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Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices

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Organic radical cations in general, and those of hydrocarbons in particular, have been studied widely by ESR spectroscopy for the last 35 years.¹⁻³ Their importance as intermediates in chemical reactions involving electron transfer and the relevance of ESR spectroscopy as the method of choice for their studies are uncontested. They can be generated from the corresponding neutral compounds in fluid solution by reaction with oxidizing agents as well as by electrolysis or photolysis. The pertinent ESR spectra often exhibit a highly resolved hyperfine pattern (line width 0.01 mT)⁴ which provides detailed structural information. However, the conventional methods fail when the oxidation potential of the neutral precursor is too high and/or when the radical cation is too reactive to persist in fluid solution. Such cases have become amenable to ESR studies by a procedure introduced in the early 1980s.⁵ This procedure makes use of Freon matrices (Freon = halocarbon, e.g., CFC₃, CF₂ClCFCl₂, or CF₃-CCl₃) which contain the precursor as a substrate and which are subjected to ionizing γ -rays from a ⁶⁰Co source at 77 K. Initially, the particles undergoing ionization are the molecules of the Freon, because they greatly outnumber those of the substrate. Subsequently, the electron holes migrate across the matrix until being trapped by the substrate, which has an ionization energy lower than the Freon (ca. 11.5 eV). In such a way, it is possible to convert organic compounds that are relatively hard to oxidize into their radical cations. Being immobilized in the rigid medium, many of these radical cations are persistent and can be investigated by ESR

spectroscopy from 77 K to the softening point of the matrix (120–160 K). Usually, only the radical cation of the substrate and/or its rearrangement product yields observable spectra, because ESR lines of paramagnetic species from Freon molecules are widened beyond detection by ¹⁹F-hyperfine anisotropy.

The handicap of ESR spectroscopy of radicals in glasses is the low resolution, due to the long rotational correlation time. In the case of hydrocarbon radical cations, lines are mostly broadened by proton-hyperfine anisotropy which is neither efficiently averaged out as in fluid solution nor resolved as in single crystals. The information provided by such spectra is, at best, incomplete. A remedy to this handicap comes from ENDOR (electron nuclear double resonance) spectroscopy.⁶ Application of the ENDOR technique to radical cations in Freon matrices reveals structural features that are hard to come by elsewhere. This statement especially holds for radical cations of small hydrocarbons presented here. In many cases, secondary radical cations can also be studied in full detail, and more insight is thus gained into the mechanisms of rearrangements and other sequential reactions.

(1) Landolt-Börnstein, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1980; Vol. 9d.

(2) Reviews: *Electron Spin Resonance, Specialist Periodical Reports*; The Chemical Society: London, 1971–1991; Vols. 1–9, 10A–13A. Courtneidge, J. L.; Davies, A. G. *Acc. Chem. Res.* **1987**, *20*, 90.

(3) See also: (a) Gerson, F.; Lopez, J.; Akaba, R.; Nelsen, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 6716. (b) Gerson, F.; Gescheidt, G.; Nelsen, S. F.; Paquette, L. A.; Teasley, M. F.; Waykole, L. *J. Am. Chem. Soc.* **1989**, *111*, 5518.

(4) Illustrative examples: ESR spectra of the radical cations of adamantylideneadamantane^{3a} and anti-sequinorbornene.^{3b}

(5) Reviews: Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. Symons, M. C. R. *Chem. Soc. Rev.* **1984**, *13*, 393. Shiotani, M. *Magn. Reson. Rev.* **1987**, *12*, 333.

Fabian Gerson was born in Lodz, Poland. He studied natural sciences at the ETH Zürich, where he received his D.Sc. degree in 1958. Since 1968 he has held a professorship at the University of Basel. His main research interests are in ESR spectroscopy of organic radical ions, in which field he has published most of his 200 papers, a textbook, and several review articles.

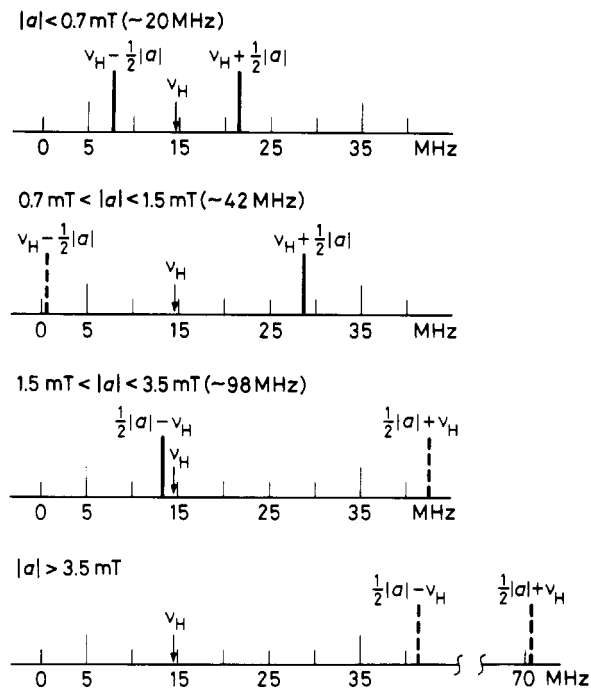


Figure 1. Schematic representation of proton-ENDOR signals, observable (solid lines) and not observable (dashed lines) on our instrument, for coupling constants $|a|$ of different size. Taken from ref 7.

Advantage of ENDOR Spectroscopy

A set of equivalent protons gives rise to a pair of ENDOR signals, so that, with increasing size and decreasing symmetry of the radical, the number of lines grows additively and not multiplicatively as in the ESR spectra.^{6a} When the value $|a|$ of the proton-coupling constant in megahertz (for $g = 2.0023$, 1 mT corresponds to 28.025 MHz) is smaller than twice the frequency, ν_H , of the free proton, the pair of signals occurs at $\nu_H \pm \frac{1}{2}|a|$; i.e., it is centered at ν_H and separated by $|a|$. For $|a| > 2\nu_H$, the low-frequency signal ($\nu_H - \frac{1}{2}|a|$) is "inverted" at the origin (0 MHz) and appears at $\frac{1}{2}|a| - \nu_H$; the pair of signals is then centered at $\frac{1}{2}|a|$ and separated by $2\nu_H$. In our ENDOR system, ν_H is typically 14.56 MHz. The upper limit of available frequencies is 35 MHz, while the lower limit for largely immobilized radicals lies at ca. 5 MHz. Consequently, the size of $|a|$ determines whether two, one, or none of the signals can be detected (Figure 1).

