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An ESR Study of the Aziridine and Azetidine Radical Cations: Evidence for the C···C Ring-Opened Aziridine Radical Cation

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The radical cations from aziridine and azetidine have been characterized by ESR spectroscopy following their generation in the solid state by γ irradiation of dilute solutions of the parent compounds in the $CFCl_3$ matrix at 77 K. The ESR parameters of the azetidine radical cation are typical of those for nitrogen-centered amine radical cations such as $Me_2NH^{\bullet+}$. On the other hand, the radical cation formed from aziridine has very different ESR parameters that compare closely to those for the isoelectronic C···C ring-opened form of the oxirane radical cation and the allyl radical. The radical cation formed from azetidine is therefore assigned a ring-closed structure with the unpaired electron in a $2p_z$ orbital on nitrogen perpendicular to the ring plane, whereas the cation from aziridine is an allylic C···C ring-opened planar isomer with the unpaired electron in a nonbonding π orbital centered mainly on the two end carbon atoms. The neutral 1-aziridinyl and 1-azetidinyl radicals have been detected as radical products following the γ irradiation of the parent compounds in the $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices. In particular, the 1-azetidinyl radical is produced cleanly from the azetidine radical cation in the $CFCl_2CF_2Cl$ matrix at ca. 100 K.

Introduction

One of the striking conclusions to emerge from recent ESR studies of radical cations in solid matrices is that the chemistry of these species at low temperatures often parallels their gas-phase reactivity observed at much higher temperatures in the mass spectrometer. That a relationship should exist between radical cation chemistry in the gas and condensed phases was proposed in connection with radiolysis mechanisms many years ago,[1-3] and is exemplified by the occurrence of McLafferty rearrangements, usually associated with mass spectrometric studies,[4,5] under cryogenic conditions.[6-8]

Another general reaction which has been widely investigated by both mass spectrometric and ESR studies is the ring opening of the radical cations from cyclopropane and oxirane. van Velzen and van der Hart[9] made the definitive observation that the oxirane cation formed by electron impact in an ICR spectrometer opens directly to give a vibrationally excited species. On the basis of previous work,[10,11] this ring-opened cation was suggested[9] to have the $CH_2OCH_2^{\bullet+}$ structure. Subsequent ESR studies of the radical cation formed in the solid state at 77 K provided the first direct evidence for the planar C_{2v} ring-opened structure.[12,13] Moreover, the generation of this species under cryogenic conditions strongly supports the conclusion from the ICR study that the barrier to ring opening must be small. The most recent theoretical calculations are in excellent accord with these results. Thus, Clark[14] estimates that the barrier to C···C ring opening of the oxirane radical cation is only 3.7 kcal mol^{-1} at the MP2/6-31G* level and may disappear completely at higher levels. Also, Radom and co-workers[15] predict that the ring-opened cation adopts a planar, but easily distorted,[16] C_{2v} structure lying 19.6 kcal mol^{-1} below the ring-closed species.[14-16]

As compared to the work on oxirane, the radical cation from aziridine, the other isoelectronic three-membered ring heterocycle, has been investigated in much less detail and no solid-state ESR studies have hitherto been reported. In a study of the metastable peaks for the fragmentation of various $C_2H_5N^{\bullet+}$ species by hydrogen-atom loss, Holmes and Terlouw[17] found that the ion generated from aziridine was indistinguishable from the open chain isomer $CH_2NHCH_2^{\bullet+}$ produced from dimethylamine, the same energy release, peak shape, and shift upon exchange deuteration being found in each case. Consequently, they were unable to decide whether the radical cation from aziridine possesses an intact ring or a ring-opened structure in the gas phase.[17] It is of interest, therefore, that recent ab initio calculations by Lien and Hopkinson[18] at the 6-31G*//4-31G level predict that the planar C_{2v} ring-opened radical cation is 26.5 kcal mol^{-1} more stable than the ring-closed cation, both species possessing minima on the $C_2NH_5^{\bullet+}$ potential energy hypersurface. However, the magnitude of the barrier to ring opening was not investigated.[18]

In this paper we present the first evidence for the ring opening of the aziridine radical cation, the cationic species detected by ESR spectroscopy following γ irradiation of a solid solution of aziridine in the $CFCl_3$ matrix at 77 K being the C···C ring-opened isomer. In contrast, the similarly generated cation from azetidine, the corresponding nitrogen heterocycle with a four-membered ring, is found to be a ring-closed species with ESR parameters characteristic of a nitrogen-centered cation radical. We also report studies of these two compounds in other Freon matrices; in particular, the previously known neutral (cyclic aminyl) 1-aziridinyl and 1-azetidinyl[19] radicals have been identified as the ultimate paramagnetic species formed from their respective parent compounds in the $CFCl_2CF_2Cl$ matrix above 82 and 110 K, respectively.

