

An EPR and Theoretical Investigation of Azoalkane and Azobenzene Radical Cations

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Results for azoethane, 1,1'-azopropane, 2,2'-azopropane, 1,1'-azoadamantane, 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (Me₂DBO) and *cis* and *trans*-azobenzene radical cations are presented, as formed in solid freon matrices at low temperatures. The azoalkane radical cations are all formed in σ -states, corresponding to ionisation of the a_g orbital (out-of-phase lone-pair combination), while for the *trans*-azobenzene radical cation the assignment to the π -state cannot be definitely excluded, although experimental evidence would appear to suggest the σ -state: the *cis*-azobenzene radical cation isomerises to the *trans*-isomer. Semi-empirical calculations were also performed on selected examples of the above species, the conclusions from which are discussed.

Radical cations of azoalkanes have been implicated as intermediates in a variety of reactions¹ involving these compounds. Definitive evidence for their structural nature has been provided by EPR spectroscopy, mostly as isolated in solid freon matrices at low temperatures,²⁻⁷ and, in the case of relatively stable bridgehead azoalkane radical cations, liquid phase spectra have been recorded.⁸⁻¹⁰ The overall conclusion from these studies is that the ionisation occurs from the out-of-phase lone-pair combination giving 2A_g radical cations, as opposed to ionisation of the N=N π -level leading to the alternative 2A_u (π) state. These conclusions are in accord with the results of photoelectron spectroscopy of simple azoalkanes, which show that the π -level lies *ca.* 2.6 eV below the a_g level, assuming that the ionisations occur vertically.¹¹

In the present paper, we examine in more detail a wider range of compounds in an effort to evaluate the generality of the above over different overall structures.

Experimental

In accord with normal practice for radical cation generation in freon matrices, dilute (*ca.* 1.0%) solutions of the azo-precursors were prepared in freon solvents, and were frozen to 77 K at which temperature the resulting polycrystalline solid solutions were exposed to γ -radiation from a ⁶⁰Co source to a nominal dose of 1 Mrad. EPR spectra were recorded at 77 K, using either Varian E9 or Bruker ER 200D spectrometers, but were annealed to higher temperatures initially by simply decanting the liquid nitrogen coolant from the Dewar and allowing the sample to warm, and using either standard Varian or Bruker variable-temperature devices when specific temperatures were required.

The origin of the open-chain azoalkanes is as quoted previously:^{2,3,5} (*E*)-azobenzene was purchased from Aldrich; 2,3-diazabicyclo[2.2.2]oct-2-ene, 1,4-dimethyl-2,3-diazobicyclo[2.2.2]oct-2-ene, 1,1'-azoadamantane and 2,3-diazabicyclo[2.2.1]hept-2-ene were generous gifts from Professors H. J. Shine and P. S. Engel; (*Z*)-azobenzene was prepared by UV irradiation of the *E*-isomer in hexane solution, followed by column chromatography of the resulting *Z-E* mixture.

