

Nitrenium ions.† Reactions of *N,N*-dimethyl-*p*-benzyloxyaniline-iminium chloride with indoles and indolizines. X-ray structure of unexpected [2-chloro-4-(4-dimethylaminophenyl-*ONN*-azoxy)-phenyl]dimethylamine (azoxy derivative)

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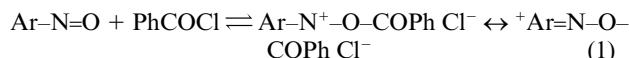
Received 17th July 2003, Accepted 8th September 2003

First published as an Advance Article on the web 1st October 2003

N,N-Dimethyl-*p*-nitrosoaniline reacts with benzoyl chloride affording a complex salt containing a cation, a hybrid between a nitrenium ion and an iminium ion. The salt reacts with nucleophiles (indoles, indolizines) yielding compounds characterized by a new carbon–nitrogen bond, derived from the nitrenium ion form. According to the type of nucleophile, the reaction, to differing extents, is in competition with an electron transfer process which leads to the formation of the dimer of the nucleophile and of the azoxy corresponding to the *N,N*-dimethyl-*p*-nitrosoaniline. In one of the reactions studied, a chlorinated azoxy derivative was also isolated, and its structure was elucidated by X-ray analysis.

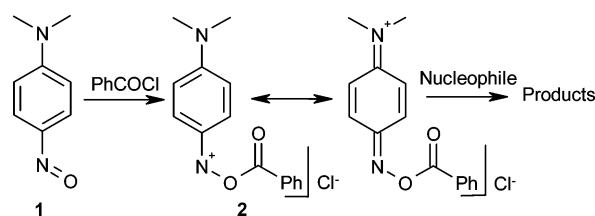
Introduction

Nitrosoarenes react with benzoyl chloride affording a benzyloxy iminium cation which can also be represented as a nitrenium ion (eqn. (1)).



In fact, in a previous study, in the reaction between 1-methyl-2-phenyl-3-nitrosoindole and benzoyl chloride, this cation was isolated and characterized by X-ray spectroscopy.¹ In this study it was shown, supported by AM1 calculations,¹ that the interaction of nitroso indoles or *N,N*-dimethyl-*p*-nitrosoaniline with benzoyl chloride produces an intermediate which can be likely represented by both the structures of an iminium ion and of a nitrenium ion. For a long time nitrenium ions were an object of discussion and many doubts arose as to their existence.^{2–4} In fact, when a double bonded nitrogen atom bearing a positive charge (nitrenium ion)^{5–7} is linked to a benzene ring, the positive charge is better localized on the conjugated aromatic system. However, we have already demonstrated that such nitrogen atoms may attack a carbon atom of an appropriate nucleophile.^{8,9}

In the present paper we report the reactions between *N,N*-dimethyl-*p*-nitrosoaniline, benzoyl chloride (Scheme 1) and different indoles and indolizines; the isolated products show that the ionic path involving a nitrenium ion is in competition with an electron transfer process (see discussion).



Scheme 1

Results

All the reactions were carried out in acetonitrile or in chloroform by adding a solution of the appropriate nucleophile **3–7** to the suspension of the salt formed from *N,N*-dimethyl-*p*-nitrosoaniline and benzoyl chloride at ca. 5 °C under magnetic stirring. In the case of compounds **3**, **4** and **5** the reaction mixture was poured into water, extracted and the products were separated by silica gel chromatography (see Experimental). In the case of nucleophiles **6** and **7**, the reaction mixture was treated with NaClO₄ in order to isolate products **13** and **15** as cation perchlorates. All products listed in Table 1 were identified by their analytical and spectroscopic data (see Experimental) or compared with authentic samples. Compound **11** was investigated by X-ray analysis in order to establish that the chlorine atom is bonded in the *ortho* position with respect to the dimethylamino group on the phenyl ring in the opposite site to the *N*-oxide aryl moiety (Fig. 1). Furthermore, X-ray analysis showed that the compound consists of two symmetry-independent molecules (called molecules A and B) showing a *trans* conformation of the aromatic rings with