The resolving power of the ENDOR technique is superior to that of ESR spectroscopy, and this enhancement of resolution is particularly impressive for radical cations in Freon matrices. Whereas the width of ESR lines is 0.2–0.5 mT under such conditions, the corresponding ENDOR signals are only 0.3 MHz or 0.01 mT wide. It is, therefore, surprising that ENDOR spectroscopy, which has been used by many research groups inside and outside the Basel laboratory for the last 20 years,^{6b} has hardly found its way into the field of radical cations in Freon matrices. An obvious advantage of the greatly enhanced resolving power of the ENDOR experiment in this field is the observation

(6) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron-Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH Publishers: New York, 1988; (a) Chapter 2, (b) Chapter 5.

(7) Arnold, A.; Burger, U.; Gerson, F.; Kloster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271.

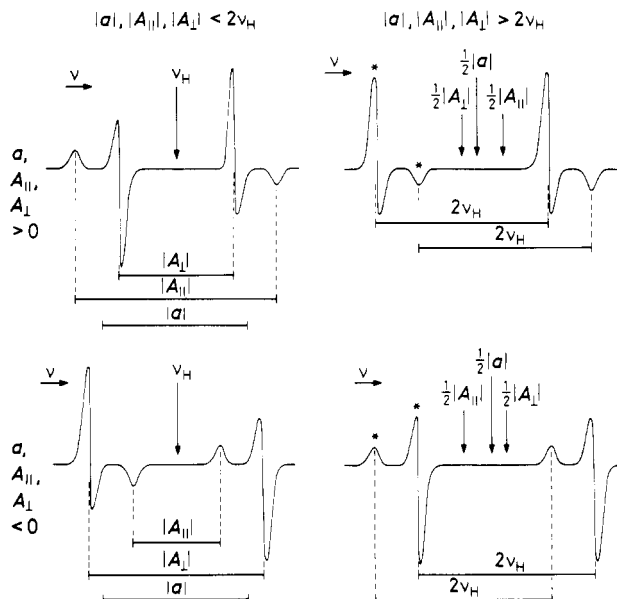
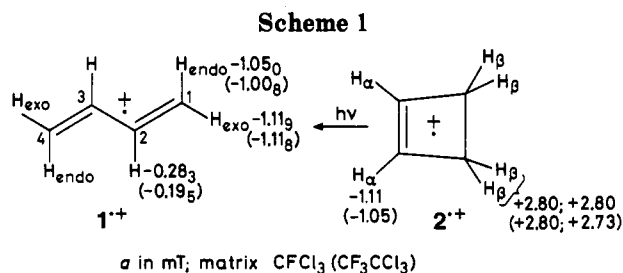


Figure 2. Idealized proton-ENDOR signals for a quasi-axial tensor of hydrocarbon radical cations in Freon matrices; connection between the sign of the isotropic coupling constant a and the relative sizes of their anisotropic counterparts $|A_{\parallel}|$ and $|A_{\perp}|$. The "inverted" signals are starred. Taken from ref 7.

of hyperfine interactions which are masked by the width of the ESR lines. Small $|a|$ values and differences between larger ones can now be measured precisely. Moreover, it is often possible to determine the sign of a , which is as relevant to the structure of a radical as the absolute value $|a|$.

In ESR spectroscopy, protons separated from a π -center by 0, 1, 2, ... sp^3 -hybridized carbon atoms are denoted $\alpha, \beta, \gamma, \dots$. Coupling constants a of substantial magnitude generally arise from α - and β -protons. They have a negative sign for the former and a positive one for the latter, due to the different mechanisms of spin transfer from the π -center to such protons (spin polarization for α and spin delocalization or hyperconjugation for β).^{8a} The sign of a can be determined, because, in contrast to the corresponding ESR spectrum, the residual hyperfine anisotropy is frequently resolved. It splits the proton-ENDOR signal into a parallel and a perpendicular feature representing the z - and (averaged) x, y -components of a quasi-axial tensor. We have found that the constant, $|A_{\parallel}|$, associated with the parallel feature is larger than its perpendicular counterpart $|A_{\perp}|$ when the isotropic value $a = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$ is positive; an opposite relation, $|A_{\parallel}| < |A_{\perp}|$, holds for a negative sign of a (Figure 2). These relations are rationalized as follows: A_{\parallel} , A_{\perp} , and a have the same sign, which is either positive or negative, whereas the anisotropic contribution B to a , defined by $A_{\parallel} = a + 2B$ and $A_{\perp} = a - B$, is throughout positive; furthermore, $|a|$, $|A_{\parallel}|$, and $|A_{\perp}|$ are much larger than B . With the sign of a thus derived from the ENDOR spectrum and a reliable prediction by theory, assignments of coupling constants to protons in the radical cation can be made when the two values have similar magnitude but differ in sign. This information is the more valuable, as a general-TRIPLE-resonance experiment^{6a} providing rel-

(8) Gerson, F. *High-Resolution ESR Spectroscopy*; Wiley and Verlag Chemie: New York and Weinheim, 1970; (a) Chapter 1.5, (b) Chapter 2.1.



ative signs of a is only rarely practicable on ENDOR signals of radical cations in rigid solutions.

Application to Specific Radical Cations

ENDOR spectroscopy has substantially contributed to the full characterization of a number of radical cations in Freon matrices which have been studied in Basel for the last five years. All radical cations were generated at 77 K by γ -irradiation of these matrices containing an organic precursor to be ionized as the substrate. The following sections are headed by the names of such precursors which formed radical cations upon ionization. When only the spectrum of a secondary radical cation was observed, the name of the corresponding neutral compound is given, along with that of the original substrate.

