

ON THE ESR IDENTIFICATION OF PARAMAGNETIC SPECIES OBSERVED DURING SET OXIDATION OF N,N-DIMETHYL-p-ANISIDINE

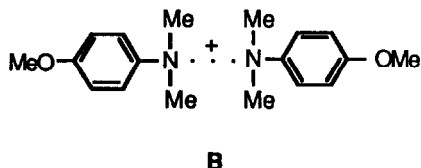
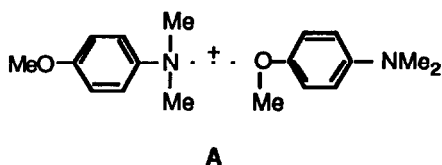
F. Ciminale,* R. Curci, M. Portacci and L. Troisi

*Centro CNR di Studio sulle Metodologie Innovative di Sintesi Organiche
Dipartimento di Chimica, Università, via Amendola 173, 70126 Bari, Italy*

Abstract. During SET oxidation of the title compound, N,N,N'-trimethyl-N'-(4-methoxyphenyl)-1,4-phenyldiamine radical cation ($3a^+$) was detected by e.s.r.; this derives from an oxidatively activated nucleophilic substitution on N,N-dimethyl-p-anisidine. Revised e.s.r. parameters for N,N-dimethyl-p-anisidinium radical are also reported.

In a preliminary e.s.r. study we identified the blue paramagnetic species that is observed when an excess of N,N-dimethyl-p-anisidine (**1**) is oxidized with $Tl(OAc)_3$ in $MeNO_2$, as a bimolecular three-electron σ -bonded aminium radical and proposed for it structure **A**.¹

The dimeric character of this radical was suggested by observations that could be interpreted in terms of a reversible formation of the blue species from the primary red cation radical 1^+ in the presence of unoxidized **1**. Actually, structure **A** with its N...O three-electron σ -bond leading three methyl groups to occupy high spin density positions, would be an obvious first choice when analysing the e.s.r. spectrum in Fig.1, and this in consideration of an unambiguous hyperfine coupling of 6.75 G with nine protons. Of course the more likely N...N bonded aminium dimer radical **B** would be inconsistent since it implies hyperfine coupling with twelve protons.



This assignment seemed interesting since, in contrast with sulphide² and phosphine³ analogous, amine dimer cation radicals had virtually not been observed before.⁴ The possibility for a nitrogen atom to give rise to three-electron σ -bonds resulted well documented just in the case of cyclic and bicyclic diamines; here, conformational constraints force the intramolecular overlap between spin-bearing and lone pair orbitals.⁵ Another challenging aspect of structure **A** was the apparent preference for N...O rather than N...N interaction; this was surprising, although justifiable by invoking steric

hindrance effects. Indeed, as pointed out by experimental data and theoretical calculations on sulphur containing systems,⁶ by increasing the difference between the electronegativities of component atoms, the stability of the three-electron bonds should be lowered. Thus, we undertook a more detailed investigation on amine dimer cation radicals in order to gain further information concerning the factors that govern nitrogen participation in intermolecular three-electron bonds. Preliminary to this, a closer look at the radical species generated in the title reaction was in order.

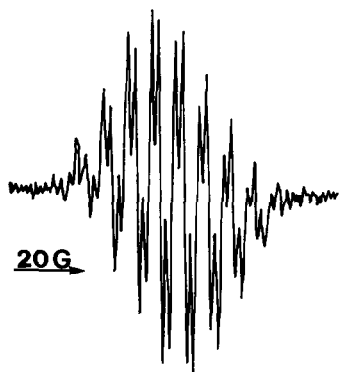


Fig. 1 - E.s.r. spectrum of $3a^{+\cdot}$, obtained by oxidation of excess **1** with $Tl(OAc)_3$ in $MeNO_2$.

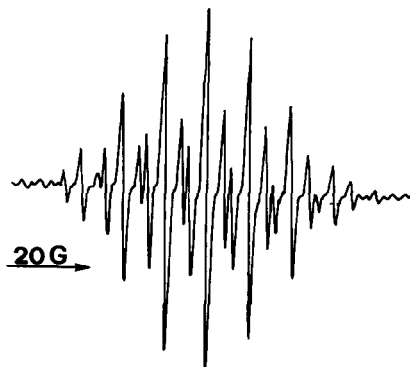
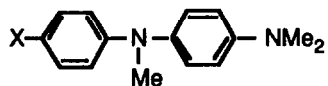


Fig. 2 - E.s.r. spectrum of $p\text{-CD}_3\text{OC}_6\text{H}_4\text{NMe}_2^{+\cdot}$ in $MeNO_2$.

