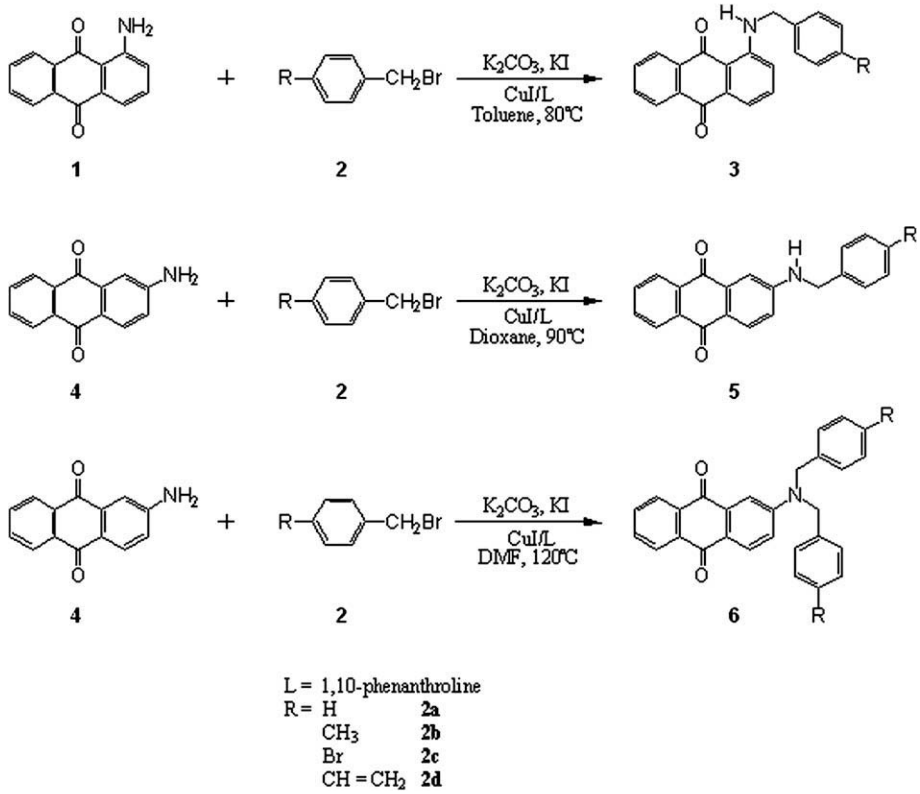

Fig. 1. Synthetic route of target molecules.

2.4.1. N,N-*Dibenzyl-2-aminoanthraquinone (**6a**)*

Yield: (0.32 g) 79%. Orange powder. M.p.: 146–147 °C (reported [11] 144.5–145.5 °C). δ_H (300 MHz, $CDCl_3$): 8.18–8.27 (m, 2Ar-H), 8.12 (d, $J = 8.8$, Ar-H), 7.66–7.76 (m, 2Ar-H), 7.62 (d, $J = 2.6$, Ar-H), 7.28–7.38 (m, 6Ar-H), 7.23 (d, $J = 7.1$, 4Ar-H), 7.01 (dd, $J_1 = 8.8$, $J_2 = 2.6$, Ar-H), 4.82 (s, $2CH_2$). δ_C (75 MHz, d_6-DMSO): 183.1, 180.3, 152.6, 137.4, 134.4, 133.6, 133.0, 129.3, 128.8, 127.2, 126.5, 126.4, 121.6, 117.0, 108.5, 54.3. FT-IR (KBr, cm^{-1}): 3378(s), 3059(w), 3025(w), 2921(w), 2852(w), 1669(s), 1644(s), 1592(m), 1567(m), 1489(m), 1452(m), 1327(s), 1297(s), 714(s). MS (*m*/*z*): 403.2 (M^+).

