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Synthesis of 1,3,6,8-Tetrakis(dimethylamino)pyrene Having Low Oxidation Potential

Naomi Ueda, Yoshiteru Sakata,* and Soichi Misumi
The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567

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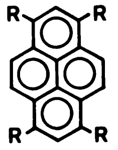
Synopsis. 1,3,6,8-Tetrakis(dimethylamino)pyrene (**1**) was synthesized starting from the corresponding tetranitro compound. The first oxidation potential of **1** shows the lowest value ($E^1_{1/2}$=−0.12 V vs SCE) among those of aromatic amines reported so far.

It is well known that the substitution of olefinic or aromatic protons with dimethylamino groups results in lowering the oxidation potential. Typical examples are tetrakis(dimethylamino)ethylene[1] and 1,4-bis(dimethylamino)benzene,[2] whose oxidation potentials ($E^1_{1/2}$) are −0.75 V and 0.04 V vs SCE, respectively. The former value is the lowest among those of all organic compounds so far reported. Our previous study[3] on the synthesis of 2,7-bis(dimethylamino)pyrene ($E^1_{1/2}$= 0.37 V) and -tetrahydropyrene ($E^1_{1/2}$=0.14 V) with fairly low oxidation potentials prompted us to prepare 1,3,6,8-tetrakis(dimethylamino)pyrene (**1**) with a view to powerful donor.



1: R = -NMe$_2$
2: R = -NO$_2$
3: R = -NH$_2$·HCl

Results and Discussion

1,3,6,8-Tetranitropyrene (**2**), prepared by nitration of pyrene according to the literature,[4] was reduced with tin powder in 6M HCl to give **3** in 87% yield. Because of the instability of free amine, **3** was used for the subsequent reaction without further purification. Methylation of **3** was carried out with dimethyl sulfate to give the desired compound **1** in 37% yield. Although **1** is very sensitive to oxygen, **1** can be kept for several months at ordinary temperature under inert atmosphere.

Figure 1 shows a cyclic voltammogram for 1 mM (mmol dm^{-3}) of **1** in 0.1 M tetraethylammonium perchlorate in acetonitrile, recorded with a scan rate of 50 mV s^{-1}. It exhibits two reversible redox waves. Judging from the peak separation (ca. 30 mV) two electron-transfer process is involved in each wave. In agreement with the initial expectation, the oxidation potentials of **1** are very low ($E^1_{1/2}$=−0.12 V, $E^2_{1/2}$=−0.05 V vs SCE). It is noteworthy that the value of $E^1_{1/2}$ is less than that of 1,4-bis(dimethylamino)benzene, which is the lowest among those of aromatic amines so far reported.

1 forms charge-transfer complex with iodine.

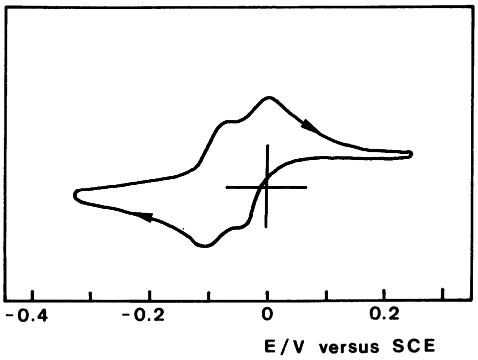


Fig. 1. Cyclic voltammogram of **1** in acetonitrile.

Experimental

All the melting points are uncorrected. The IR, NMR, MS, and electronic spectra were measured on a Hitachi EPI-G2 and a Hitachi 345, a JEOL JNM-FX-100, a Hitachi RMU-7, and a Hitachi EPS-3T spectrometer, respectively. The cyclic voltammetry was carried out at room temperature under argon using the combination of a generator of Hokuto HB-107 A and a potentiostat of Hokuto HA-104. A glassy carbon electrode (Yanagimoto P-13) was used as the anode, and platinum wire was used as the counter electrode.

1,3,6,8-Tetrakis(dimethylamino)pyrene (1). To a suspension of 1,3,6,8-tetranitropyrene (**2**) (200 mg 0.52 mmol) in 15 ml of 6M hydrochloric acid was added tin powder (372 mg, 3.13 mmol) in small portions under nitrogen and the mixture was warmed at 50—60 °C for 3.5 d. After cooling, precipitates of ammonium salt **3** were collected, washed with 6M HCl and dried to give 184 mg (87%) of **3**, which was used for the next step without further purification [**3**: MS 262 (M$^+$); IR (nujol mull) 3570, 3475, 3200—2300, and 1605 cm^{-1}].

To a stirred aqueous solution (5 ml) of crude **3** (184 mg, 0.45 mmol) was added an aqueous solution (6 ml) of sodium hydrogencarbonate (1.818 g, 21.64 mmol) and dimethyl sulfate (908 mg, 7.21 mmol) under nitrogen at room temperature. Stirring was continued at room temperature for 1 h and then at 50—60 °C for 4 h. After cooling, 2-aminoethanol (3 ml) was added and the mixture was heated at 120—130 °C for 3 h with stirring. After cooling, yellow precipitates of **1** were collected, washed with water and dried to give 102 mg of crude **1**. Purification by sublimation gave 62 mg (37%) of **1**: Yellow prisms, mp 212—213 °C; ^{1}H NMR (CDCl$_3$) δ=3.02 (24H, s), 7.43 (2H, s), and 8.17 (4H, s); IR (KBr disk) 1585 cm^{-1}; UV (CH$_3$CN) 228 (ε 4.10×10^4), 302 (2.25×10^4), and 414 nm (3.04×10^4). Found: C, 76.69; H, 8.11; N, 15.18%. Calcd for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96%.

Complexation of 1 with Iodine. Under nitrogen atmosphere, a solution of **1** (10 mg, 0.03 mmol) in benzene (2 ml) and a solution of iodine (33 mg, 0.15 mmol) in the same solvent(3 ml) were mixed at room temperature. Precipitated dark purple microcrystals were filtered, washed with benzene, and dried to give 8 mg (80% yield based on **1**) of **1**–I$_2$: black fine crystals, decomp>180 °C; IR (KBr disk) 1550 cm^{-1}: UV (CH$_3$CN) 220 (sh, ε 5.33×10^4), 256 (4.26×10^4), 296 (1.28×10^5). 368 (6.39×10^4), 456 (2.79×10^4), and 532 nm (1.06×10^4). Found: C,19.16; H,2.01; N, 3.73; I, 74.66%. Calcd for $C_{24}H_{30}N_4 \cdot 4.4I_2$: C, 18.93; H, 2.10; N, 3.84; I, 74.33%.

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