***s*-trans-Buta-1,3-diene (1) and Cyclobutene (2).** The ESR spectrum of $1^{\bullet+}$ in a CFCl_3 ^{9,10,11a} or a CF_3CCl_3 matrix^{11b} ($g = 2.0029$) is a 1.1-mT quintet due to the four protons in the 1,4-positions. Complete and more precise hyperfine data are provided by the corresponding ENDOR spectra. With CFCl_3 , the signals are of "isotropic" shape. A pair of them at $\nu_H \pm 1/2|a|$ yields the smaller $|a|$ value for the two protons in the 2,3-positions, while separate signals at $\nu_H + 1/2|a|$ from the *exo*- and *endo*-protons in the 1,4-positions indicate distinctly different coupling constants of these protons.¹⁰ A general-TRIPLE-resonance experiment carried out on the ENDOR signals indicates that all a values have the same sign. The expectation that this sign is negative, as required for α -protons, is borne out by the ENDOR spectrum of $1^{\bullet+}$ taken with the $\text{CF}_3\text{-CCl}_3$ matrix, in which each of the signals reveals its anisotropic features with $|A_{\parallel}| < |A_{\perp}|$.^{11b,c} It is noteworthy that the resulting isotropic values a are, in part, markedly altered relative to those observed with the CFCl_3 matrix (Scheme 1).

The ENDOR technique has also been applied to the isomeric $2^{\bullet+}$, which, in Freon matrices, gives rise to an easily detectable ESR spectrum ($g = 2.0030$).^{11a,b} With CF_3CCl_3 , a signal from the two α -protons is observed at $\nu_H + 1/2|a|$, along with that from the four β -protons at $1/2|a| - \nu_H$. Both of them are split into two: the former by hyperfine anisotropy with $|A_{\parallel}| < |A_{\perp}|$, thus confirming the negative sign of a , and the latter, of "isotropic" shape, by the symmetry-lowering effect of the matrix which separates the set of four protons into two pairs (Scheme 1).^{11b}

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

(10) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* 1988, 71, 1065.

(11) (a) Gerson, F.; Qin, X.-Z.; Bally, T.; Aebischer, J.-N. *Helv. Chim. Acta* 1988, 71, 1069. (b) Aebischer, J.-N.; Bally, T.; Roth, K.; Haselbach, E.; Gerson, F.; Qin, X.-Z. *J. Am. Chem. Soc.* 1989, 111, 7909. (c) Gerson, F.; Qin, X.-Z.; Schmidlin, R. Unpublished a values for $1^{\bullet+}$ in a CF_3CCl_3 matrix, slightly revised relative to those given in ref 11b.

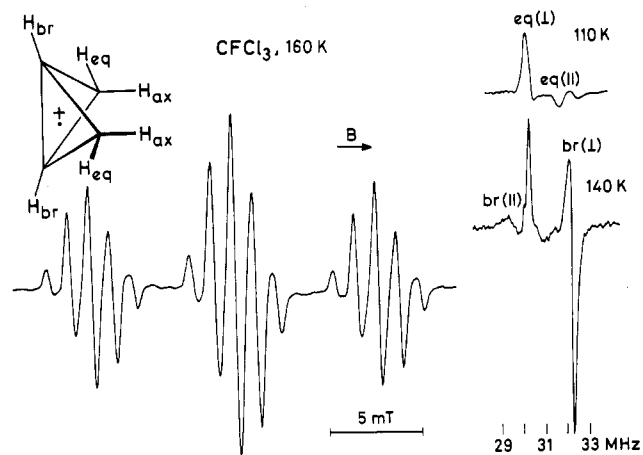


Figure 3. ESR (left) and proton-ENDOR (right) spectra of $3^{\bullet+}$; matrix and temperature as indicated. Taken from ref 7.

Upon photolysis ($\lambda = 450$ nm) of $2^{\bullet+}$ in a CFCl_3 or a CF_3CCl_3 matrix, its ESR and ENDOR spectra are replaced by those of $1^{\bullet+}$.¹¹ It has been suggested^{11b} that ring opening in $2^{\bullet+}$ occurs in a nonconcerted way, directly leading to $1^{\bullet+}$ without the intermediacy of the *cis*-configured radical cation.

Bicyclo[1.1.0]butane (3) and Its 1-Methyl (4) and 1,3-Dimethyl (5) Derivatives. Contrary to what might be expected, $3^{\bullet+}$ is persistent in a CFCl_3 matrix; i.e., it does not readily rearrange to the isomeric $2^{\bullet+}$ and/or $1^{\bullet+}$.¹² The ESR spectrum of $3^{\bullet+}$ ($g = 2.0039$; Figure 3) exhibits a 7.71-mT triplet from the two axial methylene protons (H_{ax}), each component of the triplet being split into a 1.14-mT quintet from both the two corresponding equatorial protons (H_{eq}) and the two bridgehead protons (H_{br}). The $|a(H_{eq})|$ and $|a(H_{br})|$ values differ, therefore, by less than the line width of 0.3 mT. Theory predicts that the central C(1)–C(3) bond in $3^{\bullet+}$ is essentially due to one electron only and that the singly occupied orbital at the two carbon atoms forming this bond has predominantly p-character.^{12,13} Consequently, C(1) and C(3) must be considered as π -centers and H_{br} as α -protons, while H_{ax} and H_{eq} are β . The coupling constant $a(H_{br})$ should thus be negative, whereas $a(H_{ax})$ and $a(H_{eq})$ ought to have a positive sign.

