

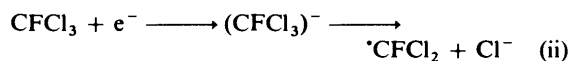
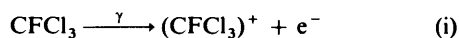
## Vinyl Radical Cations formed by Radiolysis: an Electron Spin Resonance Study

George W. Eastland,<sup>†</sup> Yukio Kurita,<sup>‡</sup> and Martyn C. R. Symons\*

Department of Chemistry, The University, Leicester LE1 7RH

Exposure of dilute solutions of a range of vinyl compounds,  $H_2C=CHX$  or  $H_2C=CMeX$  in trichlorofluoromethane to  $^{60}Co$   $\gamma$ -rays at 77 K generated the corresponding cations, most of which were well characterised by their e.s.r. spectra. Results for  $X = Me$  are discussed in terms of possible out-of-plane twisting for the cation. The 2-vinylpyridine cation favours a  $\pi$  SOMO similar to that of the styrene cation, whereas the 4-vinyl-derivative favours a SOMO which is largely the  $n(\sigma)$ -orbital on nitrogen. The cations of allyl chloride and bromide exhibit large hyperfine coupling to the halogen showing that these atoms favour the extreme out-of-plane site, with considerable delocalisation of the unpaired electron on to the halogen. Results for methyl acrylate and methyl methacrylate cations are difficult to interpret in terms of the expected  $\pi$ -structures. However, for  $X = CHO$ , the SOMO is clearly the  $n(O)$  orbital in the radical plane rather than the  $\pi$ -orbital. The cyano cations favour a  $\pi$  SOMO with significant spin density on nitrogen. For  $X = Br$ , large hyperfine coupling to bromine indicates *ca.* 39% delocalisation. For the vinyl ethers and acetate the SOMO is quite strongly localised on the  $H_2C$ -unit with  $\alpha$ -proton couplings of *ca.* 19 G. Results for  $X = SiMe_3$  are of interest in that they provide clear evidence for out-of-plane twisting, as was recently established by Sakurai and co-workers. Also, on annealing to *ca.* 120 K these cations lost methyl radicals, which were detected by their characteristic e.s.r. spectrum.

The aim of this study was to survey the character of the e.s.r. spectra of a range of vinyl cations, mainly  $(H_2C=CHX)^+$  and  $(H_2C=CMeX)^+$ . This was prompted by the advent of a new technique for preparing radical cations in solid matrices, which has proven to be very efficient.<sup>1-4</sup> The essence of the method is summarised in equations (i)–(iv) for the most popular matrix



$(CFCl_3)$ . Provided the substrate molecule  $X$  has an ionization potential less than that of the solvent, and provided it does not form clusters in the frozen solutions, radical cations,  $X^{\cdot+}$  will form. These may be detected as such, or may undergo various types of unimolecular breakdown or rearrangement. Fortunately, radicals formed by electron attachment to solvent molecules give rise to very broad e.s.r. features which do not seriously interfere.

The first olefin cation studied by e.s.r. was the relatively stable tetramethylethylene cation,<sup>5</sup> but the first extensive study of olefin cations was that of Shida *et al.*,<sup>6</sup> using  $CFCl_3$  as solvent. They obtained good results for  $(H_2C=CHEt)^+$ ,  $(MeCH=CHMe)^+$ ,  $(H_2C=CMe_2)^+$ , (cyclopentene)<sup>+</sup>, and (cyclohexane)<sup>+</sup>, in addition to various diene cations. We studied the cation  $(F_2C=CF_2)^+$ <sup>7</sup> because of our interest in the corresponding radical anion,<sup>8,9</sup> and during the period of writing this report, a most interesting note on twisting in various trimethylsilyl-substituted alkene cations has appeared,<sup>10</sup> as well as a paper by Tabata and Lund on methyl acrylate and methyl methacrylate cations.<sup>11</sup>

Many of these cations have potentially interesting structures, and some are of importance because of their role in certain types of cationic polymerisation.

### Experimental

All the vinyl derivatives were of the best commercial grades available. The solvent ( $CFCl_3$ ) was purified when necessary by standard procedures, great care being taken not to pick up trace impurities, since these can, if their ionization potentials are less than that of the solute, divert the electron-loss process away from solute molecules.

Samples were irradiated as small beads at 77 K in a Vickrad  $^{60}Co$   $\gamma$ -ray source to doses of *ca.* 1 Mrad. E.s.r. spectra were measured on a Varian E-109 spectrometer, calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl (DPPH). Samples were annealed by decanting the liquid nitrogen from the insert Dewar flask and monitoring the spectra continuously. They were re-cooled to 77 K whenever significant spectral changes were observed.

### Results and Discussion

As this is a survey of results for vinyl monomer cations, we have considered all available data, which are given in the Table. We have included our results for the  $(H_2C=CHMe)^+$  cation, which was not studied by Shida *et al.*,<sup>6</sup> but which was briefly mentioned in their comprehensive study of alkane radical cations by Toriyama *et al.*<sup>12</sup> One very interesting aspect of their results is that they claimed to have prepared two subtly different types of  $(H_2C=CHMe)^+$  cations depending upon the source (Table). The species formed thermally from  $(MeCH_2Me)^+$  and  $(Me_3CH)^+$  cations had  $a(Me) \approx 26$  G,  $a(CH_2) \approx 13$  G, and  $a(CH) \approx 0$ , whilst that formed directly from  $MeCH=CH_2$  in  $CFCl_3$  had  $a(CH_2) = 11$  and 6 G,  $a(Me) = 23.5, 23.5,$  and 47.0 G and  $a(CH) \approx 0$ . Our spectra resembled the latter. The average value for the methyl proton coupling is 31.3 G and that for the  $CH_2$  protons is 8.5 G. Thus, apart from the difference in the rotatory behaviour of the methyl group, the average coupling to the  $CH_2$  protons has decreased from 13 to 8.5 G whilst that to the methyl protons has increased from 26 to 31.3

<sup>†</sup> On leave from Department of Chemistry, Saginaw Valley State College, University Centre, MI 48710, U.S.A.

