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# Structures and Rearrangements of Bicyclo[1.1.0]butane Radical Cations: An ESR and ENDOR Study[1]

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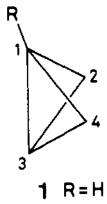
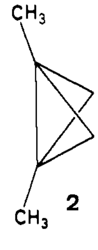
**Abstract:** Radical cations were generated by $\gamma$-irradiation in Freon matrices from bicyclo[1.1.0]butane (**1**), 1,3-dimethylbicyclo[1.1.0]butane (**2**), 1-methylbicyclo[1.1.0]butane (**3**), tricyclo[3.1.0.0$^{2,6}$]hexane (**4**), and tricyclo-[4.1.0.0$^{2,7}$]heptane (**5**), as well as from some deuterio derivatives of **1**, **3**, and **5**. Under these conditions, the bicyclic radical cations **1**$^{\bullet+}$, **2**$^{\bullet+}$, and **3**$^{\bullet+}$ were persistent and could be characterized by their hyperfine data with the use of ESR and ENDOR spectroscopy. A detailed analysis of these data indicates that a methyl group withdraws ca. 15% of the spin population from the substituted carbon atom 1 or 3 of bicyclobutane. In contrast to **1**$^{\bullet+}$–**3**$^{\bullet+}$, the tricyclic radical cations **4**$^{\bullet+}$ and **5**$^{\bullet+}$ are not sufficiently long-lived for ESR and ENDOR studies, as they readily rearrange to the radical cations of cyclohexa-1,3-diene (**6**) and cyclohepta-1,3-diene (**8**), respectively. The isomerization of **5**$^{\bullet+}$ to **8**$^{\bullet+}$ possibly proceeds via the radical cation of *cis*-bicyclo[3.2.0]hept-6-ene (**7**) which undergoes ring opening to yield **8**$^{\bullet+}$. Deuterium labelings of **5**$^{\bullet+}$ and **8**$^{\bullet+}$ point out that the initial step in this isomerization is the cleavage of a lateral bond in the bicyclobutane moiety, and the same statement should hold for the rearrangement of **4**$^{\bullet+}$ to **6**$^{\bullet+}$. The present work emphasizes the importance of ENDOR spectroscopy for the full characterization of radical cations in Freon matrices. Not only can smaller coupling constants and differences in the larger ones be determined, but it is also possible to derive the absolute sign of these values from the anisotropic components of their ENDOR signals. Because of its lower resolving power, this information is not available with the use of ESR spectroscopy alone, in particular for radicals in rigid solutions.

## Introduction

In a previous communication,[2] we have characterized the radical cation of bicyclo[1.1.0]butane (**1**) by its hyperfine-proton data determined from the ESR spectra of **1**$^{\bullet+}$ and its 1-deuterio derivative **1**-*d*$^{\bullet+}$. Contrary to what might be expected, **1**$^{\bullet+}$ does not rearrange to the radical cation of cyclobutene[1g,3] under the experimental conditions (CFCl$_3$ matrix; temperature, 77–160 K). Like the neutral compound **1**, it possesses a puckered geometry. A flap angle of 132.2° between the C(1)C(2)C(3) and C(1)C(4)C(3) planes of **1**$^{\bullet+}$ has been derived by combining hyperfine data with results of theoretical calculations[2] (for comparison, this angle is 121.7° in neutral **1**[4]). The spin distribution in **1**$^{\bullet+}$ has been interpreted[2] in terms of (i) the bulk of the spin population residing in the 2p-AO's of the two bridgehead atoms C(1) and C(3) and (ii) a hyperconjugatively favored spin transfer onto the methylene protons at C(2) and C(4). It is interesting to know how alkyl substitution in the 1,3-positions or bridging of the 2,4-positions by a polymethylene chain affects the kinetic stability and the spin distribution of **1**$^{\bullet+}$. To this aim, in addition to **1**$^{\bullet+}$, we have studied the radical cations produced by $\gamma$-irradiation in



**1** R=H
**1**-*d* R=D



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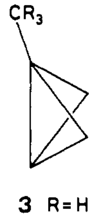
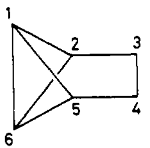


**3** R=H
**3**-*d*$_3$ R=D



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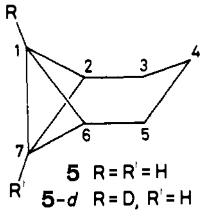
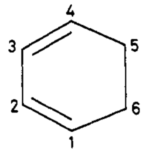


**5** R=R'=H
**5**-*d* R=D, R'=H
**5**-*d*$_2$ R=R'=D



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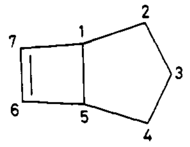

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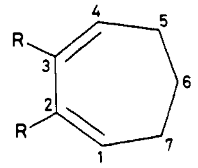

**8** R=H
**8**-*d*$_2$ R=D

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(1) Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices, Part 10. Parts 1–9: (a) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1065. (b) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498. (c) Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 1135. (d) Gerson, F.; Qin, X.-Z. *Chem. Phys. Lett.* **1988**, *153*, 546. (e) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1989**, *72*, 383. (f) Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1077. (g) Aebischer, J.-N.; Bally, T.; Roth, K.; Haselbach, E.; Gerson, F.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 7909. (h) Arnold, A.; Gerson, F. *J. Am. Chem. Soc.* **1990**, *112*, 2027. (i) Arnold, A.; Gerson, F.; Burger, U. *J. Am. Chem. Soc.* **1991**, *113*, 4359. Part 11: (j) Weber, K.; Prinzbach, H.; Schmidlin, R.; Gerson, F.; Gescheidt, G. *Angew. Chem., Int. Ed. Engl.* **1993**, in press.

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Freon matrices[5] from 1,3-dimethylbicyclo[1.1.0]butane (**2**) and 1-methylbicyclo[1.1.0]butane (**3**), as well as of tricyclo[$3.1.0.0^{2,6}$]hexane (dihydrobenzvalene; **4**) and tricyclo[$4.1.0.0^{2,7}$]heptane (Moore's hydrocarbon; **5**). Rearrangements of $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ led to the investigations of the radical cations obtained under the same conditions from cyclohexa-1,3-diene (**6**), *cis*-bicyclo[3.2.0]hept-6-ene (**7**), and cyclohepta-1,3-diene (**8**). For assignments of coupling constants to protons in individual positions and/or for elucidation of the rearrangement mechanism, isotopically labeled derivatives have also been included, namely 1-(trideuteriomethyl)bicyclo[1.1.0]butane (**3**-$d_3$), 1-deuterio- (**5**-$d$) and 1,7-dideuteriotricyclo[$4.1.0.0^{2,7}$]heptane (**5**-$d_2$), and 2,3-dideuteriocyclohepta-1,3-diene (**8**-$d_2$).

Along with the ESR spectroscopy, an important role in these studies has been played by the ENDOR technique, of which application to radical cations in Freon matrices was initiated in the Basel laboratory a few years ago.[1a]

## Results and Discussion

Frozen solutions of **1–8** and their deuterio derivatives in $CFCl_3$ were exposed to ionizing $\gamma$-rays at 77 K;[5] for **5–8** and their derivatives use was also made of $CF_2ClCFCl_2$ and $CF_3CCl_3$ as the matrix. The radical cations thus formed were studied by ESR and ENDOR spectroscopy in the temperature range between 77 K and the softening points of the matrices.

**General Remarks on Proton-ENDOR Spectra of Radical Cations in Frozen Solutions.** In our ENDOR system (see Experimental Section), the upper limit of the radio-frequency range is 35 MHz, while the lower limit of ca. 5 MHz is determined by the performance of the instrument in this special case of largely immobilized radical cations. Considering the frequency of the free $^1$H nucleus, $\nu_H$ = 14.56 MHz, the proton-coupling constants, $a$, are divided into four groups: (i) $|a| < 0.7$ mT ($\sim$20 MHz); both high- and low-frequency ENDOR signals at $\nu_H \pm {}^1/_2|a|$ may be observed in the range 5–25 MHz; (ii) 0.7 mT ($\sim$20 MHz) $< |a| <$ 1.4 mT ($\sim$40 MHz); only the high-frequency signal at $\nu_H + {}^1/_2|a|$ may be detected in the range 25–35 MHz; (iii) 1.4 mT ($\sim$40 MHz) $< |a| <$ 3.5 mT ($\sim$100 MHz); only the low-frequency signal at ${}^1/_2|a| - \nu_H$, i.e., "inverted" at the origin (0 MHz), may appear in the range 5–35 MHz; and (iv) $|a| >$ 3.5 mT ($\sim$100 MHz); both high- and low-frequency signals are beyond the reach of our ENDOR system.

A schematic representation of the ENDOR signals associated with the coupling constant $a$ is shown for i–iv in Figure 1.

In contrast to the seemingly "isotropic" ESR spectra of the radical cations, the corresponding proton-ENDOR signals often revealed a slight but significant hyperfine anisotropy. This finding is readily accounted for by the larger resolving power of the ENDOR spectroscopy. (For radical cations in Freon matrices, the ENDOR signals are typically ca. 0.3 MHz wide, as compared to the line width of 0.2–0.5 mT or 6–14 MHz in the corresponding ESR spectra.) Usually, the "anisotropic" ENDOR signals were split into only two components having a shape characteristic of parallel and perpendicular features. This pattern must be brought about by rotational averaging of two ($x,y$) out of three components ($x,y,z$). In the proton-ENDOR spectra dealt with in the present work and in our other studies of radical cations in Freon matrices,[1d,e,g,i,j] the coupling constant $|A_\parallel|$ associated with the parallel feature was larger than its perpendicular counterpart $|A_\perp|$ when the isotropic value $a = {}^1/_3(A_\parallel + 2A_\perp)$ is expected to be positive; an opposite relation $|A_\parallel| < |A_\perp|$ held for a negative sign of $a$ (Figure 2). Although we cannot provide a strict theoretical proof for these relations, we accept them as a rule which is valid for radical cations of small hydrocarbon molecules in Freon matrices, and to which no exceptions have so far been found in this special case. Tentatively, one can derive such a rule by using the equation $A_\parallel = a + 2B$ and $A_\perp = a - B$ where $B$ is the anisotropic contribution to $a$. For protons in the radical cations studied in the present and in the previous work,[1-3] it is reasonable to assume that $A_\parallel$, $A_\perp$, and $a$ have the same sign, which is either positive or negative, whereas $B$ is positive throughout. Moreover, as $|A_\parallel|$, $|A_\perp|$, and $|a|$ are much larger than $B$, the relations $|A_\parallel| > |a| > |A_\perp|$ for $a > 0$ and $|A_\parallel| < |a| < |A_\perp|$ for $a < 0$ are obvious consequences of this assumption. They enabled us to determine the absolute sign of $a$ from an ENDOR spectrum and thus, by comparison with theory, to assign coupling constants to protons in individual positions of the radical cation when two values are similar in magnitude but should differ in sign. This information is the more valuable, as general-TRIPLE resonance experiments, which provide relative signs of coupling constants,[6] are hardly practicable on the ENDOR signals of radical cations in rigid solutions.