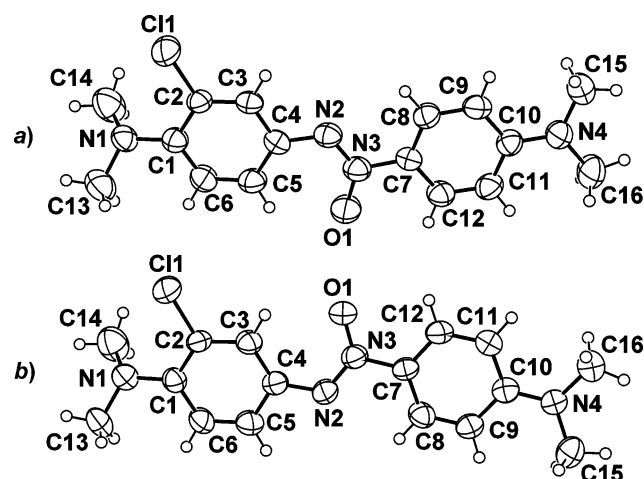
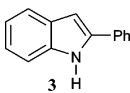
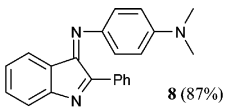
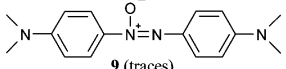
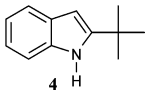
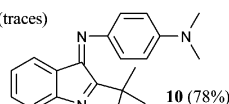
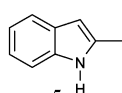
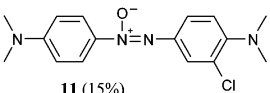
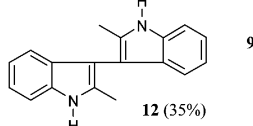
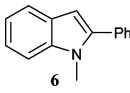
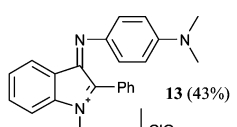
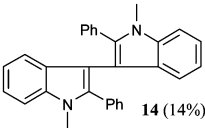
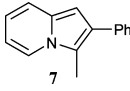
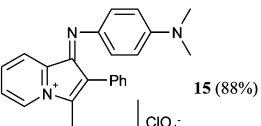


Fig. 1 An ORTEP view (50% probability ellipsoids) of (a) molecule A and (b) molecule B in compound 11.

† Part 5. For Part 4 see ref. 1

Table 1 Isolated products and yields from the reactions of salt **2** with nucleophiles **3–7**

Nucleophile	Products
	 8 (87%)  9 (traces)
	 10 (78%) 9 (traces)
	 11 (15%)  12 (35%) 9 (40%)
	 13 (43%)  14 (14%) 9 (traces)
	 15 (88%)  9 (traces)

respect to the azoxy group (Fig. 1). The two molecules however differ in the mutual orientation of the dimethylaminoazoxybenzene and dimethylaminochlorobenzene moieties, as indicated by the value of the C(1) ... C(4) ... C(7) ... C(10) *pseudo* torsion angle (158.1(10) and $-173.6(9)^\circ$ for molecules A and B, respectively). Bond distances and angles within the azoxy group are in agreement with those reported in the literature (Table 3). In particular, the N(2)=N(3) (1.273(4) and 1.283(5) Å), C(7)–N(3) (1.456(5) and 1.446(4) Å), C(4)–N(2) (1.422(5) and 1.406(5) Å) and N(3)–O(1) (1.253(5) and 1.250(4) Å) bond lengths are consistent with the presence of electron delocalization $N^+ \rightarrow O^-$ in the *N*-oxide group. In order to avoid excessively short distances between *ortho* hydrogen atoms of the aromatic rings and the azoxy group, the aromatic rings in both independent molecules are not strictly coplanar, the dihedral angle formed by the mean planes through the Cl(1), C(1) ... C(6) chlorobenzene ring and the C(7) ... C(12) benzene ring being 5.7(1) and 11.9(1)° for molecules A and B, respectively. In this conformation the interatomic distances involving the *ortho* hydrogen atoms and the azoxy group are:

Table 2 Experimental data for the X-ray diffraction study on crystal-line compound **11**

Compound	11
Formula	C ₁₆ H ₁₉ ClN ₄ O
<i>a</i> /Å	25.207(4)
<i>b</i> /Å	7.631(2)
<i>c</i> /Å	17.000(3)
$\alpha/^\circ$	90
$\beta/^\circ$	95.50(10)
$\gamma/^\circ$	90
<i>V</i> /Å ³	3255.0(13)
<i>Z</i>	8
Formula weight	318.8
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> /°C	23
λ /Å	1.54178
ρ_{calc} /g cm ⁻³	1.301
μ /cm ⁻¹	21.35
Transmission coefficient	0.928–1.000
<i>R</i> ^a	0.050
<i>wR</i> ₂	0.073
GOF	0.870
<i>N</i> -observed ^b	2468
<i>N</i> -independent ^c	6196
<i>N</i> -refinement ^d	5243
Variables	397

^a Calculated on the observed reflections having $I > 2\sigma(I)$. ^b *N*-observed is the total number of independent reflections having $I > 2\sigma(I)$. ^c *N*-independent is the number of independent reflections. ^d *N*-refinement is the number of reflections used in the refinement having $I > 0$.

Table 3 Selected bond distances (Å) and angles (°) for compound **11**

	Molecule A	Molecule B
Cl(1)–C(2)	1.730(3)	1.726(3)
O(1)–N(3)	1.253(5)	1.250(4)
N(1)–C(1)	1.402(5)	1.401(5)
N(1)–C(13)	1.466(5)	1.470(5)
N(1)–C(14)	1.445(4)	1.447(4)
N(2)–N(3)	1.273(4)	1.283(5)
N(2)–C(4)	1.422(5)	1.406(5)
N(3)–C(7)	1.456(5)	1.446(4)
N(4)–C(10)	1.367(5)	1.363(4)
N(4)–C(15)	1.426(5)	1.436(4)
N(4)–C(16)	1.447(4)	1.458(5)
C(1)–N(1)–C(13)	115.9(3)	116.6(3)
C(1)–N(1)–C(14)	114.8(3)	115.1(3)
C(13)–N(1)–C(14)	111.0(3)	110.4(3)
N(3)–N(2)–C(4)	119.3(3)	119.9(3)
O(1)–N(3)–N(2)	126.9(3)	125.9(3)
O(1)–N(3)–C(7)	116.5(3)	117.8(3)
N(2)–N(3)–C(7)	116.6(3)	116.3(3)
C(10)–N(4)–C(15)	121.9(3)	121.5(3)
C(10)–N(4)–C(16)	120.7(3)	119.2(3)
C(15)–N(4)–C(16)	117.4(3)	116.3(3)
N(2)–C(4)–C(3)	112.0(3)	129.4(3)
N(2)–C(4)–C(5)	130.1(3)	112.6(3)
C(3)–C(4)–C(5)	117.8(3)	117.9(3)

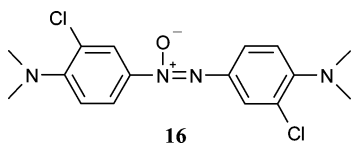
Molecule A: C(5) ... O(1), 2.715(4) Å; H(5) ... O(1), 2.15 Å; C(5)–H(5) ... O(1), 117.8°; C(12) ... O(1), 2.670(5) Å; H(12) ... O(1), 2.34 Å; C(12)–H(12) ... O(1), 100.4°; C(8) ... N(2), 2.757(5) Å; H(8) ... N(2), 2.47 Å; C(8)–H(8) ... N(2), 97.9°. Molecule B: C(3) ... O(1), 2.705(4) Å; H(3) ... O(1), 2.15 Å; C(3)–H(3) ... O(1), 117.2°; C(12) ... O(1), 2.696(4) Å; H(12) ... O(1), 2.39 Å; C(12)–H(12) ... O(1), 99.2°; C(8) ... N(2), 2.748(5) Å; H(8) ... N(2), 2.45 Å; C(8)–H(12) ... N(2), 98.6°.