Aromatic amine **1**, deuteriated at the methoxy group,⁷ was oxidized with $Tl(OAc)_3$ under the conditions affording the blue radical. If structure **A** was the correct one, isotopic labeling at one of the three methyls contiguous with the $N\cdots O$ bond was expected to yield marked changes in the e.s.r. hyperfine pattern; actually an e.s.r. spectrum practically identical to that obtained from the undeuteriated **1** was observed. This disproved structure **A** and led us to recognize that the blue radical could not be, as previously proposed, a bimolecular three-electron σ -bonded aminium radical, but it rather originated from an irreversible reaction of $1^{+\cdot}$ in the presence of excess **1**.

Since spectroscopic studies alone proved inadequate to solve the structure problem, careful product analyses were carried out. The paramagnetic reaction mixture was made diamagnetic by treatment with 10% aqueous $Na_2S_2O_3$ and analysed by TLC and GC. Along with about 80% unreacted **1** and 10% N-methyl-p-anisidine (**2**), a product was detected in about 3% yields, which significantly developed a characteristic persistent blue colour during u.v. visualization of the chromatogram (silica gel). Column chromatography (silica gel, light petroleum- Et_2O 90:10) allowed us to separate just two fractions considerably enriched in the unknown product, contaminated by either **1** or **2**. The GC/MS

analyses of both fractions gave for the unknown product a molecular peak at m/z 256, assigned to *N,N,N'*-trimethyl-*N'*-(4-methoxyphenyl)-1,4-phenyldiamine (**3a**) in comparison with the fragmentation pattern of an authentic sample.⁸



3a X = OMe
3b X = H

The *p*-phenyldiamines are known to be easily oxidized, affording quite stable radical cations (Wurster's salts).⁹ Accordingly, **3a** gave blue paramagnetic solutions of the corresponding aminium radical **3a⁺** upon oxidation with $Tl(OAc)_3$ in $MeNO_2$ or even in the absence of externally added oxidants when $CHCl_3$ was used as a solvent. The observed e.s.r. spectrum was identical with that obtained for the blue radical generated by oxidation of **1** (Fig.1), and its structural consistency with **3a⁺** is based on the following interpretation that has been checked by computer simulation: 6.75 (2N,9H); 2.0 G (4H). Comparison with spectral data of analogous tetramethyl-*p*-phenyldiamine system [Wurster's blue: 6.99 (2N), 6.76 (12H), 1.97 G (4H)]¹⁰ shows that the peculiar electron delocalization of the latter radical remains substantially unaffected by replacement of a methyl with the *p*-anisyl group in **3a⁺**.

It is conceivable that the formation of **3a⁺** during the one-electron oxidation of **1** occurs as it follows: first, the radical cation **1⁺** in the presence of excess base **1** undergoes rapid deprotonation and subsequent demethylation;¹¹ then, the demethylation product **2** behaves as a nucleophile towards **1⁺** affording **3a⁺** upon displacement of the MeO group. According to the latter event, compound **3b** could be detected by GC/MS in the reaction mixture when **1⁺** was generated in the presence of a different secondary aromatic amine, namely *N*-methylaniline. Noteworthy, this reaction would represent a clear-cut new case of oxidatively activated nucleophilic substitutions, a new class of organic reactions that has recently attracted much interest.¹²

As a closing remark, a brief comment on e.s.r. characteristics of **1⁺** seems in order. The paramagnetic resonance of this radical, which can be observed in $MeNO_2$ by treatment of a dilute solution ($\sim 10^{-3} M$) of amine with excess oxidant, exhibits a complex hyperfine structure. Our previous interpretation¹ of this spectrum was based on e.s.r. parameters reported in the literature: $a(N) = 10.0$; $a(NMe_2) = 10.40$; $a(o) = 4.25$; $a(m) = 1.82$; $a(OMe) = 1.85$ G.¹³ The considerably simpler hyperfine pattern of the spectrum (Fig.2) obtained by us in the case of the deuteromethoxy derivative now allows one to determine the following coupling constants: $a(N) = 10.12$; $a(NMe_2) = 10.12$; $a(o) = 4.30$ G. The most noticeable feature here is the absence of $a(m)$; and this cannot be ascribed to the isotopic substitution at the methoxy group. Therefore, the only possible conclusion is that, in radical cation **1⁺**, the expected meta protons coupling is undetectably smaller than line width (1.05 G). In fact, a value of 0.35 G can be roughly estimated from calculated spin densities and experimental e.s.r. parameters of several documented *p*-substituted dimethylanilinium radicals.¹⁴

