An EPR and Theoretical Study of Radicals Formed from Tetraalkylsulfamides $[(R_2N)_2SO_2]$

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A series of sulfamides has been synthesised and their primary radical cations studied by EPR spectroscopy following γ-radiolysis in low-temperature freon matrices. These species are readily bleached by visible light (>570 nm), to give secondary radicals, the nature of which varies with the sulfamide used. The ^{14}N hyperfine data show that the SOMO comprises both nitrogen centres and furthermore that the ^{14}N tensors are parallel. This implies that a distortion of the sulfamide system occurs on ionisation, since the neutral species (at least for sulfamide and its tetramethyl derivative) adopt bisected structures with an appreciable angle between the nitrogen 2p orbitals. MO calculations indicate that the obvious possibility of a twisting of the N-centres through 90° to form regular 'allylic' structures is disfavoured energetically over the retention of the basic bisected geometry, and we suggest therefore that it is a 'bent-bonding' distortion that operates to render the N-orbital axes parallel, in accord with the EPR data. Additionally, we have studied radicals formed by radiolysis of the pure sulfamides at 77 K, and conclude that much of the radiation chemistry in these pure systems is driven by electron capture events: these are not possible in the freon media which are themselves efficient electron capture materials, and thus remove them from the reaction system.

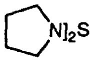
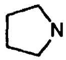
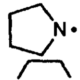
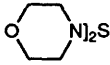
A variety of sulfur-containing radicals have been studied by EPR spectroscopy. These include sulfinyl ($RSO^{\bullet}$)[1] and sulfonyl ($RSO_2^{\bullet}$)[2,3] species, along with their amino-analogues $R_2NSO^{\bullet}$[4] and $R_2NSO_2^{\bullet}$,[5,6] and the extensive literature available on nitrogen-sulfur-containing radical cations has recently been reviewed.[7] Simple thiyl radicals ($RS^{\bullet}$) were studied in the solid state by EPR spectroscopy[8] but have never been observed in solution, apart from aminothiyl radicals.[4] Simple thiyl radicals have, however, been observed in solution by muon spin rotation spectroscopy.[9,10] We have recently undertaken the study of a range of nitrogen centred radical cations[11–18] as formed by radiolysis of their neutral precursors in solid freon matrices[19,20] and a preliminary report of work on the tetramethylsulfamide radical cation has appeared.[11] In the present work, the range of sulfamides has been extended and radicals formed therefrom by exposure to γ-radiation at 77 K, both in freon matrices and in the pure state, are characterised.

Results and Discussion

Relevant EPR data are given in Tables 1 and 2 for radicals formed by radiolysis of sulfamides, along with values taken from the literature where appropriate.

Radical Cations in Freon Matrices.—$(Me_2N)_2SO_2$. Fig. 1 shows a typical spectrum obtained from this compound by γ-radiolysis of its dilute 0.1%) solution in $CFCl_3$ at 77 K, which may be readily assigned to the primary radical cation.[11] Given the large multiplicity of the $^{14}N|0>$ features and the relatively small magnitude of the proton coupling (10.6 G), a SOMO involving a single nitrogen centre is eliminated, and so the cation does not distort in the manner of the corresponding carbamide cation (1).[15] In fact, the $|0>$ components are well reproduced as a pattern of 13 lines, arising from an equivalent coupling to four sets of CH_3 protons and shows that the SOMO is distributed equally between both nitrogen centres. Parallel $|+1\rangle$, $|+2\rangle$ nitrogen features are also resolved, giving a value for $A_{\parallel}(^{14}N)$ of 18 G, and seem to show further substructure probably from a weak matrix ^{19}F interaction.[21]

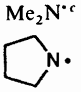
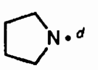
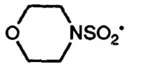
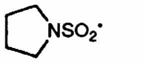
Table 1 EPR parameters for $(R_2N)_2SO_2^{+\bullet}$ radical cations and related radicals

Radical	Couplings[a,b]	g Values[c]
$(Me_2N)_2SO_2^{+\bullet}$	a(12 H) 10.6, $A_{\parallel}$ ($2^{14}N$) 18	2.0034
$(Et_2N)_2SO_2^{+\bullet}$	a(4 H) 25, a(4 H) 13, $A_{\parallel}$ (2 ^{14}N) 20	2.0035
	a(4 H) 20, $A_{\parallel}$ (2 ^{14}N) 20	2.0036
	a(2 H) 61, a(2 H) 26, $A_{\parallel}$ (^{14}N) 42	$g_{\parallel}$ 2.0023, $g_{\perp}$ 2.0056, $g_{av.}$ 2.0045
	a(4 H) 39.1, a(^{14}N) 14.4	2.0046
	a(4 H) 10, $A_{\parallel}$ (2 ^{14}N) 17	2.0036
$[(Me_2CH)_2N]_2SO_2^{+\bullet}$	a(2 H) *ca.* 7, $A_{\parallel}$ (^{14}N) 46	2.0035
$[(C_6H_{11})_2N]_2SO_2^{+\bullet}$	$A_{\parallel}$ (^{14}N) 45	2.0036

[a] In Gauss (1 G = 10^{-4} T). [b] $A_{\perp}(^{14}N)$ taken = 0. [c] g values ±0.0005. [d] Ref. 33.

An X-ray diffraction study of tetramethylsulfamide[22] shows that the molecules exist as the structure **2**. If this geometry were retained on ionisation, there would be an appreciable angle between the density axes of the two nitrogen 2p atomic orbitals in their contribution to the SOMO. The principal coupling direction would therefore bisect the N–S–N angle, corresponding to an angle (θ) between the density axis of each nitrogen 2p orbital and the external magnetic field of *ca.* 20°, so that the apparent dipolar coupling would be reduced (to *ca.* 80% of the true value, assuming a $3\cos^2\theta - 1$ dependence[23] of the anisotropic coupling). We can obtain an estimate of the *p*-orbital spin population at 0.33 on each nitrogen atom from the methyl proton couplings.[16] This enables an estimate of the

Table 2 Radicals formed by radiolysis of pure sulfamides

Radical	Couplings[a]	g Values[b]
$Me_2N^\bullet$	a (6 H) 27, $A_\parallel$ (^{14}N) 45	2.0043
$Me_2N^{\bullet c}$	a (6 H) 27.4, a (^{14}N) 14.8	2.0044
	a (2 H) 26, a (2 H) 61, $A_\parallel$ (^{14}N) 42	$g_\parallel$ 2.0023 $g_\perp$ 2.0056 $g_{av.}$ 2.0045
	a (4 H) 39.1, a (^{14}N) 14.4	2.0046
$Pr^i{}_2NSO_2^\bullet$	—	2.0036
	—	2.0035
$EtNHSO_2^\bullet$	—	2.0037
	—	2.0036
$Et_2NSO_2^\bullet$	—	2.0036
$Me_2NSO_2^\bullet$	—	2.0037

[a] In Gauss (1 G = 10^{-4} T). [b] g values ±0.005. [c] Ref. 36. [d] Ref. 33.