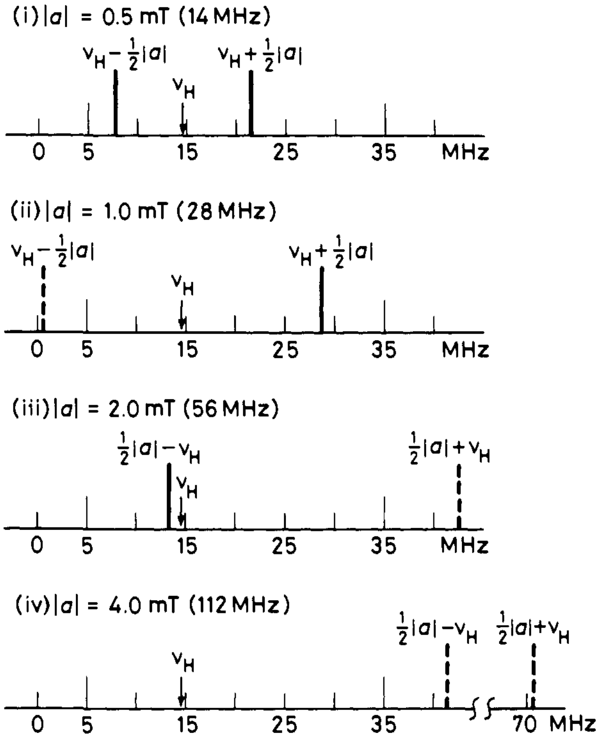

**Figure 1.** Schematic representation of proton-ENDOR signals observable (solid line) and not observable (dashed line) on our instrument for coupling constants of different size (cf. text).

In the following, we describe the ESR and ENDOR spectra obtained upon $\gamma$-irradiation of **1–8** and their deuterio derivatives in Freon matrices.

**Bicyclo[1.1.0]butane (1).** The ESR spectrum of $\mathbf{1}^{\bullet+}$ in a $CFCl_3$ matrix at 160 K was presented in the previous communication.[2] Its hyperfine pattern consists of a two-proton triplet spaced by 7.71 ± 0.05 mT, each component of the triplet being further split by 1.14 ± 0.05 mT into a four-proton quintet. The very large (and undoubtedly positive) coupling constant $a(H_{ax})$ = +7.71 mT has been assigned to the two axial methylene protons in the 2,4-positions; the smaller value of 1.14 mT thus being left for the two corresponding equatorial methylene protons, $H_{eq}$, and the two bridgehead protons, $H_{br}$, in the 1,3-positions. This assignment was confirmed by the ESR spectrum of the radical cation $\mathbf{1}\text{-}d^{\bullet+}$ deuteriated in the 1-position,[2] as the four-proton quintet of $\mathbf{1}^{\bullet+}$ was replaced by a three-proton quartet of $\mathbf{1}\text{-}d^{\bullet+}$. The coupling constants $a(H_{eq})$ and $a(H_{br})$ could not be distinguished in the ESR spectrum, and the difference in their absolute values was

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[5] Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *13*, 393.

[6] See, e.g.: Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH Publishers: New York, 1988; Chapter 2.

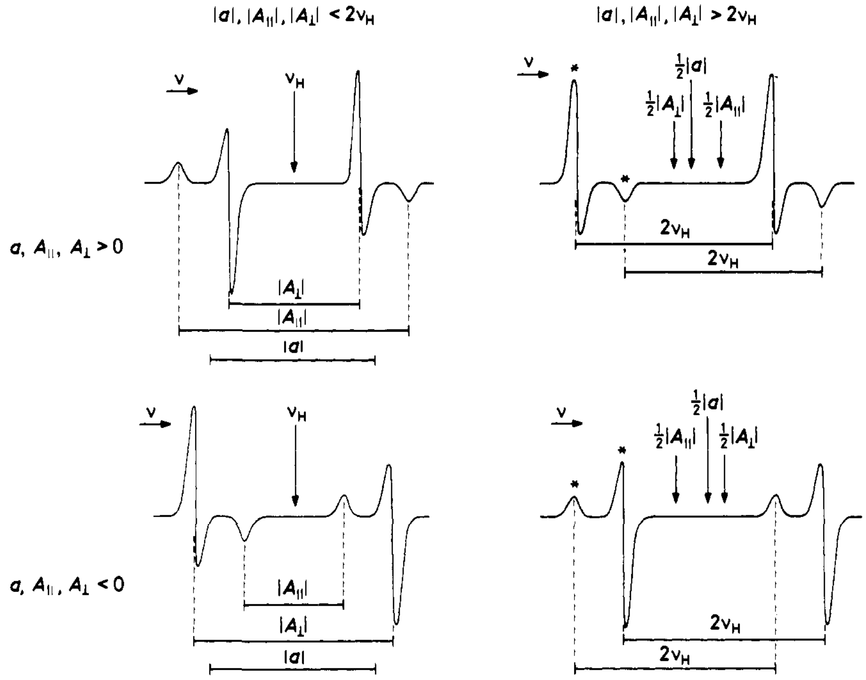

**Figure 2.** Idealized proton-ENDOR signals for quasiaxial hyperfine tensors of small hydrocarbon radical cations in a Freon matrix. Connection between the sign of the isotropic coupling constant, $a$, and the relative size of its anisotropic counterparts $|A_{\parallel}|$ and $|A_{\perp}|$. The "inverted" signals are starred.

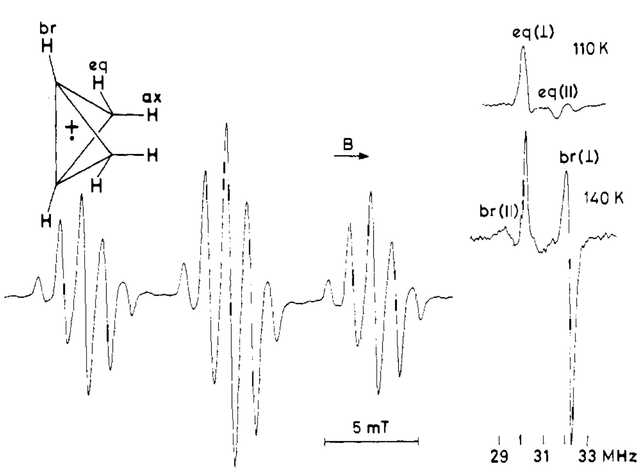

**Figure 3.** Left: ESR spectrum of $1^{\bullet+}$ in a $CFCl_3$ matrix at 160 K. Right: corresponding proton-ENDOR spectrum; temperature varied as indicated.

estimated to be smaller than 0.2 mT.[2] Theory requires a positive sign for $a(H_{eq})$ and a negative one for $a(H_{br})$, because the singly occupied orbital in $1^{\bullet+}$ is predicted to have a predominantly "p-character" at the bridgehead atoms C(1) and C(3) and thus $H_{br}$ must be regarded as an $\alpha$-proton, while $H_{ax}$ and $H_{eq}$ have to be considered as $\beta$.[7]

The proton-ENDOR spectrum of $1^{\bullet+}$ has not previously been analyzed.[2] Figure 3 shows the high-frequency ENDOR signals from $H_{eq}$ and $H_{br}$, in addition to the ESR spectrum of $1^{\bullet+}$ which is here reproduced for completeness. With a $CFCl_3$ matrix at 110 K, signals characteristic of a parallel and a perpendicular component were observed at 31.42 MHz ($\nu_H + {}^1/_2|A_{\parallel}|$) and 30.15 MHz ($\nu_H + {}^1/_2|A_{\perp}|$). They are assigned to $H_{eq}$, because $|A_{\parallel}|$ = 33.72 MHz or 1.203 mT is larger than $|A_{\perp}|$ = 31.18 MHz or 1.112 mT, as required for $a > 0$. The isotropic coupling constant $a(H_{eq})$ is thus +32.03 MHz or +1.142 mT. At 140 K, additional ENDOR signals, also representing two "anisotropic" features, became evident. From their positions at 29.28 MHz ($\nu_H + {}^1/_2|A_{\parallel}|$) and 32.19 MHz ($\nu_H + {}^1/_2|A_{\perp}|$), one calculates $A_{\parallel}$ = 29.44 MHz or 1.050 mT and $|A_{\perp}|$ = 35.26 MHz or 1.257 mT. These values yield the isotropic coupling constant $a(H_{br})$ = −33.32 MHz or −1.188 mT, the negative sign being consistent with $|A_{\parallel}| < |A_{\perp}|$. Both coupling constants $a(H_{eq})$ and $a(H_{br})$ determined in this way agree, in the limits of experimental error, with the previously reported[2] $|a(H_{eq})| \approx |a(H_{br})| = 1.14 \pm 0.05$ mT, and the difference $|a(H_{br})| - |a(H_{eq})|$ = 0.046 mT is vanishingly small, as compared to the width (0.4 mT) of the ESR lines. The anisotropic contributions $B = {}^1/_3(A_{\parallel} - A_{\perp})$ to $a(H_{eq})$ and $a(H_{br})$ are +0.030 and +0.069 mT, respectively. The larger $B$ value for $H_{br}$ than for $H_{eq}$ is in accordance with their specification of the former as $\alpha$- and the latter as $\beta$-protons and with the finding that a higher temperature is required for the signals of $H_{br}$ than for those of $H_{eq}$ to be observed in the ENDOR spectrum.