2.4.2. N,N-*Di(4-methylbenzyl)-2-aminoanthraquinone (**6b**)*

Yield: (0.35 g) 81%. Orange powder. M.p.: 163–165 °C. δ_H (300 MHz, d_6-DMSO): 8.07–8.13 (m, 2Ar-H), 7.95 (d, $J = 8.8$, Ar-H), 7.79–7.88 (m, 2Ar-H), 7.35 (d, $J = 2.2$, Ar-H), 7.17 (m, 9Ar-H), 4.86 (s, $2CH_2$), 2.27 (s, $2CH_3$). δ_C (75 MHz, d_6-DMSO): 183.2, 180.3, 152.7, 136.3, 134.5, 134.4, 134.3, 133.6, 133.5, 133.1, 129.3, 129.2, 126.5, 126.4, 121.5, 117.0, 108.5, 54.1, 20.7. FT-IR (KBr, cm^{-1}): 3328(s), 3059(w), 3027(w), 2919(w), 2849(w), 1666(s), 1641(s), 1584(m), 1563(m), 1461(m), 1326(s), 1286(s), 714(s). MS (*m*/*z*): 431.2 (M^+).

2.4.3. N,N-*Di(4-bromobenzyl)-2-aminoanthraquinone (**6c**)*

Yield: (0.37 g) 66%. Orange powder. M.p.: 182–183 °C. δ_H (300 MHz, d_6-DMSO): 8.08–8.14 (m, 2Ar-H), 7.99 (d, $J = 8.8$, Ar-H), 7.81–7.90 (m, 2Ar-H), 7.57 (d, $J = 8.2$, 4Ar-H), 7.32 (d, $J = 2.2$, Ar-H), 7.26 (d, $J = 8.2$, 4Ar-H), 7.15 (dd, $J_1 = 8.8$, $J_2 = 2.2$, Ar-H), 4.92 (s, $2CH_2$). δ_C (75 MHz, d_6-DMSO): 183.0, 180.3, 152.3, 136.9, 134.4, 134.3, 133.6, 133.5, 133.0, 131.6, 129.3, 128.7, 126.4, 126.3, 121.9, 120.1, 117.1, 108.5, 53.7. FT-IR (KBr, cm^{-1}): 3357(s), 3046(w), 2923(w), 2852(w), 1671(s), 1639(s), 1586(m), 1559(m), 1487(m), 1451(m), 1329(s), 1296(s), 720(s). MS (*m*/*z*): 559.0 (M^+).

2.4.4. N,N-*Di(4-vinylbenzyl)-2-aminoanthraquinone (**6d**)*

Yield: (0.40 g) 88%. Orange powder. M.p.: 179–180 °C. δ_H (300 MHz, $CDCl_3$): 8.19–8.26 (m, 2Ar-H), 8.12 (d, $J = 8.8$, Ar-H), 7.66–7.75 (m, 2Ar-H), 7.61 (d, $J = 2.3$, Ar-H), 7.39 (d, $J = 7.9$, 4Ar-H), 7.19 (d, $J = 7.9$, 4Ar-H), 7.00 (dd, $J_1 = 8.8$, $J_2 = 2.3$, Ar-H), 6.69 (dd, $J_1 = 17.6$, $J_2 = 10.9$, 2H, $=CH$), 5.73 (d, $J = 17.6$, 2H, $=CH_2$), 5.24 (d, $J = 10.9$, 2H, $=CH_2$), 4.79 (s, $2CH_2$). δ_C (75 MHz, $CDCl_3$): 183.9, 181.4, 153.2, 137.0, 136.2, 136.1, 135.2, 134.2, 133.9, 133.7, 133.0, 130.0, 126.9, 126.8, 126.7, 123.0, 116.6, 114.0, 109.0, 53.9. FT-IR (KBr, cm^{-1}): 3364(s), 3083(w), 3047(w), 3001(w), 2922(w), 2857(w), 1670(s), 1638(s), 1587(m), 1561(m), 1474(m), 1449(m), 1327(s), 1296(s), 719(s). MS (*m*/*z*): 455.2 (M^+).

