Matrix Isolation EPR Study of Novel Radical Cations from Bicyclic[3.2.0] and Monocyclic C_7H_8 and C_7H_{10} Compounds

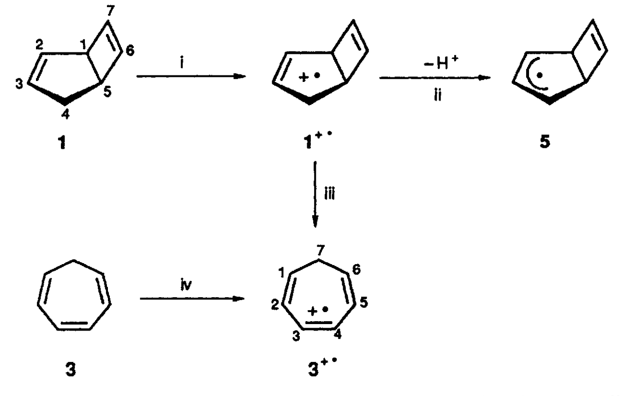
Antonio Faucitano,[*,a] **Armando Buttafava,**[a] **Fausta Martinotti,**[a] **Reiner Sustmann**[b] **and Hans-Gert Korth**[b]
[a] *Dipartimento di Chimica Generale, Università di Pavia, 27100 Pavia, Italy*
[b] *Institut für Organische Chemie, Universität - GH Essen, D-4300 Essen 1, Germany*

The radical cations of bicyclo[3.2.0]hepta-2,6-diene and bicyclo[3.2.0]hept-2-ene have been obtained by γ-irradiation of the parent compounds in Freon matrices and their structures investigated by EPR spectroscopy and MNDO and INDO calculations. In a $CFCl_3$ matrix, ring opening to the isomeric cycloheptatriene and cycloheptadiene radical cations occurred, whereas in a $CF_2ClCFCl_2$ matrix the prevalent reaction was deprotonation to the neutral bicyclo[3.2.0]hepta-2,6-dien-4-yl and bicyclo[3.2.0]hept-2-en-4-yl radicals, respectively.

Investigations of hydrocarbon radical cations are of great interest from different points of view. For instance, the singly occupied molecular orbital (SOMO) of the radical cation often corresponds to the highest occupied molecular orbital (HOMO) of the parent compound, so that the electronic structure of the latter can be deduced from the EPR spectrum of the radical cation.[1] Furthermore, the radical cations provide readily accessible and reactive electronic modifications of the parent compounds with the result that they are ubiquitous intermediates in many important classes of reaction. As part of our research program on radical cations of hydrocarbons with strained ring structures[2] we report in this work on the application of a γ-radiolytic technique using Freon matrices[3] for the generation and EPR-spectroscopic characterization of novel species (**1**$^{+\bullet}$, **2**$^{+\bullet}$) obtained by electron ejection from two compounds belonging to the C_7H_8 and C_7H_{10} hypersurface, namely bicyclo[3.2.0]hepta-2,6-diene (**1**) and bicyclo[3.2.0]hept-2-ene **2**. This work also refers to the structure and EPR properties of the related, hitherto unknown radical cations **3**$^{+\bullet}$ and **4**$^{+\bullet}$ from cycloheptatriene **3** and cycloheptadiene **4**, formed from **1**$^{+\bullet}$ and **2**$^{+\bullet}$ *via* electrocyclic ring opening.

Results and Discussion

The EPR spectrum recorded after γ-irradiation of **1** in a $CF_2ClCFCl_2$ matrix at 77 K showed an approximate quartet structure of *ca.* 15 mT overall width [Fig. 1(*a*), (*b*)]. With the aid of INDO calculations on the MNDO-optimized structures (see below) the spectrum could be roughly reproduced by computer simulation using the hyperfine splitting (hfs) constants given in Table 1 for the radical cation **1**$^{+\bullet}$ of the parent compound **1** (Scheme 1).