**1,3-Dimethylbicyclo[1.1.0]butane (2).** Figure 4 shows the ESR spectrum observed at 150 K upon $\gamma$-irradiation of **2** in a $CFCl_3$ matrix. The prominent feature of the hyperfine pattern is a two-proton triplet spaced by 6.51 mT. This very large coupling constant, which resembles the $|a(H_{ax})|$ value of 7.71 mT for $1^{\bullet+}$, is characteristic of the two methylene axial protons in the 2,4-positions of the bicyclo[1.1.0]butane radical cations. It testifies that the observed ESR spectrum arises from an unrearranged radical cation $2^{\bullet+}$. The smaller hyperfine splittings represented by a six-proton septet and a two-proton triplet are due to the six protons, $H_{me}$, of the two methyl substituents in the 1,3-positions and to the two equatorial methylene protons, $H_{eq}$, in the 2,4-positions. All protons are $\beta$ and their coupling constants, $a(H_{ax})$ = +6.51, $a(H_{me})$ = +1.65, and $a(H_{eq})$ = +0.89 mT, should be positive. For $H_{me}$ and $H_{eq}$, this expectation has been born out by the ENDOR spectrum (Figure 4), in which each of the two proton sets gives rise to a parallel and a perpendicular feature. The "inverted" low-frequency signals at 10.05 MHz (${}^1/_2|A_{\parallel}| - \nu_H$) and 7.75 MHz (${}^1/_2|A_{\perp}| - \nu_H$) arise from $H_{me}$, while the high-frequency ones at 29.68 MHz ($\nu_H + {}^1/_2|A_{\parallel}|$) and 25.69 MHz ($\nu_H + {}^1/_2|A_{\perp}|$) stem from $H_{eq}$. The pertinent anisotropic coupling constants are $|A_{\parallel}|$ = 49.22 MHz or 1.755 mT and $|A_{\perp}|$ = 44.62 MHz or 1.591 mT for $H_{me}$ and $|A_{\parallel}|$ = 30.24 MHz or 1.078 mT and $|A_{\perp}|$ = 22.26 MHz or 0.794 mT for $H_{eq}$. Their isotropic counterparts, $a(H_{me})$ = +46.15 MHz or +1.646 mT and $a(H_{eq})$ = +24.92 MHz or +0.889 mT, agree with the data derived from the ESR spectrum, the positive sign of both values being in

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(7) In ESR spectroscopy, a proton directly attached to a $\pi$(p)-center is denoted $\alpha$ and those separated by 1, 2, ... $sp^3$-hybridized C-atoms from such a center are called $\beta$, $\gamma$, ....

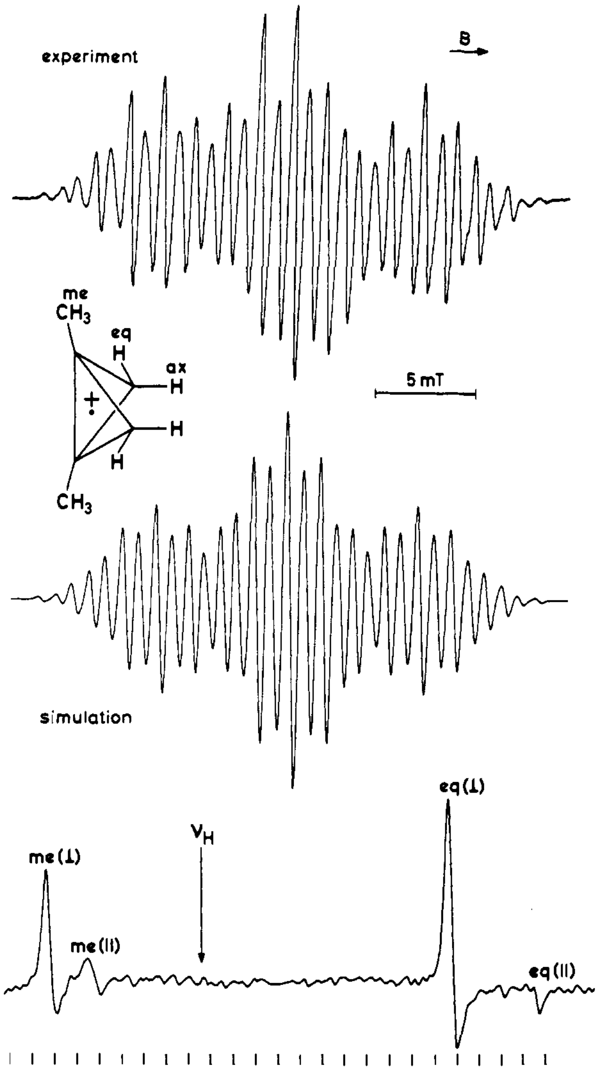

**Figure 4.** Top: ESR spectrum of $2^{\bullet+}$ in a $CFCl_3$ matrix at 150 K. The simulation below made use of the coupling constants given in the text and Table I (line shape, Gaussian; line width, 0.3 mT). Bottom: corresponding proton-ENDOR spectrum taken under the same conditions.

accordance with $|A_\parallel| > |A_\perp|$. The contribution $B = +0.095$ mT to $a(H_{eq})$ for $2^{\bullet+}$ is considerably larger than the corresponding value (+0.030 mT) for $1^{\bullet+}$, presumably because of the larger molecular size and longer rotational correlation time. Such a contribution is reduced to $B = +0.055$ mT for $a(H_{me})$, due to internal rotation of the methyl substituents.

**1-Methylbicyclo[1.1.0]butane (3).** It may be anticipated that γ-irradiation of **3** in a $CFCl_3$ matrix, like the analogous treatment of **1** and **2**, should yield an unrearranged radical cation. Indeed, the ESR spectrum, obtained upon ionization of **3** by this method and shown in Figure 5, is fully consistent with that expected for $3^{\bullet+}$. The dominant triplet, spaced by 6.89 mT, arises from the two axial methylene protons, $H_{ax}$, in the 2,4-positions, and it is further split into two three-proton quartets. One of them with the larger coupling constant of 1.73 mT must be due to the three protons, $H_{me}$, in the 1-methyl substituent, while the other with the smaller coupling constant of 0.92 mT has to be attributed to the two equatorial methylene protons, $H_{eq}$, in the 2,4-positions and to the single bridgehead proton, $H_{br}$, in the 3-position. This assignment was confirmed by the ESR spectrum of the radical cation generated from 1-(trideuteriomethyl)bicyclo[1.1.0]butane (**3**-$d_3$) under the same conditions and displayed in Figure 6. Clearly the three-proton coupling constant of 1.73 mT has here been replaced by a partially resolved hyperfine splitting from three deuterons.

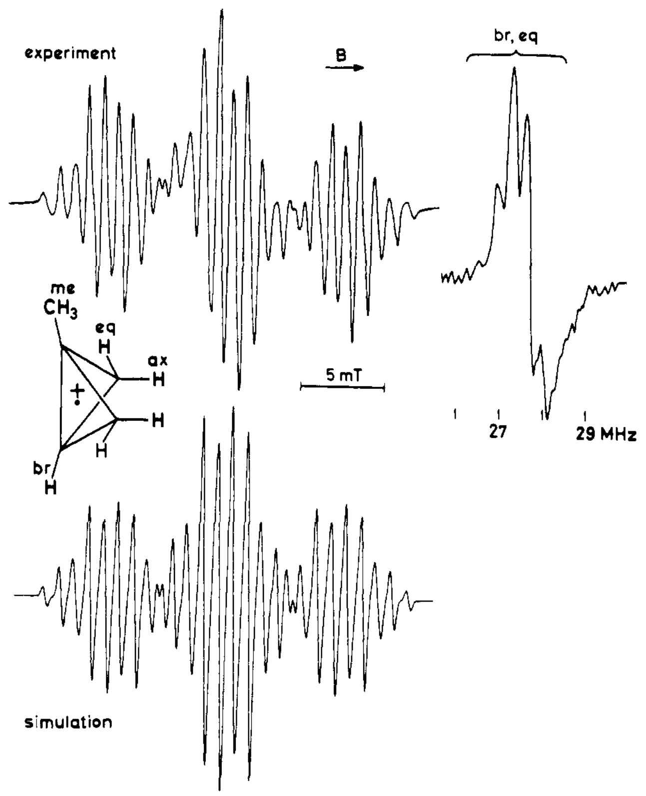

**Figure 5.** Left: ESR spectrum of $3^{\bullet+}$ in a $CFCl_3$ matrix at 150 K. The simulation below made use of the coupling constants given in the text and Table I (line shape, Gaussian; line width, 0.3 mT). Right: corresponding proton-ENDOR spectrum taken under the same conditions.

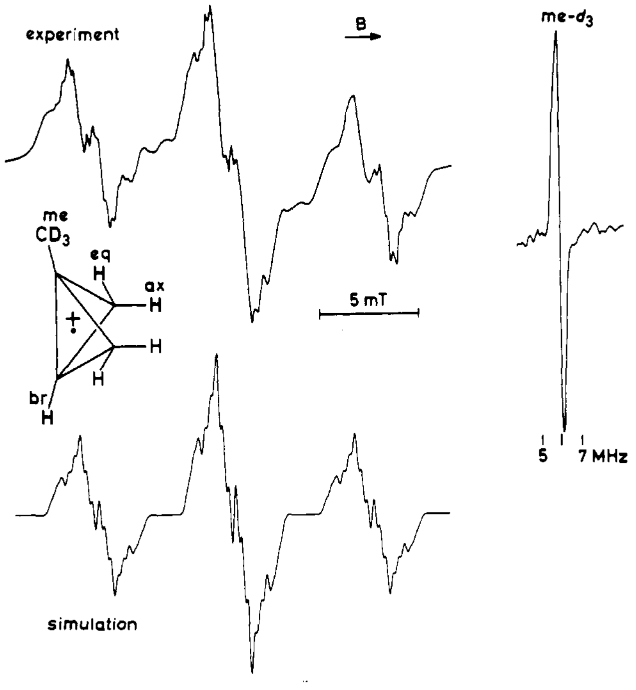

**Figure 6.** Left: ESR spectrum of **3**-$d_3^{\bullet+}$ in a $CFCl_3$ matrix at 150 K. The simulation below made use of the coupling constants given in the text and Table I (line shape, Gaussian; line width, 0.3 mT). Right: corresponding deuteron-ENDOR spectrum taken under the same conditions.

The proton-ENDOR spectra of both $3^{\bullet+}$ and **3**-$d_3^{\bullet+}$ were less informative than those of $1^{\bullet+}$ and $2^{\bullet+}$. The "anisotropic", high-frequency signals from $H_{eq}$ and $H_{br}$ in the range 26–29 MHz (Figure 5) strongly overlapped, so that a reliable analysis in terms of individual components was difficult. Nevertheless, their point

**Table I.** Proton-Hyperfine Data, in mT,[a] for the Radical Cations of Bicyclo[1.1.0]butane (**1**) and Its 1,3-Dimethyl (**2**) and 1-Methyl (**3**) Derivatives in $CFCl_3$ Matrices[b]

| | | proton | | | |
|---|---|---|---|---|---|
| | | br | eq | ax | me |
| **1**$^{\bullet +}$ | $a$ | −1.188 (2H) | +1.142 (2H) | +7.71[c] (2H) | |
| | $A_{\parallel}$ | −1.050 | +1.203 | | |
| | $A_{\perp}$ | −1.257 | +1.112 | | |
| | $B$ | +0.069 | +0.030 | | |
| **2**$^{\bullet +}$ | $a$ | | +0.889 (2H) | +6.51[c] (2H) | +1.646 (6H) |
| | $A_{\parallel}$ | | +1.078 | | +1.755 |
| | $A_{\perp}$ | | +0.794 | | +1.591 |
| | $B$ | | +0.095 | | +0.055 |
| **3**$^{\bullet +}$ | $a$ | −0.92[c] (1H) | +0.92[c] (2H) | +6.89[c] (2H) | +1.733 (3H)<br>[+0.266 (3D)][d] |

[a] Experimental error in $|a|$ is ±0.005 mT, unless specified otherwise. [b] Temperature as indicated in Figure 3 and in the captions to Figures 3–6. [c] Experimental error is ±0.05 mT. [d] Observed for **3**-$d_3^{\bullet +}$.

of gravity at 27.5 MHz corresponds to $|a(H_{eq})| \approx |a(H_{br})| = 25.9$ MHz or 0.92 mT, in agreement with the value determined from the ESR spectrum. An "inverted" low-frequency signal from $H_{me}$ appeared in the expected range of 9–10 MHz, but it was not sufficiently sharp for a precise measurement of $|a(H_{me})|$. By contrast, the three methyl deuterons in **3**-$d_3^{\bullet +}$ gave rise to a narrow and intense high-frequency signal ($^1/_2|a| + \nu_D$) of "isotropic" shape (Figure 6). From the position of this signal at 5.96 MHz and the frequency of the free $^2H$ nucleus, $\nu_D = 0.1535\nu_H = 2.23$ MHz, the deuteron-coupling constant $|a(D_{me})| = 7.46$ MHz or 0.266 mT was determined; this value is tantamount to $|a(H_{me})| = 1.733$ mT.