The deviation from coplanarity is reflected also in a significant deviation from the ideal values of the bond angles involving the C(4) carbon atom of the chlorobenzene ring (Table 3).

Discussion

The reactions here described demonstrate once again that activated nitrosoarenes having an electron donating group in a conjugated position, such as nitrosoindoles or *N,N*-dimethyl-*p*-nitrosoaniline **1**, react with nucleophiles in the nitrenium form giving rise to a new nitrogen–carbon bond. This mechanism was observed in almost all the reactions studied, affording compounds **8**, **10**, **13** and **15**, and already described elsewhere.^{1,8} These results are also in agreement with AM1 calculations,¹ which showed that the most positive position for a non-hindered nucleophilic attack is represented by the nitrogen of the nitroso group. The formation of 4,4'-bis(dimethylamino)-azoxybenzene **9**, isolated almost in all cases, and of compounds **11**, **12** and **14**, could be likely explained by an electron transfer process, which could be in competition with the ionic pathway mentioned above.¹¹ Moreover, on the basis of the obtained products, the electron transfer process seems to be the only possible mechanism in the case of 2-methylindole **5**.¹³ The reduction potential of *N,N*-dimethyl-*p*-nitrosoaniline **1** (0.392 V vs. SCE at pH 2.3)¹⁴ and the oxidation potentials of nucleophiles **3**, **4**, **5**, **6** and **7** (0.73,¹⁵ 0.57 (see Experimental), 0.46,¹⁶ 0.64,¹⁷ 0.215¹⁷ V vs. Ag/Ag⁺ in MeCN, respectively) are in agreement with an outer-sphere electron transfer process, except for indoles **3** and **6**.¹⁸ However, there is no linear correlation between the redox potentials of the reagents and the extent of the electron transfer process (in the case of indolizine **7**, which has the lowest oxidation potential, the electron transfer process should be the most favourable),¹⁸ probably because the two mechanisms (ionic and radical) depend strongly on kinetic factors. In the case of nucleophiles **3** and **6** an inner-sphere electron transfer could also be possible as discussed previously.¹⁹

In order to gain more insight into the unexpected formation of the chlorinated azoxybenzene **11**, its probable precursor **9** was reacted with chloride anion (which is formed in the reaction medium): compound **11** was however not obtained. Azoxy derivative **9** was then reacted with a donor of positive chlorine such as *N*-chlorobenzotriazole (NCBT)²⁰ in 1 : 1 ratio, and this time compound **11** was isolated in quantitative yield. In the main reactions the chlorinating agent could be molecular chlorine formed in the reaction medium by oxidation of the chloride ion promoted by the protonated salt **2**.²¹ To verify this hypothesis, the azoxy derivative **9** was then reacted with molecular chlorine, generated from hydrochloric acid and potassium permanganate, and the chlorinated-azoxy **11** was isolated together with compound **16**, probably because of the chlorine excess used. All these results confirm that compound **11** was formed by chlorination of compound **9**.



Experimental

Melting points are not corrected and were measured by an electrothermal apparatus. IR spectra were recorded in Nujol on a Perkin Elmer Spectrum MGX1 spectrophotometer equipped with a Spectra Tech. "Collector" for DRIFT measurements. ¹H NMR spectra were recorded at room temperature in CDCl₃ or DMSO-*d*₆ on a Varian Gemini 200 spectrometer (δ in ppm referred to tetramethylsilane). Mass spectra were recorded on a Carlo Erba QMD 1000 spectrometer in EI⁺ mode. Elemental analyses of the new compounds were performed with a Carlo Erba CHNSO E.A. 1108 elemental analyser.