Experimental Section

Aziridine (ethylenimine) was prepared by the reaction of 2-aminoethyl hydrogen sulfate (97% from Aldrich) with sodium hydroxide.[20] The fraction boiling at 55–60 °C was collected and

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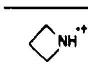
TABLE I: ESR Parameters for the Azetidine and Aziridine Radical Cations and Related Radicals

radical cation or radical	matrix or solvent	T/K	hyperfine couplings/G	g_{av} or g_{iso}	ref
	$CFCl_3$	90	$A(4\ H) = 54.2$, $A_{N-H}\ (1\ H) = 22.6$ $A_{\parallel}(^{14}N) = 41.4$, $A_{\perp}(^{14}N) = 8.0$, $A_{iso}(^{14}N) = 19.1$	2.0037	this work
		140	$A(4\ H) = 54.1$, $A_{N-H}(1\ H) = 22.7$ $A_{\parallel}(^{14}N) = 38.2$, $A_{\perp}(^{14}N) = 9.5$, $A_{iso}(^{14}N) = 19.1$	2.0038	this work
$(CH_3)_2NH^{\bullet+}$	90% H_2SO_4	304	$a(6\ H_\beta) = 34.3$, $a_{N-H}(1\ H) = 22.7$, $a(^{14}N) = 19.3$	2.0036	23a
	aqueous $HClO_4$	300	$a(6\ H_\beta) = 33.6$, $a_{N-H}(1\ H) = 22.0$, $a(^{14}N) = 19.2$	2.0035	23b
$CH_2NHCH_2^{\bullet+}$	$CFCl_3$	150	$A(4\ H) = 16.1$, $A_{N-H}(1\ H) = 4.3$, $A(^{14}N) = 7.7^a$	2.0026	this work
$CH_2NDCH_2^{\bullet+}$	$CFCl_3$	150	$A(4\ H) = 16.1$, $A_{N-D}(1\ D) = 0.66$, $A(^{14}N) = 7.7^a$	2.0024	this work
$CH_2NHCH_2^{\bullet+}$	$CFCl_3$	150	$A_{exo}(2\ H) = 17.2$, $A_{endo}(2\ H) = 14.0$, $A_{N-H}(1\ H) = 4.3$, $A(^{14}N) = 7.7^b$	2.0026	this work
$CH_2OCH_2^{\bullet+}$	$CFCl_3$	145	$A(4\ H) = 16.3$	2.0022	12
$CH_2{=}CH{-}CH_2^{\bullet}$	$CH_3CH{=}CH_2$	143	$a_{exo}(2\ H) = 14.8$, $a_{endo}(2\ H) = 13.9$, $a_{C-H}(1\ H) = 4.1$	2.0026	c

[a] An additional doublet splitting of 2.7 G was used to simulate the spectra in Figures 2 and 3. [b] An excellent fit to the spectrum of Figure 2a could also be obtained from these parameters without using an additional 2.7-G doublet splitting. The corresponding parameters for $CH_2NDCH_2^{\bullet+}$ did not yield such a good fit for Figure 3a, however. [c] Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1968**, 90, 7157. Beckwith, A. L. J.; Norman, R. O. C. *J. Chem. Soc. B* **1969**, 400.