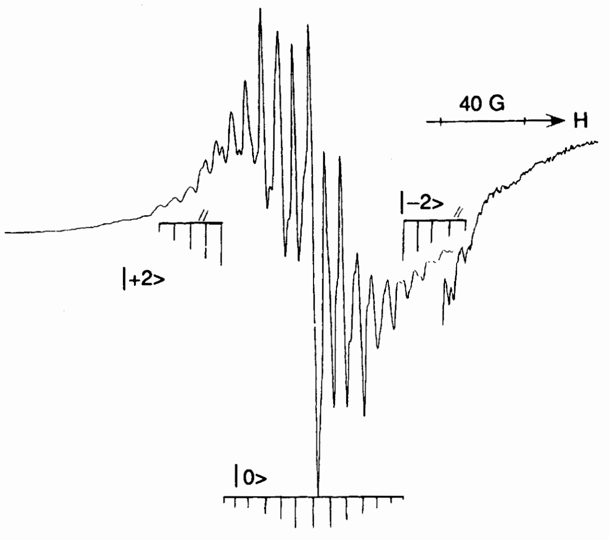
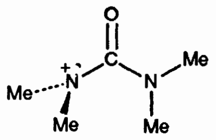


Fig. 1 EPR spectrum recorded from $(Me_2N)_2SO_2^{+\bullet}$ radical cations in a solid $CFCl_3$ matrix at 77 K

isotropic ^{14}N coupling to be made at 6.5 G, using our previously determined spin-polarisation parameters for nitrogen centred radicals,[12] and agrees well with the experimental value of 6 G which is obtained by taking $A_\perp(^{14}N) = 0$. The true dipolar coupling (2*B*) would then be 10.9 G for a spin population of 0.33[24] but would be measured at *ca.* 9 G because of the non-parallel nature of the ^{14}N hyperfine tensors discussed above.

Thus we anticipate a value for $A_\parallel(^{14}N)$ of 15.5 G for the structure **2**, which is somewhat less than observed (18 G). It seems unlikely that this difference is due to an error in the p-orbital spin populations as determined from the proton couplings, since the structural model **2** requires a spin population of the 2p orbital on each nitrogen atom of 0.44, leading to a value for $Q_N{}^{Me} = +24$ G, which appears very low indeed by comparison with data for other aminium radical cations.[16,25] In short, the data are best accommodated if the ^{14}N hyperfine tensors, and hence the nitrogen 2p orbital axes, are parallel. This could occur in two ways, one of which is *via* a substantial increase in the N–S–N angle, but this would surely put considerable strain on the molecule and thus appears unlikely. Pyramidalisation of the nitrogen centres could also render these orbitals parallel but would require the admixture of appreciable 2s character such that perpendicular $^{14}N|+1\rangle$, $|+2\rangle$ features should be observed in the EPR spectrum: this contrasts with the observation that $A_\perp(^{14}N)$ is actually within the linewidth (*ca.* 3 G) and so the nitrogen centres must be close to planar. The third possibility is that both Me_2N groups twist through 90° on ionisation so that the structure **3** is adopted. For **3**, the measured dipolar coupling will be the true value (2*B*), and we expect this to be *ca.* 10.9 G for a 2p spin population of 0.33 per nitrogen atom (above), in good agreement with that observed (18 G).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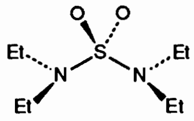
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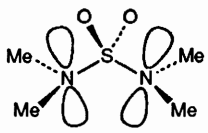
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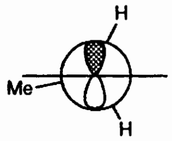
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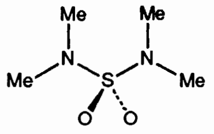
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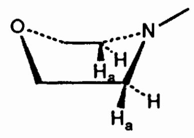
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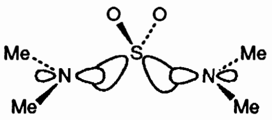
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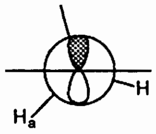
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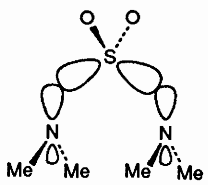
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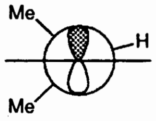
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These arguments are based on a scheme involving bond formation by the linear overlap of atomic orbitals, and do not allow for the possibility of bent-bonding, which has been proposed to be of importance in radicals and in triplet carbenes.[26] Thus a distortion on ionisation that merely increases the bending of the N–S bonds, involving the mutual motion of the bound Me_2N units could occur, leading to structures **4** or **5**, both of which comprise the requirement of parallel N(2p) orbitals, but clearly **5** is the more distorted.