3. Results and discussion

The preparation of mono benzyl- (**3a**) and bis benzyl- (**6a**) 1-aminoanthraquinones has been described [8–11] but these methods are not efficient and the yields of **3a** and **6a** were poor. Herein, a more efficient route for the synthesis of these compounds

Table 1
Benzylation of 1-aminoanthraquinone.

Entry	Benzyl bromide	Catalyst[a]	Reaction time, h	Product	Isolated yield, %
1	**2a**	KI/CuI/L	5	**3a**	83
2	**2a**	KI	18	**3a**	51
3	**2b**	KI/CuI/L	5	**3b**	86
4	**2b**	KI	18	**3b**	53
5	**2c**	KI/CuI/L	5	**3c**	69
6	**2c**	KI	18	**3c**	32
7	**2d**	KI/CuI/L	5	**3d**	91
8	**2d**	KI	18	**3d**	59

[a] L = 1,10-Phenanthroline.

Table 2
Monobenzylation of 2-aminoanthraquinone.

Entry	Benzyl bromide	Catalyst[a]	Reaction time, h	Product	Isolated yield, %
1	**2a**	KI/CuI/L	10	**5a**	73
2	**2a**	KI	24	**5a**	40
3	**2b**	KI/CuI/L	10	**5b**	76
4	**2b**	KI	24	**5b**	41
5	**2c**	KI/CuI/L	10	**5c**	61
6	**2c**	KI	24	**5c**	22
7	**2d**	KI/CuI/L	10	**5d**	80
8	**2d**	KI	24	**5d**	54

[a] L = 1,10-Phenanthroline.

Table 3
Bisbenzylation of 2-aminoanthraquinone.

Entry	Benzyl bromide	Catalyst[a]	Reaction time, h	Product	Isolated yield, %
1	**2a**	KI/CuI/L	8	**6a**	79
2	**2a**	KI	24	**6a**	49
3	**2b**	KI/CuI/L	8	**6b**	81
4	**2b**	KI	24	**6b**	52
5	**2c**	KI/CuI/L	8	**6c**	66
6	**2c**	KI	24	**6c**	31
7	**2d**	KI/CuI/L	8	**6d**	88
8	**2d**	KI	24	**6d**	55

[a] L = 1,10-Phenanthroline.

is reported. Moreover, series of novel aminoanthraquinone derivatives **3b**–**3d**, **5a**–**5d** and **6b**–**6d** were prepared via this method (Fig. 1).

It has been debated that the benzylation of neutral amines by benzyl halides is complicated from a synthetic point of view because of the possibility of multiple benzylation which can proceed to give the quaternary ammonium salt in the presence of excess benzyl halide [12], however, it is not true for aminoanthraquinones. The nucleophilicity of aminoanthraquinones is too weak owing to the two electron-attracting groups (carbonyl) attached to the amino substituted aromatic rings. So, the quaternary ammonium salt can be avoided and multiple benzylation can be controlled.

The synthetic procedure for all derivatives are outlined in Fig. 1. For 1-aminoanthraquinone, only monobenzyl substituted 1-aminoanthraquinones were produced as a consequence of the intramolecular hydrogen bonding between the 1-amino group and the C-10 carbonyl function. But for 2-aminoanthraquinone, mono- and bisbenzyl substituted 2-aminoanthraquinones can be both produced. Moreover, at higher applied temperature more bisbenzyl substituted 2-aminoanthraquinones are produced. So, during the synthesis of monobenzyl substituted 2-aminoanthraquinones, the temperature must be maintained under 100 °C. Meanwhile, the benzyl bromide **2** should be added dropwise and 2-aminoanthraquinone must be excess.

Copper(I) iodide is an efficient catalyst for Ullmann-type reactions [13,14]. Recently, CuI–phenanthroline system has been well used in amination reactions [15–17]. But it was first developed for the benzylation of aminoanthraquinones. As a result, the reactions were accelerated and products with higher yield were obtained (Tables 1–3).