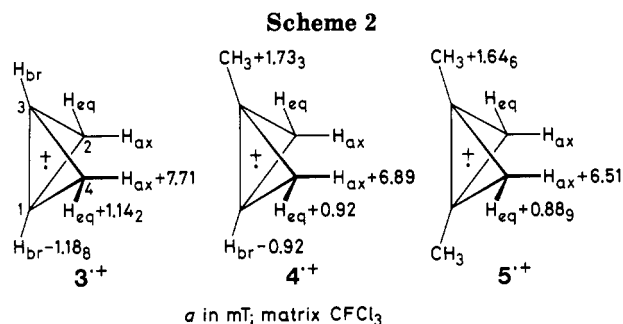
Anisotropic features of ENDOR signals are observed at $\nu_H + 1/2|a|$ from both H_{eq} and H_{br} (Figure 3).⁷ Those appearing at lower temperatures have been assigned to H_{eq} , because $|A_{\parallel}| > |A_{\perp}|$. The others, which become detectable only at higher temperatures, have $|A_{\parallel}| < |A_{\perp}|$, so that an assignment to H_{br} is indicated. The difference $|a(H_{br})| - |a(H_{eq})|$ is merely 0.046 mT (Scheme 2).

The strikingly large coupling constant $a(H_{ax})$, characteristic of bicyclo[1.1.0]butane radical cations, is due to the simultaneous linking of the methylene groups to both C(1) and C(3), at which the spin-bearing p-orbitals are in phase, as well as to the conformation of the C– H_{ax} bonds eclipsing these orbitals.^{12,14} The ratio $a(H_{ax})/a(H_{eq}) = 6.75$ points to a strongly puckered geometry of $3^{\bullet+}$. By combining the experimental data with theoretical calculations, a flap angle of 132.2° between the C(1)C(2)C(3) and C(1)C(4)C(3) planes is obtained,

(12) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* 1989, 111, 6456.

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

(14) Whiffen, D. H. *Mol. Phys.* 1963, 6, 223.



along with a C(1)–C(3) distance of 178.6 pm.¹² (The corresponding values for the neutral **3** are 121.7° and 149.7 pm.¹⁵)

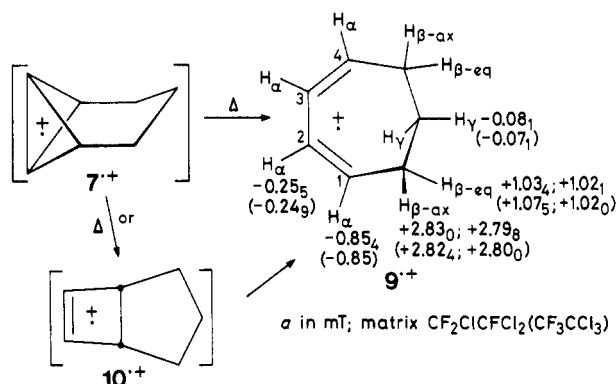
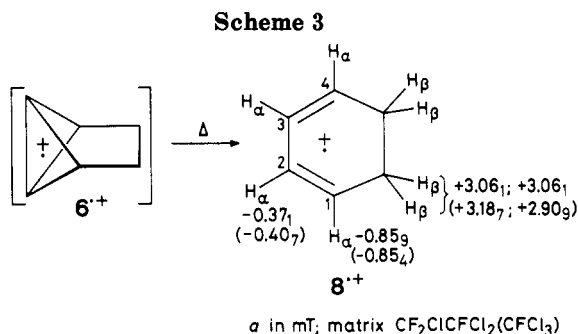
The radical cations **4⁺** and **5⁺** (Scheme 2) are also persistent in CFC_3 matrices, and they give rise to intense and well-defined ESR spectra ($g = 2.0039$).⁷ The positive sign required for the coupling constants of the six methyl and the two equatorial methylene β -protons in **5⁺** has been confirmed by the observation of their ENDOR signals at $\frac{1}{2}|a| - \nu_H$ and $\nu_H + \frac{1}{2}|a|$, respectively; the anisotropic features of these signals display $|A_{||}| > |A_{\perp}|$. Moreover, it has been inferred from the hyperfine data for **3⁺** and **5⁺** that a methyl group at a quasi- π -center C(1) or C(3) of bicyclo[1.1.0]butane withdraws ca. 15% of the spin population from this center,⁷ an amount somewhat larger than in methyl-substituted “classical” π -radical cations.^{3b}

Cyclohexa-1,3-diene (8) from Tricyclo[3.1.0.0^{2,6}]-hexane (Dihydrobenzvalene; 6) and Cyclohepta-1,3-diene (9) from Tricyclo[4.1.0.0^{2,7}]heptane (Moore’s Hydrocarbon; 7). In sharp contrast to **3⁺**–**5⁺**, the radical cations **6⁺** and **7⁺**, i.e., those of bicyclo[1.1.0]butanes bridged in the axial 2,4-positions, do not persist in Freon matrices at 77 K, but isomerize to those of corresponding cycloalka-1,3-dienes **8⁺** and **9⁺** (Scheme 3).⁷

The ESR spectra of the rearrangement products, **8⁺** and **9⁺** ($g = 2.0029$),¹⁶ have been analyzed in detail by ENDOR.⁷ The study of **9⁺**, in particular, provides a paradigm for the utility of this technique when applied to radical cations in Freon matrices. The wealth of information derived from the ENDOR signals contrasts with the relative paucity of data obtained from the corresponding ESR spectrum. For instance, with a $\text{CF}_2\text{ClCFCl}_2$ matrix, the ESR spectrum of **9⁺**, at its best resolution (Figure 4), is a 2.81-mT triplet from the two axial methylene β -protons ($H_{\beta\text{-ax}}$); a further splitting into a 0.95-mT quintet arises from both the two corresponding equatorial protons ($H_{\beta\text{-eq}}$) and the two α -protons ($H_{\alpha\text{-1,4}}$) in the 1,4-positions. The 0.25-mT triplet from the two α -protons in the 2,3-positions is barely indicated, while the difference $|a(H_{\beta\text{-eq}})| - |a(H_{\alpha\text{-1,4}})|$ and the coupling constant, $a(H_{\gamma})$, of the two methylene γ -protons entirely escape detection. The ENDOR spectrum of **9⁺** in a $\text{CF}_2\text{ClCFCl}_2$ matrix shows signals of “isotropic” shape for all protons (Figure 4). Those from $H_{\beta\text{-eq}}$ and $H_{\alpha\text{-1,4}}$, both at $\nu_H + \frac{1}{2}|a|$, can be clearly distinguished. A split signal from $H_{\beta\text{-ax}}$ appears

(15) Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* 1969, 50, 1976.