*AM*1 (*MO*) *calculations on* $(Me_2N)_2SO_2$ *and its radical cation.* In order to try to gain some further insight into the structural problems discussed above, we have carried out semi-empirical AM1 calculations[*] on neutral $(Me_2N)_2SO_2$ and its

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[*] AM1 calculations (M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902) were made using version 6.0 of the MOPAC system (J. J. P. Stewart, QCPE No. 455, Version 6.0) implemented on a network of SUN work-stations: atomic parameters were taken from the literature (M. J. S. Dewar and Y.-C. Yuan, *Inorg. Chem.*, 1990, **29**, 3881; J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; 221), and the PRECISE option was used throughout. Except when constraints are explicitly defined, all independent geometrical variables ($3N - 6 = 57$) were simultaneously optimised. Calculations for open-shell species were made using both RHF and

Table 3 Calculated $\Delta H_f°$ (kJ mol^{-1}) for species discussed in the text

$(Me_2N)_2SO_2$	freely optimised (C_{2v})	−282.3
	SN_2C_4 fixed flat	−238.0
$(Me_2N)_2SO_2^{+\bullet}$	freely optimised	+576.2
	C_{2v} on N_2SO_2	+642.5
	C_{2v} and SN_2C_4 flat	+694.8
$Me_2NSO_2^+$		+571.4
$Me_2N^{\bullet}$		+130.2
$Me_2NH^{+\bullet}$		+783.2
$MeN{=}CH_2$		+76.0
SO_2		−196.7

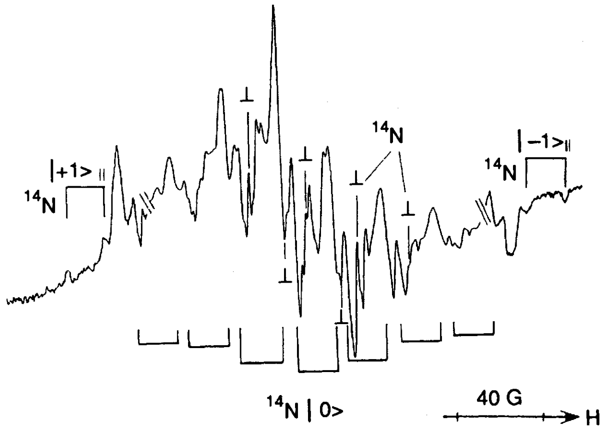


Fig. 2 EPR spectrum assigned to $Me_2NH^{+\bullet}$ radical cations formed by irradiation of the sample from Fig. 1 with red light (>570 nm)

radical cation. Extensive exploration of the conformational space for $(Me_2N)_2SO_2$ reveals only a single energy minimum having the same C_{2v} structure as that found by X-ray crystallography (**2**).[22] The nitrogen atoms are exactly planar (*cf.* the experimental sum of 351°): the HOMO (at −10.26 eV) is the out-of-phase combination of the nitrogen 2p orbitals, while the next occupied orbital (at −10.49 eV) is the corresponding in-phase combination. When the SN_4C_4 subunit was constrained to be coplanar, as in **3**, the calculated energy rose by *ca.* 45 kJ mol^{-1} (Table 3); similarly, for the radical cation, this coplanar structure was found to be 52 kJ mol^{-1} higher in energy than the overall C_{2v} geometry (**2**).

With the N_2SO_2 core of the $(Me_2N)_2SO_2^{+\bullet}$ radical cation constrained to C_{2v} symmetry, conformational exploration led again to a single minimum, having a conformation (**2**) identical with that found for the neutral molecule.[22] The SOMO is formed from the out-of-phase N(2p) combination, while the first doubly occupied orbital is the in-phase combination. Possibly associated with the ionisation of an electron from the out-of-phase orbital, the N ··· N distance in the radical cation, 2.566 Å, is marginally shorter than that, 2.605 Å, in the neutral molecule, despite the S–N bonds being longer (1.702 Å as against 1.638 Å in the neutral).

When all constraints on the structure of $(Me_2N)_2SO_2^{+\bullet}$ were removed, an entirely new geometry was obtained, with an energy (Table 3) 67 kJ mol^{-1} below that of the 'non-planar' C_{2v} conformer **2**. In this freely optimised structure, while the conformation defined by the Me_2N groups is essentially unchanged, the two S–N bonds now have different lengths, 1.569 Å and 1.925 Å, associated with S–N bond orders of 0.76 and 0.31 respectively. Both nitrogen atoms remain accurately planar but the SOMO is now localised almost exclusively on the more remote nitrogen atom. The fact that this structure is not observed experimentally may imply some limitation in the calculational method *per se*, or more likely that the structure of the radical cation is influenced by the solid matrix which impedes this distortion that otherwise might operate, as predicted, for a 'gas-phase' molecule. However, even after annealing to 155 K in an attempt to relax the matrix and release any intrinsic distortion, no EPR signal was obtained that could be attributed to a radical with a localised SOMO of this kind, and so there may be an appreciable activation energy that we were unable to overcome under our conditions.

Overall, we favour the structure **4** for $(Me_2N)_2SO_2^{+\bullet}$, for the following reasons. We are inclined to disfavour structure **3** because our calculations show it to have a significantly higher energy (Table 3) than the basic C_{2v} geometry **2**: this leaves us with either **4** or **5** to explain the parallel N(2p) orbitals observed experimentally. Structure **5** requires a very great angular distortion (*ca.* 70°) and the substantial geometry change that this implies is not born out by our calculations. On the other hand, we need only bend the N–S bonds by a relatively modest 20° to arrive at the structure **4** which is in better accord with the relatively small geometry change on ionisation predicted theoretically.

Other configurations of $(Me_2N)_2SO_2^{+\bullet}$. Subject to the constraints of C_{2v} symmetry on the N_2SO_2 core, the effect of variation of the N–S–N angle was investigated over the range 30°–180°. The neutral-type conformation **2** was retained throughout the scan, although pyramidalisation of the nitrogen atoms was apparent for N–S–N angles below 70°. Aside from the distorted minimum alluded to earlier, having $\Delta H_f°$ of +642.5 kJ mol^{-1} (Table 3), only one other minimum was found on this pathway. This was characterised by $\Delta H_f°$, +735.0 kJ mol^{-1}, *d*(N–S), 2.329 Å, and *d*(N–N), 1.423 Å. The geometry, charge distribution and SOMO all characterise this species as an adduct of $SO_2^{+\bullet}$ and $Me_2N{-}NMe_2$: indeed, this would approximate to the structure **5** with strong bonding between the N–N centres and is clearly less stable by *ca.* 93 kJ mol^{-1} than **4**. A potential decomposition product of this is the $Me_2N{-}NMe_2^{+\bullet}$ radical cation,[27] however, this was not observed as a product of either a thermal or a photochemical (see below) route.