Scheme 1 *Reagents:* i, $CFCl_2CF_2Cl$ or $CFCl_3$; γ-irrad., 77 K; ii, $CFCl_2CF_2Cl$, 123 K; iii, $CFCl_3$, 113 K; iv, $CFCl_2CF_2Cl$; γ-irrad., 77 K

Table 1 EPR hyperfine splittings/mT of radical cations **1**$^{+\bullet}$–**4**$^{+\bullet}$

Radical cation	T/K	a_1	a_2	a_3
1$^{+\bullet a}$	77	3.5 (H-1)	4.5 (H-4_{syn})	6.2 (H-4_{anti})
2$^{+\bullet a}$	77	3.8 (H-1)	4.5 (H-4_{syn})	6.4 (H-4_{anti})
3$^{+\bullet}$	113	0.52 (H-1,6)	0.52 (H-3,4)	5.15 (2H-7)
4$^{+\bullet}$	153	0.9 (H-1,4)	0.9 (H-5,6_{eq})	2.8 (H-5,6_{ax})

[a] Approximate values.

According to the INDO and MNDO calculations (Tables 2, 3) the given hfs features are in agreement with **1**$^{+\bullet}$ having a structure similar to that of the parent compound, the major difference being the lengthening of the C(2)–C(3) bond of the five-membered ring from 133 to 145 pm. This geometry effect is a consequence of the loss of an electron from the HOMO, in which most of the bonding character is located at C(2) and C(3). Delocalization of the unpaired spin onto the cyclobutene moiety is limited to *ca.* 15% of the overall spin density (Fig. 2) and is accompanied by a small lengthening of the C(6)–C(7) double bond from 133 to 135 pm. Most of the unpaired spin density (and the positive charge) is localized on the p-orbitals at C(2) and C(3), thus leading to a dominant magnetic interaction by the three β-hydrogen atoms at C(1) and C(4). The other couplings are smaller than the experimental linewidth.

On warming to 123 K, the radical cation **1**$^{+\bullet}$ undergoes deprotonation with formation of the allyl-type bicyclo[3.2.0]hepta-2,6-dien-4-yl radical (**5**), the corresponding hfs constants being identical to those reported[6] [Fig. 1(*c*), (*d*)]. The deprotonation of alkane radical cations to form alkyl radicals has been reported to take place selectively from the C–H bonds carrying the highest unpaired spin density.[7] In **1**$^{+\bullet}$ this property is shared by the two C–H bonds at C(4). Deprotonation may involve proton transfer to the parent compound or to nucleophiles such as Cl ions, formed by dissociative electron capture of the matrix molecules. In both cases diffusion of the reactants is required for the reaction to occur. This is not unreasonable since some softening of the matrix already occurs at 113 K as can be deduced from the improved EPR spectral resolution.

γ-Irradiation of **1** in a $CFCl_3$ matrix afforded somewhat different results. At 77 K the EPR spectrum again showed the 'quartet' structure of radical cation **1**$^{+\bullet}$ as the major component [Fig. 3(*a*)]. However, a different change in the EPR spectrum took place on warming to temperatures above 113 K, leading to

Table 2 Selected MNDO parameters of radical cations $1^{+\bullet}$ and $2^{+\bullet a}$

Bond length/pm			Bond angle/°			Dihedral angle/°		
	$1^{+\bullet}$	$2^{+\bullet}$		$1^{+\bullet}$	$2^{+\bullet}$		$1^{+\bullet}$	$2^{+\bullet}$
C(1)–C(2)	149	148	C(2)–C(1)–C(5)	10.5	105.9	C(1)–C(2)–C(3)–C(5)	−2.7	−0.9
C(2)–C(3)	144	144	C(1)–C(2)–C(3)	11.4	111.2	C(4)–C(5)–C(1)–C(7)	−118.7	−121.6
C(3)–C(4)	150	149	C(2)–C(3)–C(4)	111.5	110.5	C(2)–C(1)–C(5)–C(6)	113.6	118.8
C(4)–C(5)	154	155	C(3)–C(4)–C(5)	106.2	106.6	H(5)–C(5)–C(1)–H(1)	0.3	0
C(1)–C(5)	160	158	C(4)–C(5)–C(1)	106.1	105.8	C(5)–C(6)–C(7)–C(1)	−0.1	−1
C(1)–C(7)	155	157	C(5)–C(6)–C(7)	95.3	91.0	H(3)–C(3)–C(4)–$H(4)_{ax}$	57.5	55.9
C(5)–C(6)	152	156	C(6)–C(7)–C(1)	94.2	90.1	H(3)–C(3)–C(4)–H_{eq}	−58.4	−59.5
C(6)–C(7)	135	155	H(4)–C(4)–H(4)	105.1	104.5	H(3)–C(3)–C(2)–H(2)	−5	0.4

[a] Numbering scheme as given in Schemes 1, 2.