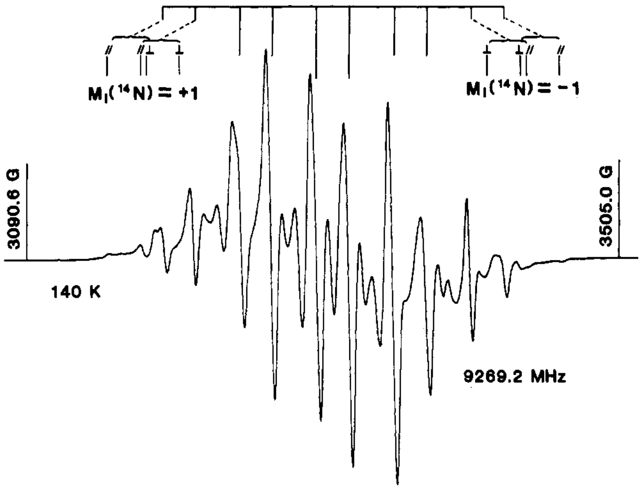


Figure 1. First-derivative ESR spectrum of the radical cation of azetidine in $CFCl_3$. The stick diagram shows a reconstruction of the spectrum in terms of a binomial quintet-(4 H) of-doublets (1 H) pattern augmented by the outermost parallel and perpendicular $M_I = \pm 1$ components of a ^{14}N (I = 1) hyperfine interaction.

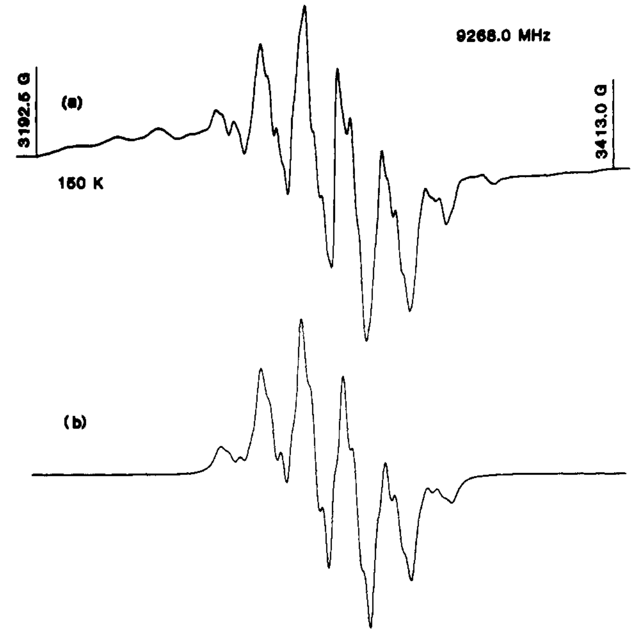


Figure 2. Observed (spectrum a) and computer-simulated (spectrum b) first-derivative ESR spectra of the aziridine-*N-d* radical cation in $CFCl_3$. Spectrum b was simulated by using the ESR parameters in Table I and a Lorentzian line width of 3.0 G.

its ^1H NMR spectrum consisted of a single peak at 1.6 ppm (4 H), as expected since the N–H hydrogen signal for aziridine is undetectable,[21] probably because of rapid exchange broadening.[21] Aziridine-*N-d* was made by stirring 0.2 g of aziridine with a 2-g solution of 10% KOD in D_2O for 10 h at room temperature. Azetidine (trimethylenimine) was supplied by Fluka Chemical Corp. and used as received, the stated purity being 97% by GC.

The Freon solvents consisted of trichlorofluoromethane and 1,1,2-trichlorotrifluoroethane from PCR/SCM Specialty Chemicals, and 1,1,1-trichlorotrifluoroethane from Aldrich.

The radical species were generated by γ irradiation of 0.8–1.0 mol % solid solutions of the cyclic amines in the halocarbon solvents at 77 K. Procedures for sample preparation and ESR measurements were as described previously.[12] ESR spectra were simulated by using the EPRSRC program (IBM Instruments, Inc.) with the Aspect 2000 computer.