Photolysis of $(Me_2N)_2SO_2^{+\bullet}$. The sample of γ-irradiated $(Me_2N)_2SO_2$ in solid $CFCl_3$, which was initially sky-blue in colour, could be bleached by exposure to red light (>570 nm), accompanied by the complete change in its EPR spectrum to that shown in Fig. 2. This can be ascribed to the formation of the $Me_2NH^{+\bullet}$ radical cation, the spectrum showing apparent 10 G doublet features which arise from the difference between the methyl (34.5 G) and the N–H (24.2 G) proton couplings. The hyperfine data (Table 1) are seen to be in accord with those measured previously for this radical, both in solid $CFCl_3$[28] and in a fluid acidic solution.[29] We suggest that the fragmentation in eqn. (1) takes place, succeeded by the proton transfer [eqn. (2)]. According to our calculations (earlier), although the freely

$$(Me_2N)_2SO_2^{+\bullet} \longrightarrow Me_2N^{\bullet} + Me_2{-}SO_2^{+} \qquad (1)$$

$$Me_2N^{\bullet} + Me_2NSO_2^{+} \longrightarrow Me_2NH^{+\bullet} + H_2C{=}NMe + SO_2 \qquad (2)$$

optimised isomer (Table 3) was distorted with a SOMO and charge distribution indicative of incipient dissociation to give $Me_2N^{\bullet}$, and might lie on the pathway of eqn. (1), nevertheless this dissociation is in fact endothermic by *ca.* 126 kJ mol^{-1} However, the photons of red light are certainly energetic enough (peaking at 570 nm = 210 kJ mol^{-1}) to promote this process, so long as sufficient energy from the $(N-N) \longleftarrow (N+N)$

UHF wave functions, with essentially identical results: similarly, when all the calculations were repeated using the PM3 Hamiltonian (J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; 221) the results again were concurrent with those from the AM1 calculations.

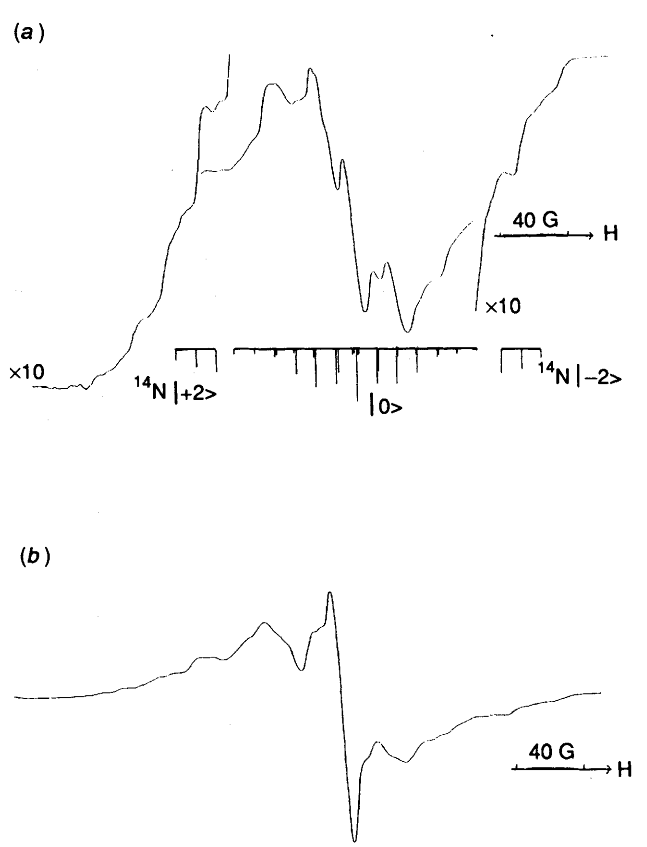


Fig. 3 EPR spectra from (*a*) $(Et_2N)_2SO_2$, γ-irradiated in solid $CFCl_3$ at 77 K and assigned to the primary radical cations, and (*b*) following subsequent bleaching with red light (> 570 nm)

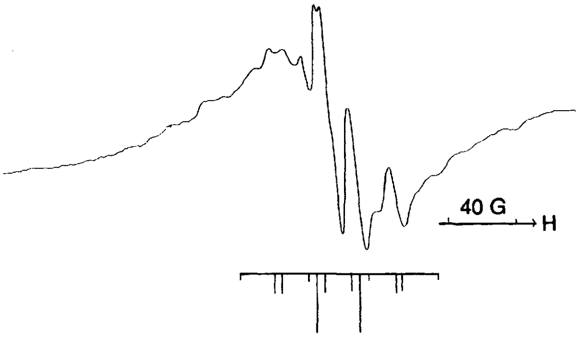


Fig. 4 EPR spectrum recorded following γ-irradiation of $(EtNH)_2SO_2$ in solid $CFCl_3$ at 77 K, showing features assigned to free ethyl radicals

transition is channelled into N–S vibrational excitation. Reaction (2), on the other hand, is calculated to be exothermic by *ca.* 39 kJ mol^{-1}.

$(Et_2N)_2SO_2$. The spectrum [Fig. 3(*a*)] recorded from γ-irradiated $(Et_2N)_2SO_2$ in solid $CFCl_3$ at 77 K shows that all 8β-protons cannot be equivalent. Our best fit for this pattern is as a quintet (25 G) of quintets (13 G), with a parallel coupling to two equivalent nitrogen nuclei of *ca.* 20 G. This can be accommodated by structure **6** in which dihedral angles of *ca.* 15° and 45° are taken by the two β-protons of each ethyl group (**7**). It is apparent that the lines are rather broad and we suggest that this is due to a small range of conformations of ethyl groups being adopted, but all very close to **7**, giving an additional line broadening. On annealing, the spectrum was slightly sharpened, but in contrast with results for $Et_3N^{+\bullet}$ radical cations,[25] where all 6β-protons became equivalent at *ca.* 140 K, even up to the limit of the melting point of the $CFCl_3$ matrix the 8β-protons remained in two inequivalent sets; this is most likely a consequence of steric hindrance in $(Et_2N)_2SO_2^{+\bullet}$ which is partly relieved in the structure **6**/**7**.