By analogy to **1**$^{\bullet +}$ and **2**$^{\bullet +}$ and as required by theory, $a(H_{ax})$, $a(H_{eq})$, $a(H_{me})$, and $a(D_{me})$ should be positive, whereas $a(H_{br})$ is expected to have a negative sign.

The hyperfine data of **1**$^{\bullet +}$, **2**$^{\bullet +}$, and **3**$^{\bullet +}$ are collected in Table I. The $g$ factor of all three radical cations is 2.0039 ± 0.0001.[8]

**Tricyclo[3.1.0.0$^{2,6}$]hexane (4) and Cyclohexa-1,3-diene (6).** The ESR spectrum observed upon $\gamma$-irradiation of **4** in a $CFCl_3$ matrix exhibited a four-proton quintet spaced by 3.05 mT and further split by 0.85 and 0.41 mT, each due to a two-proton triplet ($g = 2.0029 \pm 0.0001$). The largest coupling constant of ca. 3 mT from four equivalent or nearly equivalent protons is incompatible with the structure of the primary radical cation **4**$^{\bullet +}$, in which the two axial methylene protons are removed by bridging the bicyclo[1.1.0]butane in 2,4-positions. On the other hand, the hyperfine data agree with those reported for cyclohexa-1,3-diene (**6**) ionized in a $CFCl_3$[9] or $CF_3CCl_3$ matrix[10] and, thus, the observed ESR spectrum must be attributed to the radical cation **6**$^{\bullet +}$, a rearrangement product of **4**$^{\bullet +}$.

The assignment of the coupling constants to the two pairs of $\alpha$-protons in the 1,4- and 2,3-positions and to the four $\beta$-protons in **6**$^{\bullet +}$ in the 5,6-positions is straightforward: $|a(H_{\alpha\text{-}1,4})| = 0.85$ mT, $|a(H_{\alpha\text{-}2,3})| = 0.41$ mT, and $|a(H_{\beta})| = 3.05$ mT. As the three coupling constants fall in the frequency range, where they should be observable by our ENDOR system (see above), the radical cation **6**$^{\bullet +}$ was generated by $\gamma$-rays from **6** in $CFCl_3$, $CF_2ClCFCl_2$, and $CF_3CCl_3$ matrices and studied by ENDOR spectroscopy. In fact, ENDOR signals associated with all coupling constants were detected; they are reproduced in Figure 7. With $CF_2ClCFCl_2$ as the matrix, signals of "isotropic" shape appeared at 28.35 MHz ($^1/_2|a| - \nu_H$) for $H_\beta$, at 26.60 MHz ($\nu_H + {}^1/_2|a|$) for $H_{\alpha\text{-}1,4}$, and at 19.76 and 9.36 MHz ($\nu_H \pm {}^1/_2|a|$) for $H_{\alpha\text{-}2,3}$. The coupling constants derived therefrom are $|a(H_\beta)| = 85.82$ MHz or 3.061 mT, $|a(H_{\alpha\text{-}1,4})| = 24.08$ MHz or 0.859 mT, and $|a(H_{\alpha\text{-}2,3})| = 1.040$ MHz or 0.371 mT. Upon replacing $CF_2ClCFCl_2$ by $CFCl_3$ or $CF_3CCl_3$ as the matrix, the ENDOR signals of the $\alpha$-protons became "anisotropic" and exhibited parallel and perpendicular components, while those of $\beta$-protons retained their "isotropic" shape, but split into two, denoted $\beta$-ax and $\beta$-eq in ref 9 (Figure 7). The pertinent hyperfine data are listed in Table II. The finding that $|A_\perp| > |A_\parallel|$ for $H_{\alpha\text{-}1,4}$ and $H_{\alpha\text{-}2,3}$ is again consistent with the required negative sign of the coupling constants of these $\alpha$-protons. Although the sign of the $\beta$-proton coupling constants, $a(H_{\beta\text{-ax}})$ and $a(H_{\beta\text{-eq}})$, could not be verified experimentally, it is certainly positive. Their difference $\Delta a(H_\beta)$ is matrix dependent and, expectedly, increases on lowering the temperature, as noted in a previous work.[10] Thus, with a $CFCl_3$ matrix, on going from 150 to 135 K, the coupling constants $a(H_{\beta\text{-ax}}) = +3.187$ and $a(H_{\beta\text{-eq}}) = +2.909$ mT (Figure 7 and Table II) changed to +3.243 and +2.838 mT, respectively. Above 125 K, the ESR spectrum of **6**$^{\bullet +}$ in a $CF_2ClCFCl_2$ matrix was replaced by that of cyclohexadienyl radical[11,12] with $|a(H_{\alpha\text{-}2,6})| = 0.91$, $|a(H_{\alpha\text{-}3,5})| = 0.27$, $|a(H_{\alpha\text{-}4})| = 1.28$, and $|a(H_\beta)| = 4.85$ mT.

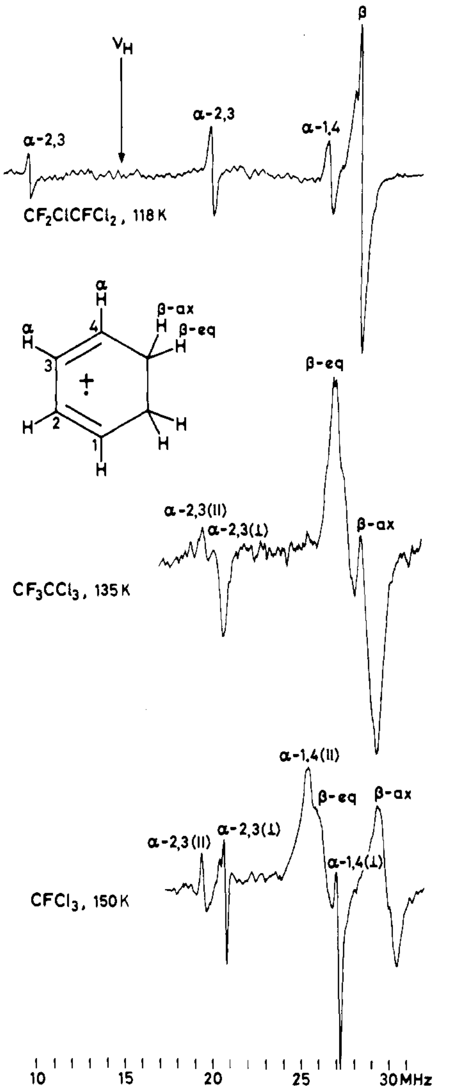

**Figure 7.** Proton-ENDOR spectra of **6**$^{\bullet +}$ in Freon matrices. Experimental conditions as indicated.

**Tricyclo[4.1.0.0$^{2,7}$]heptane (5), *cis*-Bicyclo[3.2.0]hept-6-ene (7), and Cyclohepta-1,3-diene (8).** Irradiation of **5** by $\gamma$-rays in $CFCl_3$, $CF_2ClCFCl_2$, and $CF_3CCl_3$ matrices led to essentially the same ESR spectrum that is shown for $CF_2ClCFCl_2$ in Figure 8. Its

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(8) The $g$ factor of **1**$^{\bullet +}$ was erroneously reported as 2.0030 ± 0.0002 in the previous communication.[2]

(9) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.

(10) Tabata, M.; Lund, A. *Chem. Phys.* **1983**, *75*, 379.

(11) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *38*, 773. (b) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(12) Formation of the cyclohexadienyl radical at higher temperatures was also observed for the radical cation of cyclohexa-1,4-diene in a $CF_3CCl_3$ matrix.[10]

**Table II.** Proton-Hyperfine Data, in mT,[a] for the Radical Cations of Cyclohexa-1,3-diene (**6**) and Cyclohepta-1,3-diene (**8**) in $CFCl_3$, $CF_2ClCFCl_2$, and $CF_3CCl_3$ Matrices[b]

| | | | proton | | | |
|---|---|---|---|---|---|---|
| | | | $\alpha$-1,4 | $\alpha$-2,3 | $\beta$-ax | $\beta$-eq |
| $6^{\bullet+}$ | $CF_2ClCFCl_2$ | $a$ | −0.859 (2H) | −0.371 (2H) | +3.061 (2H) | +3.061 (2H) |
| | $CF_3CCl_3$ | $a$ | | −0.402 (2H) | +3.090 (2H) | +3.008 (2H) |
| | | $A_\parallel$ | $c$ | −0.354 | | |
| | | $A_\perp$ | $c$ | −0.426 | | |
| | | $B$ | | +0.024 | | |
| | $CFCl_3$ | $a$ | −0.854 (2H) | −0.407 (2H) | +3.187 (2H) | +2.909 (2H) |
| | | $A_\parallel$ | −0.773 | −0.338 | | |
| | | $A_\perp$ | −0.895 | −0.442 | | |
| | | $B$ | +0.041 | +0.035 | | |

| | | | proton | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\alpha$-1,4 | $\alpha$-2,3 | $\beta'$-ax | $\beta''$-ax | $\beta'$-eq | $\beta''$-eq | $\gamma$ |
| $8^{\bullet+}$ | $CF_2ClCFCl_2$ | $a$ | −0.854 (2H) | −0.255 (2H) | +2.830[c] (1H) | +2.798 (1H) | +1.034 (1H) | +1.021 (1H) | −0.081 (2H) |
| | $CF_3CCl_3$ | $a$ | −0.85[d] (2H) | −0.249 | +2.824 | +2.800 (1H) | +1.075 (1H) | +1.020 | −0.071 (2H) |
| | | $A_\parallel$ | (−0.77)[e] | −0.176 | +2.849 | +2.825 | +1.122 | +1.058 | |
| | | $A_\perp$ | −0.895 | −0.286 | +2.811 | +2.788 | +1.052 | +1.001 | |
| | | $B$ | (+0.04) | +0.037 | +0.013 | +0.012 | +0.023 | +0.019 | |
| | $CFCl_3$ | $a$ | | | +2.828 (1H) | +2.775 (1H) | | | $f$ |
| | | $A_\parallel$ | $f$ | $f$ | +2.887 | +2.834 | $f$ | $f$ | |
| | | $A_\perp$ | $f$ | $f$ | +2.799 | +2.746 | $f$ | $f$ | |
| | | $B$ | | | +0.029 | +0.029 | | | |

[a] Experimental error is ±0.003 and ±0.008 mT in $|a|$ smaller than 1 mT and larger than 2 mT, respectively, unless specified otherwise. [b] Temperature as indicated in Figures 7 and 9 and in the caption to Figure 8. [c] ENDOR signals masked by those for $\beta$-eq (Figure 7). [d] Experimental error is ±0.02 mT. [e] ENDOR signal masked by those of $\beta$-ax (Figure 9); value estimated within ±0.03 mT. [f] Not detected by ENDOR spectroscopy (Figure 9).