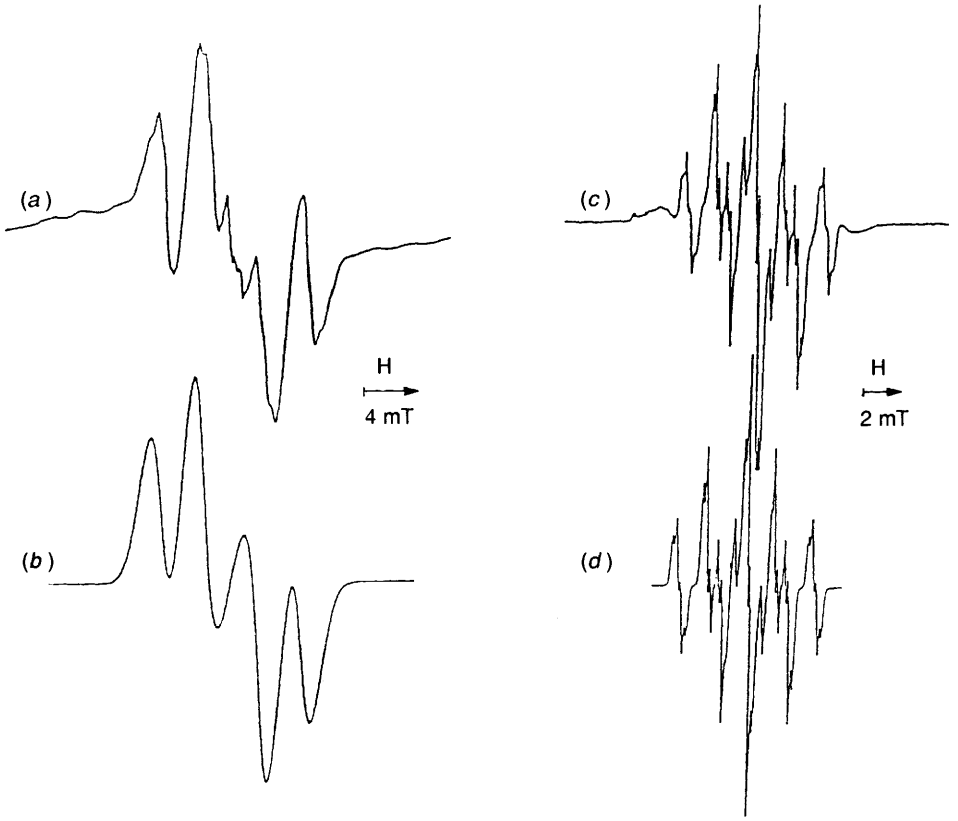
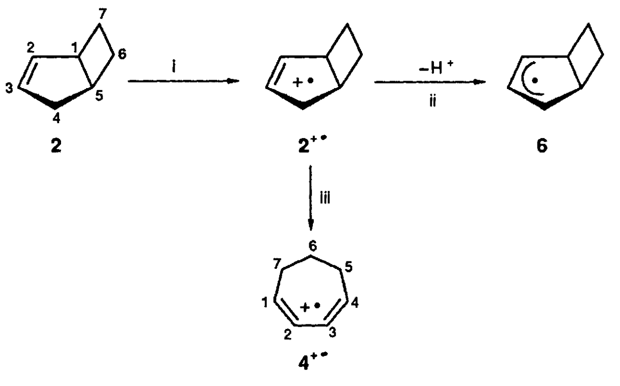


Fig. 1 (*a*) EPR spectrum recorded at 77 K immediately after γ-irradiation of **1** at 77 K in $CF_2ClCFCl_2$; (*b*) computer simulation using the hfs constants given in Table 1 for $1^{+\bullet}$; (*c*) spectrum from (*a*) after warming to 123 K; (*d*) computer simulation using the hfs constants of radical **5** (ref. 12)



