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EPR Characterization of Radical Cations Generated by One-electron Oxidation of N-Methyl-p-anisidine

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Abstract. *The two persistent radical cations arising from N-methyl-p-anisidine (3) upon oxidation with $Tl(OAc)_3$ in the absence ($4^{+\cdot}$: 1,2-dimethyl-1,2-bis(p-anisyl)hydrazine r. c.), or in the presence ($3^{+\cdot}$) of F_3CSO_3H, have been identified by EPR spectroscopy. Based on the spectrum of $3^{+\cdot}$, a revision of the EPR characterization of the radical cation from 4'-methoxy-N-methylbenzenesulfenanilide (5) is also suggested.*

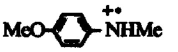
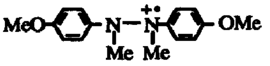
Several years ago we reported an EPR study on the one-electron oxidation of N,N-dimethyl-p-anisidine (1) with thallium triacetate.[1] Depending on the experimental conditions, either of two paramagnetic species could be detected: the direct one-electron oxidation product $1^{+\cdot}$, or a more persistent species which was identified as the radical cation of N,N,N'-trimethyl-N'-(p-anisyl)-1,4-phenylendiamine (2).

As part of the additional chemical and spectroscopic work required for the latter identification, a parallel EPR investigation had been carried out on N-methyl-p-anisidine (3) providing helpful results which, however, did not find space on that report. Eventually, a very recent paper,[2] dealing with EPR characterization of paramagnetic species forming in the reaction of some benzenesulfenanilides with Lewis acids, prompted us to disclose those results in this note.

The addition of $Tl(OAc)_3$ to an $MeNO_2$ solution (5×10^{-3} M) of 3, previously bubbled with He for 10 min, instantaneously developed a deep violet coloration and allowed us to record the paramagnetic resonance shown in Fig. 1, which was attributed to the long lived radical cation of 1,2-dimethyl-1,2-bis(p-anisyl)hydrazine (4). In fact, as reported in Table 1, the coupling constants determined by best matching with a calculated spectrum,[3] reveal equally sized magnetic interactions with two nitrogen nuclei and six protons, which are strongly indicative of two equivalent N-Me groups. The values of splitting constants and *g*-factor we have attributed to $4^{+\cdot}$ are in good agreement with those reported in the literature for analogous hydrazyne cations.[4] On the other hand, the detection of $4^{+\cdot}$ under conditions that should firstly produce $3^{+\cdot}$ is not surprising: according to the known reactivity of secondary aminium cations,[5] $3^{+\cdot}$, once formed in the presence of a base such as the parent anisidine 3, would undergo a rapid deprotonation yielding the N-methyl-p-anisidino radical; the latter would then dimerize to the hydrazine 4, a compound that, compared with the starting secondary amine 3, would be easily oxidizable[6] to a very persistent radical cation, $4^{+\cdot}$.

Further support to the above assignment came from a successful attempt to attain hydrazinium cation $4^{+\cdot}$ by a different route to N-methyl-p-anisidino radical. Thus, exploiting the ability of the 2,2-diphenyl-1-picrylhydrazyl (DPPH)[7] radical to abstract N-H hydrogen atoms and, in certain cases to behave as a one-electron oxidant, we were able to obtain an EPR spectrum identical to that reported in Fig. 1 simply by treatment of a solution of 3 with DPPH.

Table 1. Hyperfine splitting constants and *g*-factors of radical cations from N-methyl-p-anisidine.