Substituted benzyl bromides **2a**–**d** can strongly influence the activity of the reactions. Yields of **3d**, **5d** and **6d** are much higher than those of **3c**, **5c** and **6c**, respectively (Tables 1–3, entries 5–8). Furthermore, the electrochemical and spectrochemical properties of anthraquinone are tuned because the substituted groups extend the degree of conjugation of the anthraquinone nucleus.

The redox properties of **3**, **5** and **6** were investigated by CV in CH_2Cl_2 and TBAP as an electrolyte (Figs. 2–4). Reduction potentials were measured relative to the internal SCE. For all the aminoanthraquinone derivatives, two reduction waves were revealed, indicating the formation of stable radical anions and dianions, respectively. These observations are quite different from that of the unsubstituted anthraquinone which has only one redox peak under the same conditions. So, the broad CVs are specific to the substituted anthraquinones. These derivatives show different

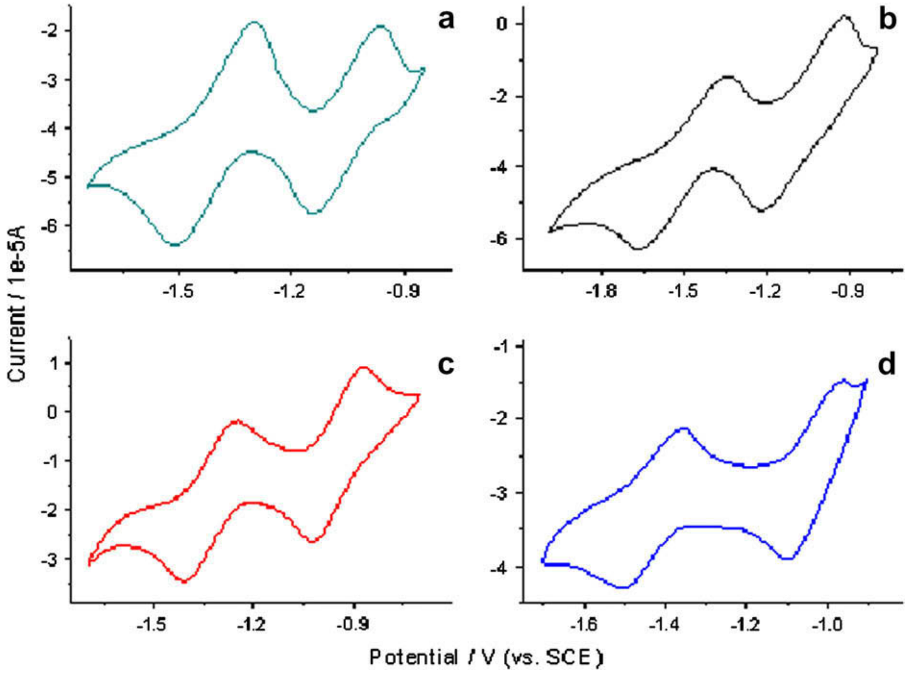

Fig. 2. Cyclic voltammetry of (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d** in CH_2Cl_2/TBAP (0.1 M) at room temperature, scan rate of 100 mV/s.

