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N,N-DIMETHYL-p-ANISIDINIUM CATION. ESR EVIDENCE FOR INTERMOLECULAR SPIN-LONE PAIR INTERACTION

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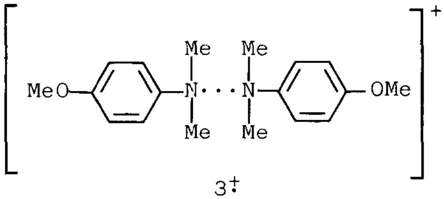
Abstract. ESR characterisation of N,N-dimethyl-p-anisidinium dimer radical cation is reported.

Exceptionally long-lived radical cations have been obtained from certain bicyclic diamines with bridgehead nitrogens and the peculiar reason of their remarkable persistency has been accounted for by the substantial stabilization (10-20 Kcal mol^{-1}) due to the formation of an intramolecular N-N three-electron σ bond involving spin-bearing and lone pair orbital.[1]
By analogy, in the case of monoamines stabilized dimer radical cations might be generated upon an intermolecular interaction between aminium radicals and neutral amines. This kind of interaction has been recently invoked in order to rationalize some results concerning the quenching of singlet trans-stilbene-amine exciplexes by ground-state amines.[2] However, to our present knowledge, just an early report[3] exists in which the formation of a dimer such as the bimolecular triphenylamine radical cation could be directly deduced from ESR spectra.

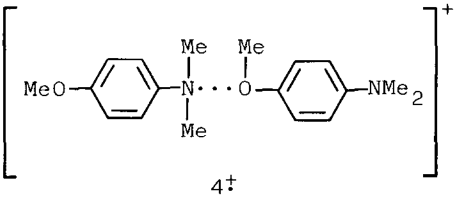
In the course of our recent studies on the mechanisms of oxidation of tertiary amines with metal peroxides we needed information for an unequivocal interpretation of ESR experiments in which an aminium radical cation was believed to be involved.To this purpose we undertook an ESR investigation of the N,N-dimethyl-p-anidisine (**1**)/$Tl(CH_3COO)_3$ system. We believe the results reported here provide an intriguing example of aminium dimer radical that deserves separate reporting.

Coloured paramagnetic solutions were obtained from **1** by treatment with tallium triacetate (**2**) in $CHCl_3$ or $MeNO_2$. However, while a blue (λ_{max}=607.9nm) solution invariably resulted in the first solvent, differently coloured solutions

could be generated in $MeNO_2$ depending on the ratio of the reactants.
At 2:1≤1 a blue solution (λ_{max}=609.4nm) was still obtained, while a red one (λ_{max}=481.9nm) appeared when a large excess of 2 (2:1>3) was employed.[5]
At intermediate values of the 2:1 ratio we observed a red colour initially developing and then becoming violet or blue within a few minutes.
The $MeNO_2$ red solution showed a complex ESR spectrum (Fig. 1) which persisted suitably intense for one or two hours. This spectrum can be undoubtedly assigned to N,N-dimethyl-p-anisidinium cation ($1^{+\cdot}$) since it could be satisfactorily simulated on the basis of the hyperfine splitting constants reported in the literature[6] for $1^{+\cdot}$, as obtained by electrochemical oxidation in MeCN.
The spectrum recorded for both the $CHCl_3$ and $MeNO_2$ solutions remained unchanched for a longer time (15 hours) and, as shown in Fig. 2, it displays a different hyperfine structure, although the "g" factor (2.0027) resulted the same within the experimental error. Furthermore, it is worth noting that, when an appropiate amount of 1 or 2 was added to the red or the blue $MeNO_2$ solution respectively, the colours as well as the ESR spectra of these solutions resulted reciprocally replaceable. These findings clearly indicate that the blue radical is reversibly related to the red amine radical cation $1^{+\cdot}$, and this through a process involving parent amine 1, precisely as expected for a three-electron σ bonded dimer amine radical cation.
In principle two distinct possibilities of spin-lone pair interaction exist in our case, one leading to the formation of a symmetric N-N bonded bimolecular ion ($3^{+\cdot}$) and the other to an unsymmetric N-O dimer ($4^{+\cdot}$).