(16) Former reports on ESR spectra of **8⁺** and **9⁺** in Freon matrices; see, for **8⁺**, ref 9 and the following: Tabata, M.; Lund, A. *Chem. Phys.* 1983, 75, 379. See, for **9⁺**: Faucitano, A.; Buttafava, A.; Martinotti, F.; Sustmann, R.; Korth, H. G. *J. Chem. Soc., Perkin Trans. 2* 1992, 865.



at $\frac{1}{2}|a| - \nu_H$, while $H_{\alpha\text{-2,3}}$ and H_{γ} are represented by pairs of signals at $\nu_H \pm \frac{1}{2}|a|$. As in the case of β -protons in **2⁺** (see above), the splitting of the signals from $H_{\beta\text{-ax}}$ and $H_{\beta\text{-eq}}$ is due to the symmetry-lowering effect of the matrix. On changing to CF_3CCl_3 , all signals, except those from H_{γ} , exhibit anisotropic features (Figure 4). The relations $|A_{||}| < |A_{\perp}|$ for $H_{\alpha\text{-1,4}}$ and $H_{\alpha\text{-2,3}}$ and $|A_{||}| > |A_{\perp}|$ for $H_{\beta\text{-ax}}$ and $H_{\beta\text{-eq}}$ are in accord with a negative sign of the α - and a positive one of the β -proton-coupling constants. For $a(H_{\gamma})$, of which the residual anisotropy is not resolved, theory requires a negative sign and suggests that the observed signals are due to both γ -protons.

Deuterium labelings of **7** and **9** establish that the first step in the isomerization of **7⁺** to **9⁺** is the cleavage of the *lateral* (and not of the central) bond in the bicyclo[1.1.0]butane moiety of **7⁺**; an analogous statement should hold for the initial step in the rearrangement of **6⁺** to **8⁺**. It is possible that **7⁺** isomerizes into **9⁺** via the short-lived radical cation of *cis*-bicyclo[3.2.0]hept-6-ene (**10**), which readily undergoes ring opening to yield **9⁺** (Scheme 3).⁷

Tricyclo[3.1.0.0^{2,6}]hex-3-ene (Benzvalene; 11). As **11** is a monoene derivative of **6**, one may expect, by analogy with the facile rearrangement of **6⁺** to **8⁺**, that **11⁺** will rapidly isomerize to the radical cation of benzene (**12**). Surprisingly, **11⁺** persists in a CF_3CCl_3 matrix up to 125 K, above which temperature it rearranges to **12⁺**.¹⁷ The ESR spectrum of **11⁺** ($g = 2.0029$) exhibits 2.79- and 0.835-mT triplets from the two methine γ -protons and the two ethenic α -protons, respectively. A third triplet-splitting from the two allylic β -protons is too small to be resolved, but it is revealed by a pair of ENDOR signals at $\nu_H \pm \frac{1}{2}|a|$, a negative sign of $a(H_{\beta})$ being derived from the anisotropic features with $|A_{||}| < |A_{\perp}|$.

The hyperfine data for **11⁺** (Scheme 4) are rationalized in terms of the singly occupied orbital represented

(17) Gerson, F.; Arnold, A.; Burger, U. *J. Am. Chem. Soc.* 1991, 113, 4359.

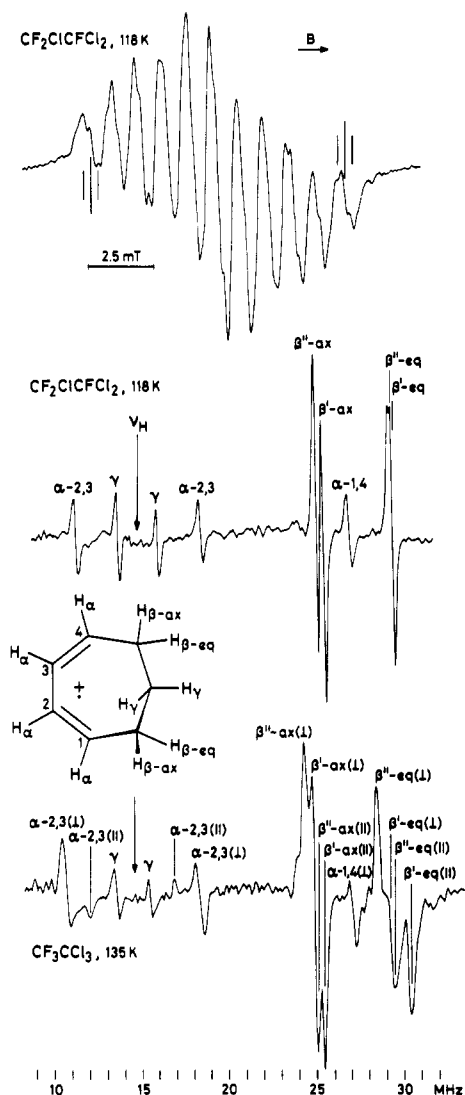
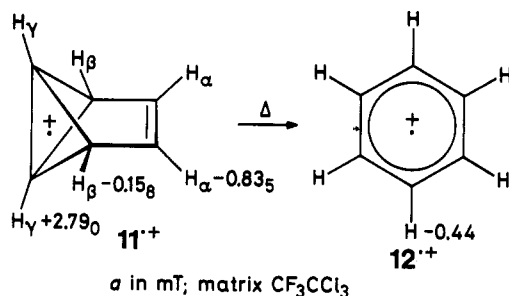


Figure 4. ESR (top) and proton-ENDOR (center and bottom) spectra of 9^{++} ; matrix and temperature as indicated. The feature $\alpha-1,4(II)$ in the lowermost spectrum is masked by signals from β -ax. Taken from ref. 7.