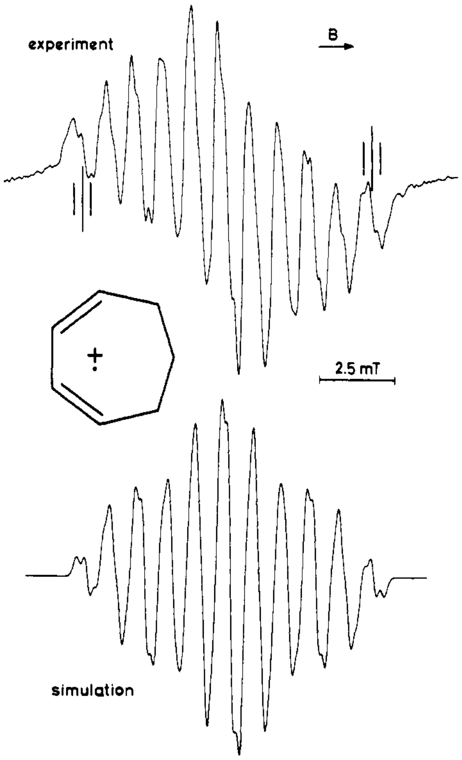
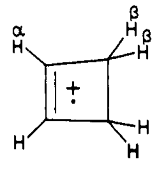


**Figure 8.** ESR spectrum of $8^{\bullet+}$ in a $CF_2ClCFCl_2$ matrix at 118 K. The simulation below made use of the coupling constants given in Table II (line shape, Gaussian; line width, 0.2 mT).

hyperfine pattern stems from a two-proton triplet of 2.81 mT which is split into a four-proton quintet of 0.95 mT and a further, partially resolved, two-proton triplet of 0.25 mT ($g$ = 2.0029 ± 0.0001). As in the case of **4**, this spectrum can hardly be reconciled with that expected for a bicyclo[1.1.0]butane radical cation bridged in the two axial 2,4-positions, but it must arise from a rearranged product. Such a conclusion has been endorsed by the ESR spectra obtained with 1-deuterio- (**5**-*d*) and 1,7-dideuterio-tricyclo[4.1.0.0$^{2,7}$]heptane (**5**-$d_2$) as starting material. These spectra differed only slightly from that in Figure 8; the sole effect of labeling was the replacement of the partially resolved two-proton triplet of 0.25 mT (**5**) by a corresponding one-proton doublet (**5**-*d*) or a complete removal of this triplet splitting (**5**-$d_2$). If the observed ESR spectrum were due to the primary radical cation $5^{\bullet+}$, one would expect that deuteriation in the 1,7-positions should affect the coupling constant of 0.95 mT, appropriate for the $\alpha$-protons, $H_{br}$, at the bridgehead carbon atoms in the bicyclobutane radical cations (Table I).

The two promising candidates for the ESR spectrum in Figure 8 are the radical cations of *cis*-bicyclo[3.2.0]hept-6-ene (**7**) and cyclohepta-1,3-diene (**8**).[13] The ESR spectra observed upon $\gamma$-irradiation of both **7** and **8** in Freon matrices were identical with those obtained from **5** under the same conditions, and the major coupling constants 2.81 and 0.95 mT could well be accommodated in both $7^{\bullet+}$ and $8^{\bullet+}$, as is evident from comparison with the hyperfine data for the radical cations of cyclobutene (**10**) and cyclohexa-1,3-diene (**6**): $10^{\bullet+}$, $|a(H_\alpha)|$ = 1.1 and $|a(H_\beta)|$



$10^{\bullet+}$

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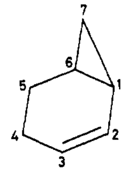
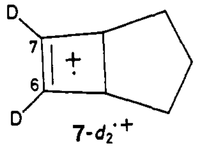
(13) The radical cation of bicyclo[4.1.0]hept-2-ene (norcar-2-ene, **9**) has been suggested as the rearrangement product of $5^{\bullet+}$ produced by photolytically induced electron transfer from **5** to an acceptor in acetonitrile solution: Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711. The ESR spectrum observed upon $\gamma$-irradiation of **9** in a $CFCl_3$ matrix was, however, completely different from that obtained under the same conditions with **5** as the starting material (Figure 8). It consisted of a broad one-proton doublet spaced by ca. 5 mT, a value comparable to the coupling constant of 5.4 mT reported for the two axial $\beta$-protons in the radical cation of cyclohexene.[9] The observed spectrum has, therefore, been attributed to the primary radical cation $9^{\bullet+}$, in which the coupling constant of 5 mT is due to a single axial $\beta$-proton in the 4-position.

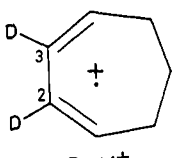


**9**

= 2.8 mT;[1g,3] $\mathbf{6}^{\bullet+}$, $|a(H_{\alpha\text{-}1,4})| = 0.85$ and $|a(H_{\beta})| = 3.1$ mT (Figure 7 and Table II). This finding indicated that either ring opening of $\mathbf{7}^{\bullet+}$ to $\mathbf{8}^{\bullet+}$ or ring closure of $\mathbf{8}^{\bullet+}$ to $\mathbf{7}^{\bullet+}$ occurred, the latter rearrangement corresponding to the photolytic method of preparation of **7** from **8** (see Experimental Section). Identification of *the radical cation of cyclohepta-1,3-diene* (**8**) *as the paramagnetic species giving rise to the observed ESR spectrum*[14] rests on the findings for the 2,3-dideuterio derivative ($\mathbf{8}$-$d_2$) of this compound. The ESR spectra of $\mathbf{8}$-$d_2^{\bullet+}$ generated by $\gamma$-irradiation of $\mathbf{8}$-$d_2$ in Freon matrices were identical with those obtained from $\mathbf{5}$-$d_2$ as the starting material, i.e., the coupling constant of 0.25 mT was replaced by the hyperfine splitting from two deuterons. This coupling constant is of the correct magnitude for the two $\alpha$-protons in the 2,3-positions of $\mathbf{8}^{\bullet+}$ (see below), but it is too small for such protons in the corresponding 6,7-positions of $\mathbf{7}^{\bullet+}$ which should bear the two deuterons upon ring closure of $\mathbf{8}$-$d_2^{\bullet+}$ to $\mathbf{7}$-$d_2^{\bullet+}$ (the corresponding value for $\mathbf{10}^{\bullet+}$ is 1.1 mT).



$\mathbf{7}$-$d_2^{\bullet+}$



$\mathbf{8}$-$d_2^{\bullet+}$

Figure 9 shows the proton-ENDOR spectra obtained for $\mathbf{8}^{\bullet+}$ in $CFCl_3$, $CF_2ClCFCl_2$, and $CF_3CCl_3$ matrices from either **5** or **7** or **8**. As in the case of $\mathbf{6}^{\bullet+}$ (Figure 7), the signals observed with the matrix $CF_2ClCFCl_2$ had an "isotropic" shape. The two axial methylene $\beta$-protons, $H_{\beta\text{-ax}}$, in the 5- and 7-positions are not equivalent and give rise to two conspicuously narrow, close-lying signals at 25.12 and 24.67 MHz ($^1/_2|a| - \nu_H$). Their two equatorial counterparts, $H_{\beta\text{-eq}}$, are also not strictly equivalent, being represented by two overlapping signals at 29.05 and 28.87 MHz ($\nu_H + {}^1/_2|a|$). The broad signal in between at 26.54 MHz ($\nu_H + {}^1/_2|a|$) stems from the two $\alpha$-protons, $H_{\alpha\text{-}1,4}$, in the 1,4-positions. The two remaining $\alpha$-protons, $H_{\alpha\text{-}2,3}$, in the 2,3-positions are responsible for the pair of signals at 18.13 and 10.99 MHz ($\nu_H \pm {}^1/_2|a|$), while the other pair at 15.70 and 13.42 MHz, also centered at $\nu_H$, arises from one or both $\gamma$-protons, $H_{\gamma\text{-syn}}$ and $H_{\gamma\text{-anti}}$, in the 6-position. The following coupling constants, the signs and assignments of which will be justified below, were derived from the ENDOR signals: $a(H_{\beta'\text{-ax}}) = +79.36$ MHz or $+2.830$ mT, $a(H_{\beta''\text{-ax}}) = +78.46$ MHz or $+2.798$ mT, $a(H_{\beta'\text{-eq}}) = +28.98$ MHz or $+1.034$ mT, $a(H_{\beta''\text{-eq}}) = +28.62$ MHz or $+1.021$ mT, $a(H_{\alpha\text{-}1,4}) = -23.96$ MHz or $-0.854$ mT, $a(H_{\alpha\text{-}2,3}) = -7.14$ MHz or $-0.255$ mT, and $a(H_{\gamma}) = -2.28$ MHz or $-0.081$ mT.

On passing from the matrix $CF_2ClCFCl_2$ to $CF_3CCl_3$, all ENDOR signals were still observable but turned "anisotropic", except those of the $\gamma$-protons which retained their "isotropic" shape. With the matrix $CFCl_3$, on the other hand, the hyperfine anisotropy caused the signals to broaden beyond recognition and only those of the axial $\beta$-protons could be detected (Figure 9). The hyperfine data for $\mathbf{8}^{\bullet+}$ in all three matrices are collected in Table II, below the corresponding values for $\mathbf{6}^{\bullet+}$.