Scheme 2 *Reagents*: i, $CFCl_2CF_2Cl$ or $CFCl_3$; γ-irrad., 77 K; ii, $CFCl_2CF_2Cl$, 123 K; iii, $CFCl_3$, 77 K

the spectrum shown in Fig. 3(*b*). This spectrum is interpreted in terms of the interaction of two and four equivalent hydrogen atoms with hfs of 5.15 and 0.57 mT, respectively [Fig. 2(*c*)]. We consider such hfs as being diagnostic of the cycloheptatriene radical cation ($3^{+\bullet}$) because of the following arguments. (i) The same spectrum has been obtained by γ-irradiation of cycloheptatriene (**3**) in a $CF_2ClCFCl_2$ matrix (Scheme 1), and (ii) the observed EPR features are consistent with those predicted by INDO calculations (Table 3) based on a planar geometry[8] for $3^{+\bullet}$ (Table 4).

According to the INDO results, the triplet splitting is assigned to the methylene hydrogen atoms and the quintet to the four hydrogens at C(1), C(3), C(4) and C(6). The hfs of the two hydrogens at C(2) and C(5) respectively, are predicted to be significantly smaller and, hence, are probably not resolved. These hfs features are consistent with the unpaired electron being located in a b_1 orbital of the cycloheptatriene cation radical of C_{2v} symmetry (Fig. 2). The uncommonly large hfs of the methylene hydrogens are a consequence of hyperconjugation and appear to be typical for β-protons at carbon atoms bound to two contiguous spin density centres with equal phases. In this respect the EPR properties of the cycloheptatriene radical cation can be related to those of the cyclohexadienyl radical.[9] It is inferred from the identification of $\mathbf{3}^{+\cdot}$ that the $CFCl_3$ matrix favours the isomerization of radical cation $\mathbf{1}^{+\cdot}$ [by cleavage of the endocyclic C(1)–C(5) bond followed by a 1,4-hydrogen transfer] over deprotonation. The electrocyclic reaction is expected to take place in a disrotatory mode and to be assisted by gain of resonance stabilization in the resulting radical cation $\mathbf{3}^{+\cdot}$. The other major factor certainly contributing to the driving force of this reaction is the release of ring strain, facilitated by the weakening of the C(1)–C(5) bond in $\mathbf{1}^{+\cdot}$. The latter effect can be deduced from the MNDO calculations, which predict an elongation of this bond from 152 to 160 pm in going from the neutral parent compound **1** to its radical cation $\mathbf{1}^{+\cdot}$. The fact that neither the cyclopentene radical cation[10] nor the radical cation of norbornadiene[11] undergo ring opening is in line with this view.

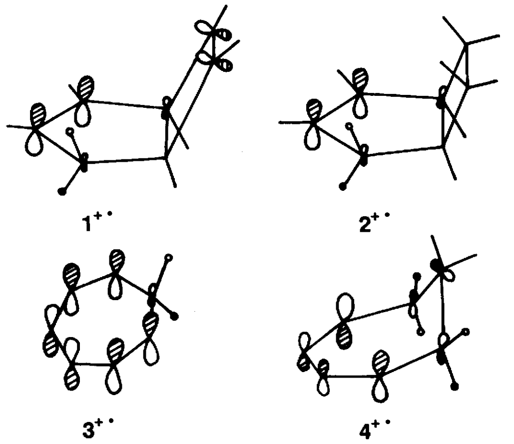


Fig. 2 Schematic representation of the MNDO SOMOs of radical cations $\mathbf{1}^{+\cdot}$–$\mathbf{4}^{+\cdot}$