Results and Discussion

Hyperfine coupling and g -parameters for azoalkane (and

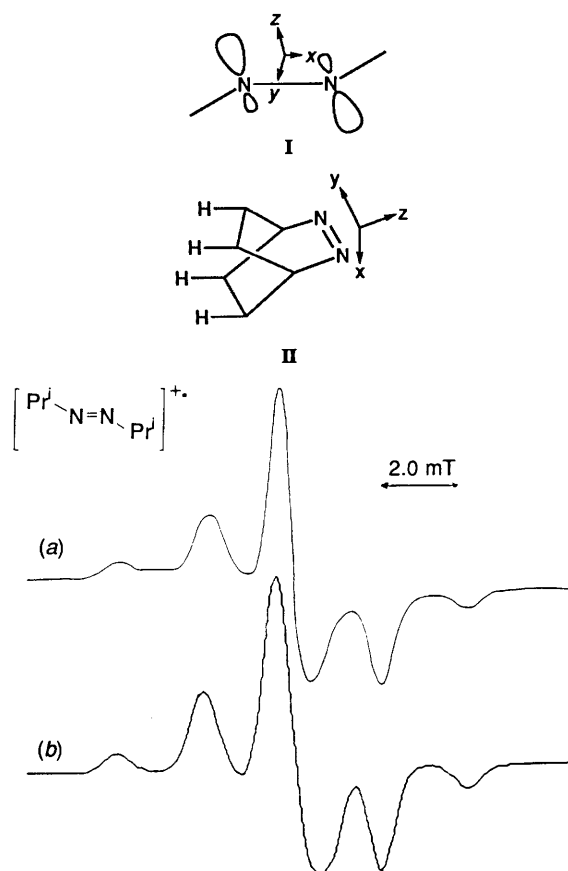


Fig. 1 EPR spectrum assigned to 2,2'-azopropane radical cations in a CFCl_3 matrix at 77 K, along with simulation; simulation parameters: $g_1 = 1.9974$; $g_2 = 2.0063$; $g_3 = 2.0034$; $A_1 = 0.10$ mT; $A_2 = 0.65$ mT; $A_3 = 2.30$ mT; linewidth = 0.7 mT

azobenzene) radical cations, both from the present work and from the literature, are collated in Table 1. We now discuss our results for specific cases.

$\text{Me}_2\text{CHN}=\text{NCHMe}_2$.—The spectrum in Fig. 1 is that of the $\text{Me}_2\text{CHN}=\text{NCHMe}_2^{+\cdot}$ radical cation, along with its computer

Table 1 EPR parameters for azo-radical cations measured at 77 K

Radical	(¹⁴ N) coupling ^a	g-Value
EtN=NEt ⁺	$A_{ }$ 24 (A_{\perp}) ^b 7	2.0033/2.0064/1.9975
Pr ⁿ N=NPr ⁿ⁺	$A_{ }$ 24 (A_{\perp}) ^b 7	2.0032/2.0062/1.9972
Pr ⁱ N=NPr ⁱ⁺	$A_{ }$ 23 (A_2) 6.5 (A_3) 1.0	2.0034/2.0063/1.9974
AdN=NAd ⁺ ^c	$A_{ }$ 23 (A_{\perp}) ^b 7	2.0034/2.0065/1.9974
DBO ⁺	$A_{ }$ 41 A_{\perp} 26 a (4 H) 15	$g_{ }$ 2.0036, g_{iso} = 2.002 ^d
Me ₂ DBO ⁺	$A_{ }$ 41 A_{\perp} 26 a (4 H) 15	g_{\perp} 2.0035
PhN=NPh ⁺ -CFCl ₃	A 7.0/7.0/30.7	g_{iso} = 2.0018
PhN=NPh ⁺ -CF ₂ ClCFCl ₂	A 7.5/7.5/28.0	2.0002/2.0002/2.0038

^a In Gauss, 1 G = 10⁻⁴ T. ^b Probably a single A -component, the other being close to zero. ^c Ad = 1-adamantyl. ^d From ref. 6.

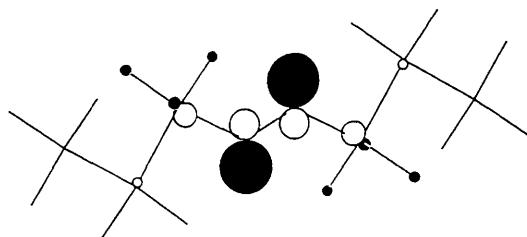


Fig. 2 Representation of SOMO for σ 1,1'-azopropane radical cation calculated by AM1 semiempirical methods