Compounds **1**, **3**, **5** and **6** were purchased from Aldrich. Compounds **4**¹⁹ and **7**²² were prepared according to the literature reports.

Reaction of indoles **3–6** and indolizine **7** with salt **2**. General procedure

Benzoyl chloride (0.5 mmol in 10 ml of MeCN) was added dropwise and under magnetic stirring to a solution of *N,N*-dimethyl-*p*-nitrosoaniline (0.5 mmol in 20 ml of MeCN) cooled at ca. 5 °C with an ice/water bath. The green colour of the nitroso compound became lighter and a yellow precipitate of salt **2** formed. A solution of the nucleophile (0.5 mmol in 15 ml of MeCN) was then added dropwise to this mixture under stirring. After 3 h the reaction was worked up.

In the case of indoles **3**, **4** and **5** the reaction mixture was poured into 10% NaOH (50 ml) and extracted with toluene (2 × 50 ml). The organic layer was washed with water (2 × 30 ml), dried with Na₂SO₄ and evaporated to dryness; the residue was then chromatographed on a silica gel column eluting with cyclohexane–ethyl acetate 9 : 1.

In the case of nucleophiles **6** and **7** the reaction mixture was treated with an excess of 10% NaClO₄ under stirring and the solution was kept overnight. The sodium chloride formed was then filtered off and the solution reduced to a small volume. By addition of dry diethyl ether the perchlorate salt **13** or **15** (respectively) was precipitated, filtered off and crystallized from chloroform–diethyl ether. The filtrate was evaporated to dryness and chromatographed on a silica gel column eluting with cyclohexane–ethyl acetate 9 : 1.

The reaction with indoles **3**, **4** and **5** was also carried out in chloroform under the same conditions and the results were almost the same.

Compounds **8**⁸ (*N,N*-dimethyl-*N'*-(2-phenylindol-3-ylidene)-benzene-1,4-diamine), **9**¹⁰ {[4-(4-dimethylaminophenyl)-*ONN*-azoxy]phenyl}dimethylamine}, **12**¹¹ (2,2'-dimethyl-1*H*,1'*H*-[3,3']biindolyl) and **14**¹² (1,1'-dimethyl-2,2'-diphenyl-1*H*,1'*H*-[3,3']biindolyl) were identified by comparison with authentic samples. Analysis and spectroscopic data of isolated products are reported below.

N,N-Dimethyl-*N'*-(2-phenylindol-3-ylidene)benzene-1,4-diamine **8**: mp 214–215 °C (from benzene–petroleum ether); $\nu_{\max}/\text{cm}^{-1}$ 1600 (C=N); δ_{H} (200 MHz; CDCl₃; Me₄Si) 3.08 (6H, s, NMe₂), 6.84 (2H, A₂B₂, *J* 9.0, Ph), 7.01 (1H, dt, *J* 7.6 and 1.2, Ph), 7.20 (2H, A₂B₂, *J* 9.0, Ph), 7.46 (6H, m, Ph), 8.41 (2H, m, Ph); *m/z* (EI) 325 (M⁺, 5), 311 (3), 283 (12), 205 (4), 69 (100).

N-(2-*tert*-Butylindol-3-ylidene)-*N'*,*N'*-dimethylbenzene-1,4-diamine **10**: mp 137–138 °C (from benzene–petroleum ether); (Found: C, 78.58; H, 7.62; N, 13.73. Calc. for C₂₀H₂₃N₃: C, 78.651; H, 7.5905; N, 13.7583%); $\nu_{\max}/\text{cm}^{-1}$ 1588 (C=N), 1547, 1513; δ_{H} (200 MHz; CDCl₃; Me₄Si) 1.54 (9H, s, Bu^t), 3.03 (6H, s, NMe₂), 6.78 (2H, A₂B₂, *J* 9.0, Ph), 7.05 (2H, A₂B₂, *J* 9.0, Ph), 6.65–7.45 (4H, m, Ph); *m/z* (EI) 305 (M⁺, 100%), 290 (33), 275 (18), 262 (21), 248 (27), 185 (4), 171 (9).