Table 3 INDO proton hfs constants of radical cations $\mathbf{1}^{+\cdot}$–$\mathbf{4}^{+\cdot\, a}$

	hfs/mT			
Position[b]	$\mathbf{1}^{+\cdot}$	$\mathbf{2}^{+\cdot}$	$\mathbf{3}^{+\cdot}$	$\mathbf{4}^{+\cdot}$
C(1)	*2.39*	*3.8*	*−0.78*	*−0.84*
C(2)	−0.39	−0.53	0.07	−015
C(3)	−0.67	−0.79	*−0.39*	
C(4)	*4.1* (*syn*) *6.18* (*anti*)	*4.33* (*syn*) *6.44* (*anti*)	*−0.39*	*−0.84*
C(5)	1.31	0.9	0.07	*3.1* (ax) *0.65* (eq)
C(6)	1.24	0.31 (*syn*) 0.12 (*anti*)	*−0.78*	−0.26 (ax) −0.14 (eq)
C(7)	1.33	0.29 (*syn*) 0.037 (*anti*)	*6.98* (2 H)	*3.1* (ax) *0.65* (eq)

[a] Data used in the spectral simulations given in italics. [b] Numbering scheme as given in Schemes 1, 2.

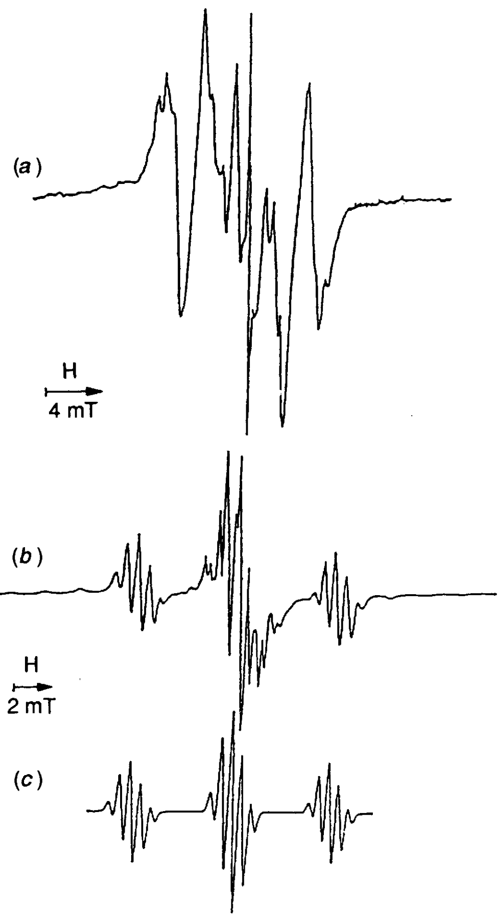


Fig. 3 (*a*) EPR spectrum recorded at 77 K after γ-irradiation of **1** at 77 K in $CFCl_3$ matrix; (*b*) spectrum from (*a*) after warming to 113 K; (*c*) computer simulation of spectrum (*b*) using the hfs constants given in Table 1 for $\mathbf{3}^{+\cdot}$

The SOMO and EPR properties of the radical cation $\mathbf{2}^{+\cdot}$ are predicted by the MNDO and INDO methods to be similar to that of $\mathbf{1}^{+\cdot}$ with most (>70%) of the unpaired spin density located at C(2) and C(3) (Fig. 2). The major hfs constants are expected to be due to the three hydrogen atoms at C(1) and C(4) (Table 3). Also, the geometry changes accompanied with the electron loss are predicted to be similar to those in $\mathbf{1}^{+\cdot}$, resulting mainly in the lengthening of the C(2)–C(3) and the C(1)–C(5) bonds from 133 to 144 pm and from 153 to 158 pm, respectively (Table 2). In agreement, the EPR spectrum obtained at 77 K in a $CF_2ClCFCl_2$ matrix [Fig. 4(*a*), (*b*); Table 1] consists of a partially-resolved quartet with an average line separation of *ca.* 3.0 mT. On warming to temperatures above 123 K the radical cation $\mathbf{2}^{+\cdot}$ deprotonates to give the neutral bicyclo[3.2.0]hept-2-en-4-yl radical (**6**)[12] [Scheme 2; Fig. 4(*c*), (*d*)].