As with the $(Me_2N)_2SO_2^{+\bullet}$ radical cation, the sample of γ-irradiated $(Et_2N)_2SO_2/CFCl_3$ was an intense blue colour, and could be bleached with red light, although with more reluctance. Fig. 3(*b*) shows the resulting change in the EPR spectrum, which is actually recorded at half the gain of that in Fig. 3(*a*), and it is clear that an intense central line has 'grown-in' at the expense of features from the primary $(Et_2N)_2SO_2^{+\bullet}$ species. This line has a *g*-value of 2.0036 and is typical for $R_2NSO_2^{\bullet}$ radicals.[6] We propose therefore that reaction (3) has occurred. The species

$$(Et_2N)_2SO_2^{+\bullet} \longrightarrow Et_2NSO_2^{\bullet} + Et_2N^{+} \qquad (3)$$

Et_2N^+ may be stabilised either by bonding to a matrix $CFCl_3$ molecule[30] ($CFCl_2\text{–}Cl\cdot\overset{+}{\cdot}\cdot NEt_2$) or by rearrangement to the protonated amine [eqn. (4)]. Thus the direction of $+/^{\bullet}$

$$Et\overset{+}{N}\text{–}\overset{H}{C}HCH_3 \longrightarrow Et\overset{+}{N}(H){=}CHCH_3 \qquad (4)$$

separation accompanying the N–S bond cleavage is different in reactions (1) and (3), and is probably a consequence of the expected lower electron affinity of the Et_2N^+ than the Me_2N^+ fragment, judging by ionisation potential data for the corresponding amines, Et_2NH and Me_2NH.[31]

$(EtNH)_2SO_2$. We found no evidence for the primary radical cation following γ-radiolysis of $(EtNH)_2SO_2$ in solid $CFCl_3$ at 77 K, and apart from features that may be attributed to ethyl radicals, the spectrum (Fig. 4) shows only signals from solvent radicals. [The latter could be reduced relative to those from the organic radical by the use of low microwave powers (*ca.* 1 μW) as a consequence of the differential power response but the low solubility of the compound led to very weak signals overall at this power level.] Thus the reaction (5) is implicated. As with

$$EtNHSO_2NHEt^{+\bullet} \longrightarrow Et^{\bullet} + EtNHSO_2NH^{+} \qquad (5)$$

previous examples,[17,32] it is most likely that dissolution of this polar compound in the non-polar freon solvent occurs in the form of H-bonded clusters so that reaction (5) actually occurs within an extended molecular unit which is able to stabilise the resulting cation fragment. This would explain the difference in behaviour of this compound from the others in this study, which are apparently isolated as monomers, as expected in dilute solutions where H-bonding is absent.

$[(CH_2)_4N]_2SO_2$. As shown in Fig. 5(*a*), the spectrum from this compound comprises a central five line pattern for the |0⟩ features: this is certainly from the four pseudo-axial protons of the pyrrolidine rings. Curiously, the coupling from the corresponding pseudo-equatorial protons is not resolved and must be contained within the rather broad lines, but would be expected at *ca.* 10 G given the general rule[16] that the axial/equatorial couplings in a five membered ring radical are in the ratio of *ca.* 2, regardless of the nature of the radical centre.

Again, the sample was a (greenish) blue colour and was sensitive to red light which changed the form of the EPR spectrum to that shown in Fig. 5(*b*). This shows an intense central singlet with a *g*-value of 2.0058 and is incompatible with an $R_2NSO_2^{\bullet}$ radical (*g* = 2.0036),[6] but is in accord with typical values for $R_2NSO^{\bullet}$ radicals (2.006).[4] Thus it appears that reaction (6) has occurred. Additionally, there are weaker

(6)

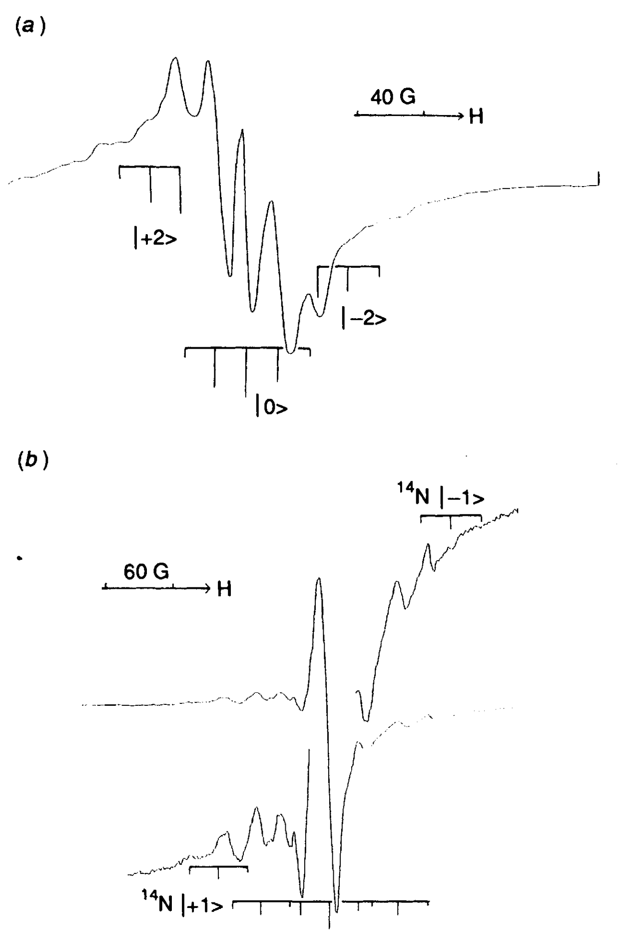
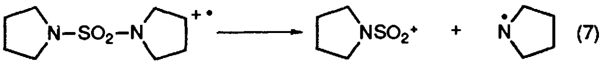


Fig. 5 EPR spectra recorded from (*a*) intact $(C_4H_8N)_2SO_2{}^{+\bullet}$ radical cations at 77 K, and (*b*) following subsequent bleaching with red light (> 570 nm)

features present which we assign to the pyrrolidinyl radical.[33] At 77 K, the pseudo-axial and pseudo-equatorial couplings for this radical are distinct but a two-jump averaging process, as expected for the ring inversion, gives an average of 43.5 G which is in reasonable accord with the value measured in an adamantane matrix;[33] the *g*-tensor data (Table 1) also average to the previously observed isotropic value. Thus reaction (7) probably also occurs.



(7)

$[O(CH_2)_4N\text{–}]_2SO_2$. The spectrum similarly recorded from dimorpholinesulfamide is shown in Fig. 6(*a*). The central |0⟩ region appears as a five line pattern with a common spacing of 10 G. Since there are shoulders present that establish the parallel coupling at *ca.* 17 G, close to the typical range, the 10 G coupling seems rather low because it has to be assigned to the four equivalent pseudo-axial protons (the corresponding equatorial proton coupling being normally fairly close to zero).[16] As in a previous study of the 1,4-dioxane radical cation,[34] where similarly low proton couplings were observed compared with those in other ether radical cations, we propose that a transannular bonding occurs (**8**) which moves the β-protons closer to the nodal region of the SOMO (**9**). In which case, the slight fall in the $A_{\parallel}(^{14}N)$ coupling may be taken as being due to some delocalisation onto the oxygen atom, and the dihedral angle for the H_a protons would be in the range 40–50° leading to a coupling of *ca.* 10 G as observed.