simulation. A_3 must be assigned to the z -axis (**I**) and, if the A - and g -tensors are nearly coincident, the g -value should be close to free spin; however, the actual g -value (2.0034) is slightly shifted from this. One approach to the assignment of the other A - and g -values, within the axis system in **I**, is to make recourse to the normal form of hyperfine tensors for nuclei of atoms which (*a*) bear spin density themselves and (*b*) are proximal (α) to a position of spin density. Within the axis system **I**, that for (*a*) will take the form $+2B$, $-B$, $-B$ (z, x, y), and for (*b*) 0 , $+B_x - B_x$ (z, x, y). Since *each* nitrogen nucleus in this delocalised unit is expected to experience dipolar contributions from spin density on *both* nitrogen atoms, the negative dipolar components are seen to reinforce along y , but partly to cancel along x ; for the z -direction, only the positive dipolar component is of any consequence. On this basis, the positive isotropic coupling will be cancelled least along x but most along y , leading to the assignment of $A_x = 6.5$, $A_y = 1.0$.

This would lead to the assignment of $g_x = 2.0076$, $g_y = 1.9972$, which could be explained if $B(x)$ resulted in promotion of an electron from the π into the SOMO, in accord with the PES/UV-derived energies for neutral azomethane shown in Fig. 2. However, it is very difficult to explain how an appreciable *negative* g -shift could occur when the field lies along the y -direction, unless coupling with C-N σ^* orbitals was particularly dominant, and we note that this assignment order is at odds with that for the very simple σ -radical HCO[•] in which the α -proton tensor establishes clearly that the negative g -shift arises when the field is in the C=O direction.

We feel, on balance, that the negative shift is from the N=N (x) direction and arises from coupling with the N-N π^* level: the observed opening of the C-N=N angles, discussed presently, would bring the n_{\perp} and π^* levels closer together (they would be degenerate for the fully linear case). The positive shift along the y axis we propose is a consequence of electron promotion from filled σ -orbitals (C-N, N-N). In this interpretation, our simple picture of two mutually interacting dipolar tensors does not hold, since the x ($-B + B_x$) and y ($-B - B_y$) contributions appear to be reversed. We suggest that a modification of the normal dipolar (α) tensor stems from *negative* spin density in the system which, at least qualitatively, accounts for this. While our

INDO calculations do indeed predict substantial negative spin densities, the full details are as yet unclear.

The existence of appreciable dipolar contributions from more than a single source complicates slightly the derivation of the true perpendicular coupling for each nitrogen nucleus. However, by taking all signs as positive for the x , y , z A -components, an isotropic coupling of 10.2 G is obtained: if A_z is close to the true 'parallel' coupling, we determine a $2B$ value of 12.8 G and thus $A_{\perp} = +3.8$ G. This leads to a $2p$ orbital population on each nitrogen atom of 0.39 with $2s$ populations of 0.02. Notably the $p:s$ ratio is 21 which is *compatible with the normal range for planar nitrogen-centred π -radicals*, but we have eliminated this assignment, and shows that the bond angle opening (C-N=N) in an azoalkane on ionisation is substantial. MNDO calculations on azoethane and 1,1'-azopropane radical cations give C-N=N angles of 136°, in accord with this overall picture, but the usual approximate procedure for estimating bond angles from $p:s$ ratios, using Coulson's equation for C_{2v} symmetry,¹³ leads to an angle in excess of 160°, so that the bonds are probably strongly bent and there is a great expansion of 'inter-orbital angles' at each nitrogen centre in order to maximise the 3-electron π -bonding between the nitrogen centres. Clearly these angles have not opened to the 180° (π) limit since the radical cation would be electronically degenerate and extremely large g -shifts are expected in cases of this kind, even in the presence of strong matrix perturbations, well outside of that observed in the present study.

EtN=NEt, PrⁿN=NPrⁿ and 1,1'-Azoadamantane.—The assignments for the radical cations of these substrates are very similar (Table 1) with only small changes in the g - and A -parameters arising from minor substituent effects on the N=N⁺ unit. This shows that the SOMO is strongly confined to the C-N=N-C moiety, as shown in Fig. 2, which was calculated using the AM1 method, further extensions of the C-C σ -system providing only marginal influences on its structure. Published results for the 1,1-azonorbornane radical cation⁸ also accord with this view since the reported $A_{||}$ value is close to that measured by us in these other cases discussed, and the isotropic ¹⁴N couplings measured directly from liquid solution⁸⁻¹⁰ (11–12 G) are in accord with those obtained by averaging our anisotropic data (10–11 G), allowing for the potential environmental differences between solid and liquid phases.