Radical cation	a (G)	$g^{\dagger}$
 $(3^{+\bullet})$	8.17 (1N), 10.15 (3H), 9.42 (1H) 4.00 (1H), 4.45 (1H), 0.25 (2H), 2.07 (3H)	2.0034
 $(3\text{-}d_3{}^{+\bullet})$	8.15 (1N), 10.15 (3H), 9.50 (1H) 3.95 (1H), 4.45 (1H)	
 $(4^{+\bullet})$	6.20 (2N), 6.20 (6H), 2.62 (4H)	2.0033

† Measured using DPPH as a standard: $g = 2.0037$

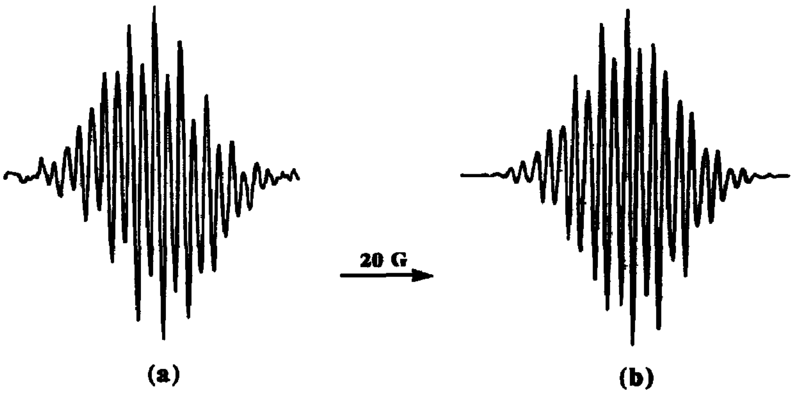


Fig. 1 ESR spectrum of $4^{+\bullet}$ obtained from 3 in $Tl(OAc)_3/MeNO_2$: (a) experimental; (b) simulated with a linewidth of 1.25 G.

The radical cation $3^{+\bullet}$, which has been presumed to be a competent intermediate in the process leading to $4^{+\bullet}$, became detectable when its intrinsic propensity to lose a proton was repressed by performing the oxidation with $Tl(OAc)_3$ in the presence of trifluoromethanesulfonic acid. The identity of $3^{+\bullet}$ was reliably inferred from its EPR spectrum reported in Fig. 2. The computation of the complex experimental hyperfine structure (Fig. 2b) can be considered more than satisfactory because it succeeds in accommodating an evident magnetic non-equivalence of the protons at C-2 and C-6 as expressed by the values of 4.00 and 4.45 G (see Table 1). This non-equivalence, which is clearly exhibited through an alternating linewidth effect (Fig. 2a), is due to restricted rotations pertaining, as ascertained in related systems, to both the C(1)-N^8 and the C(4)-O^9 bonds.

Further evidence in the spectroscopic characterization of $3^{+\bullet}$ derived from the analysis of the spectrum (Fig. 3) obtained upon similar oxidant treatment of N-methylanisidine deuterated at the methoxy group ($3\text{-}d_3$):[10] the coupling constants of the computer simulation are listed in Table 1.

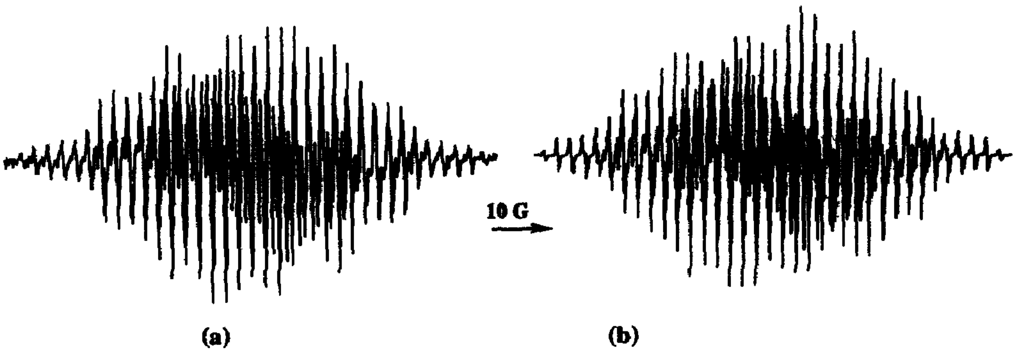


Fig. 2 ESR spectrum of $3^{+\cdot}$ in $Tl(OAc)_3$-$CF_3SO_3H/MeNO_2$: (a) experimental; (b) simulated with a linewidth of 0.2 G.