[2-Chloro-4-(4-dimethylaminophenyl)-*ONN*-azoxy]phenyl]-dimethylamine **11**: mp 97–98 °C (from ligroin 60–80 °C); (Found: C, 60.31; H, 6.12; N, 17.53. Calc. for C₁₆H₁₉ClN₄O: C, 60.279; H, 6.0071; N, 17.5743%); $\nu_{\max}/\text{cm}^{-1}$ 1592 (N(O)=N), 1177 (N—O); δ_{H} (200 MHz; CDCl₃; Me₄Si) 2.90 (6H, s, NMe₂), 3.07 (6H, s, NMe₂), 6.67 (2H, A₂B₂, *J* 9.3 and 1.7, Ph), 7.08 (1H, d, *J* 9.8, Ph), 8.10 (1H, dd, *J* 9.8 and 2.0, Ph), 8.17 (2H, A₂B₂, *J* 9.3 and 1.7, Ph), 8.33 (1H, d, *J* 2.0, Ph); *m/z* (EI) 320 (M⁺, 19%), 318 (M⁺, 54), 168 (50), 135 (32), 133 (100), 120 (69).

3-(4-Dimethylaminophenylimino)-1-methyl-2-phenyl-3*H*-indolium perchlorate **13**: mp 174–176 °C (from chloroform–diethyl ether); (Found: C, 62.83; H, 5.08; N, 9.50. Calc. for C₂₃H₂₂N₃ClO₄: C, 62.799; H, 5.0409; N, 9.5524%); $\nu_{\max}/\text{cm}^{-1}$ 1610 (C=N); δ_{H} (200 MHz; DMSO-*d*₆; Me₄Si) 3.03 (6H, s, NMe₂), 3.97 (3H, s, NMe), 6.96 (2H, m, Ph), 7.3–7.7 (9H, m, Ph), 7.90 (1H, d, *J* 7.7, Ph), 8.02 (1H, d, *J* 7.8, Ph); *m/z* (EI) 341 (M⁺ – ClO₄ + 1, 100%), 327 (33), 221 (9), 207 (26).

1-(4-Dimethylaminophenylimino)-3-methyl-2-phenyl-1*H*-indolizinium perchlorate **15**: mp 200–201 °C (from chloroform–diethyl ether); (Found: C, 62.78; H, 5.05; N, 9.59. Calc.

for $C_{23}H_{22}N_3ClO_4$: C, 62.799; H, 5.0409; N, 9.5524%; $\nu_{\max}/\text{cm}^{-1}$ 1610 (C=N); δ_{H} (200 MHz; DMSO- d_6 ; Me $_4$ Si) 2.58 (3H, s, Me), 3.10 (6H, s, NMe $_2$), 6.65 (2H, br s, Ph), 7.08 (2H, br s, Ph), 7.32 (2H, br s, Ph), 7.43 (3H, br s, Ph), 8.01 (1H, td, J 6.4 and 1.6, Ph), 8.31 (1H, br d, J 7.2, Ph), 8.39 (1H, t, J 7.4, Ph), 9.10 (1H, d, J 6.2, Ph); m/z (EI) 341 (M^+ – ClO $_4$ + 1, 34%), 326 (11), 221 (8), 206 (13).

Reaction of compound 9 with *N*-chlorobenzotriazole

Compound 9 (71 mg, 0.25 mmol, in 5 ml of CHCl $_3$) and *N*-chlorobenzotriazole (39 mg, 0.25 mmol, in 5 ml of CHCl $_3$) were mixed at room temperature. After 30 min the reaction solution was evaporated to dryness and the residue was chromatographed on silica gel TLC plates eluting with cyclohexane–ethyl acetate 9 : 1. Compound 11 and benzotriazole were isolated almost quantitatively.