Scheme 4

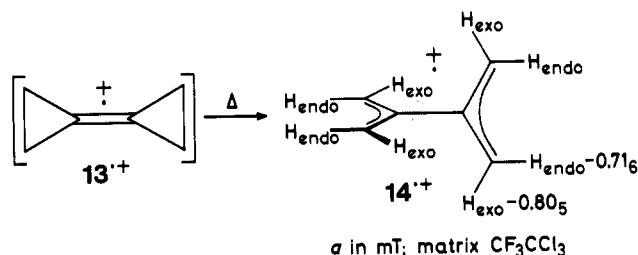


by the HOMO of ethene, albeit with very efficient spin delocalization onto the bicyclo[1.1.0]butane moiety. In accord with the results of a CIDNP study on the oxidation of 11,¹⁸ MO models predict a reduced negative value of $a(H_\alpha)$ and an unusually large positive one of $a(H_\gamma)$, due to a W or zigzag arrangement of bonds¹⁹ favoring a strong long-range π - σ interaction (through-

(18) Abelt, C. J.; Roth, H. D.; Schilling, M. L. *J. Am. Chem. Soc.* 1985, 107, 4148.

(19) Russell, G. A.; Holland, G. W.; Chang, K. Y.; Keske, R. G.; Mattox, J.; Chung, C. S. C.; Stanley, K.; Schmitt, K.; Blankespoor, R.; Kosugi, Y. *J. Am. Chem. Soc.* 1974, 96, 7237.

Scheme 5



bond mechanism²⁰). The small negative coupling constant $a(H_\beta)$ is accounted for by the position of the protons in the nodal plane of the π -system; this geometry makes hyperconjugation ineffective, so that only spin polarization (often neglected for β -protons) contributes to $a(H_\beta)$.

Tetramethyleneethane (14) from Bicyclopropylidene (13). In a CF_3CCl_3 matrix, 13^{++} is not persistent at 77 K and undergoes opening of the two three-membered rings to yield 14^{++} .²¹ While the ESR spectrum of 14^{++} ($g = 2.0029$) is a 0.75-mT nonet from the eight protons of 14^{++} ,²² the corresponding ENDOR spectrum shows two distinctly separate signals at $\nu_H \pm 1/2|a|$ of "isotropic" shape, due to the sets of four *exo*- and four *endo*-protons. The pertinent coupling constants (Scheme 5) compare favorably with halves of the a values (-1.481 and -1.390 mT) found for the analogous protons in the 1,3-positions of the allyl radical.²³

The neutral molecule 14, for which no Kekulé formula with fewer than two unpaired electrons can be drawn, has presumably a triplet ground state of D_{2d} symmetry.²⁴ The same geometry, with two mutually orthogonal allyl moieties, has been assumed for 14^{++} , which should thus be considered as positively charged bialllyl with the spin evenly distributed over both π -moieties.

Bicyclo[2.2.1]hepta-2,5-diene (Norbornadiene; 15), Bicyclo[2.2.2]octa-2,5-diene (Dihydrobarrelene; 16), and Bicyclo[2.2.2]octa-2,5,7-triene (Barrelene; 17). The ESR spectra of 15^{++} ,^{25,26} 16^{++} (both $g = 2.0030$),²⁶ and 17^{++} ($g = 2.0025$)²⁷ in Freon matrices exhibit splittings from protons with the largest coupling constants only. The remaining smaller $|a|$ values have been determined from the corresponding ENDOR signals at $\nu_H \pm 1/2|a|$.^{26,27} The signs of the coupling constants (Scheme 6) are based on the observed anisotropic components, $|A_{||}|$ and $|A_{\perp}|$, and/or on theoretical arguments.

Common to all three radical cations is the spin delocalization over the two (15^{++} and 16^{++}) or three (17^{++}) ethenic π -systems; it manifests itself by the α -proton-coupling constants being one-half or one-third of that

(20) Hoffmann, R. *Acc. Chem. Res.* 1971, 4, 1.

(21) Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Am. Chem. Soc.* 1989, 111, 1135.

(22) A similar nonet was reported for the radical anion 14^{--} : Bauld, N. L.; Stevenson, G. R. *J. Am. Chem. Soc.* 1969, 91, 3675.

(23) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* 1968, 90, 7157.

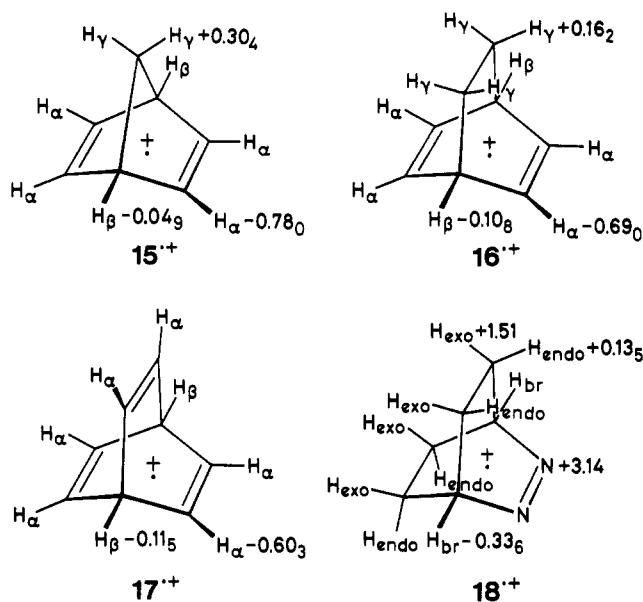
(24) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* 1986, 108, 7416. For a very recent discussion on the ground-state multiplicity and geometry of the neutral 14, see: Dowd, P.; Chang, W.; Partian, C. J.; Zhang, W. *J. Phys. Chem.* 1993, 97, 13408.

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(26) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* 1989, 72, 383.

