An ESR Study of the Radical Cation of *trans*-Azobenzene

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ESR spectroscopy shows that the radical cation of *trans*-azobenzene exists as the (n_-) σ-state, with negligible delocalisation of spin density onto the phenyl groups.

There is currently considerable interest in the properties of radical cations formed from azo-compounds. Most of the information to date has been obtained on the basis of product studies,[1] but, recently, more direct evidence has been obtained by ESR spectroscopy[2—6] for azoalkane radical cations formed in freon matrices under cryogenic conditions. Ionisation of an azo-group can, in principle, take place from either the N=N π-orbital or the out-of-phase lone-pair combination (n_-) giving π- or σ-cations, respectively.[7] Photoelectron studies indicate that in azoalkanes, the n_- level lies at higher energy than the π-level and so σ-cations are expected. While ESR results for the 2,3-diazabicyclo[2.2.2]octene (DBO) cation show that it is indeed formed in the σ-state, in which the SOMO is extensively delocalised into the C–C σ-system,[4—6] the small isotropic (^{14}N) couplings and large nitrogen 2p spin densities found in open-chain azoalkane radical cations have led their assignment to the π-state.[2,3]

In this communication, results are reported for the radical cation of *trans*-azobenzene. Figure 1(a) shows a spectrum recorded from PhN=NPh following *X*-irradiation in a solid

Table 1. ESR data for azobenzene radical cations and related radicals.

Radical	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}
$PhN{=}NPh^{+\bullet}$	30.8	7.5	15.3	2.0026	2.0014	2.0018
$Me_2CHN{=}NCHMe_2^{+\bullet}$	24.0	0	8.0	2.0026	2.0080	2.0062
$PhN{=}NPh^{-\bullet}$	14.0	0	4.7	—	—	*ca.* 2.003

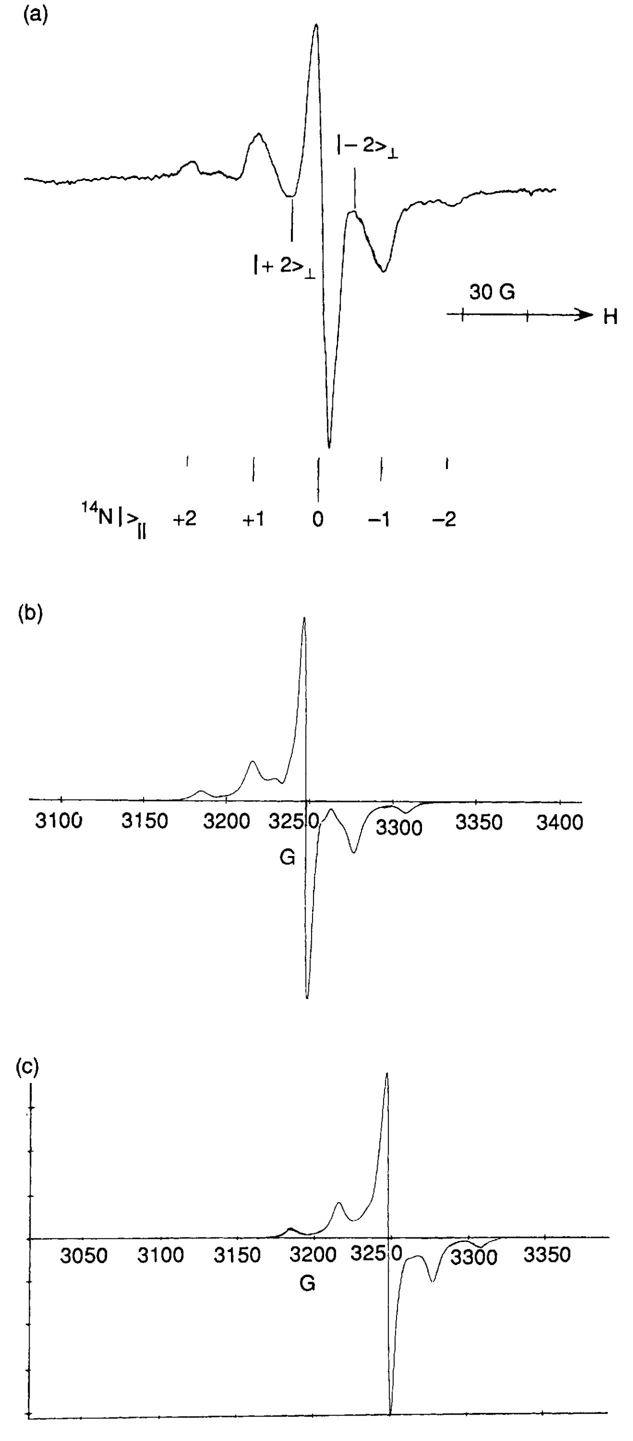

Figure 1. (a) ESR spectrum of azobenzene radical cations isolated in a solid $CFCl_3$ matrix at 77 K, (b) σ-simulation obtained using the parameters given in Table 1, (c) π-simulation; see text.