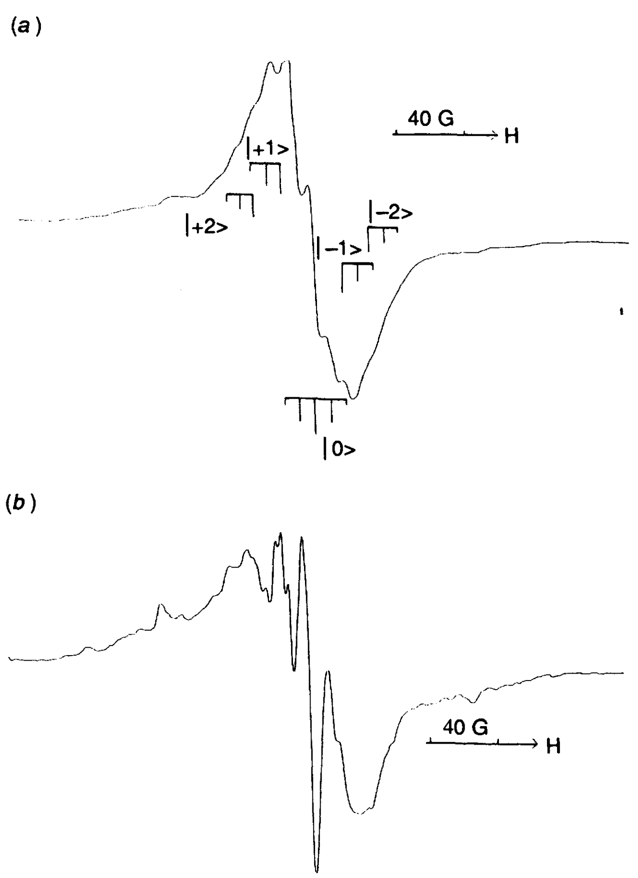


Fig. 6 EPR spectra recorded from $[O(C_4H_8)N]_2SO_2$ (*a*) following γ-irradiation in solid $CFCl_3$ at 77 K and (*b*) after bleaching with red light (> 570 nm)

The (blue) sample was partly bleached with red light accompanied by the formation of a structureless singlet at $g = 2.0036$ [Fig. 6(*b*)] so that a reaction analogous to reaction (3) is implicated.

$[(Me_2CH)_2N]_2SO_2$. The spectrum [Fig. 7(*a*)] from this compound is quite different from those considered so far and consists of just three lines. This establishes that the SOMO is now localised to a single nitrogen centre with a typical $A_{\parallel}(^{14}N) = 45$ G. The lines are broad and barely resolve a weak (2 H) proton coupling of *ca.* 7 G (most apparent as shoulders on the |+ 1⟩ feature, which is sharper than the |− 1⟩ feature because $A_{\parallel} \gg A_{\perp}$ and $g_{\perp} > g_{\parallel}$, and on the central |0⟩ feature. Therefore, the Me_2CH groups are oriented with the β-C–H protons near to the radical plane (**10**). It is interesting that a freely optimised minimum of this kind, with a localised SOMO, was predicted in our calculation on the $(Me_2N)_2SO_2{}^{+\bullet}$ radical cation, although this was never observed experimentally. We have invoked a matrix effect to account for this that impedes the required distortion involving an appreciable elongation of the $N^{+\bullet}\text{–}S$ bond: in the present example, there is a very appreciable steric congestion that would be relieved by such a distortion which is no longer retarded by the matrix.

In accord with the view that the blue colour of these cations is due to the (N–N) ⟵ (N + N) transition involving the out-of-phase and in-phase N(2p)/N(2p) combination, we note that this colour is absent for the localised $[(Me_2CH)_2N]_2SO_2{}^{+\bullet}$ cation. Instead, a yellow colour was observed, but the sample was bleached by unfiltered visible light; the resulting EPR spectrum [Fig. 7(*b*)] showing a seven-line pattern, $a(6\ H) = 24$ G. It seems most likely that an intramolecular H-atom transfer has occurred, *e.g.* reaction (8).

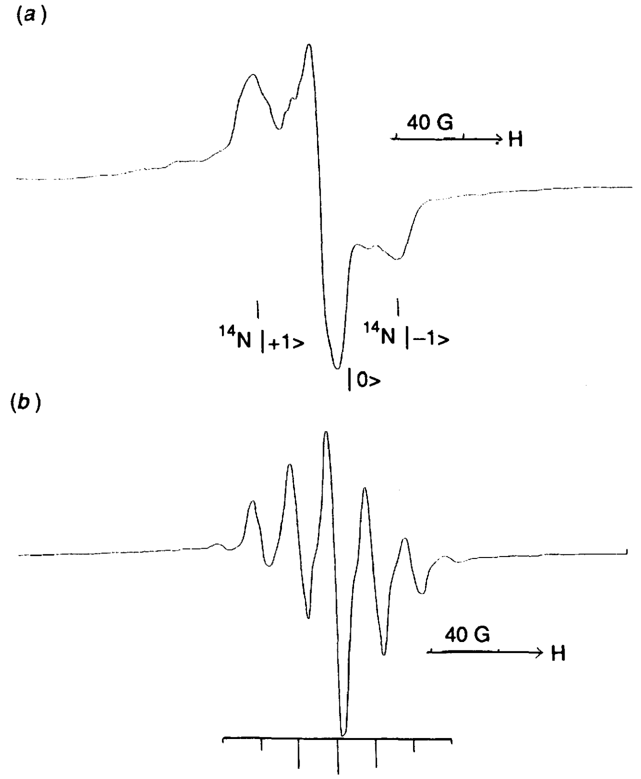


Fig. 7 EPR spectra recorded from $[(Me_2CH)_2N]_2SO_2$ (*a*) following γ-irradiation in solid $CFCl_3$ at 77 K and (*b*) after subsequent photobleaching with red light (> 570 nm)