Acknowledgements. Financial support by the Italian National Research Council (C.N.R., Rome), in the frame of "Progetto Strategico Processi di Trasferimento Monoelettronico", and by the Italian Ministry of Education is gratefully acknowledged.

References and Notes

1. F. Ciminale, R. Curci, and L. Troisi, *Tetrahedron Lett.*, **26**, 6369 (1985).
2. L. Lunazzi, G.F. Pedullì, in *Organic Sulphur Chemistry. Theoretical and Experimental Advances* (Edited by F. Bernardi, I.G. Csizmadia, A. Mangini), chap. 9, Elsevier (1985).
3. W.B. Gara, B.P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 150 (1978).
4. Bimolecular triphenylamine radical cation ($\text{Ph}_3\text{N}^+\cdot\text{NPh}_3$) is the only early documented case : D.N. Stamires, J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963).
5. R.W. Alder, R.B. Sessions, in *The Chemistry of Amino, Nitroso and Nitro compounds and their Derivatives*, (Edited by S. Patai), chap. 18, Wiley, Chichester, (1982).
6. K.D. Asmus, M. Gobel, K.O. Hiller, S. Mahling, J. Monig, *J. Chem. Soc., Perkin Trans. 2*, 641 (1985); and refs. therein.
7. This compound was prepared by adopting literature procedures following the sequence: (i) F/CD₃O substitution on p-FC₆H₄NO₂ [M.J. Rarick, R.Q. Brewster, *J. Am. Chem. Soc.*, **55**, 1289 (1933)]; (ii) reduction of p-CD₃OC₆H₄NO₂ to the corresponding amine [K. Hanaya, T. Muramatsu, H. Kudo, *J. Chem. Soc., Perkin Trans. 1*, 2409 (1979)]; (iii) methylation of p-CD₃OC₆H₄NH₂ [F.G. Bordwell, P.J. Boutan, *J. Am. Chem. Soc.*, **78**, 87 (1956)]: m.p. 45-46 °C; ¹H NMR: δ (CDCl₃, TMS) 6.92-6.78 (m, 4H), 2.90 (s, 6H); mass spectrum: m/z (relative intensities) 154 (M⁺ 54), 136 (100).
8. **3a** was synthesized by methylation of commercial N-(4-methoxyphenyl)-1,4-phenylenediamine [see previous ref. step (iii)]. This compound was separated from the accompanying N,N-dimethyl-N'-(4-methoxyphenyl)-1,4-phenylenediamine by column chromatography (silica gel, light petroleum-Et₂O 70:30), and crystallized by n-hexane/CH₂Cl₂: m.p. 104-105 °C; ¹H NMR: δ [(CD₃)₂O, TMS] 6.95-6.73 (m, 8H), 3.73 (s, 3H), 3.16 (s, 3H), 2.88 (s, 6H); mass spectrum: m/z (relative intensities) 256 (M⁺ 100), 241 (68), 226 (41).
9. A.R. Forrester, J.M. Hay, R.H. Thomson, *Organic Chemistry of Stable Free Radicals*, chap. 6, Academic Press (1968).
10. J.R. Bolton, A. Carrington, J. dos Santos-Veiga, *Mol. Phys.*, **5**, 615 (1962).
11. R.N. Butler, *Chem. Rev.*, **84**, 249 (1984).
12. L. Ebersson, *Electron Transfer Reactions in Organic Chemistry*, chap. X, Springer-Verlag (1987); and refs. therein.
13. E.T. Seo, R.F. Nelson, J.M. Fritsch, L.S. Marcoux, N.W. Leedy, R.N. Adams, *J. Am. Chem. Soc.*, **88**, 3498 (1966).
14. M.J. Drews, P.S. Wong, P.R. Jones, *J. Am. Chem. Soc.*, **94**, 9122 (1972); and refs. therein.