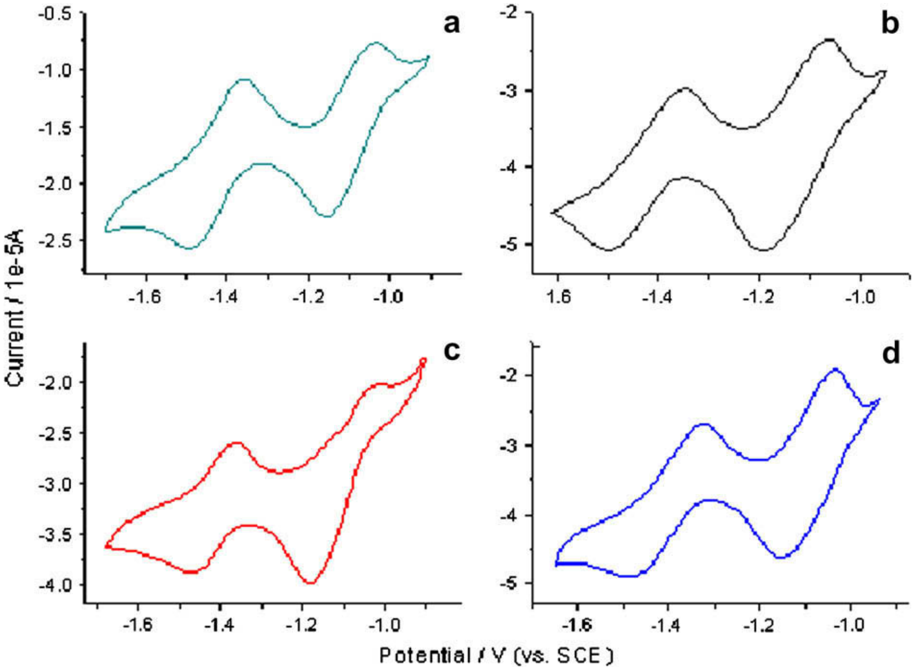

Fig. 3. Cyclic voltammetry of (a) **5a**, (b) **5b**, (c) **5c** and (d) **5d** in CH_2Cl_2/TBAP (0.1 M) at room temperature, scan rate of 100 mV/s.

reduction potentials just because of the different substituted groups of **2**. This result suggests that the electrochemical properties of aminoanthraquinones can be efficiently tuned by introducing different substituted groups.

The spectrochemical properties of **3**, **5** and **6** were determined by UV–vis in dichloromethane. Fig. 5 shows the UV–vis absorptions of **3**. The λ_{max} values of UV–vis spectra for **5** and **6** are listed in Table 4. The broad absorption peaks of **3** at about 499 nm, **5** at about 442 nm and **6** at about 458 nm correspond to electronic transition from the ground state to the intramolecular charge transfer state. The strong absorption peaks of **3** at about 315 nm, **5** at about 311 nm with a shoulder absorption peak at about 329 nm and **6** at about 312 nm with double shoulder absorption peaks at about 336 nm and 350 nm are assigned to the typical π–π* transition, locally excited state [18]. The distinction between **5** and **6** is induced by the second benzyl group of **6**. It illustrates that a substituted group can strongly influence the spectrochemical properties of the materials.