2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) and its 1,4-Dimethyl Derivative (Me₂DBO).—The DBO radical cation has been studied both by EPR^{6,7} and ENDOR⁷ spectroscopy in a CF₂ClCFCl₂ matrix, in which the DBO cation rotates sufficiently rapidly on the spectral timescale at temperatures above 100 K that isotropic g - and A -parameters can be determined. The results show the presence of a long-range coupling of 15 G to the four equivalent *anti*-protons, as in **II**, and thus that the SOMO is delocalised into the C-C σ -system. However, no anisotropic parameters have been reported but

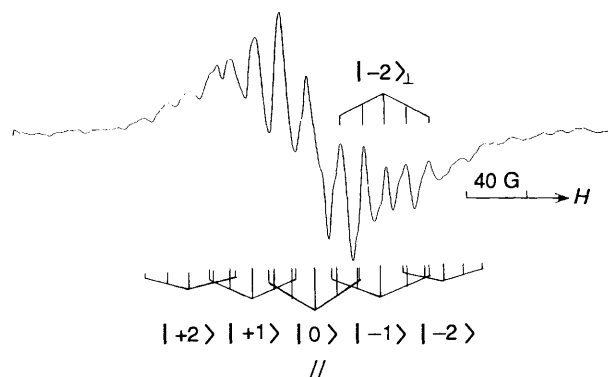


Fig. 3 EPR spectrum of $\text{DBO}^{\bullet+}$ radical cations in solid CFCl_3 at 77 K

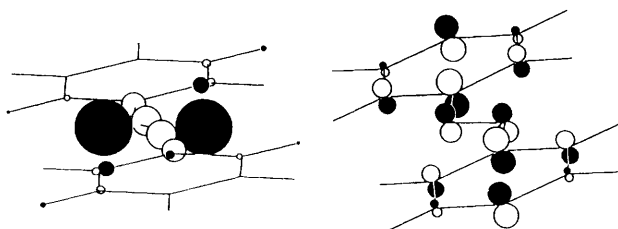


Fig. 4 σ - and π -SOMOs for azobenzene radical cation calculated by AM1 semiempirical methods. Each ground state is associated with a particular geometrical distortion (see the tables for details).

these are important in the aspect of determining the structural details of a *cis* C=N=N-C unit. We therefore obtained spectra from the DBO and Me_2DBO radical cations at 77 K in a CFCl_3 matrix, as is typified by Fig. 3. Williams *et al.*⁶ reported that the $\text{DBO}^{\bullet+}$ cation is readily bleached by visible light, giving the cyclohexene radical cation by loss of N_2 : we find that $\text{Me}_2\text{DBO}^{\bullet+}$ displays similar sensitivity to light, and by analogy make a tentative assignment of the resulting spectrum to a dimethylcyclohexene radical cation.

The (^{14}N) A -parameters are identical for $\text{DBO}^{\bullet+}$ and $\text{Me}_2\text{DBO}^{\bullet+}$, and may be processed in the usual way to yield 2s and 2p orbital populations of 0.056 and 0.303, respectively. Their sum, over both nitrogen atoms, shows that 72% of the total spin is borne by the N=N unit; this contrasts with the sum of $85 \pm 2\%$ found for the *trans* azoalkane analogues and it is significant that the sum of the spin densities on the *anti* protons (12%) accounts for the difference. The p : s ratio is now 5.4, which tells us immediately that the C-N=N bond angles are reduced from the unconstrained *trans* azoalkane radical cations; using Coulson's equation¹³ we estimate a bond angle of 137° taking the observed s-character as a true measure of the hybridisation state of each nitrogen centre. Allowing for the induced s-component^{3,14} arising from spin-polarisation of the N σ -orbitals, we obtain a very similar value of 139° ; this is to be compared with results from an AM1 calculation which gives the value 117.3° .⁶ We attribute the substantial difference of 22° to bent-bonding in the $\text{DBO}^{\bullet+}$ cation and rationalise this in terms of a distortion in the molecule on ionisation, which serves to maximise the N-N $^+$ π -overlap alluded to earlier for the *trans* cases. This will force the C-N=N bond angles to 'open' but the constraints of the rigid DBO framework precludes full relaxation, so the compromise is for the C-C(N) bonds to bend.