Results

Studies in the $CFCl_3$ Matrix. The ESR spectrum of the radical generated from azetidine, shown in Figure 1, consists of a set of sharp components that are readily analyzed into a binomial quintet (4 H) of doublets (1 H). A closer examination also reveals that anisotropic features are present in the wings with the doublet spacing of the nearly isotropic main pattern. As indicated in the stick diagram, these broad wing features can be assigned to the parallel and perpendicular $M_I = \pm 1$ components of a $^{14}N(I = 1)$ hyperfine interaction, the corresponding $M_I = 0$ components constituting the outermost lines of the well-resolved quintet structure. That only the outermost ^{14}N anisotropic features are resolved is because the inner components are subject to considerable spectral congestion. In fact, the poorly resolved structure between the sharp $M_I(^{14}N) = 0$ lines probably results from the overlap of these $M_I(^{14}N) = \pm 1$ components. Thus the overall pattern is that expected for a ring-closed and nitrogen-centered radical cation of azetidine in the solid state, the nearly isotropic couplings arising from the 4 β and 1 α hydrogens. The ESR parameters are summarized in Table I.

The form of the spectrum in Figure 1 showed only a slight reversible change with temperature between 80 and 150 K, this change occurring primarily in the values of the ^{14}N anisotropic couplings. At 90 K, $A_{\parallel}$ increased and $A_{\perp}$ decreased (Table I) from the values recorded at 140 K resulting in a better resolution of the low-field anisotropic components. As expected, however, the calculated value of the isotropic ^{14}N coupling remains constant (Table I), lending further support to the analysis.

For aziridine, a very different ESR spectrum was obtained as shown in Figures 2 and 3. Not only is the appearance dissimilar but the total width (ca. 87 G) of the spectrum from aziridine-*N-h* in Figure 2 is less than a third of that for the spectrum of the azetidine cation (ca. 316 G) in the same matrix. Such a large

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TABLE II: ESR Parameters for the 1-Azetidinyl and 1-Aziridinyl Radicals

radical	matrix or solvent	T/K	hyperfine couplings/G	g_{av} or g_{iso}	ref
	$CFCl_2CF_2Cl$	115	$A(4\ H_\beta) = 38.4$, $A(^{14}N) = 13.6$	2.0045	this work
	cyclopropane	173	$a(4\ H_\beta) = 38.3$, $a(^{14}N) = 14.0$	2.0045	19
	$CFCl_2CF_2Cl$	114	$A(4\ H_\beta) = 30.3$, $A(^{14}N) = 12.4$	2.0047	this work
	cyclopropane	173	$a(4\ H_\beta) = 30.7$, $a(^{14}N) = 12.5$	2.0043	19

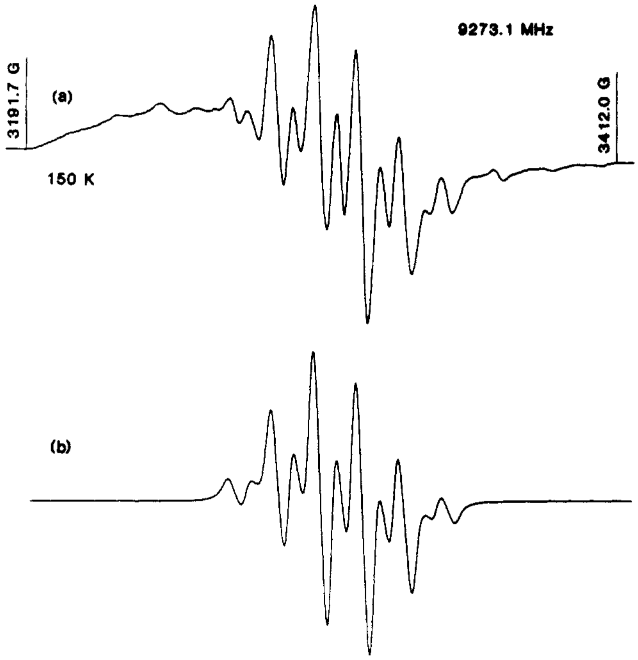


Figure 3. Observed (spectrum a) and computer-simulated (spectrum b) first-derivative ESR spectra of the aziridine-*N*-*h* radical cation in $CFCl_3$. Spectrum b was simulated by using the ESR parameters in Table I and a Lorentzian line width of 3.0 G.

difference would not be expected if the radical cation from aziridine also possessed a ring-closed structure.