Reaction of compound 9 with chlorine

Gaseous chlorine, generated by dropping aqueous 37% hydrochloric acid in a solution of KMnO $_4$ (500 mg in 10 ml of water), was blown for a few seconds into a solution of compound 9 (71 mg, 0.25 mmol, in 5 ml of CHCl $_3$). After 5 min the mixture was evaporated to dryness and the residue was chromatographed on silica gel TLC plates eluting with cyclohexane–ethyl acetate 9 : 1 yielding compounds 9 (20%), 11 (80%) and 16 (10%).

[2-Chloro-4-(3-chloro-4-dimethylaminophenyl)-*ONN*-azoxy-phenyl]dimethylamine 16: mp 106–108 °C (from ligroin 60–80 °C); (Found: C, 54.42; H, 5.10; N, 15.85. Calc. for C $_{16}$ H $_{18}$ Cl $_2$ N $_4$ O: C, 54.402; H, 5.1361; N, 15.8606%); $\nu_{\max}/\text{cm}^{-1}$ 1585 (N(O)=N), 1130 (N→O); δ_{H} (200 MHz; CDCl $_3$; Me $_4$ Si) 2.93 (12H, s, NMe $_2$), 7.07 (1H, d, J 9.0, Ph), 7.09 (1H, d, J 8.8, Ph), 8.12 (1H, dd, J 8.9 and 2.9, Ph), 8.13 (1H, dd, J 9.0 and 2.2, Ph), 8.31 (1H, d, J 2.8, Ph), 8.38 (1H, d, J 2.2, Ph); m/z (EI) 356 (M^+ , 3%), 354 (M^+ , 7), 352 (M^+ , 24), 254 (3), 184 (6), 168 (60), 133 (100), 118 (12).

Electrochemical measurements

The oxidation potential of compound 4 was measured at room temperature under nitrogen in a three-electrode cell, using 5×10^{-3} M acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate (TEAP). Cyclic voltammetric experiments were performed at sweep rate 0.5 V s $^{-1}$ using a stationary platinum disk (AMEL 492) of about 1 mm diameter as working electrode, a platinum wire as auxiliary electrode and a Ag/0.1 M AgClO $_4$ electrode as reference. The experiments were performed using a multipolarograph AMEL 472/WR coupled with a digital x/y recorder AMEL 863.

Crystal structure of [2-chloro-4-(4-dimethylaminophenyl)-*ONN*-azoxy]phenyl]dimethylamine 11 ‡

C $_{16}$ H $_{19}$ ClN $_4$ O, M_r = 318.8, monoclinic, space group $P2_1/n$, a = 25.207(4), b = 7.631(2), c = 17.000(3) Å, β = 95.50(10)°, V = 3255.0(13) Å 3 , Z = 8, ρ = 1.301 g cm $^{-3}$; λ (Cu-K α) = 1.54178 Å, μ (Cu-K α) = 21.35 cm $^{-1}$; pale yellow prism, crystal dimensions

‡ CCDC reference number 213658. See <http://www.rsc.org/suppdata/ob/b3/b308088a/> for crystallographic data in .cif or other electronic format.

0.32 × 0.35 × 0.47 mm. The structure was solved by direct methods (SIR97 23) and anisotropically refined for all the non-H atoms. The hydrogen atoms were located from a difference Fourier map and thereafter allowed to ride on their attached atoms with isotropic displacement parameter 1.2 greater than the U_{eq} of the attached atom. The structure was refined on F^2 values (SHELXL93 24) by using the weighting scheme $w = 1/\sigma^2(F_o^2)$. For 5243 unique reflections having $I > 0$ collected at T = 296(2) K on an Enraf-Nonius CAD4 diffractometer ($3 < 2\theta < 140^\circ$) and corrected for absorption the final R is 0.050 ($wR2$ = 0.073; S = 0.870). Further details concerning the X-ray diffraction study on crystalline compound 11 are given in Table 2.

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