The g -value along the parallel hyperfine direction, (z) (\parallel), is very similar to that for the open-chain analogues; however, the isotropic g -value⁶ is reduced from this (2.002) indicating the contribution to the motional average from a substantial negative shift for one of the other directions: in accord with our previous discussion, we attribute this to n_-/π^* mixing along the N=N (x) direction.

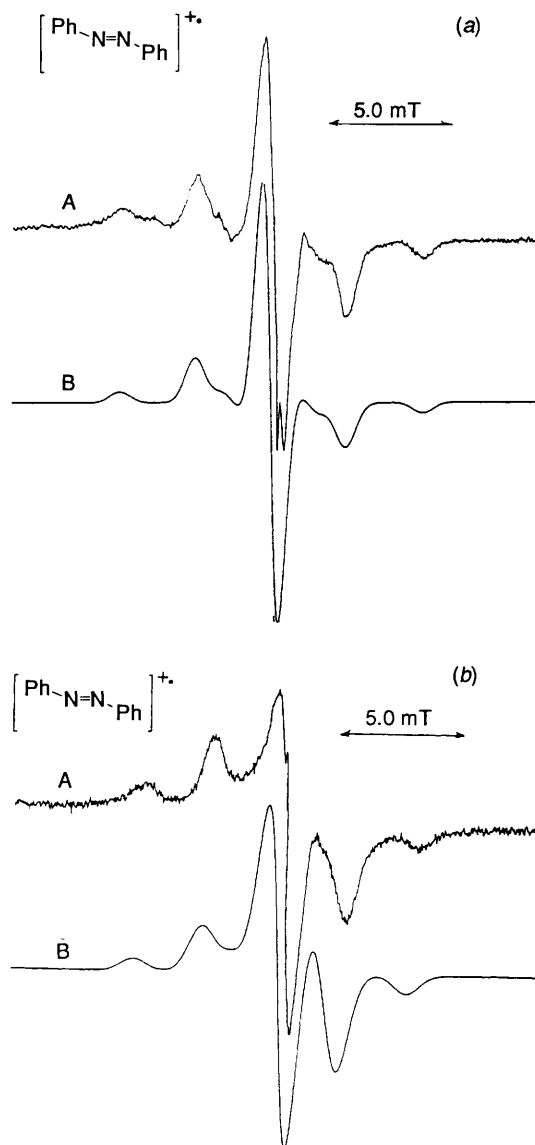


Fig. 5 EPR spectra of azobenzene radical cations (a) in CFCl_3 and (b) in $\text{CF}_2\text{ClCFCl}_2$, both recorded at 77 K; simulation parameters: $A_1 = A_2 = 0.70$ mT; $A_3 = 3.07$ mT; $g_{\text{iso}} = 2.0018$; linewidth = 0.8 mT (a); $g_1 = g_2 = 2.0002$; $g_3 = 2.0038$; $A_1 = A_2 = 0.775$ mT; $A_3 = 2.80$ mT; linewidth = 1.0 mT (b)

Azobenzene.—A preliminary report⁴ of work on the *trans* azobenzene radical cation in a CFCl_3 matrix has been published. The A_{\parallel} (^{14}N) coupling is, at 31 G, larger than that for the *trans* azoalkane radical cations, and was taken as conclusive evidence for the formation of the σ -state, particularly in view of the large derived isotropic coupling (14.9 G). As shown in Fig. 4, according to an AM1 calculation, the π -SOMO for this radical cation is strongly delocalised which further contrasts the experimentally derived sum of the 2s + 2p populations over both nitrogen atoms which is close to unity. This is more in accord with the highly localised SOMO shown for the σ -state. The anisotropy in the g -tensor is rather low: previously we assigned⁴ $g_{\parallel} = 2.0026$, $g_{\perp} = 2.0014$, giving an average of $g = 2.0018$. However, a good fit is also obtained as shown in Fig. 5(a) when an isotropic g -value of 2.0018 is used.