$CFCl_3$ matrix at 77 K. It is evident that there are five major hyperfine features present, from which a parallel coupling ($A_{\|}$) of 30.8 G can be measured. In contrast with the spectra of the open-chain azoalkane cations,[2,3] where $A_{\perp}$ was not clearly resolved, there are additional perpendicular components, giving $A_{\perp}$ 7.5 G; this is confirmed by the simulation shown in Figure 1(b). From this data, an isotropic coupling of 15.3 G can be derived. Therefore, the contribution from the nitrogen 2s component to the SOMO has increased substantially from that observed for the RN=NR cations (*e.g., ca.* 8 ± 2 G in $Me_2CHN{=}NCHMe_2^{+\bullet}$, Table 1); a result most reasonably explained in terms of a σ-structure for the azobenzene cation. The simulation in Figure 1(c) was obtained using a value of $A_{\perp}$ 5.9 G, which is the minimum possible for a π-structure according to the atomic parameters[8] for a N=N *localised* SOMO with a 2p spin density of 0.5 on each nitrogen atom. Any delocalisation of the electron would increase $A_{\perp}$ so that the perpendicular features were fully resolved, since A_{iso} would require a larger value in this case. At any rate, the minimum possible isotropic coupling is 14.2 G, which is incompatible with a π-structure.[3]

From the ratio of p/s electron spin densities of 16.5, $\widehat{\mathrm{Ph{-}N{=}N}}$ bond angles of *ca.* 160° can be estimated by the usual approximate procedure.[8] Since this is much greater than the *ca.* 130° obtained from MO calculations on $RN{=}NR^{+\bullet}$ cations,[9—11] for which σ-structures are predicted, a high degree of bent-bonding (incomplete orbital following) is implicated,[12] although the value calculated from the ESR data may be taken as a measure of interorbital angles and suggests that substantial bonding character is introduced between the nitrogen atoms (represented by: $-\ddot{\mathrm{N}}{=}\dot{\mathrm{N}}^{+}- \longleftrightarrow -\dot{\mathrm{N}}^{+}{=}\ddot{\mathrm{N}}-$) on ionisation. As the sum of the p + s orbital spin densities on the nitrogen atoms is 0.97, the SOMO must be very highly confined to the N=N unit, and hence the degree of delocalisation onto the phenyl groups can be only very small. This implies a structure in which both phenyl rings and the N=N group are coplanar, so that direct π-delocalisation of spin density from the n_- orbital is prevented.

Further evidence for a difference in the electronic structure of the azobenzene cation from that of open-chain azoalkane cations is provided by its *g*-tensor data; this is compared in Table 1 with that for the azoisopropane cation. The $g_{\|}$ axis is taken as being close to the A_z axis, and is near the spin-only value; however, the $g_{\perp}$ component is below free-spin, in contrast with the azoisopropane cation for which $g_{\perp} = 2.0080$. These $g_{\perp}$ shifts will be discussed more fully elsewhere.[11]

It has been suggested previously[13] that the five-line spectrum (A_{iso} 9.3 G) observed in a flow-system during reduction of PhN_2^+ ions with sodium dithionite, and assigned to $PhN_2^\bullet$ radicals,[14] is in fact due to the azobenzene radical cation. If this assignment is correct, the much lower A_{iso} value was observed in solid freon suggests that the proposed reaction (1)[15] leads to the alternative π-state of the azobenzene cation.

$$PhN{=}N^+ + Ph^\bullet \rightarrow PhN{=}NPh^{+\bullet} \qquad (1)$$

However, the magnitude of the isotropic coupling implies that the spin density on the N=N unit must be close to unity† (*i.e.*, that there is virtually no delocalisation onto the phenyl groups). This contrasts with ESR results for other π-radical cations with phenyl substituents which show them to be partially delocalised species,[3,16] and with hyperfine data for the corresponding azobenzene π-radical *anion* (see Table 1)

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† By means of the spin-polarisation parameters derived in ref. 3, and assuming that the spin densities on the two nitrogen atoms are equivalent, by symmetry, a total π-spin density is obtained on the two nitrogen atoms of:

$$\rho_1^{\pi} + \rho_2^{\pi} = (2 \times 9.3)/(S^{N} + \sum_{X} Q^{N}{}_{N\text{-}X} + Q^{X}{}_{X\text{-}N}) = 0.99$$

This suggests a near absence of delocalisation onto the phenyl groups, which is surprising for the π-cation.

which establish significant delocalisation of *ca.* 30%; the assignment[13] is therefore believed to be tentative.

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