Effect of Ring Size on Hyperconjugation in Heterocycloalkanes. An E.S.R. Study

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The β-hydrogen hyperfine coupling constant for the thietane cation is 31.1 G (1 G = 10^{-4} T) whereas the corresponding value for the thiirane cation is only 16.1 G, demonstrating that CH_2 hyperconjugation in sulphur heterocycles is much diminished in going to a three-membered ring.

Although the conjugative properties of strained ring systems are believed to have an important bearing on the structure and reactivity of these compounds, there appear to be no quantitative experimental studies that describe the extent of hyperconjugation as a function of ring size. Usually, a reliable measure of hyperconjugation is available through the determination of β-hydrogen hyperfine coupling constants in π radicals by e.s.r. spectroscopy.[1] However, this approach is precluded for heterocycloalkane radical cations where the heteroatom is derived from first-row elements because the $^2B_1$ and $^2A'$ (π) states of the oxirane and aziridine cations are unstable and undergo C · · · C ring opening to give allylic structures.[2,3] We therefore turned to sulphur heterocycles in an attempt to obtain the required information, and here we report e.s.r. data that are directly applicable to the problem.

It was found some time ago that the solid-state Freon ($CFCl_3$) radiolysis technique[4,5] provides a very suitable method for the generation of monomer radical cations from alkyl sulphides in a $CFCl_3$ matrix,[6] in contradistinction to oxidation methods in solution which almost invariably result in the rapid formation of the corresponding dimer radical cations.[7,8] Using this solid-state technique, the monomer radical cation of the four-membered sulphur heterocycle (thietane) was generated almost exclusively and gave an e.s.r. spectrum with the expected g anisotropy consisting of two binomial quintet patterns [A(4H) 31.1 G; 1 G = 10^{-4} T] associated with $g_\perp$ (2.027) and $g_\parallel$ (2.008). Similar experiments for the three-membered heterocycle (thiirane) gave e.s.r. signals from both monomer and dimer cations, as shown in Figure 1, where the lower spectrum at 90 K can be analysed into two sets of overlapping features with the expected quintet [A(4H) 16.1 G] and nonet [A(8H) 5.8 G] patterns for the monomer and dimer species. Although only the low-field components of the perpendicular features are unobscured for the monomer cation, the assignment is definitive for two reasons. First, as would be expected, the $g_\perp$ value of 2.028 is close to the corresponding value for the thietane cation, and, secondly, the ratio of 2.8 of the hyperfine couplings for the thiirane monomer and dimer cations is similar to the ratio of 3.1 for the corresponding cations from dimethyl sulphide.[6]

Our hyperfine data for the thiirane, thietane, and dimethyl sulphide cations summarized in Table 1 reveal a striking effect of ring size on the β-hydrogen coupling constant. Essentially, the coupling of 31.1 G in the thietane cation is 'normal' since it agrees within experimental error with the value of 30.6 G which would be expected from the results for the dimethyl sulphide cation by considering only the angular dependence.[9] A similar 'normal' value is found for the oxetane cation by reference to the dimethyl ether cation.[10] Thus, the hyperconjugative effect in the four-membered heterocycles is very similar to that in acyclic hetero-compounds. On the other hand, our result for the thiirane cation shows that there is almost a 50% reduction in hyperconjugation on going to the three-membered ring system.

In contrast to this finding, a previous e.s.r. study of these cations reported virtually no difference between the results for thietane and thiirane.[11] Since the conflicting data pertain to the thiirane cation, we repeated these experiments using samples from both Aldrich and Fluka and confirmed our observations. Also, the stated purity (99%) of these thiirane samples was verified by g.c. and n.m.r. spectroscopy, the ^1H and ^{13}C spectra consisting of single peaks at δ 2.38 and 17.7, respectively. Our confidence in the data is thereby reaffirmed, and we conclude that the large reduction in the β-hydrogen coupling in going from the thietane to the thiirane cation is real.†

Recent MNDO calculations by Glidewell[12] provide strong support for this decreased hyperconjugation effect in the three-membered ring. In the table of his paper,[12] the calculated 1s spin densities for the four β-hydrogens in the thiirane and thietane cations are reported to be 0.016 and