$3^{+\cdot}$



$4^{+\cdot}$

However, analysis of the ESR characteristics allows an unambiguous identification of the blue radical as $4^{+\cdot}$. In fact the spectrum of Figure 2 exhibits a main hyperfine pattern consisting of an even number of equally spaced lines which would be determined by the situation at the three-electron bond where an higher spin density should be envisaged for both of the proposed structures.
This even number of resonances can be attributed to magnetic interaction of the unpaired electron with a set of accidentally equivalent nuclei including one nitrogen and nine protons (total spin=5.5) such as that contained in radical $4^{+\cdot}$,

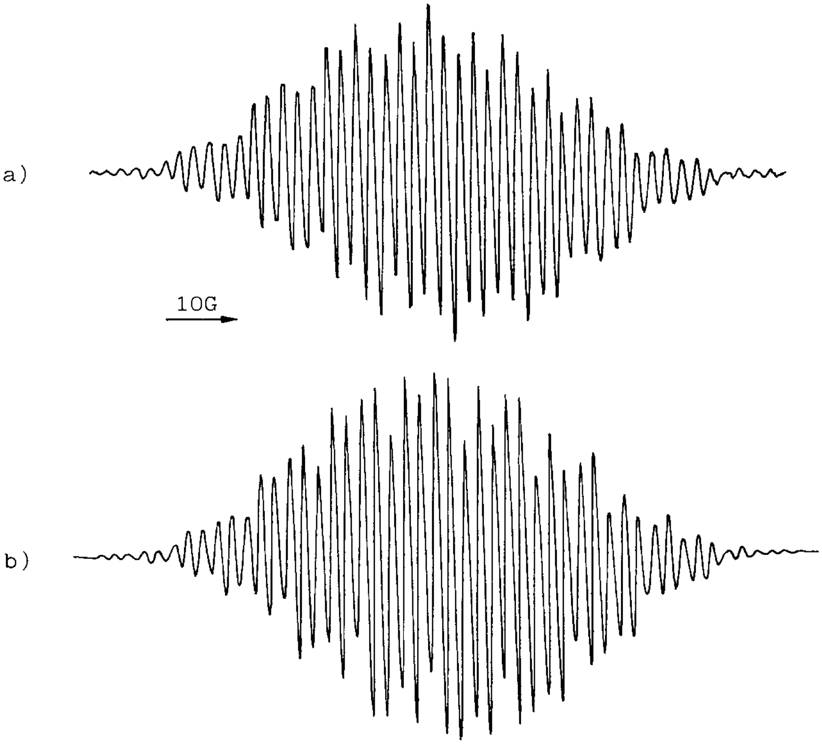


Figure 1: ESR spectrum of the red radical obtained by oxidation of **1** with **2**: a) observed; b) simulated using the coupling constants reported for **1**$^{+}$ in reference 6 and a line-width of 1G.

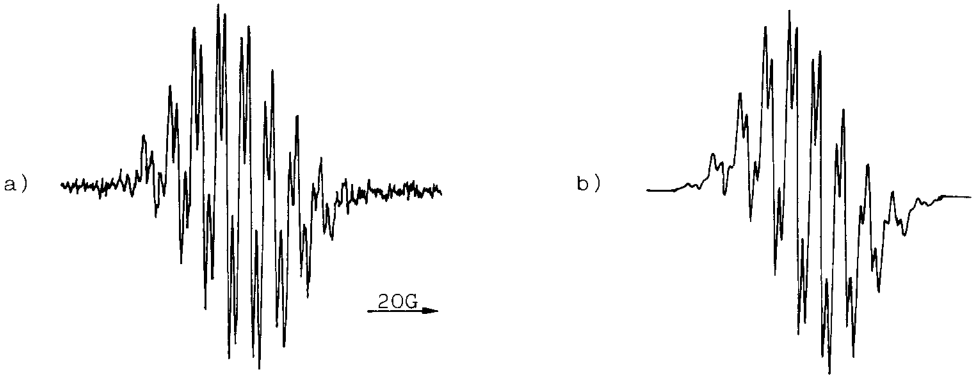


Figure 2: ESR spectrum of the blue radical obtained by oxidation of **1** with **2**: a) observed; b) simulated using the splitting constants reported (see text) and a line-width of 1G.

while a major odd multiplet should be expected for a system of accidentally equivalent nuclei consisting of two nitrogens and twelve protons (total spin=8) such as that present in radical $\underset{\sim}{3}^{+\cdot}$.

Moreover this interpretation is substantiated by the satisfactory computer simulation which could be obtained using the following splitting constants: a=6.75G (1N,9H) and a=2.0G (4H). The minor differences persisting between the experimental and simulated spectrum might be taken as to reflect possible differences among the splitting constants of nitrogen and methyl protons of $N(CH_3)_2$ and OCH_3 group; however, interferences due to the simultaneous presence of minor amounts of N-N dimer $\underset{\sim}{3}^{+\cdot}$ cannot be completely ruled out.

In summary, this study demonstrates that radical cation $\underset{\sim}{1}^{+\cdot}$ can be stabilized by spin lone-pair interaction with parent amine $\underset{\sim}{1}$. This interaction becomes favoured in a less polar solvent such as $CHCl_3$ as compared with $MeNO_2$ and it leads, for evident steric reasons, to the formation of N-O bonded dimer radical $\underset{\sim}{4}^{+\cdot}$.

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References and Notes

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5. Under similar conditions red-brown solutions was sometimes obtained in $CHCl_3$, but no ESR signal appeared evident.
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