The spectrum derived from aziridine-*N*-*h* in Figure 2 appears to consist of six lines with some poorly resolved substructure. The precise form of this pattern only becomes clear, however, after examination of the spectrum from the *N*-*d* compound in Figure 3. In this case the spectrum is better resolved and fits an analysis in terms of hyperfine interaction with four hydrogens and one nitrogen, providing that A(4 H) is approximately twice the value of $A(^{14}N)$. Also, the difference in the total width of the two spectra indicates about a 4-G coupling to the N–H hydrogen. Starting from these deductions, we made attempts to simulate the pattern from aziridine-*N*-*h* and a good fit was obtained (lower spectrum of Figure 2) with the parameters given in Table I, the small (2.7 G) additional doublet splitting being included to improve the quality of fit in the profile of the substructure. This apparent doublet splitting could arise from a matrix superhyperfine interaction.[12,13] At any rate, the inclusion of this additional interaction in the simulation also improved the fit to the spectrum obtained from aziridine-*N*-*d* (Figure 3), the parameters being the same as those obtained for the undeuterated species except for the replacement of $A_{N-H}(H) = 4.3$ G by $A_{N-D}(D) = 0.66$ G.

Although the 150 K spectra in Figures 2 and 3 show better resolution than those recorded at lower temperatures, there was no indication of any other spectral change on warming and the reversibility of the temperature dependence was established between 85 and 150 K. It seems clear from this and other work that the $CFCl_3$ matrix maintains an unusually high rigidity almost up to its softening point of 150–160 K. As a result, the diffusion-controlled reactions of cations with their corresponding neutral molecules are not observed in $CFCl_3$ except in competition with the eventual decomposition of the cations at the softening temperature. In this respect, the $CFCl_3$ and $CFCl_2CF_2Cl$ matrices have very different properties, as will be apparent from the results presented in the next section.

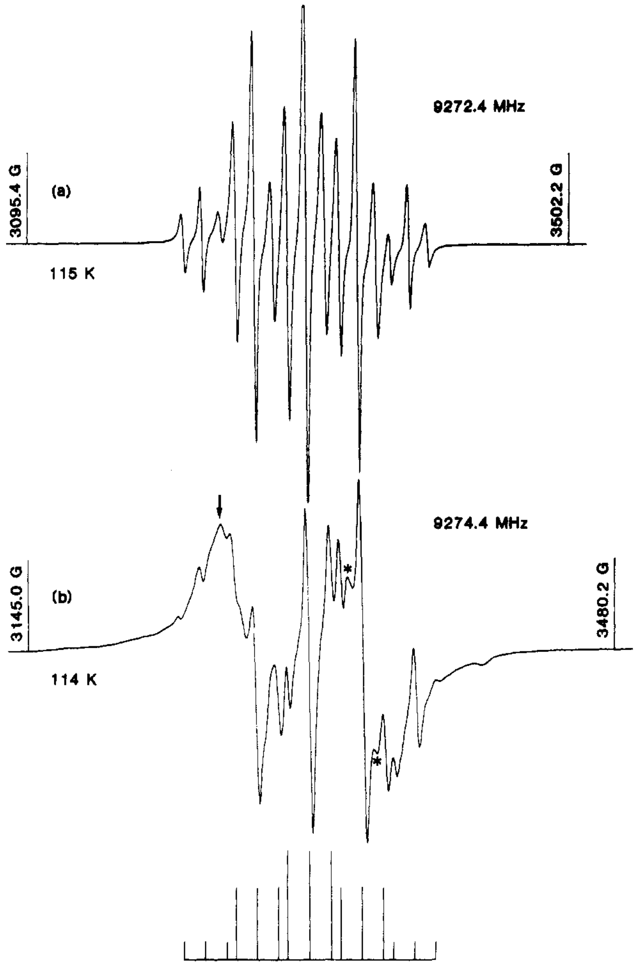


Figure 4. First-derivative ESR spectra of radicals derived from (a) azetidine and (b) aziridine by γ irradiation (dose, ca. 0.5 Mrad) of 1 mol % solutions in $CFCl_2CF_2Cl$. In spectrum b, the arrow shows the low-field hump of a broad doublet spectrum attributed to a matrix radical (see text) while the asterisks represent unidentified components. The stick diagram under spectrum b identifies the components attributed to the 1-aziridinyl radical.