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Scheme 6



a in mT; matrix $\text{CF}_2\text{ClCFCl}_2$ (15^+ , 17^+ , 18^+), CF_3CCl_3 (16^+)

expected for the radical cation of ethene (-1.4 to -1.8 mT^{8b}). The interaction between the nonconjugated π -systems in **15** and **16** is dominated by the through-space mechanism,^{20,28} so that the singly occupied orbitals in 15^+ and 16^+ are represented by the *antibonding* combination (π_-) of the two ethene HOMOs which lie energetically above their bonding counterparts (π_+). Likewise, the corresponding orbital of 17^+ has three nodal planes between the three constituent ethene HOMOs; these planes coincide with those of the individual π -systems and pass through the bridgehead carbon and hydrogen atoms. It is noteworthy that **17** is an archetype of a Möbius molecule with D_{3h} symmetry and that the relevant orbital belongs to A_2' .²⁹ The nondegeneracy of this orbital and, therewith, of the ground state of 17^+ complies with the fact that the ESR lines can be saturated, which is the prerequisite for a successful ENDOR experiment. (A contrary behavior is usually found for the ESR spectra of radicals with degenerate ground states.³⁰)

Additional structural features of 15^+ , 16^+ , and 17^+ are the small negative coupling constants of the β -protons lying in the nodal planes of the singly occupied orbitals. For 15^+ and 16^+ , these a values are surpassed by the positive ones of the γ -protons, due to an arrangement of bonds favoring long-range π - σ interaction.¹⁹

2,3-Diazabicyclo[2.2.2]oct-2-ene (18). The presence of an azo group in **18** has far-reaching consequences for 18^+ , the only radical cation in this Account containing heteroatoms. In contrast to 15^+ , 16^+ , and 17^+ , which are π -radicals, 18^+ must be classified as a σ -radical obtained by removal of an electron from an

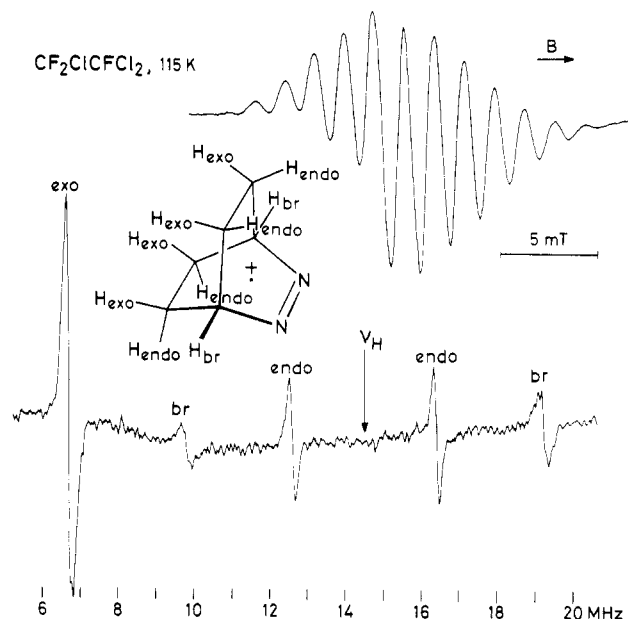


Figure 5. ESR (top) and proton-ENDOR (bottom) spectra of 18^+ ; matrix and temperature as indicated. Reprinted with permission from ref 34. Copyright 1988 Verlag Helvetica Chimica Acta.

antibonding combination (n_-) of the two N lone pairs.³¹ The very large ^{14}N -coupling constant, diagnostic of the σ -character of the singly occupied orbital, has a pronounced hyperfine anisotropy which, together with the anisotropic g factor, makes the ESR spectra of 18^+ in CFCl_3 and CF_3CCl_3 matrices difficult to analyze,³²⁻³⁴ even with the aid of the ENDOR technique. However, when a $\text{CF}_2\text{ClCFCl}_2$ matrix is used, the ESR spectrum ($g = 2.0022$) becomes essentially "isotropic" above 110 K. Whereas from the hyperfine spacing of this spectrum by ca. 1.55 mT only the ^{14}N - and the largest proton-coupling constant can be derived with a modest precision,³³ the $|a|$ values of all protons are readily determined from the likewise "isotropic" ENDOR signals at $1/2|a| - \nu_{\text{H}}$ for *exo*-protons and at $\nu_{\text{H}} \pm 1/2|a|$ for the *endo*-protons and the bridgehead protons (Figure 5).³⁴ The signs of a are those required by theory, and they are in line with the general-TRIPLE-resonance experiment performed on the ENDOR signals (Scheme 6). The ratio $a(\text{H}_{\text{exo}})/a(\text{H}_{\text{endo}}) = 11.2$ emphasizes the dependence of the long-range coupling on the orientation of the C-H bonds relative to the spin-bearing orbital n_- .

Naphthalene (19). Although **19** is the next aromatic hydrocarbon after benzene, reliable hyperfine data for 19^+ were missing until a few years ago. This is because oxidation of **19** in fluid solution yields merely the dimeric radical cation 19_2^{+} ,³⁵ while the poor resolution of a highly "anisotropic" ESR spectrum of monomeric 19^+ in glassy boric acid has led to an incorrect analysis.³⁶ Only in a more recent work³⁷ could a better resolved ESR spectrum of 19^+ in a CFCl_3 matrix ($g = 2.0029$)

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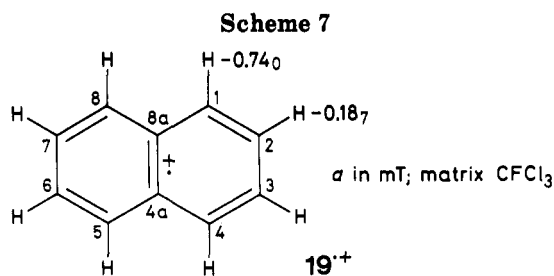
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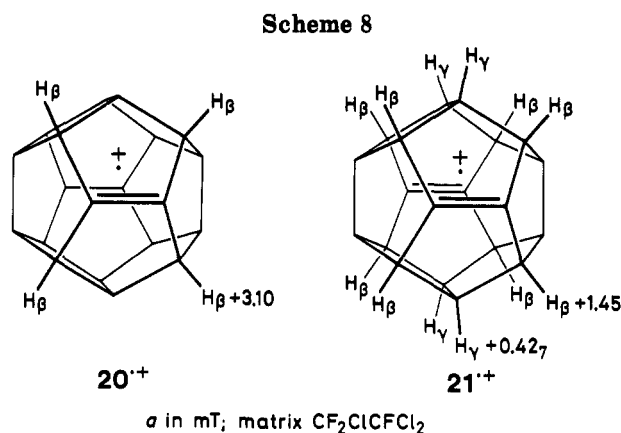