<sup>‡</sup> On leave from Faculty of Engineering, Yokohama National University, Yokohama, Japan.

Table. E.s.r. parameters for a range of vinyl radical cations

Cation	Nucleus	Hyperfine coupling (G) <sup>a</sup>				Ref.
		x	y	z	iso	
	H <sub>2</sub> C=				13.3	6
	=CH				3.5	
	-CH <sub>2</sub> -				37.1	
	<sup>2</sup> H <sub>2</sub> C=				13	12
	-CH <sub>3</sub>				26	
	<sup>1</sup> H <sub>2</sub> C=				11, 6	
	-CH <sub>3</sub>				23.5, 23.5, 47.0	
	H <sub>2</sub> C=				14.0	6
	-CH <sub>3</sub>				16.0	
	H ( <i>para</i> )				10	
	H <sub>2</sub> C=				10	
	H ( <i>para</i> )				10	
	H <sub>2</sub> C=				10	
	H ( <i>para</i> )				10	
	H <sub>2</sub> C=				10	
	<sup>14</sup> N	56	29	29	38	
	<sup>1</sup> H (2,6)				ca. 28	
	<sup>1</sup> H (3,5)				ca. 10	
	<sup>14</sup> N	62	31	31	42	13
	<sup>1</sup> H (2,6)				29	
	<sup>35</sup> Cl	45	ca. 10	ca. 10	ca. 22	
	H <sub>2</sub> C=				16	
	<sup>81</sup> Br	287	ca. 70	ca. 70	ca. 142	
	H <sub>2</sub> C=				ca. 16	
	<sup>1</sup> H				125	11
	H <sub>2</sub> C=				24	
	=CH				12	
	<sup>14</sup> N	20	0	0	ca. 7	
	<sup>81</sup> Br	240				
	<sup>81</sup> Br				ca. 15	
	<sup>1</sup> H					
	H <sub>2</sub> C=				19	
	H <sub>2</sub> C=				19.4	
	H <sub>2</sub> C=				19.4	14
	H <sub>2</sub> C=				3.5	
	OCH <sub>2</sub> -				19	
	H <sub>2</sub> C=				18	
	H <sub>2</sub> C=				18	
	H <sub>2</sub> C=					
	H <sub>2</sub> C=				13,	
					18	
	-N-CH <sub>2</sub> -				32, 0	
	H <sub>2</sub> C=				40	
	CH				18	
	H <sub>2</sub> C=				44.2	10
	H <sub>2</sub> C=					

<sup>a</sup> G = 10<sup>-4</sup> T. <sup>b</sup> From (MeCH<sub>2</sub>Me)<sup>+</sup>. <sup>c</sup> From MeCH=CH<sub>2</sub>.

G. No explanation for these marked differences was offered. One possibility is that the species formed from the alkene cations was not this olefin cation, but it is difficult to understand what other species could be formed. If the assignment is accepted, the only difference lies in the proximity of the ejected H<sub>2</sub> or CH<sub>4</sub> molecules for the thermally generated species.

This suggests that these radicals have structures which are readily modified by minor changes in environment. One possibility is that there is weak bonding to a solvent molecule for the cation formed from H<sub>2</sub>C=CHMe but not for that formed from the alkane cations. Another is that the cations are slightly twisted about the 'double' bond, as is clearly the case for the trimethylsilyl derivatives.<sup>10</sup>

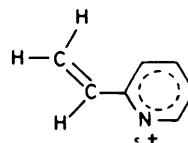
We consider two effects that might be observed on twisting. The first applies if there is no major shift in spin density on twisting. For the  $\alpha$ -protons, there will be a positive coupling from hyperconjugation, which will increase on a sin<sup>2</sup> $\theta$  law as  $\theta$  goes from 0° for the planar radical to 90° for the 90° twisted limit. Coupling to the methyl protons is not expected to be very sensitive to the extent of twisting. However, as we have previously proposed,<sup>15</sup> we expect a tendency towards spin-charge separation for unsymmetrical cations, as in the limiting

structure H<sub>2</sub>C<sup>+</sup>-CMe<sub>2</sub>, since electron release from methyl groups stabilises carbocations more than radicals. This effect will be greatly enhanced as overlap between the two  $p(\pi)$ -orbitals is reduced on twisting. This will result in a concomitant increase in the (negative) coupling to the -CH<sub>2</sub> protons and a fall in the coupling to the methyl protons. We propose that the degree of twist is a subtle balance of steric and electronic forces, and that this can be modified by small changes in the environment. Only detailed calculation can show quantitatively how a small change in  $\theta$  will modify the parameters, but the differences observed by Iwasaki and co-workers seem to be reasonable in terms of a small change in  $\theta$ .

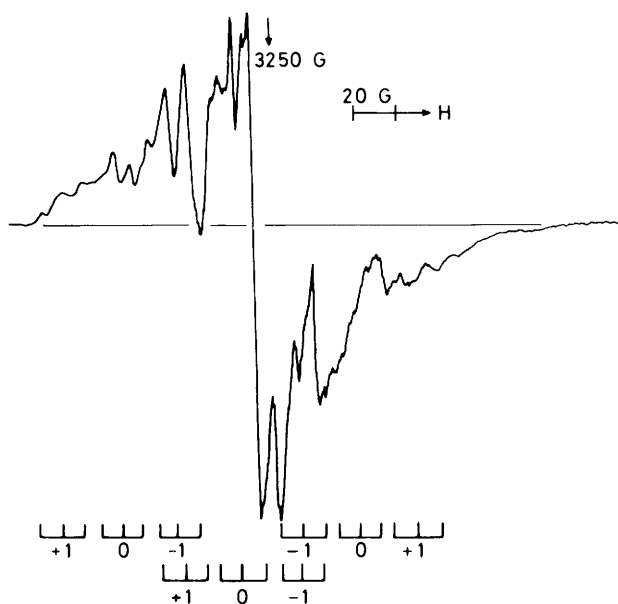
*Styrene and Related Cations.*—The e.s.r. spectrum for the styrene cation is a broad 1:3:3:1 quartet centred close to the free-spin  $g$ -value (2.0023) with  $a \approx 10$  G. One of the three protons responsible for this is surely the *para*-proton, the other two being assigned to the =CH<sub>2</sub> protons. Our INDO calculations support this assignment, the predicted isotropic coupling constants for these protons being (-) 6.5 and (-) 9 G, respectively, couplings to the remaining protons being too small to detect (< 3.6 G).