Studies in the $CFCl_2CF_2Cl$ Matrix. Except for inferior resolution, the 85 K spectrum derived from azetidine in this matrix resembled that obtained in $CFCl_3$. Essentially all the strong components present in the $CFCl_3$ spectrum (Figure 1) were reproduced in a much broader envelope leaving no doubt that the identical azetidine radical cation is also generated in the $CFCl_2CF_2Cl$ matrix at 77 K. On raising the temperature, however, very different results were obtained in the two matrices. Instead of just an improvement in resolution, strong new signals appeared irreversibly in the spectrum of the $CFCl_2CF_2Cl$ solution between 95 and 100 K, and evidently another radical grew in to replace the original cation. The spectrum of this secondary radical was well resolved at 115 K (Figure 4a) and consists of a quintet (4 H) of ^{14}N triplets with coupling constants (Table II) that are almost identical with those previously reported for the 1-azetidinyl radical in the liquid phase.[19] Hence, the ring-closed radical cation undergoes a clean reaction to produce this neutral radical in the

$CFCl_2CF_2Cl$ matrix at ca. 100 K. It should be added, perhaps, that a much smaller yield of neutral radicals may also be formed initially at 77 K but their unequivocal detection by ESR is extremely difficult because of the low spectral resolution at this temperature.

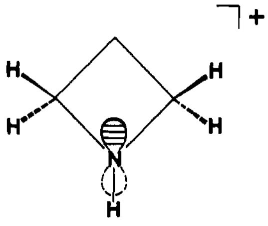
Only the neutral 1-aziridinyl radical[19] was detected in γ-irradiated $CFCl_2CF_2Cl$ solutions of aziridine. Even at 82 K, there was no evidence for the apparent six-line spectrum of the cation observed in $CFCl_3$ and the spectrum was dominated by a quintet pattern belonging to the $M_I(^{14}N) = 0$ components of the 1-aziridinyl radical. The additional $M_I(^{14}N) = \pm 1$ components of the spectrum became partially resolved at 114 K, as shown in Figure 4b, and the ESR parameters are given in Table II. Above 115 K, a broad doublet spectrum, probably associated with a matrix radical, grew in strongly and obscured the spectrum of the 1-aziridinyl radical so that improved resolution could not be achieved at higher temperatures.

Studies in the CF_3CCl_3 Matrix. The spectrum of the γ-irradiated azetidine solution was dominated from 85 to 144 K by the pattern associated with the ring-closed cation previously described in connection with Figure 1. Above 115 K, some additional lines belonging to the 1-azetidinyl radical could be detected. The spectrum of the cation showed little intensity change until it disappeared abruptly in the region between 144 and 150 K which is close to the softening point of the matrix. After the loss of the cation, the spectrum at 150 K consisted mainly of well-resolved isotropic patterns from the 1-azetidinyl and CF_3CCl_2[22] radicals. However, the signal intensity of the 1-azetidinyl radical was not commensurate with the loss of the cation signal, suggesting that the conversion clearly observed in the $CFCl_2CF_2Cl$ matrix does not occur to the same extent in CF_3CCl_3. Also, the CF_3CCl_2 radical is normally detected at 150 K after the γ irradiation of CF_3CCl_3, even in the absence of a solute.[22]

The results for the aziridine solutions in this matrix were similar to those obtained in $CFCl_2CF_2Cl$ insofar as the 1-aziridinyl radical was the only detectable product from the solute. The spectrum of this radical was not as well resolved as in $CFCl_2CF_2Cl$, however, since only the quintet corresponding to the central components of the ^{14}N hyperfine interaction was observed, even at 143 K.

Discussion

Structures of the Azetidine and Aziridine Radical Cations. The ESR parameters of the azetidine radical cation listed in Table I strongly support the structure represented by the ring-closed and nitrogen-centered π radical **1**, the configuration at nitrogen being planar. Perhaps the clearest proof of this assignment comes from a comparison of these parameters with those of the dimethylamine radical cation,[23] also given in Table I. Direct comparison of the isotropic parameters is appropriate except in the case of the β-hydrogens, where the assumption of the $\cos^2 \theta$ relation[24] would lead to an expected ratio of 1.5 for the quotient of A(4 H) for the azetidine cation to A(6 H) for the dimethylamine cation. The actual ratio is 1.61, suggesting that hyperconjugation may be slightly more important in the four-membered ring heterocycle. It is interesting that the corresponding ratio for the oxetane and dimethyl ether cations is 1.52.[12a] One difference between the ESR results for the oxetane[12a] and azetidine cations is that the γ-hydrogen coupling in the former is 10.8 G whereas this coupling was not observed for the azetidine cation. Considering that a long-range coupling of this type would be almost entirely isotropic in character, the failure to observe this γ coupling suggests that it must be less than the line width of about 5 G.