By way of contrast, the EPR spectrum obtained upon γ-

Table 4 Selected MNDO parameters of radical cations $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot\, a}$

$\mathbf{3}^{+\cdot}$				$\mathbf{4}^{+\cdot}$					
Bond length/pm		Bond angle/°		Bond length/pm		Bond angle/°		Dihedral angle/°	
C(1)–C(2)	139	C(7)–C(1)–C(2)	129.8	C(6)–C(7)	154	C(5)–C(6)–C(7)	120.1	C(3)–C(2)–C(1)–C(7)	0
C(2)–C(3)	142	C(1)–C(2)–C(3)	128.9	C(7)–C(1)	152	C(6)–C(7)–C(1)	110	C(1)–C(7)–C(5)–C(6)	110
C(3)–C(4)	141	C(2)–C(3)–C(4)	129.1	C(1)–C(2)	146	C(7)–C(1)–C(2)	129		
C(1)–C(7)	149	C(1)–C(7)–C(6)	125.7	C(2)–C(3)	146	C(1)–C(2)–C(3)	129		

[a] Numbering scheme as given in Schemes 1 and 2. The structure of $\mathbf{3}^{+\cdot}$ is planar. Both $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ have a symmetry plane bisecting the C(1)–C(7)–C(6) and C(5)–C(6)–C(7) angles respectively. The orientations of the CH_2 groups are such that the C–C–C planes bisect the H–C–H angles.

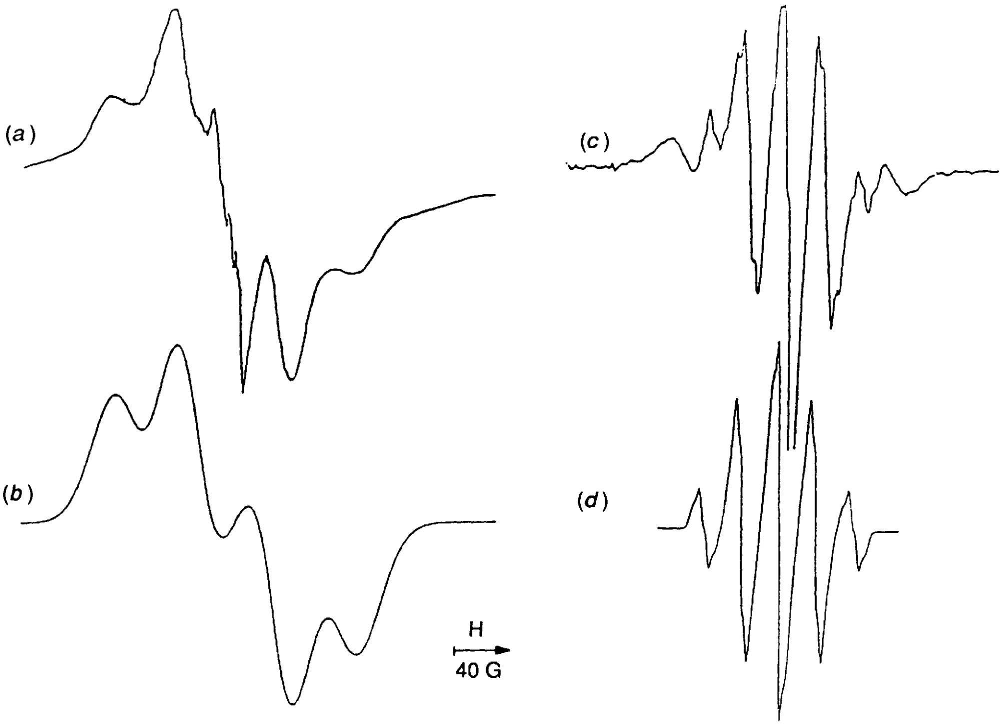


Fig. 4 (*a*) EPR spectrum recorded at 77 K immediately after γ-irradiation of **2** at 77 K in $CF_2ClCFCl_2$; (*b*) computer simulation using the hfs constants given in Table 1 for $\mathbf{2}^{+\bullet}$; (*c*) spectrum from (*a*) after warming to 123 K; (*d*) computer simulation using the hfs constants of radical **6** (ref. 12)