Results for the cation of 2-vinylpyridine were very similar. Thus the  $\pi$ -cation was again favoured. However, weak outer features similar to those obtained from substituted pyridine cations<sup>16</sup> were also obtained, showing that the  $n(\sigma)$ -cation (1) was formed in low abundance. This is one of the few examples we know of in which two alternative electronic structures are significantly populated. It shows that these two orbitals are truly orthogonal and that electron transfer between them is slow. INDO calculations predict that the  $n(\sigma)$ -structure should be favoured.

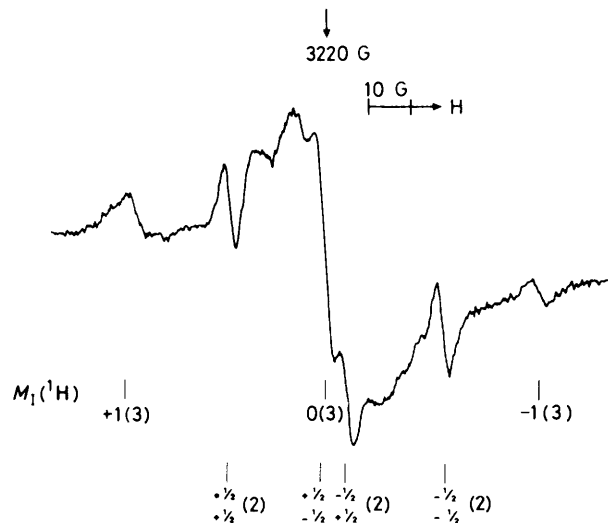
Curiously, this is the case for the 4-vinylpyridine cation (Figure 1). There is possibly a small yield of the  $\pi$ -cation, [ $A(2H) \approx 10$  G] but certainly the  $n(\sigma)$ -cation dominates. The e.s.r. parameters for the  $n(\sigma)$ -cation are comparable with those for the parent pyridine cations<sup>13,16</sup> as indicated in the Table.



(1)

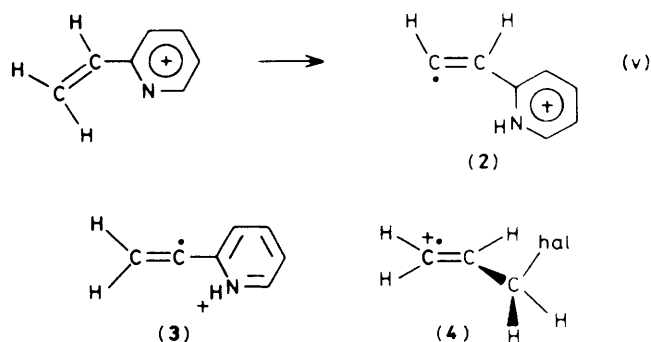


**Figure 1.** First-derivative X-band e.s.r. spectrum for 4-vinylpyridine in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the  $\pi(\sigma)$ -pyridine cation. The central triplet may be due in part to the  $\pi$ -cation



**Figure 2.** First-derivative X-band e.s.r. spectrum for 2-vinylpyridine in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the vinyl radicals (2) and (3) formed after annealing to *ca.* 120 K

On annealing, the  $\pi$ -cation for 2-vinylpyridine was lost, and a new spectrum grew in (Figure 2). This change is tentatively interpreted in terms of an intramolecular proton transfer from the vinyl group to nitrogen, one possibility being shown in equation (v). The alternative transfer to give  $\text{H}_2\text{C}=\dot{\text{C}}-\overset{+}{\text{N}}\text{R}$  (3) radicals must also be considered. We think that two different vinyl cations are formed, one having one proton with  $a = 21$  G and another with  $a = 27$  G and a second with  $\Sigma a = 94$  G in lower abundance. By analogy with results for other vinyl radicals,<sup>17,18</sup> the former is tentatively assigned to the radical (2) and the latter to radical (3), which probably has two equivalent hydrogen atoms ( $a = 47$  G). As expected, we were unable to detect breakdown products of this type with the 4-vinyl-derivative.



**Allyl Halide Cations.**—Well defined spectra for the radical cations of allyl chloride and bromide were obtained, but not from the iodide. We have never been able to prepare  $\beta$ -iodo radicals,  $\text{R}_2\dot{\text{C}}-\text{CH}_2\text{I}$ , and suggest that they lose iodine atoms too readily.

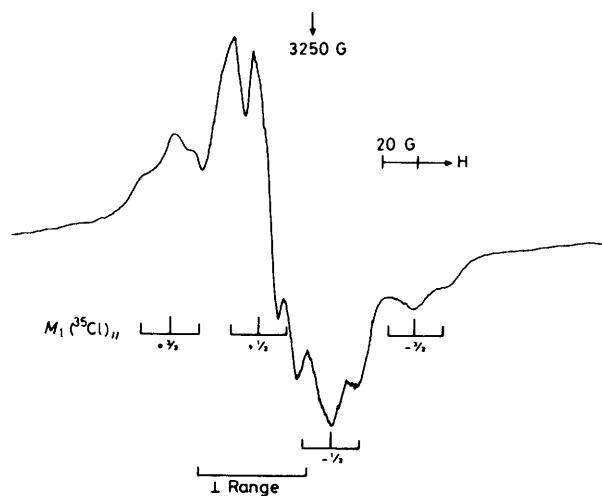
The results (Table) show conclusively that the chlorine and bromine atoms adopt the out-of-plane configuration (4) which gives maximum overlap between the  $\pi$ -orbital and the C-hal bond. This is the favoured conformation for  $\beta$ -chloro and  $\beta$ -bromo radicals<sup>19-22</sup> (unless the case proposed by Wood and Lloyd is accepted<sup>23,24</sup>), but curiously, it is not the conformation detected for benzyl chloride cations.<sup>25</sup> These gave an undetectably small coupling to chlorine, suggesting that the chlorine atom lies close to the molecular plane. In contrast, the bromine atom in benzyl bromide cations gave a large hyperfine coupling and is clearly well removed from the radical plane.