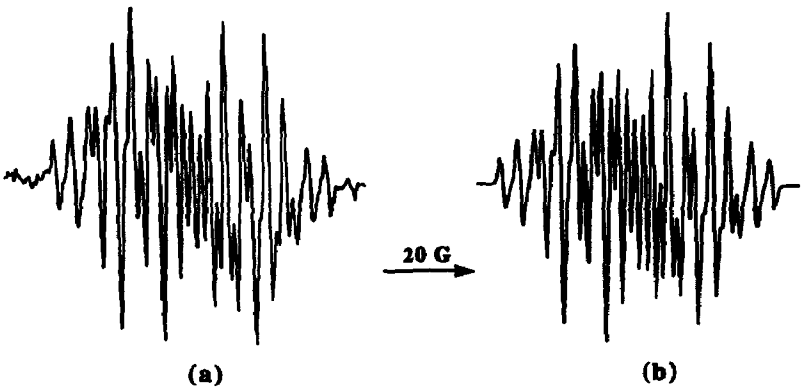


Fig. 3 ESR spectrum of 3-$d_3^{+\cdot}$ in $Tl(OAc)_3$-$CF_3SO_3H/MeNO_2$: (a) experimental; (b) simulated with a linewidth of 1.2 G.

The spectrum of Fig. 2a exhibits a great similarity to the one recently obtained[2] from a solution of 4'-methoxy-N-methylbenzenesulfenanilide (5) in $BF_3/MeCN$. By virtue of the resemblance of the two spectra, identical in all respects but for a minor difference between the corresponding overall spectral ranges, at least three separate chemical and spectroscopic aspects of the reaction of the sulfenanilide 5 with BF_3 seem to call into question the original identification of the observed radical, indicating this could be $3^{+\cdot}$ rather than $5^{+\cdot}$. Firstly, under the conditions of EPR experiments, the benzenesulfenanilide 5, according to its character of sulphenyl transfer reagent, was found to lose the SPh group, thus turning into the anisidine 3, which was isolated in 40% yield. Secondly, since the *g*-factor of 2.0034 is identical to that determined in the present work for $3^{+\cdot}$ (cf. Table 1), its attribution to $5^{+\cdot}$ should imply that on the latter radical cation the sulfur atom does not participate at all in unpaired electron delocalization. This, though not completely unreasonable on account of the presence of the methoxy group which might limit the distribution of spin density only within the anisyl moiety, is not in agreement with most of the reported radical cations of sulfenamides,[11] for which higher *g*-factors[12] reflect a substantial sulfur π spin density.[13] The last point deserving consideration is the finding that deuteration at the phenylthio moiety of the starting sulfenanilide left the hyperfine structure of the observed radical completely unaffected. While, by referring to $\mathbf{5}^{+\cdot}$, the interpretation given to this result, that there is no unpaired electron density on the SPh group, would appear as surprising as the small *g*-factor, its consistency with $\mathbf{3}^{+\cdot}$ is unquestionable, simply because this is a species lacking the group concerned by isotopic substitution.

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References and Notes

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10. (a) **N-methyl-4-trideuteromethoxyaniline** (**3-d$_3$**) was synthesized by methylation of 4-trideuteromethoxyaniline[12b] (6.8 mmol) with MeI (6.9 mmol), following a standard procedure. Pure **3-d$_3$** was obtained after separation from its dimethyl analogue by column chromatography (silica gel, n-hexane/Et$_2$O 70/30): m.p. 31-33 °C; ^{1}H NMR (CDCl$_3$, 60 MHz) δ 2.70 (s, 3H), 3.20 (s, 1H, disappears on exchange with D$_2$O), 6.33-6.80 (m, 4H). (b) The synthesis of 4-trideuteromethoxyaniline has been already reported.[1]
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