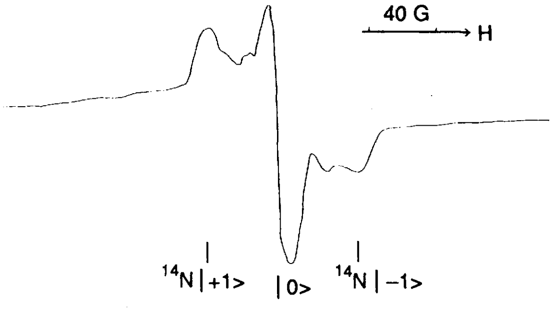


Fig. 8 EPR spectrum from $[(C_6H_{11})_2NSO_2]_2O^{+\bullet}$ radical cations in solid $CFCl_3$ at 77 K

$$Me_2CHN(CHMe_2)SO_2\overset{+\bullet}{N}(CHMe_2)_2 \longrightarrow Me_2\dot{C}\text{–}N(CHMe_2)SO_2\overset{+}{N}(H)(CHMe_2)_2 \quad (8)$$

$[(C_6H_{11})_2NSO_2]_2O$. Doubtless because of its highly sterically congested nature, we have found considerable difficulty in the preparation of the tetracyclohexylsulfamide. From one attempt, however, we managed to isolate instead the sulfamic anhydride $[(C_6H_{11})_2NSO_2]_2O$. As expected, its radical cation possesses a SOMO which is localised to one nitrogen centre with a coupling $A_{\parallel}(^{14}N) = 45$ G. There is no resolved proton structure, however, and so the two β-protons are again close to the radical plane as in **10**. The sample was yellow in colour, but in contrast with the similarly coloured $[Me_2CH)_2N)]_2SO_2^{+\bullet}$ radical cation, it was apparently resistant to bleaching with unfiltered visible light. Owing to the large size (and therefore very restricted librational mobility at 77 K) of this cation, its spectrum (Fig. 8) was found to saturate very readily, despite the appreciable anisotropy in A and g, and this could only be avoided by the use of very low microwave powers in the range 0.05–0.5 μW.

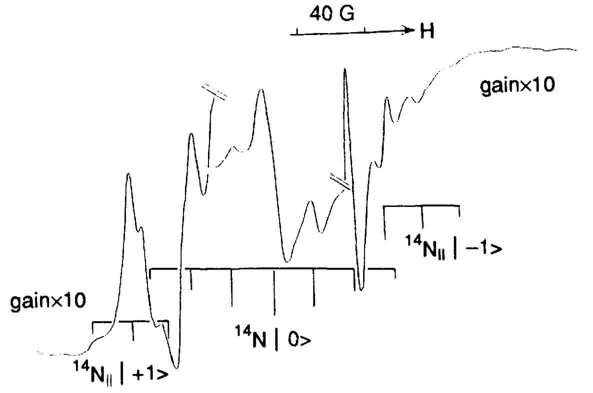


Fig. 9 EPR spectrum recorded following γ-irradiation of pure $(Me_2N)_2SO_2$ at 77 K

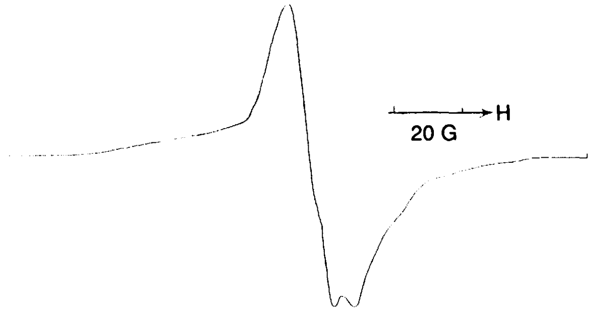


Fig. 10 EPR spectrum recorded following γ-irradiation of pure $(Et_2N)_2SO_2$ at 77 K

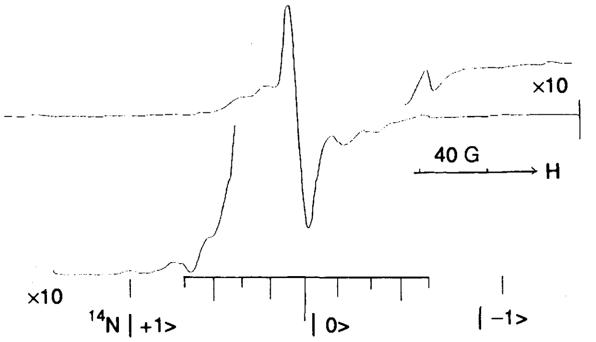


Fig. 11 EPR spectrum recorded following γ-irradiation of pure $(C_4H_8N)_2SO_2$ at 77 K

Radiolysis of the Pure Sulfamides.—Figs. 9–11 show typical EPR spectra obtained from representative sulfamides after γ-irradiation as pure solids at 77 K. In each case, the central region of the spectrum shows a structureless feature in the region of $g = 2.0036$, and we attribute this to $R_2NSO_2^{\bullet}$ radicals formed by dissociative electron capture by neutral $(R_2N)_2SO_2$ molecules [eqn. (9)]. In the cases of $(Me_2N)_2SO_2$ and $(C_4H_8N)_2SO_2$, $Me_2N^{\bullet}$ and pyrrolidinyl radicals were additionally observed implying that dissociation of the proposed intermediate radical anion may also occur in the opposite sense to eqn. (9), leading to $R_2N^{\bullet}$ radicals and $R_2NSO_2^-$ anions. The g values (Table 2) measured for the $R_2NSO_2^{\bullet}$ radicals are in agreement with those reported in the literature (2.0036 ± 0.0005)[5,6] from solid state studies, and the absence of ^{14}N structure accords with the very small (<4 G) couplings observed. We consider that the only other reasonable possibility is

$$e^- + (R_2N)_2SO_2 \longrightarrow [(R_2N)_2SO_2]^{-\bullet} \longrightarrow R_2N^- + R_2NSO_2^{\bullet} \quad (9)$$