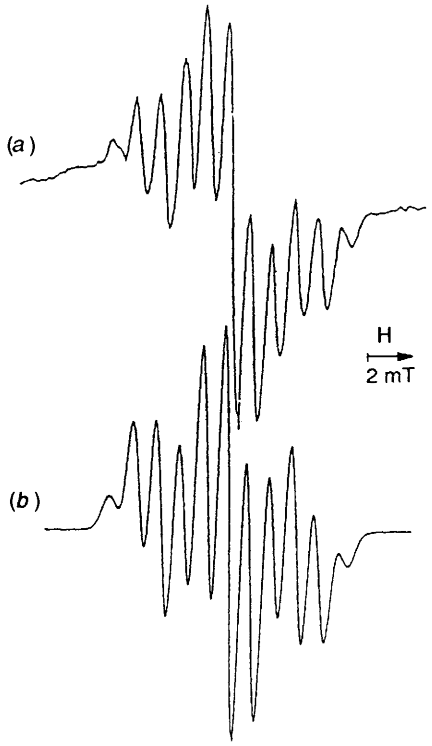


Fig. 5 (*a*) EPR spectrum recorded at 77 K after γ-irradiation of **2** at 77 K in $CFCl_3$ matrix; (*b*) spectrum from (*a*) after warming to 153 K; (*c*) computer simulation of spectrum (*b*) using the hfs constants given in Table 1 for $\mathbf{4}^{+\bullet}$

irradiation of **2** at 77 K in a $CFCl_3$ matrix did not appear to be that of $\mathbf{2}^{+\bullet}$. When recorded at a higher temperature (153 K) it acquired sufficient resolution to be analysed in terms of a 1:2:1 triplet of 2.8 mT and a binominal quintet of 0.9 mT (Fig. 5). Based on the MNDO and INDO calculations (Tables 3 and 4) this spectrum is attributed to the cycloheptadiene radical cation ($\mathbf{4}^{+\bullet}$). The hfs constants (Table 1) are consistent with the characteristics of the a_2 HOMO of the neutral parent compound of C_{2v} symmetry (Fig. 2). It follows from this observation that, like $\mathbf{1}^{+\bullet}$, the radical cation $\mathbf{2}^{+\bullet}$ also undergoes isomerization in a $CFCl_3$ matrix. This reaction most feasibly occurs by ring-opening followed by 1,4-H atom transfer. Contrary to expectation (less resonance stabilization is involved in both the intermediate state and in the cycloheptadiene system), radical $\mathbf{2}^{+\bullet}$ seems to be even less stable than $\mathbf{1}^{+\bullet}$, which can be judged from the fact that its isomerization has already occurred at 77 K during the irradiation process. In order to rationalize this observation one might conclude that stabilization by electron delocalization is not of prominent importance in these isomerization reactions. As mentioned above, other factors such as the weakening of the C(1)–C(5) bond, and primarily, the release of ring strain may be of major importance. It is worth mentioning that the neutral bicyclo[3.2.0]hept-2-en-4-yl radical (**6**) does not undergo ring opening in a similar fashion. Instead, rupture of the exocyclic C(1)–C(7) bond followed by 1,3-H shift is observed at much higher temperature.[12]

As demonstrated by the above results, the stability and chemical behaviour of radical cations $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ are markedly influenced by the nature of the Freon matrix. Several examples of similar matrix effects have been reported in the literature,[13,14] however, the origin of the phenomenon is not yet clear. It has been suggested that differences in the solvation energies may play some role. Alternatively, the constraints exercised by the matrix on the type of motions needed for diffusion or for the rearrangement of the molecular framework were invoked. Diffusion may control the competition between a monomolecular and bimolecular reaction; monomolecular ring opening is expected to be favoured with respect to bimolecular proton transfer when, as predicted for a $CFCl_3$ matrix, the diffusion of the reactants is more severely hindered.

Experimental

Frozen 0.1 mol% solutions of the hydrocarbons in $CF_2ClCFCl_2$ and $CFCl_3$ matrices were γ-irradiated at 77 K in a Co-60 source with total doses of *ca.* 2 Mrads. EPR spectra were recorded on a

Varian E-9 spectrometer equipped with a variable-temperature unit. Compounds **1** and **2** were prepared and purified by GLC as described previously;[4] commercially available cycloheptatriene (Aldrich) was distilled prior to use. Input geometries for MNDO calculations on the radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ were obtained from electron diffraction and MM2 studies on the parent compounds.[5] Fully optimized MNDO geometries were used as input data for the INDO calculations.

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