Unfortunately it is difficult to extract the  $x$  and  $y$  components for the halogen hyperfine tensors from these powder spectra (Figures 3 and 4). Nevertheless, we have used the results given in the Table to produce reasonably good simulations of the experimental spectra, and consider that they are not far removed from the correct values. These can be processed in the usual way<sup>26</sup> to give a measure of the spin density on the halogen. We find *ca.* 23% on chlorine and 29% on bromine in this way. The remaining spin must be quite strongly localised on the  $\text{CH}_2$  moiety since the isotropic proton coupling in both cases was *ca.* 16 G. This corresponds to *ca.* 70% localisation.

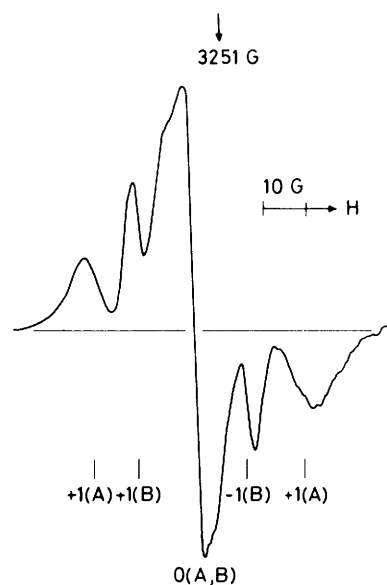
The results can be compared with those for other  $\beta$ -halogeno radicals by comparing values for  $A_{\text{max}}(\text{hal})$ . Thus for  $\text{Me}_2\dot{\text{C}}=\text{CH}_2\text{Cl}$ , and  $\text{CH}_2=\dot{\text{C}}\text{HCH}_2\text{Cl}^+$ , we have *ca.* 45 G for both. This is a remarkable result in view of the extra delocalisation of the SOMO in the alkene cation, and illustrates the well established positive charge effect for hyperconjugating systems.

For the series of  $\beta$ -bromo radicals we have  $\text{Me}_2\dot{\text{C}}\text{CH}_2\text{Br}$  ( $A_{\text{max}} = 350$  G) ( $\text{CH}_2=\dot{\text{C}}\text{HCH}_2\text{Br}^+$ ) ( $A_{\text{max}} \approx 287$  G), and  $(\text{PhCH}_2\text{Br})^+$  ( $A_{\text{max}} = 193$  G). Thus, in this case the coupling falls as delocalisation increases. The very large coupling for  $\text{Me}_2\dot{\text{C}}\text{CH}_2\text{Br}$  probably reflects a major structural distortion in which the bromine moves significantly towards the bridging position.

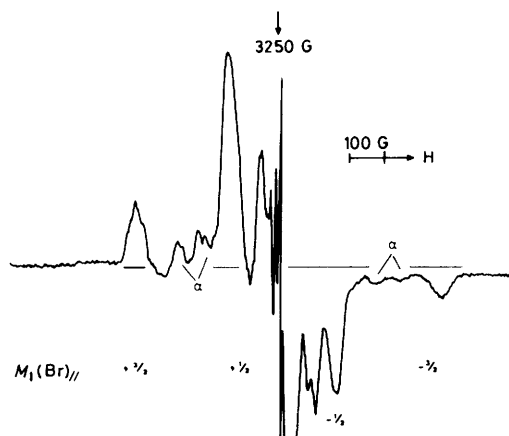
One puzzling aspect of these results is the presence of relatively intense signals in the central spectral regions for both the chloro and bromo derivatives, which grew on annealing, relative to the main cation signals. These are thought to be due to some radicals from which the halogen has been eliminated, but we are, as yet, unable to make specific assignments. We also call attention to extra features ( $\alpha$ ) between the  $+\frac{3}{2}$  and  $+\frac{1}{2}$  and the  $-\frac{1}{2}$  and  $-\frac{3}{2}$  features in the spectra of the bromo cations (Figure 4). These could be forbidden transitions for the bromo cations, but may possibly be due to a second bromine radical, which remains unidentified.



**Figure 3.** First-derivative X-band e.s.r. spectrum for allyl chloride in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the allyl chloride cation



**Figure 5.** First-derivative X-band e.s.r. spectrum for methyl acrylate in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features tentatively assigned to methyl acrylate cations A and B, see text



**Figure 4.** First-derivative X-band e.s.r. spectrum for allyl bromide in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the allyl bromide cation

**Methyl Acrylate and Methacrylate Cations.**—The formation of these cations in  $\text{CF}_3\text{CCl}_3$  matrices has been reported by Tabata and Lund.<sup>11</sup> These and other related cations have also been studied by Shiotani *et al.*<sup>27</sup> The spectrum assigned to the cation of methyl acrylate comprised a 1:2:1 triplet of broad lines with  $A(^1\text{H}) \approx 25$  G.<sup>11</sup> We have obtained a similar triplet using  $\text{CFCl}_3$ , but with  $A = 22$  G (Species A). However, we also detected an extra triplet with narrower components, having  $A(^1\text{H}) = 12$  G (Species B) (Figure 5). The latter was lost on annealing to *ca.* 100 K. Tabata and Lund suggest a SOMO having high density on the  $\text{CH}_2$ - group. However, to obtain 22 or 25 G from the  $\text{CH}_2$  protons for the  $\pi$ -cation the spin must either be *ca.* 100% localised on the  $\text{CH}_2$  group, or the coupling must be positive due to extensive twisting. We think the former is unlikely in view of the bonding character of the  $\pi$ -orbitals and the high electronegativity of oxygen. The ionization potentials of ethene and methyl formate are 10.5 and 10.82, respectively,<sup>28</sup> so the  $\pi$  SOMO is expected to be considerably delocalised over both units. [Our results for various ester cations<sup>29</sup> establish that the SOMO is  $\pi$  in character rather than  $n(\text{O})$  as for aldehyde and ketone cations.<sup>30</sup>] In that case we would expect to detect significant coupling to the  $\text{CH}_2$  protons and to the

methyl protons. [The methyl formate  $\pi$ -cation has two strongly coupled methyl protons with  $A(^1\text{H}) = 23$  G.<sup>31,32</sup>] Since only two protons appear to give significant coupling we need to extend these studies before a proper assignment can be made.