It is very interesting that the magnetic parameters change significantly [Fig. 5(a)/(b) and Table 1] when a $\text{CF}_2\text{ClCFCl}_2$ matrix is used. Such differences have been observed previously,¹⁵ and could be readily explained in terms of a matrix effect which selects between different electronic states. If, however, this were the case for azobenzene $^{\bullet+}$ the other obvious

possibility would be the π -state, but, at 14.3 G, the isotropic coupling still appears very large for this assignment, and a total 2p population of 82%, though significantly less than that for the CFCl_3 case (96%), does seem unprecedented for a phenyl conjugated π -radical ion.

We also attempted to study the *cis*-azobenzene radical cation, but this appeared to isomerise rapidly to the *trans* form in CFCl_3 . This accords with liquid-phase work on the *cis*-1,1'-azonorbomane radical cation which rapidly isomerises to the *trans* isomer.¹⁰

MO Calculations.—The geometric and electronic structures of selected substituted azo-cations were performed employing the MNDO and AM1 semiempirical methods developed by Dewar and Thiel¹⁶ available in the MOPAC package [QCPE No. 506]. Isotropic hyperfine splittings were calculated using the INDO method¹⁷ in a program originating from Olaff and Huttermann¹⁸ using the optimised cation structures. Dipolar couplings were calculated using a program developed by Edlund *et al.*¹⁹

In Tables 2–4 are presented theoretical results for energies, geometries, isotropic ¹⁴N couplings and *g*-tensors of azopropane and azobenzene radical cations. For azobenzene^{•+}, it can

Table 2 Geometrical parameters of the centre C–N=N–C moiety of azobenzene and azopropane radical cations from MNDO(RHF)

	Azobenzene ^{•+}		Azopropane ^{•+} ^a
	π -state	σ -state	σ -state
$\Delta_f H/\text{kcal mol}^{-1}$	275.1	292.9	202.9
$R(\text{N}=\text{N})/\text{\AA}$	1.271	1.186	1.165
$R(\text{C}-\text{N})/\text{\AA}$	1.378	1.423	1.503
Bond angle (N=N–C)/deg	118.2	131.6	135.7

^a No π -state could be found for the alkyl substituent.

be seen that the calculated relative stability of the σ/π states depends on the method chosen, with MNDO(RHF) and INDO favouring a more stable π -state, while AM1 selects the σ -state as being the lower in energy. Regarding the ¹⁴N isotropic coupling, the π -state is predicted to have a larger value than the σ -state,