Assignments of the coupling constants to protons in individual positions of $\mathbf{8}^{\bullet+}$ are based on the following arguments: (i) Comparison with the analogous data for the structurally related radical cations of 1,3-dienes, such as those of *trans*-buta-1,3-diene,[1a,g,3] cyclopenta-1,3-diene,[9] and, in particular, $\mathbf{6}^{\bullet+}$. (ii) Width and amplitude of the ENDOR signals which are, in general, broader and less high for the $\alpha$- than for the $\beta$-protons. (iii) Sign of the coupling constants as derived from their anisotropic features, i.e., a positive sign for the $\beta$-protons with $|A_\parallel| > |A_\perp|$ and a negative one for $\alpha$-protons with $|A_\parallel| < |A_\perp|$. (iv) Effect of deuteriation in the 2,3-positions, which leads to the absence of the 0.25 mT hyperfine splitting in the ESR spectrum (see above) and to disappearance of the pertinent proton-ENDOR signals. (v) INDO calculations[15] which reproduce satisfactorily the observed positive coupling constants of the $\beta$-protons and the negative ones of the $\alpha$-protons.[16] As for the $\gamma$-protons, of which the small coupling constant is masked by the width of the ESR lines (Figure 8), the INDO method points to a similar magnitude and negative sign for $a(H_{\gamma\text{-syn}})$ and $a(H_{\gamma\text{-anti}})$. Therefore, we tentatively attribute the observed ENDOR signals to both $\gamma$-protons, all the more as only signals diagnostic of one sort of such protons were detected (Figure 9).

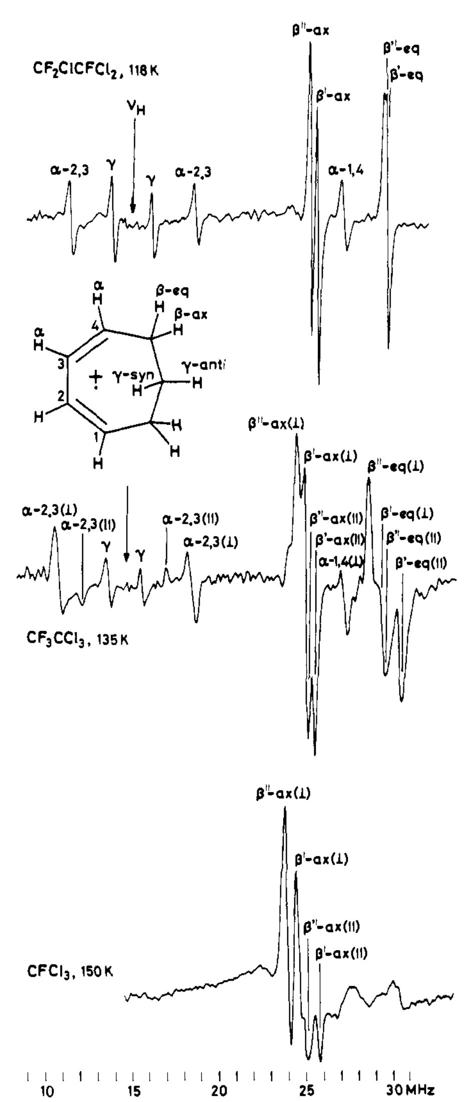


**Figure 9.** Proton-ENDOR spectra of $\mathbf{8}^{\bullet+}$ in Freon matrices. Experimental conditions as indicated.

The study of $\mathbf{8}^{\bullet+}$ provides a paradigm for the utility of ENDOR spectroscopy as applied to radical cations in Freon matrices. The wealth of information derived from the ENDOR spectra of $\mathbf{8}^{\bullet+}$ contrasts with the relative paucity of data obtained by the corresponding ESR record. The non-equivalence of the two axial $\beta$-protons and, likewise, of their two equatorial counterparts point

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(14) After the present work was finished, a paper appeared in which $\mathbf{8}^{\bullet+}$ was proposed as the rearrangement product of the radical cation of bicyclo[3.2.0]hept-2-ene: Faucitano, A.; Buttafava, A.; Martinotti, F.; Sustmann, R.; Korth, H.-G. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 865. The ESR spectrum shown there and correctly attributed to $\mathbf{8}^{\bullet+}$ was less resolved than that in Figure 8, and its analysis was not complete.

(15) Pople, L. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

(16) Coupling constants for $\mathbf{8}^{\bullet+}$ calculated by the INDO procedure[15] and based on an MNDO[17]-optimized geometry are as follows (in mT): $a(H_{\alpha\text{-}1,4}) = -0.84$, $a(H_{\alpha\text{-}2,3}) = -0.17$, $a(H_{\beta\text{-ax}}) = +3.9$, $a(H_{\beta\text{-eq}}) = +0.91$, $a(H_{\gamma\text{-syn}}) = -0.29$, and $a(H_{\gamma\text{-anti}}) = -0.21$.

(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

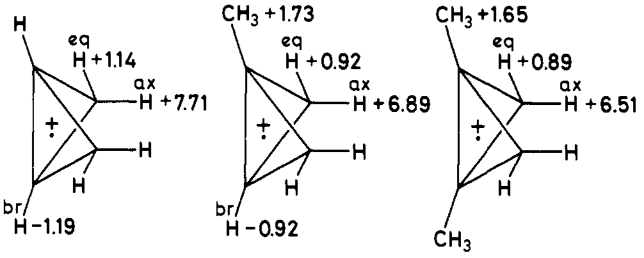
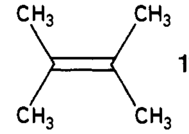


**Figure 10.** Proton-coupling constants, in mT, for **1**$^{\bullet+}$, **3**$^{\bullet+}$, and **2**$^{\bullet+}$.

to an absence of a mirror plane passing across the C(2)–C(3) bond and the C(6) atom. The radical cation **8**$^{\bullet+}$ in a Freon matrix thus deviates from the $C_s$ symmetry found by electron diffraction,[18] vibrational analysis,[19] and microwave spectroscopy[20] for the neutral **8**, although the diene $\pi$-system of **8**$^{\bullet+}$ seems to locally preserve this symmetry, according to the pairwise equivalence of the $\alpha$-protons.[21]

**Spin Distribution in the Bicyclo[1.1.0]butane Radical Cations. Effect of Methyl Substitution.** The hyperfine data for the radical cations, **2**$^{\bullet+}$ and **3**$^{\bullet+}$, of the methyl-substituted bicyclo[1.1.0]butanes (Table I and Figure 10) support the MO model of the parent **1**$^{\bullet+}$, in which the two bridgehead atoms C(1) and C(3) are regarded as a quasi two-center $\pi$-system.[2] The methyl protons, which are $\beta$ with respect to C(1) and C(3), have coupling constants $a(\mathrm{H_{me}})$ = +1.65 and +1.73 mT, for **2**$^{\bullet+}$ and **3**$^{\bullet+}$, respectively. These values compare favorably with 1.72 mT reported for the methyl $\beta$-protons in the radical cation of 2,3-dimethylbut-2-ene (**11**), a "classical" tetramethyl-substituted two-center $\pi$-system.[9]



**11**

The withdrawal of spin population by a methyl substituent from a $\pi$-center $\mu$ can be expressed by[11b,22]

$$\rho'_\mu = \rho_\mu(1 - \Delta X_{\mathrm{me}})$$

where $\rho'_\mu$ and $\rho_\mu$ are the spin populations at this center in the substituted and the parent radical, respectively; for the radical cations **1**$^{\bullet+}$–**3**$^{\bullet+}$, $\mu$ = 1 and 3. The lowering of the spin population from $\rho_{1(3)}$ to $\rho'_{1(3)}$ should manifest itself in decreasing coupling constants of the methylene $\beta$-protons, $a(\mathrm{H_{ax}})$ and $a(\mathrm{H_{eq}})$, and, in fact, such an effect is observed on going from **1**$^{\bullet+}$ to **3**$^{\bullet+}$ to **2**$^{\bullet+}$. Assuming that the conformation of the methylene bridging group is not significantly altered by the methyl substitution, comparison of the $a(\mathrm{H_{ax}})$ and $a(\mathrm{H_{eq}})$ values for **1**$^{\bullet+}$ with those for **2**$^{\bullet+}$ and **3**$^{\bullet+}$ should enable one to determine $\Delta X_{\mathrm{me}}$ for these radical cations. The coupling constants $a(\mathrm{H_{ax}})$ = +7.71 mT for **1**$^{\bullet+}$ and +6.51 mT for **2**$^{\bullet+}$ seem to be most suitable for the estimation of $\Delta X_{\mathrm{me}}$, because (i) **2**$^{\bullet+}$ has the same effective symmetry ($C_{2v}$) as **1**$^{\bullet+}$, (ii) the $a(\mathrm{H_{ax}})$ values are very large and so is the decrease on passing from **1**$^{\bullet+}$ to **2**$^{\bullet+}$, and (iii) the dihedral angle $\theta_{\mathrm{ax}}$ between the C(2)–H$_{\mathrm{ax}}$ or C(4)–H$_{\mathrm{ax}}$ bond and the 2p$_z$-axis at C(1) or C(3) has been determined as 203.5°;[2] in this range of $\theta$, the $\cos^2\theta$ function changes very slowly with $\theta$, so that the same value of $\cos^2\theta_{\mathrm{ax}}$ can be taken for **1**$^{\bullet+}$ and **2**$^{\bullet+}$. The relevant relations are[23]

$$7.71\ \mathrm{mT} \propto (\sqrt{\rho_1} + \sqrt{\rho_3})^2 \cos^2\theta_{\mathrm{ax}} \quad \text{and} \quad 6.51\ \mathrm{mT} \propto (\sqrt{\rho'_1} + \sqrt{\rho'_3})^2 \cos^2\theta_{\mathrm{ax}}$$

which reduce to

$$7.71\ \mathrm{mT} \propto 4\rho_1 \cos^2\theta_{\mathrm{ax}} \quad \text{and} \quad 6.51\ \mathrm{mT} \propto 4\rho'_1 \cos^2\theta_{\mathrm{ax}}$$

as $\rho_1 = \rho_3$ and $\rho'_1 = \rho'_3$. Thus $\rho'_1/\rho_1$ = 6.51 mT/7.71 mT = 0.844 and $\Delta X_{\mathrm{me}}$ = 0.156. This value of $\Delta X_{\mathrm{me}}$ is somewhat higher than that (0.111) recently suggested for $\pi$-radical cations.[24]