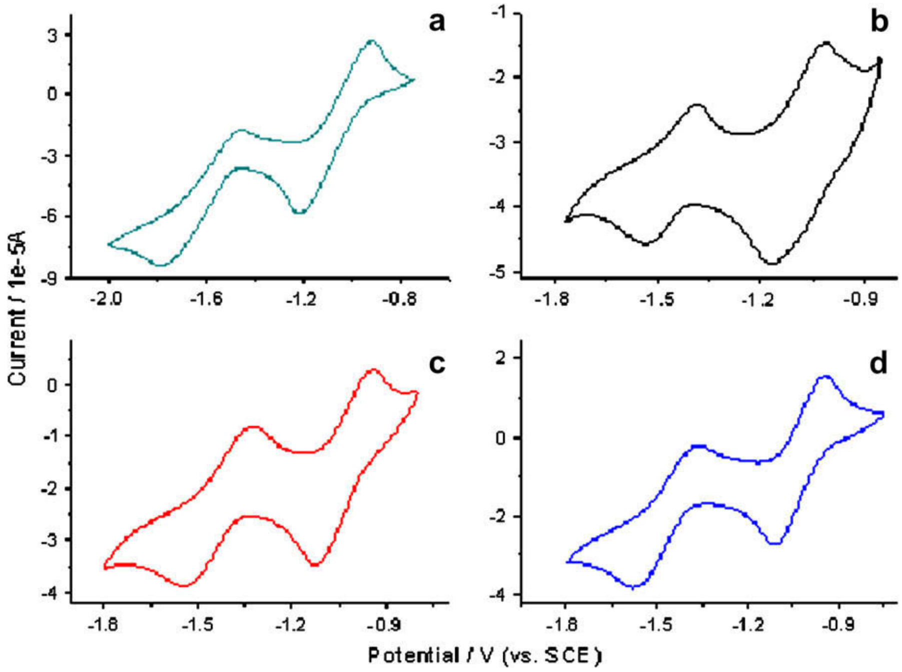

Fig. 4. Cyclic voltammetry of (a) **6a**, (b) **6b**, (c) **6c** and (d) **6d** in CH_2Cl_2/TBAP (0.1 M) at room temperature, scan rate of 100 mV/s.

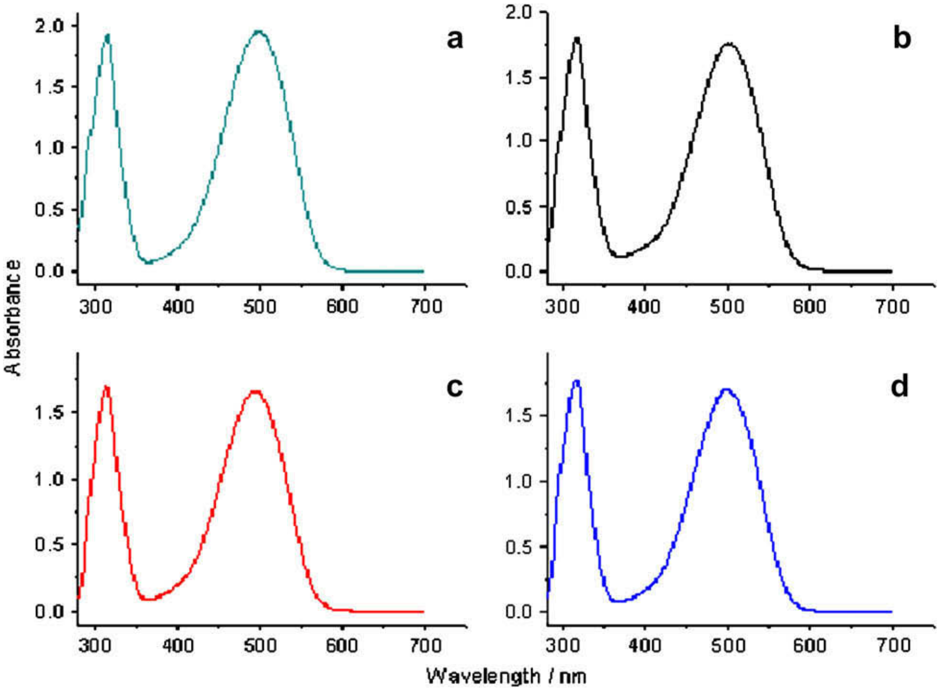

Fig. 5. UV–vis absorption spectra of (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d** in CH_2Cl_2 at room temperature.

Table 4
The λ_{max} values of UV–vis spectra for **5** and **6**.[a]

Entry	Compounds	λ_{max}, nm
1	**5a**	311, 327, 442
2	**5b**	312, 329, 442
3	**5c**	307, 325, 437
4	**5d**	311, 329, 441
5	**6a**	312, 336, 350, 458
6	**6b**	312, 338, 351, 463
7	**6c**	308, 333, 346, 450
8	**6d**	314, 340, 350, 459

[a] UV–vis absorption spectra were determined in CH_2Cl_2 at room temperature.

4. Conclusions

A series of mono- and bisbenzyl substituted 1-/2-aminoanthraquinones were synthesized and characterized by NMR, IR spectroscopy and mass spectrometry, and the conditions for the synthesis were discussed. Copper(I) iodide accelerated the reactions and enhanced the reaction yields. The electrochemical and spectrochemical properties of these compounds were studied. They are redox active and potentially useful as electrochromic materials and for biological studies.

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