In the case of the methyl methacrylate cation, even studying the  $\text{CD}_3\text{O}$  derivative was not enough to provide a clear assignment of the spectrum. The e.s.r. spectrum of the initially formed species has been given by Tabata and Lund.<sup>11</sup> Our resolution is better than theirs, but the major 'quintet' is the same. The spectrum of the  $\text{CD}_3\text{O}$  derivative was identical. The major interpretative problem lies in the extra fine-structure which varies across the spectrum. We confirm that this species is very photosensitive, but have difficulty interpreting the multi-line spectrum produced.

The fact that the  $\text{CH}_3\text{O}$  protons make no contribution to the spectrum must mean that delocalisation onto the ester moiety is small, as was inferred by Tabata and Lund for the methyl acrylate cation.<sup>11</sup> The extra methyl group will favour electron loss from the  $\text{H}_2\text{C}=\overset{\text{Me}}{\text{C}}$  unit but it is surprising that this should be so marked. We have considered a wide range of structures but none is compatible with the spectra. We defer further discussion until studies with specifically deuterated units have been undertaken.

The related cation of acrolein<sup>11</sup> is of interest since, in this case, the SOMO is clearly localised on the *n*-oxygen orbital, the aldehydic proton coupling of 125 G being quite close to that for the acetaldehyde cation (*ca.* 145 G).<sup>30</sup> Our results were identical with those of Tabata and Lund.<sup>11</sup>

**Acrylonitrile and Methacrylonitrile Cations.**—The spectrum for  $(\text{H}_2\text{C}=\text{CHCN})^+$  cations consists of a set of broad lines (Figure 6), which we interpret in terms of two protons (24 G), one proton (12 G), and a parallel nitrogen coupling (20 G). The spectra were complicated by varying contributions from a broad singlet which we were unable to avoid. The central lines comprise the  $M_1 = 0$  features for  $^{14}\text{N}$ , which are almost isotropic. The  $^{14}\text{N}$  perpendicular coupling is thought to be close to zero, as expected for a  $\pi$ -orbital delocalised onto the CN unit. It is logical to assign the 24 G splitting to the two  $\text{CH}_2$

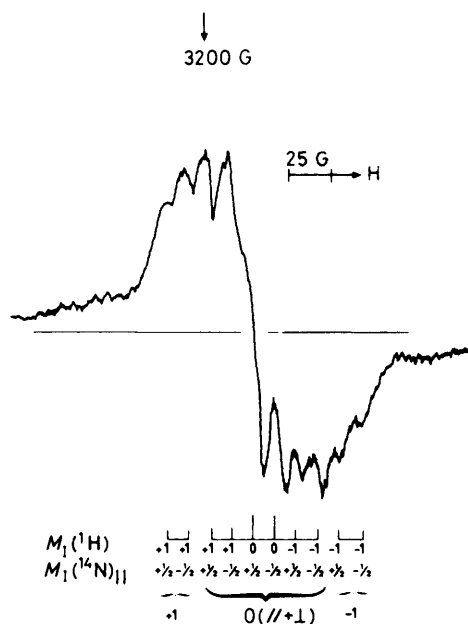


Figure 6. First-derivative X-band e.s.r. spectrum for acrylonitrile in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the acrylonitrile cation

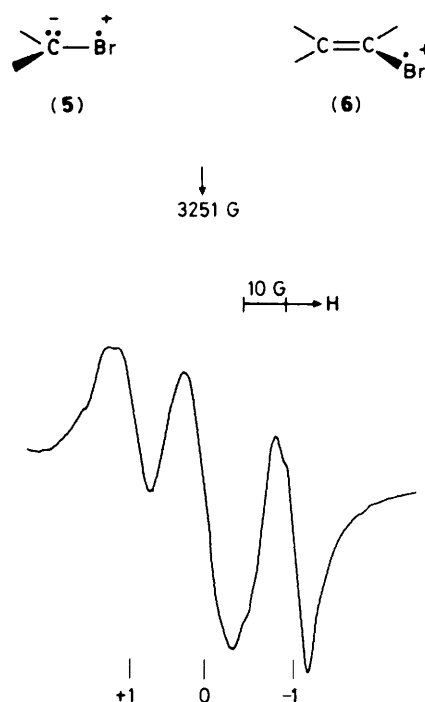


Figure 8. First-derivative X-band e.s.r. spectrum for vinyl acetate in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the vinyl acetate cation

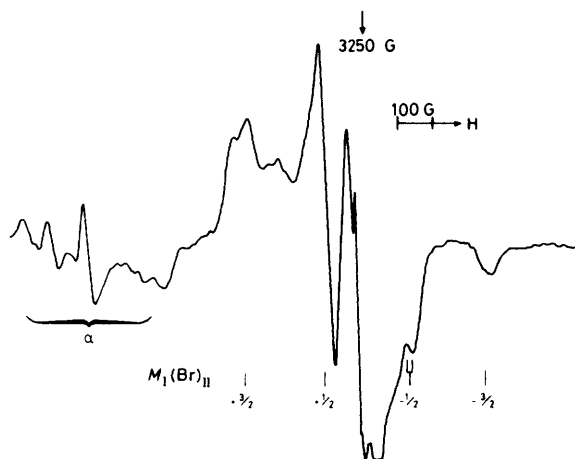


Figure 7. First-derivative X-band e.s.r. spectrum for vinyl bromide in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the vinyl bromide cation

protons and the 12 G splitting to the CH proton. However, the former seems to us to be unacceptably large for the planar cation, so we tentatively conclude that there is extensive twisting. From the  $^{14}\text{N}$  coupling we estimate a spin density of *ca.* 39%, which is surprisingly high. The e.s.r. spectrum obtained from the methacrylonitrile cation was less well defined, and we hesitate to attempt any interpretation.