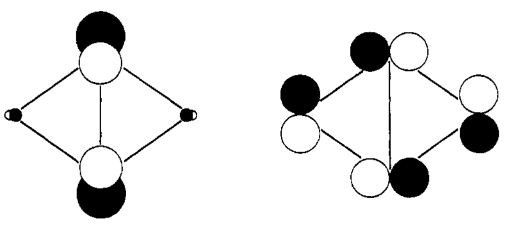


**Figure 11.** Diagrams of the two highest occupied MO's of bicyclo[1.1.0]butane (**1**).

**Rearrangements of Radical Cations 4**$^{\bullet+}$ **and 5**$^{\bullet+}$**.** Figure 11 shows the two uppermost occupied orbitals of bicyclo[1.1.0]butane (**1**).[25] The dominant feature of the HOMO 7a$_1$ is the bonding contribution to the transannular C(1)–C(3) linkage. As pointed out previously,[2] removal of an electron from **1** thus yields a radical cation **1**$^{\bullet+}$, in which this central bond is essentially due to one electron only. The change in geometry upon ionization of **1** manifests itself in a lengthening of the pertinent C(1)–C(3) bond and, to a lesser extent, in an increase of the flap angle between the planes C(1)C(2)C(3) and C(1)C(4)C(3).[2,26] However, the carbon framework of bicyclobutane is, on the whole, preserved on passing from **1** to **1**$^{\bullet+}$, as the connectivity of the atoms remains unaltered. Methyl substitution in the 1,3-positions or bridging of the 2,4-positions by a di- or trimethylene chain decreases substantially the ionization potential of **1** by raising the HOMO 7a$_1$, but the "shape" of this orbital is not markedly modified. Although the energy difference between 7a$_1$ and 1a$_2$ decreases on going from **1**–**3** to **4** and **5**, the sequence, i.e., 7a$_1$ above 1a$_2$, is not reversed. This conclusion has been drawn from both MO-theoretical calculations[27,28] and experimental studies by photoelectron spectroscopy in the gas phase[27] and polarography in solution.[28] Therefore, one expects the radical cations **2**$^{\bullet+}$–**5**$^{\bullet+}$ not only to exhibit a spin distribution similar to that in **1**$^{\bullet+}$ but also to be thermodynamically at least as stable as **1**$^{\bullet+}$. An analogous statement need not, however, hold with regard to the kinetic stability (persistence) of these radical cations. In fact, **2**$^{\bullet+}$ and **3**$^{\bullet+}$, which are substituted by methyl groups in 1,3-positions, prove to be as persistent as **1**$^{\bullet+}$ in Freon matrices at low temperatures, whereas **4**$^{\bullet+}$ and **5**$^{\bullet+}$, which are bridged by a polymethylene chain in 2,4-positions, rapidly isomerize to the radical cations, **6**$^{\bullet+}$ and **8**$^{\bullet+}$, of cyclohexa-1,3-diene and cyclohepta-1,3-diene, respectively, under the same conditions. In this place, it is appropriate to consider the mechanism of the rearrangements in question.

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(21) Reduction of symmetry, due to nonequivalence of $\beta$-protons, is presumably an effect of the matrix. Similar observation has been made for the radical cations of cyclobutene (**10**)[1g] and, quite recently, for those of dodecahedrene and dodecahedradiene.[1j]

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(25) Calculated by the MNDO method.[17]

(26) See also: Bally, T. *J. Mol. Struct.* (*Theochem*) **1991**, *227*, 249.

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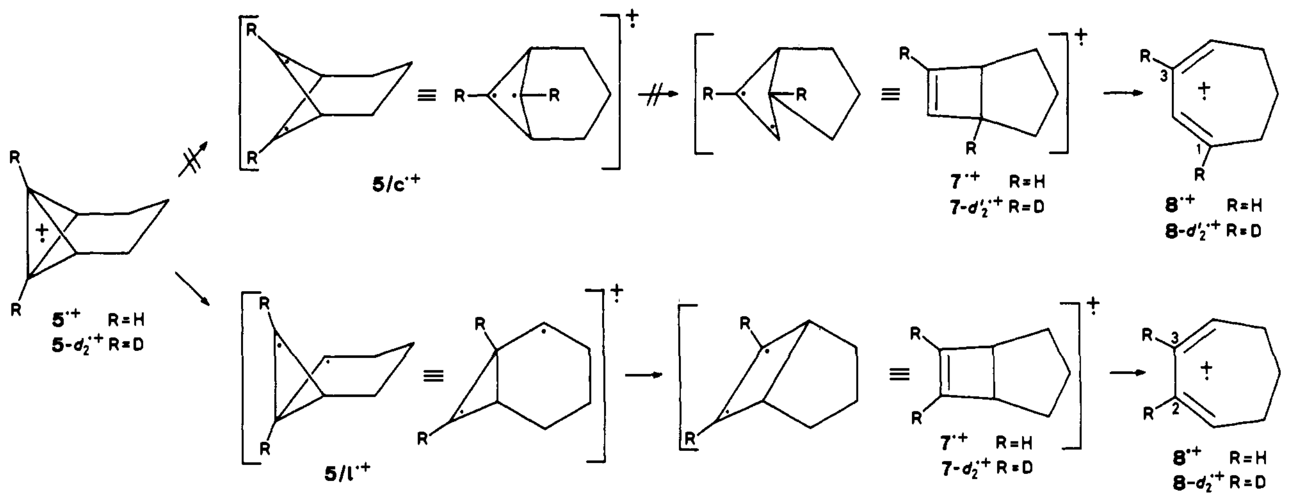
**Scheme I**



Thermally and photolytically induced isomerizations of radical cations in Freon matrices are quite common.[29] Notably, those involving polycyclic hydrocarbons and proceeding via 1,3- and 1,4-diyl radical cations have been studied by Williams and coworkers.[30] A recent paper of this research group[30d] is particularly relevant to the present work, as it deals with rearrangement of closely related bicyclo[2.1.0]pentane radical cations.

According to the arguments presented above, the most likely initial step in the isomerization of **4**$^{\bullet+}$ and **5**$^{\bullet+}$ to **6**$^{\bullet+}$ and **8**$^{\bullet+}$, respectively, should be the cleavage of the *central* bond in the bicyclobutane moiety of the two primary radical cations. In the case of **5**$^{\bullet+}$, a pathway, which begins with this step and leads to the 6,7-diyl radical cation **5/c**$^{\bullet+}$, is depicted in Scheme I. The rearrangement would then proceed via a 1,2-bond shift to the radical cation, **7**$^{\bullet+}$, of *cis*-bicyclo[3.2.0]hept-6-ene, which isomerizes to **8**$^{\bullet+}$. The postulated occurrence of **7**$^{\bullet+}$ as an intermediate is consistent with the finding that **7** yields **8**$^{\bullet+}$ upon $\gamma$-irradiation in Freon matrices. However, the mechanism involving **5**$^{\bullet+}$ → **5/c**$^{\bullet+}$ as the initial step is at variance with the experimental results for the radical cation, **5**-$d_2^{\bullet+}$, of 1,7-dideuteriotricyclo[4.1.0.0$^{2,7}$]heptane, because, in this case, the radical cation of 1,3-dideuteriocyclohepta-1,3-diene (**8**-$d'_2$) should finally be obtained and not that of the 2,3-labeled isomer (**8**-$d_2$), as is actually observed. An alternative pathway, also outlined in Scheme I, implies the cleavage of a *lateral* bond in the bicyclobutane moiety of **5**$^{\bullet+}$ as the initial step, thus generating the 2,7-diyl radical cation **5/l**$^{\bullet+}$. This pathway likewise requires a 1,2-bond shift to produce **7**$^{\bullet+}$ and, subsequently, the isomeric **8**$^{\bullet+}$, but it correctly ends up with the 2,3-deuteriated radical cation **8**-$d_2^{\bullet+}$ when starting from **5**-$d_2^{\bullet+}$.

Several reports on the rearrangement of neutral tricycloheptane **5** to bicycloheptene **7** and/or cycloheptadiene **8** exist in the literature. At high temperatures, **5** was thermally converted to a mixture of **7** and **8**, the share of the latter increasing from 9% at 593 K to 71% at 673 K.[31] Two different mechanisms were considered to account for these isomerizations. In addition to a concerted opening of both rings at the lateral bonds in the bicyclobutane moiety of **5** as the initial step, a biradical process was suggested starting with the cleavage of one such bond and closely analogous to the reaction sequence presented in Scheme I and beginning with **5**$^{\bullet+}$ → **5/l**$^{\bullet+}$. Later on, Paquette and coworkers[32a] found out that **5** rearranges to **8** at ambient temperature with the use of Ag$^+$ ion as catalyst. This finding has given rise to a series of investigations by the same research group[32] who also extended the reaction to deuterio and alkyl substituted derivatives of **5**. The fact that, starting from **5**-$d_2$, the 2,3-dideuteriocycloheptadiene **8**-$d_2$ was obtained clearly established **5** → **5/l** as the initial step. (Use was made of this reaction in the present work to prepare **8**-$d_2$ from **5**-$d_2$; see Experimental Section.) The authors first proposed a concerted mechanism for the rearrangement of **5** to **8** by Ag$^+$ ions;[32a] subsequently, in order to account for the isomerization of methyl substituted tricyclo[4.1.0.0$^{2,7}$]heptanes, other mechanisms were also considered.[32d-j]

To which extent the mechanisms suggested in the literature for the isomerization of **5** are relevant to the rearrangements observed for **4**$^{\bullet+}$ and **5**$^{\bullet+}$ in the present work is open to discussion. In particular, as has been pointed out,[1g] concerted electrocyclic pathways are not readily applicable to rearrangements of radical cations, and orbital correlation diagrams are not very helpful for the interpretation of such reactions, although generalization of this statement is contradicted by some recent cases in the literature.[30c]

The crucial point in the rearrangement of **5**$^{\bullet+}$ to **8**$^{\bullet+}$ is the cleavage of the *lateral* bond in the bicyclobutane moiety of **5**$^{\bullet+}$ as an initial step. Although no experiments on the analogous isomerization of **4**$^{\bullet+}$ to **6**$^{\bullet+}$ have been carried out for a labeled radical cation, one may reasonably assume that the ring opening in **4**$^{\bullet+}$ also occurs at this bond.[33] The cleavage of the lateral instead of the central bond is difficult to rationalize, as it presupposes a removal of an electron from the second uppermost occupied MO, 1a$_2$, of bicyclobutane which is bonding in the lateral and antibonding in the central linkage (Figure 11). However, as argued at the beginning of this section, a change in the

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[29] For a recent review, see: Shida, T. *Annu. Rev. Phys. Chem.* **1991**, *42*, 55 and references therein.