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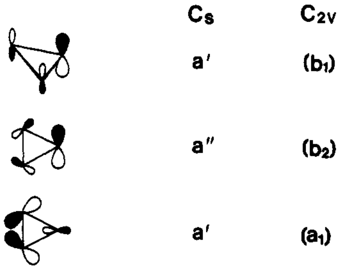
Judging from its ESR parameters (Table I), the aziridine radical cation formed in the $CFCl_3$ matrix must have a very different structure from that of the azetidine cation. The orbital ordering shown in **2**,[25] however, predicts that a ring-closed aziridine cation should also be nitrogen centered. Only an excited $^2A'$ state analogous to the $^2A_1$ state of the ring-closed oxirane cation[13] would seem to offer the possibility of a more suitable spin distribution in a ring-closed cation but the energetics are even less favorable than in the case of oxirane.[25] There is no question that the results from photoelectron spectroscopy[25] and theoretical calculations[18,25] strongly support a radical cation structure with the spin on the hetero atom if the heterocyclopropane structure is retained.



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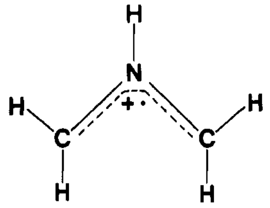
Thus, by analogy with oxirane,[12,13] we turn to consider the C···C ring-opened structure **3** which is isoelectronic with the allyl radical.



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The g factors and A(4 H) hyperfine couplings for these three radicals, listed in Table I, are strikingly similar. Moreover, the A_{N-H}(1 H) coupling of 4.3 G for the aziridine cation is very close to the corresponding coupling of 4.1 G for the hydrogen attached to the 2-carbon of the allyl radical. Lastly, the isotropic ^{14}N coupling of 7.7 G for the aziridine cation is not unreasonable given that most of the spin density in **3** is expected to reside on the two carbon atoms; unfortunately, the ^{13}C coupling for the 2-carbon atom of the allyl radical is unavailable to make a suitable comparison in this case. We conclude that the ESR data for the aziridine cation are entirely consistent with structure **3**.

Our ESR results for the aziridine cation are therefore in keeping with the prediction[18] that the energy of the ring-opened structure **3** lies well below (26.5 kcal mol^{-1}) that of the ring-closed cation in its $^2A'$ ($^2B_1$) ground state. They also imply that the barrier to ring opening is small enough to be easily surmounted at 77 K, as was previously concluded for the oxirane cation.[12-14] In light of our further work[26,27] demonstrating that the C···C ring opening of epoxide cations is a general reaction, it will be of much interest to carry out corresponding ESR studies of substituted aziridine cations.

Cyclic Aminyl Radical Formation. Both the 1-azetidinyl and 1-aziridinyl neutral radicals (**4**) were detected in the course of this work. A particularly interesting byproduct of this investigation

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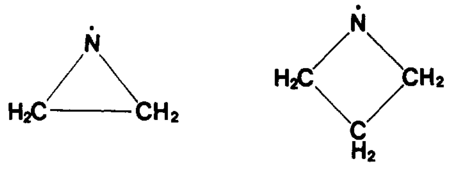

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is the direct observation of 1-azetidinyl radical formation from the azetidine radical cation in the $CFCl_2CF_2Cl$ matrix. This reaction does not appear to proceed in the $CFCl_3$ matrix and it is also much less efficient in CF_3CCl_3. Consequently, an interpretation of this reaction as a simple transfer of the N–H proton from the cation to a halocarbon solvent molecule seems most unlikely. Instead, it appears that the reaction is correlated with the higher mobility associated with the $CFCl_2CF_2Cl$ solvent,[26] suggesting that the cation reacts with a neutral azetidine molecule or a halide ion in a diffusion-controlled reaction. Although the reaction in both cases is easily formulated as a proton transfer to a nucleophilic center, a cation–molecule reaction with azetidine could also occur by hydrogen atom abstraction from the neutral molecule to give identical products, namely the cyclic aminyl radical and a protonated azetidine.