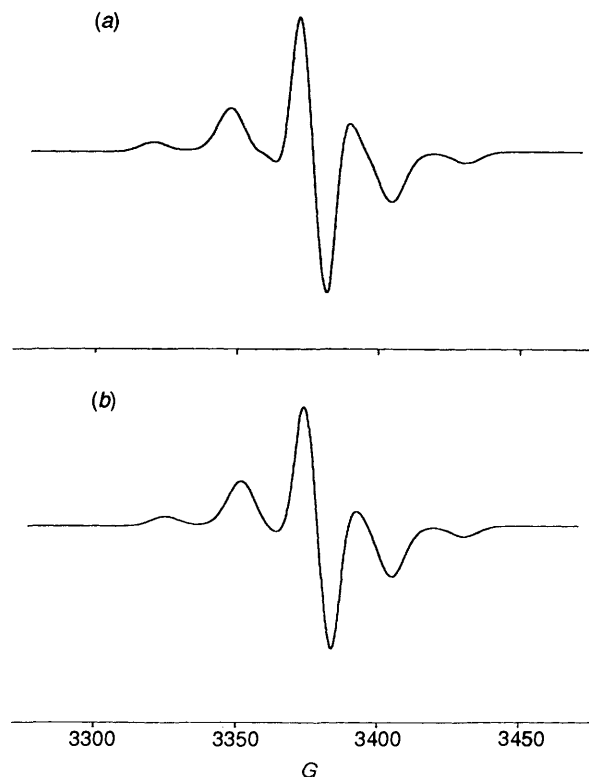


Fig. 6 Simulation using semiempirical data (a) for π -PhN=NPh^{•+} and (b) for σ -PhN=NPh^{•+} radical cations

Table 3 Magnetic^a parameters for the azobenzene and azopropane radical cations from INDO. The *x*-axis is along the N=N bond. The *z*-axis is perpendicular to the plane of the molecules.

	Azobenzene ^{•+}		Azopropane ^{•+}
	π -state	σ -state	σ -state
$E_{\text{tot}}/E_{\text{h}}$	–111.685	–111.648	–74.015
$^{14}\text{N}_{\text{iso}}/\text{mT}$	1.66	1.52	1.37
g_{xx}	2.0004	2.0000	1.9952
g_{yy}	2.0023	2.0023	2.0023
g_{zz}	2.0033	2.0029	2.0029
Dir. cos.	$\begin{bmatrix} -0.831 & -0.557 & 0.000 \\ -0.557 & 0.831 & 0.000 \\ 0.000 & 0.000 & 1.000 \end{bmatrix}$	$\begin{bmatrix} -0.908 & -0.419 & 0.000 \\ -0.419 & 0.908 & 0.000 \\ 0.000 & 0.000 & 1.000 \end{bmatrix}$	$\begin{bmatrix} -0.934 & -0.356 & 0.000 \\ -0.356 & 0.934 & 0.000 \\ -0.000 & 0.000 & 1.000 \end{bmatrix}$

^a The *g*-tensors were calculated using the closed-shell option of INDO. The hfs constants were calculated with the open-shell option. Pople's parameters were used throughout.

Table 4 Geometrical parameters for the –C–N=N–C– moiety of the azobenzene cation radical calculated using semiempirical theory

	Azobenzene ^{•+}			
	π -structure		σ -structure	
	AM1	MNDO	AM1	
$H_f/\text{kcal mol}^{-1}$	297.68	275.01	287.10	292.9
$R(\text{N}=\text{N})/\text{\AA}$	1.2706	1.271	1.177	1.186
$R(\text{C}-\text{N})/\text{\AA}$	1.3809	1.377	1.4108	1.423
Bond angle (N=N–C)/deg	120.32	118.16	137.26	131.6

which, as discussed earlier, is very surprising, if indeed it is real. What is most interesting is that simulations based on the *calculated* (from INDO spin densities) hyperfine and *g*-tensor data are in very reasonable agreement with the observed spectra for *either* the σ - or the π -states [Fig. 6(a)/(b)]. Thus, at least on the basis of this semiempirical theory, it is not possible to distinguish between the two cases and a slight adjustment of the parameters for either could obtain agreement with σ or π . Nonetheless, by comparison with other π -radicals which are (i) more delocalised and (ii) show, in any case, smaller isotropic couplings, we maintain some reservation regarding the π -assignment to either of our experimental spectra. We note also that a liquid-phase EPR spectrum has been assigned to the azobenzene radical cation²⁰ with an isotropic coupling to two equivalent nitrogen nuclei of 9.3 G; if correct, this would accord more with a normal π -radical cation.³

The *g*-tensor data for the 1,1'-azopropane radical cation is particularly significant, since it accords with the ordering of *g*-axes made earlier. For instance, the large negative *g*(*x*) shift is predicted, as is a smaller positive shift for the direction perpendicular to the radical plane; the free spin value is, as expected, predicted to lie along the SOMO axis direction. Once again, a simulation made using only the semiempirical parameters gives a good reconstruction of the experimental spectrum.

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