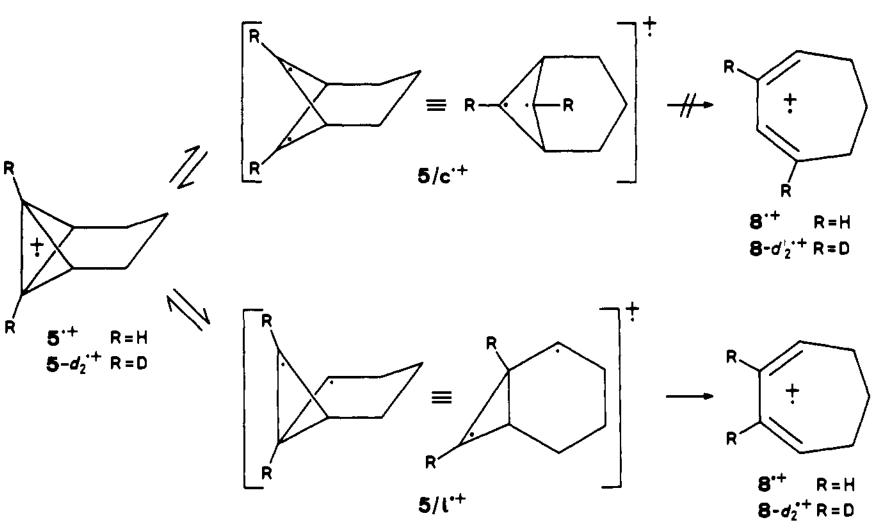
[30] (a) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835. (b) Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133. (c) Chen, G.-F.; Wang, J. T.; Williams, F.; Belfield, K. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 9853. (d) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007.

[31] Wiberg, K. B.; Szeimies, G. *Tetrahedron Lett.* **1968**, 1235.

[32] (a) Paquette, L. A.; Allen, G. R., Jr.; Henzel, R. P. *J. Am. Chem. Soc.* **1970**, *92*, 7002. (b) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280. (c) Paquette, L. A.; Wilson, S. E.; Henzel, R. P. *J. Am. Chem. Soc.* **1971**, *93*, 1288. (d) Paquette, L. A.; Henzel, R. P.; Wilson, S. E. *J. Am. Chem. Soc.* **1971**, *93*, 2335. (e) Paquette, L. A.; Wilson, S. E. *J. Am. Chem. Soc.* **1971**, *93*, 5934. (f) Paquette, L. A.; Wilson, S. E.; Henzel, R. P.; Allen, G. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 7761. (g) Paquette, L. A.; Wilson, S. E.; Henzel, R. P. *J. Am. Chem. Soc.* **1972**, *94*, 7771. (h) Zon, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 4456. (i) Paquette, L. A.; Zon, G. *J. Am. Chem. Soc.* **1974**, *96*, 203, 215. (j) Paquette, L. A.; Zon, G. *J. Am. Chem. Soc.* **1974**, *96*, 224.

[33] Recently, rearrangement products of **4** and **5** obtained upon photolysis at 185 nm were examined: Adam, W.; Alt, C.; Braun, M.; Denninger, U.; Zang, G. *J. Am. Chem. Soc.* **1991**, *113*, 4563. Among other products, the tricyclohexane **4** yielded 15% cyclohexadiene **6** and the tricycloheptane **5** afforded 85% bicycloheptene **7**. Starting from **5**-$d_2$, both 6,7- and 1,6-dideuterio derivatives, **7**-$d_2$ and **7**-$d'_2$, respectively, were obtained. According to these findings, the authors concluded that the initial step in the rearrangement of **4** is the cleavage of a lateral bond in the bicyclobutane moiety, whereas in the isomerization of **5**, ring opening at this bond competes with that of the central linkage.

**Scheme II**

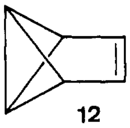


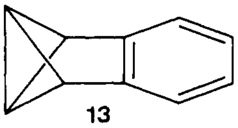
"character" of the HOMO, which would require a reversal in the energetic sequence of $7a_1$ and $1a_2$ on going from **1**–**3** to **4** and **5**, is improbable on theoretical and experimental grounds. For want of arguments involving pure electronic factors, one may invoke steric constraint by the bridging polymethylene chain, in order to rationalize the unexpected site of the bond cleavage and the facile isomerization of $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$. Such a constraint could make the ring opening at the lateral energetically more favorable than at the central bond, the more so as the energy difference between $7a_1$ and $1a_2$ should decrease on passing from **1**–**3** to **4** and **5**. The cleavage of the lateral bond in the bicyclobutane moiety of $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ presumably induces the facile isomerization of these radical cations, by contrast to $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ in which this bond is not broken. It is noteworthy that bridging of the 3,4-positions in cyclobutene (**10**) to yield *cis*-bicyclo[3.2.0]hept-6-ene (**7**) also has a detrimental effect on the persistence of the radical cation. Whereas $\mathbf{10}^{\bullet+}$ is persistent in a Freon matrix and opens to the radical cation of *trans*-buta-1,3-diene only upon photolysis,[1f,3] $\mathbf{7}^{\bullet+}$ is too unstable for characterization by ESR spectroscopy under the same conditions, as it readily isomerizes to $\mathbf{8}^{\bullet+}$.

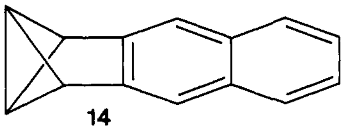
As another attempt to account for the seeming preference of $\mathbf{5}^{\bullet+}$ to cleave the lateral instead of the central bond, a somewhat different reaction mechanism is presented in Scheme II.[34] The assumption that $\mathbf{7}^{\bullet+}$ occurs as an intermediate, which is admittedly consistent with but not necessarily required by experimental evidence, has been abandoned. Moreover, formation of both 6,7- and 2,7-diyl radical cations, $\mathbf{5/c}^{\bullet+}$ and $\mathbf{5/l}^{\bullet+}$, respectively, is considered to be reversible, because the two pertinent C atoms cannot get far apart in the rigid bicyclic framework. The argument that $\mathbf{5}^{\bullet+} \rightarrow \mathbf{5/c}^{\bullet+}$ should be greatly favored over $\mathbf{5}^{\bullet+} \rightarrow \mathbf{5/l}^{\bullet+}$ is kinetically not relevant to the further course of the reaction, if conversion to $\mathbf{8}^{\bullet+}$ is regarded as the rate-controlling step. Only for $\mathbf{5/l}^{\bullet+}$ would the facile opening of the 3-membered ring in this step directly lead to the end product $\mathbf{8}^{\bullet+}$.

Finally, in order to emphasize the difficulties in discussing rearrangement of radical cations in terms of orbitals, one may consider our findings for tricyclo[3.1.0.0$^{2,6}$]hex-3-ene (benzvalene; **12**),[1i] 1,2,3-methenoindane (naphthvalene, **13**),[35] and 1,2,3-metheno-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene (naphtho[2,3]benzvalene; **14**)[35] irradiated by $\gamma$-rays in Freon matrices.

Connecting the bicyclobutane moiety to a "classical" $\pi$-system shifts the bulk of the spin population from this moiety to the respective $\pi$-system which is ethene in **12**, benzene in **13**, and naphthalene in **14**. Naively, one may expect that the extension of the $\pi$-system on going from **12** to **13** to **14** should enhance the thermodynamic and kinetic stabilities of the radical cations, as is the case with the corresponding ions of ethene, benzene, and naphthalene. Actually, the opposite behavior has been observed. Whereas $\mathbf{12}^{\bullet+}$ is persistent in a Freon matrix below 120 K and isomerizes to the radical cation of benzene only upon thermal or photolytic excitation,[1i] $\mathbf{13}^{\bullet+}$ and $\mathbf{14}^{\bullet+}$ are too short-lived under the same conditions,[35] and only the ESR spectra of the radical cations of naphthalene and anthracene, respectively, could be observed.[36]


**12**


**13**


**14**

## Experimental Section

**Bicyclo[1.1.0]butane (1) and its 1-deuterio and 1,3-dimethyl derivatives (1-*d* and 2), tricyclo[3.1.0.0$^{2,6}$]hexane (4), and tricyclo[4.1.0.0$^{2,7}$]heptane (5) and its 1-deuterio and 1,7-dideuterio derivatives (5-*d* and 5-$d_2$)** were synthesized according to known procedures: **1**,[37] **1**-*d*,[2,37] **2**,[38] **4**,[39] **5**,[40] **5**-*d*,[41] and **5**-$d_2$.[42]

**1-Methylbicyclo[1.1.0]butane (3).**[43] **1** (0.08 g) was condensed into a 20% excess of *n*-propyllithium in degassed diethyl ether in a 25 mL evacuated flask cooled in liquid $N_2$. After the mixture was stirred at 0 °C for 24 h and the volatiles were removed in vacuum, 2 mL of THF was condensed in, followed by addition of 0.23 g of methyl iodide. The contents were stirred for another 24 h at room temperature and fractionated on a vacuum line from –65 to 25 °C. Purification by gas chromatography on $\beta,\beta'$-oxodipropionitrile at 43 °C yielded **3**, as confirmed by $^1$H NMR and MS.

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(34) We are indebted to one of the Referees for suggesting this mechanism to us.

(35) Arnold, A.; Burger, U.; Gerson, F., unpublished results.

(36) ESR spectra of acene radical cations in $CFCl_3$ matrices: naphthalene, ref 1d; anthracene, Gerson, F.; Qin, X.-Z., unpublished.

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(43) For a general procedure see ref 41.

**1-(Trideuteriomethyl)bicyclo[1.1.0]butane** (**3**-$d_3$) was prepared as described for **3**, using *n*-butyllithium and trideuteriomethyl iodide.

**Cyclohexa-1,3-diene (6) and cyclohepta-1,3-diene (8)** were purified commercial products (FLUKA).

***cis*-Bicyclo[3.2.0]hept-6-ene** (**7**) was prepared by UV irradiation of **8** in pentane at 254 nm[44] (Hg-lamp, Gräntzel, Karlsruhe).

**2,3-Dideuteriocyclohepta-1,3-diene (8-*d*₂)** was obtained as a rearrangement product of **5**-$d_2$ with silver tetrafluoroborate as catalyst.[32a,e–g]

**Norcar-2-ene (9), benzvalene (12), naphthvalene (13), and 2,3-naphthobenzvalene (14)** were synthesized following procedures described in the literature: **9**,[45] **12**,[46] **13**,[46] and **14**.[47]

A $^{60}$Co source was used for $\gamma$-irradiation (dosis ca. 0.5 Mrad; concentration of the substrates $10^{-1}$–$10^{-2}$ mol dm$^{-3}$). The ESR spectra were taken on a Varian-E9 instrument, while a Bruker ESP-300 spectrometer served for the ENDOR studies.

**Acknowledgment.** This work was supported by the Swiss National Science Foundation. We thank Ms. Patricia Millasson, Université de Genève, for synthesizing **2**, **4**, **5**-$d_2$, and **8**-$d_2$ and Mr. Urs Buser, Universität Basel, for preparing **7**. We are also obliged to Professor Wolfgang Lüttke, Universität Göttingen, for a generous gift of **5** and to Professor Edwin Haselbach, Université de Fribourg, for the permission to use his $^{60}$Co source of $\gamma$-rays.

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