The corresponding 1-aziridinyl radical was found to be the major radical product after the 77 K irradiation of aziridine in both the $CFCl_2CF_2Cl$ and CF_3CCl_3 matrices, no radical cation being detected in either case. These results are more puzzling than those for azetidine, and cannot be explained by proton transfer from the C···C ring-opened cation unless the neutral CH_2–N–CH_2 radical undergoes a subsequent ring closure. A more acceptable explanation is that weakly associated neutral aziridine dimers or higher mers are present initally in these two matrices, and that the radical cation abstracts a hydrogen atom from the N–H bond of a neutral hydrogen-bonded aziridine molecule.

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Simultaneous Measurements of the Diffusion Coefficients of the Dye Molecule and Its Photoproduct by the Holographic Relaxation Technique

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Using the laser-induced holographic relaxation technique, we have demonstrated that the diffusion coefficients of camphorquinone and its photoproduct in the PMMA host can be simultaneously determined. The diffusion coefficients of CQ and its photoproduct show a Williams–Landel–Ferry (WLF) type of temperature dependence.

Although holography is widely known as a technique for producing a three-dimensional picture, it can also be used as a powerful tool for the investigation of a variety of photochemical and photophysical processes.[1] In this Letter, we are concerned with the application of the holographic grating relaxation (HGR) technique to measure the diffusion coefficient of dye molecules dissolved in a polymer host. The dye molecule of focus is camphorquinone (CQ) and the polymer host is amoprhous poly(methyl methacrylate) (PMMA).

Recent HGR experiments have revealed the presence of a decay–growth–decay diffracted intensity curve when the object beam is blocked.[2] This effect is correctly interpreted as due to the presence of multiple gratings associated with the dye molecules and their photoproducts.[3] In ref 3, the multiple grating effect is utilized to investigate the kinetics of the photochemical process of bovine serum alumin labeled with benzospiropyran. We demonstrate here that the multiple grating effect can be used to simultaneously measure the translational diffusion coefficients of CQ and its photoproduct (CQP) in PMMA.

General techniques to prepare the dye–polymer host system for the experiment have been described elsewhere.[2,4] The CQ concentration used is only between 0.5% to 1% to warrant the self-diffusion measurement. The molecular weight of PMMA is 460 000 with $M_w/M_n = 1.76$. The holographic grating is induced by crossing two bleaching (writing) beams from an Ar^+ laser radiating at 5145 Å at the CQ–PMMA sample. The maximum of CQ absorption spectrum is at about 4600 Å and $\lambda = 5145$ Å locates at the tail end of the absorption curve. The angle between two writing beams is varied between $\theta = 8.8°$ and $\theta = 90°$. Immediately after bleaching (the bleaching time is about $^1/_2$ to $^1/_{15}$ s and the laser power at the sample is about 20 mW), one of the two beams is shuttered and the other attenuated by a factor of 10^{-3} to 10^{-4} acts as the reading beam. The diffracted intensity in the first order detected with a photomultiplier–amplifier system is stored in a digital recorder from which a data file of the diffracted intensity vs. time during the reading period is obtained.

Shown in Figure 1 is the time dependence of the diffracted intensity. The unusual decay–growth–decay shape has been interpreted as due to the interference of the light diffracted from CQ and its photoproduct.[2] Since the optical properties and diffusion coefficients of CQ and CQP differ, there will be interference of the light diffracted from the grating associated with CQ and that associated with CQP. Such an interference effect owing to dual gratings has escaped detection (or proper interpretation) for several years because, when a dye molecule is labeled to a polymer chain, the ground and excited states have practically the same diffusion coefficient. However, in the present case, CQ is not attached to a polymer chain. After interacting with the laser beam, the size of the photoproduct CQ is somewhat different from that of CQ,[5] and hence different translational diffusion coefficients.

As pointed out in ref 2, the decay–growth–decay shown in Figure 1 can be fitted to the equation

$$I = [A \exp(-t/\tau_1) - B \exp(-t/\tau_2)]^2 \qquad (1)$$

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