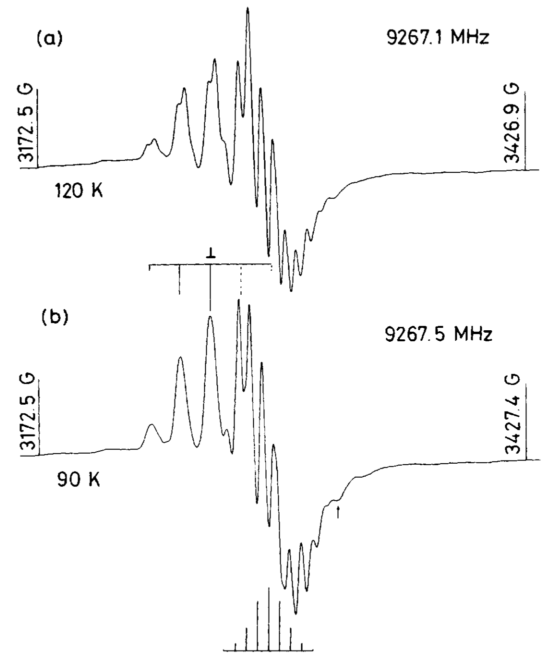

Figure 1. First-derivative e.s.r. spectra at 90 and 120 K of radicals derived by γ-irradiation of a 1 mol % solution of thiirane in $CFCl_3$ at 77 K. The upper stick diagram in (b) shows the perpendicular features of the thiirane monomer radical cation while the arrow on the right is taken to represent the outermost highfield peak of the corresponding parallel features. The fine structure which is superimposed on the monomer cation features in spectrum (a) is attributed to a weak $CFCl_3$ solvent interaction. The lower stick diagram in (b) represents the hyperfine components of the thiirane dimer radical cation.

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† Professor Symons has informed us that he fully accepts these results, and can only assume that his sample of thiirane must have contained thietane, whose spectrum dominated under the conditions used.

Table 1. E.s.r. parameters for the radical cations of thiirane, thietane, and dimethyl sulphide.

Radical cation	Matrix	T/K	Hyperfine coupling/G	g-values			Ref.
				$g_\perp$	$g_\parallel$	$g_{av.}$	
$\overline{CH_2CH_2S}^+$	$CFCl_3$	90	16.1 (4H)	2.028	2.008	2.021	[a]
		ca. 120	31[b] (4H)	2.024	2.002	2.017	11
$\overline{CH_2CH_2CH_2S}^+$	$CFCl_3$	90	31.1 (4H)	2.027	2.008	2.021	[a]
		ca. 120	31 (4H)	2.023	2.002	2.016	11
Me_2S^+	$CFCl_3$	124	20.4 (6H)			2.014	6
		77	21.2[c] (6H)			2.017	[d]
		77	21 (6H)			2.016[e]	11
	CF_3CCl_3	81	20.4 (6H)				[a]

[a] This work. [b] This value appears to be anomalous (see text). [c] Average value. [d] L. Bonazzola, J. P. Michaut, and J. Roncin, *J. Chem. Phys.*, 1985, **83**, 2727. [e] Determined for $(CD_3)_2S^+$.

0.027, respectively. Using the recommended scale factor of *ca.* 1000 G for the conversion of hydrogen spin density into hyperfine coupling for sulphur-centred radicals,[12] these results correspond to predicted hyperfine couplings of 16 and 27 G, in reasonable accord with the present experimental values (Table 1). Glidewell did not discuss these results, presumably because experimental data were not available at the time.[12] That these calculations are reliable is also indicated by the good agreement between theory and experiment for dimethyl sulphide.[6,12]

The conclusion presented here also fits in nicely with the work of Mollere and Houk[13] on the photoelectron spectroscopy of heterocycloalkanes. These authors interpreted the trend in the lowest ionization potentials of these compounds in terms of differences in hyperconjugative interactions, the b_1 orbital in the heterocyclopropanes being destabilized less than in the four-membered rings or acyclic systems. Essentially this effect is attributed to the more bonding character of the symmetric combination of π (CH_2) orbitals in the strained cyclopropane ring which lessens the interaction with the topmost b_1 orbital on the heteroatom. A corollary of this explanation is there should be a smaller admixture of the CH_2 group orbital into the b_1 orbital for the heterocyclopropanes, and this is now precisely demonstrated by our e.s.r. results.

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