Results for vinyl bromide were more readily interpreted since the spectra were dominated by a large quartet splitting characteristic of an  $\alpha$ -bromine radical (Figure 7). The proton coupling is not resolved in this overall spectrum, but careful study of individual features suggests a value of *ca.* 15 G for two protons. The central features in this spectrum are in part due to some unidentified organic radicals. The low-field features ( $\alpha$ ) were absent after irradiation at 77 K, but grew in at the expense of the major features on annealing. These features are almost

certainly due to a bromine-containing species, but we are unable to offer any clear assignment at present.

As usual with powder spectra for  $\alpha$ -bromo radicals, only  $A_{||}(A_x)$  is readily measured. However, we can use the well authenticated equation [equation (vi)] proposed by Oloff and Hüttermann which relates the spin density on halogen ( $\rho_{\text{hal}}$ ) to the maximum hyperfine coupling, ( $A_x$ ).<sup>33</sup>

$$\rho_{\text{hal}} = A_x f_{\text{hal}} / 2B^0 \quad (\text{vi})$$

where  $f_{\text{hal}} = 0.81$  for  $^{81}\text{Br}$ , and  $2B^0$  is the calculated anisotropic coupling for unit population of the  $p(\pi)$  orbital. This gives  $\rho_{\text{Br}}$  *ca.* 39%, which is surprisingly large. Thus for simple bromoalkyl radicals,  $\text{R}_2\dot{\text{C}}-\text{Br}$ , this equation gives  $\rho_{\text{Br}}$  *ca.* 18%.<sup>34</sup> For the cation of bromobenzene,  $\text{PhBr}^+$ , we obtained  $\rho_{\text{Br}} = 30\%$ .<sup>35</sup> The large increase relative to  $\text{R}_2\text{C}-\text{Br}$  radicals is even more surprising in view of the delocalisation of the electron within the  $\text{CH}_2=\text{CH}$  moiety. It reflects, in our view, the positive charge effect. This can most readily be appreciated by comparing the limiting structures (5) and (6) having unit spin density on the halogen. The former is strongly opposed by charge separation, which is not involved in the latter.

*Vinyl Ether and Ester Cations.*—We have already reported our results for the cation of vinyl ethyl ether,  $\text{EtOCH}=\text{CH}_2$ .<sup>14</sup> These showed that the limiting structure,  $\text{H}_2\dot{\text{C}}-\text{CH}=\text{OEt}^+$ , dominates, since the proton hyperfine coupling to the methylene protons was 19.4 G. We also showed that the cation derived from the acetal  $(\text{MeO})_2\text{CHCH}=\text{CH}_2$  was the rearranged species,  $(\text{MeO})_2\dot{\text{C}}-\dot{\text{C}}\text{HMe}$ , which is a particularly stable cation radical.<sup>36,37</sup> We have extended this study to include the methyl and butyl vinyl ethers, and have obtained similar results (Table).

The spectrum obtained from vinyl acetate cations was a very similar triplet, with  $A(^1\text{H}) = 18$  G (Figure 8). Clearly the

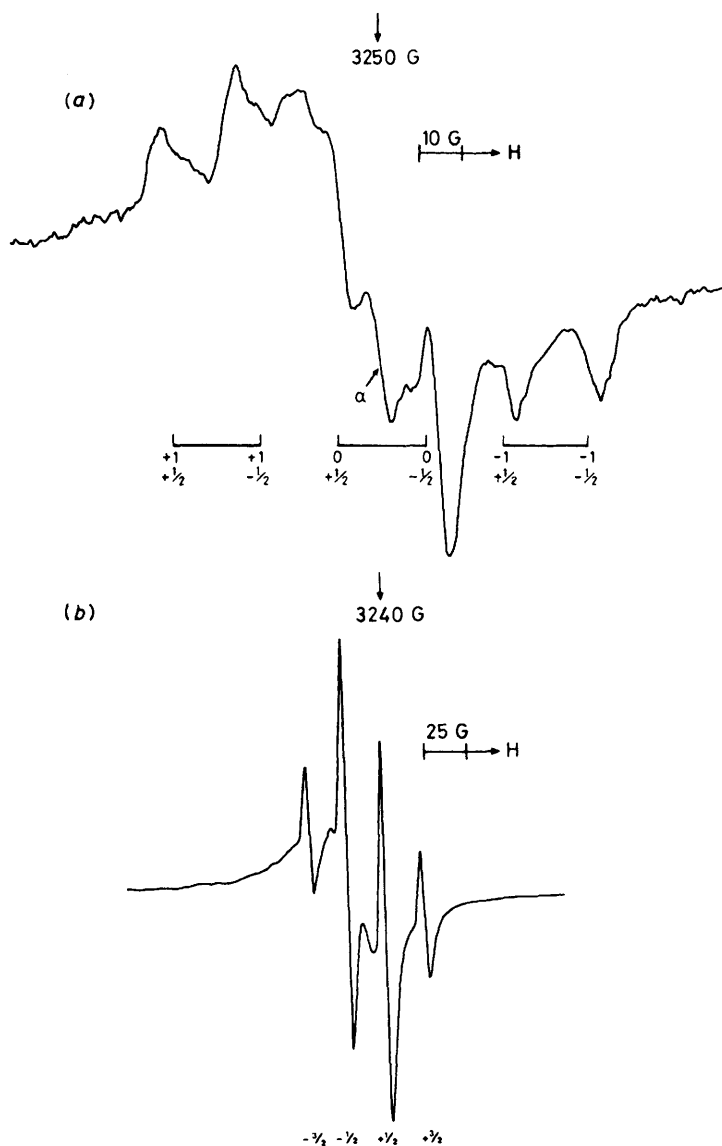
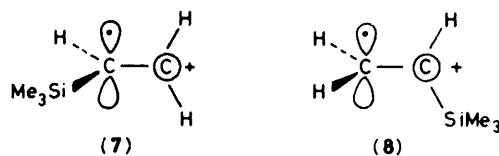
limiting structure,  $\text{H}_2\dot{\text{C}}-\overset{+}{\text{C}}\text{H}-\text{CO}_2\text{Me}$ , is again of major importance. (Note that the arguments are weakened by the possibility of extensive twisting.)