be properly analyzed and satisfactorily reproduced by computer simulation, owing largely to the use of the ENDOR technique. The signals with pronounced anisotropic features appear at $\nu_H + 1/2|a|$ from the protons in the 1,4,5,8-positions and at $\nu_H \pm 1/2|a|$ from those in the 2,3,6,7-positions. The relation $|A_{\parallel}| < |A_{\perp}|$, followed throughout in the spectrum, is in accord with the negative sign required for the coupling constants of these α -protons (Scheme 7).

The singly occupied orbitals in $19^{\bullet+}$ and in the radical anion $19^{\bullet-}$, having a vertical nodal plane through C(4a) and C(8a), can be considered as a combination of the corresponding orbitals in the radical ions, $1^{\bullet+}$ and $1^{\bullet-}$, of buta-1,3-diene. Interestingly, the ratios of the largest a values, $(-0.740 \text{ mT})/(-0.495 \text{ mT})^{37,38}$ for $19^{\bullet+}/19^{\bullet-}$ and $(-1.119 \text{ mT})/(-0.762 \text{ mT})^{10,39}$ for $1^{\bullet+}/1^{\bullet-}$, are almost identical (ca 1.5) and distinctly higher than for the radical ions of other alternant benzenoid hydrocarbons.^{8b}

Dodecahedrene (20) and Dodecahedradiene (21). ESR spectra of both $20^{\bullet+}$ and $21^{\bullet+}$ in Freon matrices are dominated by g anisotropy ($g_1 = 1.9881$; $g_2 = 2.0039$; $g_3 = 2.0329$) and consist of three groups of equidistant lines.^{40a} From the quintets for $20^{\bullet+}$ and the nonets for $21^{\bullet+}$, one derives average $|a|$ values of 3.10 and 1.45 mT for four and eight equivalent β -protons, respectively. These values are corroborated by the corresponding ENDOR spectra, which exhibit signals at $1/2|a| \pm \nu_H$ with distinct anisotropic features of a quasi-axial tensor;^{40a,b} the expected positive sign of the coupling constants, $a(H_{\beta})$, in question is confirmed by $|A_{\parallel}| > |A_{\perp}|$. The ENDOR spectra reveal also the presence of further interacting protons with smaller $|a|$ values; a pair of signals at $\nu_H \pm 1/2|a|$ with $|A_{\parallel}| \gg |A_{\perp}|$ can be assigned by MO calculations to one set of four γ -protons in $21^{\bullet+}$ ^{40c} (Scheme 8).

The finding that the major coupling constant for $21^{\bullet+}$ arises from eight equivalent β -protons and that it amounts to half the corresponding a value of four β -protons in $20^{\bullet+}$ is of eminent structural interest. It means that, upon ionization, a four-center, three-electron system of D_{2h} symmetry is formed in $21^{\bullet+}$, despite the transannular distance of 352 pm between the two π -bonds. This system resembles that in 7,8:12,19-diseco-1,16-dodecahedradiene (pagodadiene), where the corresponding distance is, however, only 262



pm. Accordingly, in contrast to $21^{\bullet+}$, the radical cation of pagodadiene is stable enough to be studied in fluid solution.⁴¹

Concluding Remarks

The radical cations described in this Account comprise a variety of basic organic species, starting from the three C_4 isomers, $1^{\bullet+}$ – $3^{\bullet+}$, proceeding to several C_6 – C_8 hydrocarbons, such as $8^{\bullet+}$, $9^{\bullet+}$, $11^{\bullet+}$, and $14^{\bullet+}$ – $17^{\bullet+}$, and ending with the C_6N_2 bicyclus $18^{\bullet+}$, the C_{10} acene $19^{\bullet+}$, and the two C_{20} “cages” $20^{\bullet+}$ and $21^{\bullet+}$. As the ENDOR technique is particularly efficient for radical cations which do not exhibit very pronounced g and hyperfine anisotropies, molecules containing heteroatoms, an extended π -system, or a bulky carbon framework are generally disfavored. Oncoming studies should reveal whether $18^{\bullet+}$ – $21^{\bullet+}$ represent borderline cases in this respect. Because of anisotropic contributions to the coupling constants, ENDOR signals from α -protons are usually broader and less readily detected than those from the β - and γ -protons. These contributions tend to average out at temperatures as high as allowed by the persistence of the radical cation and the softening point of the Freon glass; a similar effect is achieved by using the “mobile” matrix $CF_2ClCFCl_2$ instead of $CFCl_3$ or CF_3CCl_3 . Nevertheless, while strong anisotropies are detrimental to the observation of the ENDOR spectra, small residual hyperfine anisotropy is often welcome, because its resolved features provide valuable information not available from signals of “isotropic” shape. This information on the sign of the proton-coupling constant a is a further bonus of the ENDOR spectroscopy, in addition to the full and precise characterization of the radical cation by its $|a|$ values. Summing up, it may be said that the combination of the powerful spectroscopic ENDOR tool with the ingenious method to ionize organic molecules by γ -rays in Freon matrices has been very fruitful for the past five years and it will certainly be so in the near future.

I thank all colleagues and co-workers whose names are quoted in the references. In particular, I am grateful to Dr. Xue-Zhi Qin, who initiated these studies, and to Dr. Anton Arnold, who continued them. Professor Edwin Haselbach, Université de Fribourg, is acknowledged for the permission to use his ^{60}Co source of γ -rays and Professor Thomas Bally, in the same place, for stimulating discussions. Last but not least, I am indebted to the Swiss National Science Foundation for financial support.

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