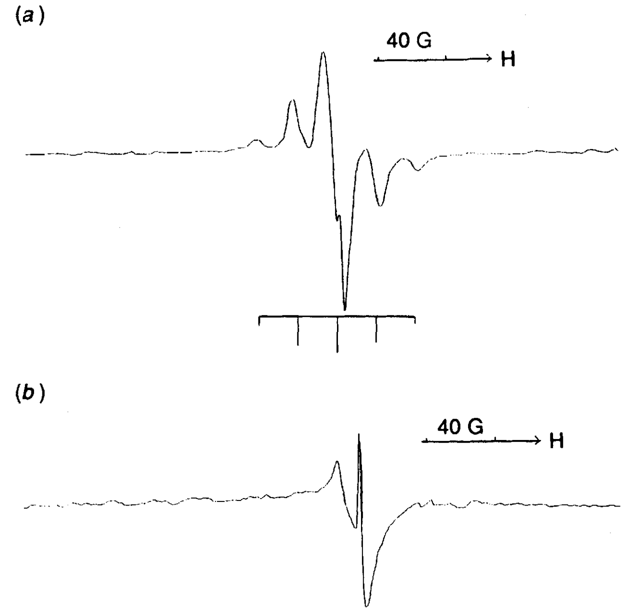


Fig. 12 EPR spectra recorded (*a*) following γ-irradiation of pure $(EtNH)_2SO_2$ at 77 K and (*b*) after subsequent bleaching with unfiltered visible light

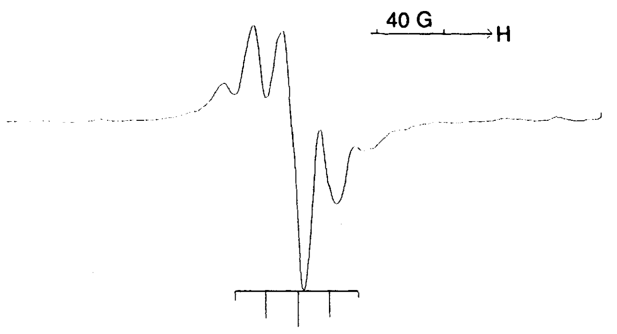


Fig. 13 EPR spectrum recorded following γ-irradiation of pure $[(Me_2CH)_2N]_2SO_2$ at 77 K

$R_2NSO^{\bullet}$ radicals, as observed from the photolysis of $(C_4H_8N)_2SO_2^{+\bullet}$ radical cations [eqn. (6)]. However, in this case, and for other radicals of this kind reported in the literature,[4] the *g* value is close to 2.006 which is too high.

In the other cases, alkyl radicals were observed. For instance, $(EtNH)_2SO_2$ gave a five line pattern [Fig. 12(*a*)] assigned to $CH_3\dot{C}HSO_2NHEt$ [a(4 H) = 24 G]; $(Pr^i{}_2N)_2SO_2$ also gave a five line pattern, but with a(4 H) = 22 G, assigned to $CH_3\dot{C}HN(Pr^i)SO_2NPr^i{}_2$ radicals (Fig. 13). We consider that these radicals arise from cation–electron combination events, leading to, respectively, C–H and C–CH_3 bond cleavage in the excited neutral sulfamide molecules. The alternative possibility, that these patterns are due to coupling to two equivalent ^{14}N nuclei is eliminated by the fact that there was no shift in the line positions on annealing to the point at which all radical signals were lost, *ca.* 230 K. In the latter case, the parallel lines should show a decrease in their separation as the more rapid tumbling of the radicals in the solid matrix averages the ^{14}N hyperfine anisotropy: the lines merely sharpen but maintain their field positions. Interestingly, the signal attributed to $CH_3\dot{C}HNHSO_2NHEt$ was bleached completely on irradiation with visible light at 77 K, without the formation of secondary radical species [Fig. 12(*b*)]. We propose that this is due to ionisation of the radical, $C^{\bullet} \longrightarrow C^{+} + e^{-}$, but there is no resulting trapped electron signal nor evidence for radicals formed by dissociative electron capture. Since the R_2NSO_2 signal is also bleached simultaneously, we suggest that reaction (10) occurs. The alternative possibility, that these radicals

$$CH_3\dot{C}HNHSO_2NHEt + R_2NSO_2^{\bullet} \xrightarrow{h\nu} CH_3CH{=}\overset{+}{N}(H)SO_2NHEt + R_2NSO_2^{-} \quad (10)$$

simply recombine, appears much less likely given that all the procedures were carried out at 77 K, and while light adsorption has been shown to increase the librational rate of matrix isolated radicals,[35] sharpening their spectra, we are not aware of any report of actual diffusion being promoted in this way.

Comparison between Freon and Sulfamide (Self-) Matrices.— As expected in freon matrices, the primary radical cations are observed or, in the case of $(EtNH)_2SO_2$, neutral radicals formed therefrom by unimolecular processes. In the self-matrices the dominant event appears to be dissociative electron capture, leading to $R_2NSO_2^{\bullet}$ radicals, and there is evidence for radical cation–electron recombination at thermal energies, leading to C–H (C–C) bond homolysis *via* excited molecular states. These electron induced reactions are not possible in the freon media, which themselves remove electrons efficiently from the reaction system by dissociative capture.

Experimental

Other than tetramethylsulfamide, which was purchased from Aldrich, the tetraalkylsulfamides were synthesised by a dropwise addition of sulfuryl chloride to a twofold excess of the corresponding dialkylamine (dried over 4X molecular sieves). The solution was filtered from the precipitate of the amine hydrochloride and evaporated to yield the crude product. This was purified by chromatography on silica, using diethyl ether as eluent. All compounds were found to have proton NMR, mass spectral and IR data consistent with the desired structures.

For EPR measurements, the pure compounds were γ-irradiated to a dose of 1 Mrad in silica tubes using a ^{60}Co source at 77 K, and for radical cation studies, dilute (*ca.* 0.1–1.0%) solutions of the sulfamides were prepared in trichlorofluoromethane and frozen at 77 K, prior to γ-irradiation, as above. The EPR spectra were recorded using a Varian E9 spectrometer using liquid-nitrogen-filled insert Dewars; sample annealing was accomplished usually by decanting the liquid nitrogen coolant and allowing the sample to warm while continuously monitoring the EPR signal for changes, and rapidly cooling back to 77 K when these were observed. Matrix signals (most evident in the low concentration range) were reduced by filtration of the freon solvent through activated silica before use, and by the subsequent use of low microwave powers (*ca.* 1 μW). Photobleaching was carried out, also at 77 K, by irradiation with visible light from a 300 W halogen lamp fitted with Oriel filters.

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