**Trimethylsilyl Derivatives.**—Our work on the cation of  $\text{H}_2\text{C}=\text{CHSiMe}_3$  has been nicely complimented by the recent study of Kira *et al.* on a range of di- and tri-substituted trimethylsilylalkene cation radicals.<sup>10</sup> The key to understanding their results is that the cations have twisted structures, the effect on the proton coupling being a trend from small negative couplings (*ca.*  $-10$  G) to large positive couplings as hyperconjugative overlap begins to dominate.

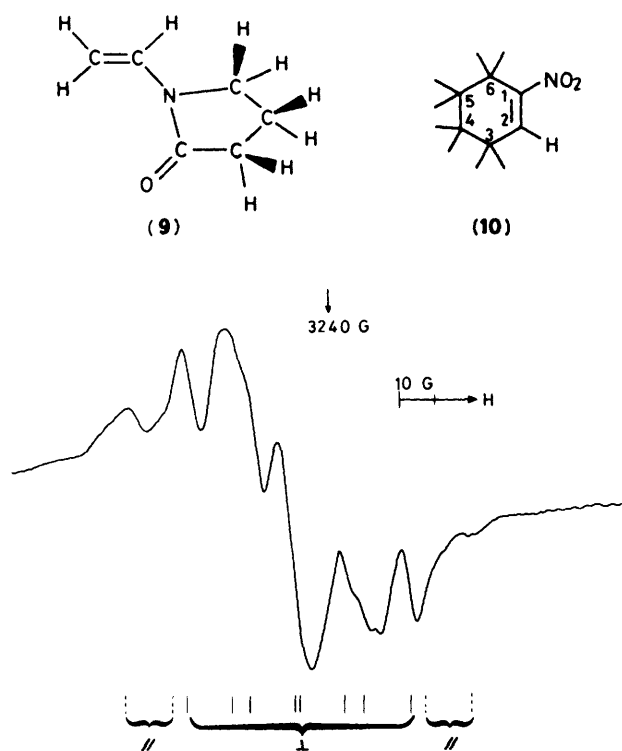
For the cation  $\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)^+$ , the methylene proton coupling was (+) 44.2 G, indicating extensive twisting. Their theoretical calculations for the cation of  $\text{H}_2\text{C}=\text{CHSiMe}_3$ , which they did not study experimentally, showed that the limiting  $90^\circ$  twist should give a radical having two protons with  $A(^1\text{H}) \approx 60$  G, and one with  $A(^1\text{H}) \approx -20$  G. This surely implies the

structure (7) rather than the alternative extreme (8). As we have stressed previously,<sup>13</sup> hyperconjugative electron release is more important for carbocations than for radicals. Furthermore, such  $\sigma-\pi$  overlap is particularly important for second-row atoms,<sup>38,39</sup> hence the former structure should indeed be favoured.

Our spectra for this cation (Figure 9a), though less well defined than those of Kira *et al.*, were reasonably well interpreted in terms of two protons having  $A(^1\text{H}) = 40$  G and one with  $A(^1\text{H}) = 18$  G. The former, which must be +40 G, is assigned to the  $\text{H}_2\text{C}$ - unit. The latter is probably +18 G but



**Figure 9.** First-derivative X-band e.s.r. spectra for vinyltrimethylsilane in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned (a) to the vinyltrimethylsilane cation, and (b) to methyl radicals formed therefrom at *ca.* 120 K. [The central feature in (a) and (b) is due to an impurity]



**Figure 10.** First-derivative X-band e.s.r. spectrum for *N*-vinyl-2-pyrrolidinone in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing features assigned to the corresponding radical cation

could be  $-18$  G. A value of  $-18$  G would imply a  $90^\circ$  twist with confinement of the electron to the  $\text{HC}(\text{SiMe}_3)$  unit. This seems to us to be unlikely. If it is  $+18$  G, the marked decrease compared with  $+40$  G for the  $\text{CH}_2$  protons still implies a drift in spin density away from the  $\text{CH}_2$  group onto the  $\text{HC}(\text{SiMe}_3)$  group, as predicted.

It is a pity that our spectra for the vinyl bromide cation are so poorly resolved, since a similar twist and polarisation might be expected in this case also. Certainly the coupling for the  $\text{CH}_2$  protons is much less than  $40$  G. We suggest only *ca.*  $15$  G, so we cannot tell if this is  $+15$  G with marked twisting, or  $-15$  G implying a planar structure.

To probe the role of halogen substituents further, we studied the cation of  $\text{H}_2\text{C}=\text{CCl}_2$ , in the hope of observing a large proton coupling in addition to coupling to the two chlorine atoms. Unfortunately, all that was obtained was a very broad, highly asymmetric single line.

One interesting result of our work on  $\text{H}_2\text{C}=\text{CHSiMe}_3$  was the detection of methyl radicals when the matrix was warmed in the  $120$ – $140$  K range (Figure 9b). This unexpected reaction implies that the residual cation,  $\text{H}_2\text{C}=\text{CH}-\text{Si}^+\text{Me}_2$ , or some rearranged or cyclised product therefrom, must be particularly stable to favour unimolecular breakdown of the primary cation.

Finally, although we have not undertaken a systematic study of nitrogen substituents, we did obtain the cation of *N*-vinyl-2-pyrrolidinone (9) and of the nitro derivative (10).

The spectrum for the former (Figure 10) was reasonably well defined, giving three proton splittings of  $28$  G,  $17$  G, and  $13$  G, and a nitrogen parallel splitting of  $17$  G [ $A_{\parallel}(^{14}\text{N}) \approx 0$ ].

We have previously shown that for the dimethylformamide cation,  $A_{\parallel}(^{14}\text{N}) = 38$  G, with  $A(\text{Me}) = 32$  G.<sup>40</sup> Thus the spin density on the amide moiety has fallen by *ca.*  $55\%$ . If this is largely centred on the  $(\text{CH}_2=)$  unit, then  $13$  and  $17$  G is

acceptable though rather high for these protons. The  $28$  G splitting is then assigned to the axial proton of the  $\text{N}-\text{CH}_2$  unit, the equatorial coupling being close to zero.

Results for the nitro derivative (10) show that the SOMO is largely confined to the olefin moiety. A good spectral fit was obtained using splittings of  $17$  G (1H),  $25$  G (3H), and  $50$  G (1H). There was no obvious anisotropy and hence no resolved coupling to  $^{14}\text{N}$ . We tentatively assign the  $17$  G splitting to the  $=\text{CH}-$  unit. For the parent cyclohexene cation, this coupling is  $9$  G.<sup>35</sup> This increase in the magnitude of the coupling probably indicates an increase in spin density on C(2). We therefore assign couplings of  $50$  and  $25$  G to the C(3) protons, and the remaining two splittings of  $25$  G for the C(6) protons. If this is correct, it seems that a skew conformation is adopted, which makes these protons equivalent. It is interesting that on annealing there was no evidence for the formation of the  $\text{NO}_2$ -like cations formed from nitroalkanes, which are thought to be the rearranged species  $\text{RONO}^+$ .<sup>14</sup>

We conclude that vinyl cations are, in general, quite stable species with normal structures. Apart from the  $\text{SiMe}_3$  derivatives there is no clear proof of twisted structures, though some indication of twisting has been inferred in several cases. The correct interpretation of the spectra derived from the acrylates remains obscure, but it is hoped that the synthesis of suitably deuteriated compounds will aid interpretation.

#### Acknowledgements

G. W. E. would like to thank Saginaw Valley State College for a leave of absence and Y. K. thanks the Ministry of Education (Japanese Government) for financial support.

#### References

- H. Kubodera, T. Shida, and K. Shimokoshi, *J. Phys. Chem.*, 1981, **85**, 2563.
- J. T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 666.
- I. G. Smith and M. C. R. Symons, *J. Chem. Res. (S)*, 1979, 382.
- M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1981, 1251; 1982, 869.
- R. M. Dessau, *J. Am. Chem. Soc.*, 1970, **92**, 6356.
- T. Shida, Y. Egawa, H. Kubodera, and T. Kato, *J. Chem. Phys.*, 1980, **73**, 5963.
- A. Hasegawa and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 93.
- M. C. R. Symons, *J. Chem. Res. (S)*, 1981, 286.
- A. Hasegawa and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1565.
- M. Kira, H. Nakazawa, and H. Sakurai, *J. Am. Chem. Soc.*, 1983, **105**, 6983.
- M. Tabata and A. Lund, *Z. Naturforsch., Teil A*, 1983, **38**, 687.
- K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, 1982, **77**, 5891.
- T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869.
- D. N. R. Rao and M. C. R. Symons, *Tetrahedron Lett.*, 1983, **24**, 1293.
- M. C. R. Symons and L. Harris, *J. Chem. Res.* 1982, (S) 268; (M), 2746.
- D. N. R. Rao, G. W. Eastland, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1984, 2803.
- E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1963, **40**, 213.
- G. W. Neilson and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1405.
- M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1897.
- S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1280.
- A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, 1970, **5**, 552.
- M. C. R. Symons and I. G. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1362.
- D. E. Wood and R. V. Lloyd, *J. Am. Chem. Soc.*, 1975, **97**, 5986.

- 24 D. E. Wood and R. V. Lloyd, *Tetrahedron Lett.*, 1976, 45.
- 25 S. P. Maj, D. N. R. Rao, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1984, 2767.
- 26 M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold, Wokingham, Berkshire, 1978.
- 27 M. Shiotani, T. Iwama, and J. Sohma, personal communication (paper presented at the 1983 Meeting of the Chemical Society of Japan).
- 28 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionization Potentials and Electron Affinities,' Arnold, London, 1966.
- 29 D. N. R. Rao, J. Rideout, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1221.
- 30 M. C. R. Symons and P. J. Boon, *Chem. Phys. Lett.*, 1982, **89**, 516; 1983, **100**, 203.
- 31 D. Becker, K. Plante, and M. D. Sevilla, *J. Phys. Chem.*, 1983, **87**, 1948.
- 32 G. W. Eastland, D. N. R. Rao, J. Rideout, M. C. R. Symons, and A. Hasegawa, *J. Chem. Res (S)*, 1983, 258.
- 33 H. Oloff and J. Hüttermann, *J. Magn. Reson.*, 1977, **27**, 197.
- 34 S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1165.
- 35 S. P. Maj, A. Hasegawa, and M. C. R. Symons, *J. Chem. Soc. Faraday Trans. 1*, 1983, **79**, 1931.
- 36 G. Behrens, E. Bothe, G. Koltzenburg, and D. Schulte-Frohlinde, *J. Chem. Soc., Perkin Trans. 2*, 1981, 143.
- 37 G. Behrens, E. Bothe, G. Koltzenburg, and D. Schulte-Frohlinde, *J. Chem. Soc., Perkin Trans. 2*, 1980, 883.
- 38 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846.
- 39 A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 622.
- 40 D. N. R. Rao and M. C. R. Symons, *Chem. Phys. Lett.*, 1982, **93**, 495.

Received 16th March 1984; Paper 4/424