

**48. The Radical Cations of Bicyclo[2.2.1]hepta-2,5-diene  
(8,9,10-Trinorborna-2,5-diene) and Bicyclo[2.2.2]octa-2,5-diene  
(2,3-Dihydrobarrelene).**

**An ESR and ENDOR Study<sup>1)</sup>**

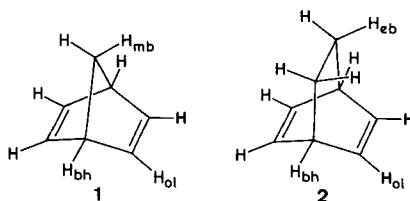
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(17.I.89)

The radical cation of bicyclo[2.2.1]hepta-2,5-diene (8,9,10-trinorborna-2,5-diene; **1**) in  $\text{CF}_2\text{ClCFCl}_2$  and  $\text{CF}_2\text{CCl}_3$  matrices and that of bicyclo[2.2.2]octa-2,5-diene (2,3-dihydrobarrelene; **2**) in  $\text{CFCl}_3$  and  $\text{CF}_3\text{CCl}_3$  matrices have been studied by ESR and ENDOR spectroscopy. For **1<sup>+</sup>**, the coupling constants of the olefinic, methano-bridge, and bridgehead protons are  $-0.780 \pm 0.005$ ,  $+0.304 \pm 0.002$ , and  $-0.049 \pm 0.002$  mT, respectively. The hyperfine tensor for the methano-bridge protons is axial,  $A_{\parallel} = +0.263 \pm 0.002$  and  $A_{\perp} = +0.386 \pm 0.002$  mT, while that for the olefinic protons is orthorhombic,  $A_x = -0.594 \pm 0.005$ ,  $A_y = -0.913 \pm 0.005$ , and  $A_z = -0.834 \pm 0.005$  mT ( $x$  parallel to C-H bond;  $z$  parallel to  $2p_x$  axis). For **2<sup>+</sup>**, the coupling constants of the olefinic, ethano-bridge, and bridgehead protons are  $-0.68 \pm 0.01$ ,  $+0.162 \pm 0.005$ , and  $-0.108 \pm 0.005$  mT, respectively. The hyperfine data for **1<sup>+</sup>** and **2<sup>+</sup>** fully support the presentation of their singly occupied orbitals as antisymmetric combinations,  $b_2(\pi_-)$ , of the two bonding ethene  $\pi$ -MO's.

**Introduction.** – Bicyclo[2.2.1]hepta-2,5-diene (8,9,10-trinorborna-2,5-diene; **1**) and bicyclo[2.2.2]octa-2,5-diene (2,3-dihydrobarrelene; **2**) are, after bicyclo[2.2.0]hexa-2,5-diene (*Dewar benzene*), the simplest bicyclic dienes of  $C_{2v}$  symmetry.



A few years ago, *Iwasaki* and coworkers [2] reported the hyperfine data for **1<sup>+</sup>** in a  $\text{CF}_2\text{ClCFCl}_2$  matrix and discussed the electronic structure of this radical cation in terms of its singly occupied molecular orbital. In that work, only the coupling constants of the four olefinic and the two methano-bridge protons in **1<sup>+</sup>** were determined, because the hyperfine splittings by the bridgehead protons remained unresolved due to the large line-width in the ESR spectrum [2]. As for **2<sup>+</sup>**, its hyperfine data have, to our knowledge, not yet been reported.

Here, we fully characterize the two radical cations with the use of both ESR and ENDOR spectroscopy. Application of the ENDOR- and TRIPLE-resonance techniques to **1<sup>+</sup>** in a  $\text{CF}_2\text{ClCFCl}_2$  matrix not only enabled us to obtain precise values and signs for the isotropic

<sup>1)</sup> Part 5 of 'Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices'. Part 4: [1].

coupling constants of all protons, but, owing to the ENDOR method, we could also measure the corresponding major anisotropic parameters for  $\mathbf{1}^\ddagger$  in a glassy  $\text{CF}_3\text{CCl}_3$ . In the case of  $\mathbf{2}^\ddagger$ , the complete isotropic hyperfine data were determined by ESR and ENDOR spectroscopy with  $\text{CFCl}_3$  and  $\text{CF}_3\text{CCl}_3$  used as matrices.

**Experimental.** – Bicycloheptadiene **1** (Aldrich, 99%) and the solvents  $\text{CFCl}_3$ ,  $\text{CF}_3\text{CCl}_3$ , and  $\text{CF}_2\text{ClCFCl}_2$  (Fluka, puriss.) were commercial products, while bicyclooctadiene **2** was synthesized according to a known procedure [3]. The radical cations  $\mathbf{1}^\ddagger$  and  $\mathbf{2}^\ddagger$  were generated from the corresponding neutral compounds by  $\gamma$  irradiation of their rigid solns. at 77 K (concentration: ca. 1% by volume; dose: 0.5 Mrad from a  $^{60}\text{Co}$  source).

The ESR spectra were taken on a Varian-E9 instrument, while a Bruker-ESP-300 spectrometer system served for the ENDOR studies. The 'powder program' for the simulations of the anisotropic ESR spectra has been adapted from that of Kasai [4].

**Results.** – Bicycloheptadiene **1** in  $\text{CF}_2\text{ClCFCl}_2$ . The radical cation  $\mathbf{1}^\ddagger$  was persistent in a  $\text{CF}_2\text{ClCFCl}_2$  matrix up to 120 K, and its ESR spectrum became essentially isotropic at 115 K. This spectrum (Fig. 1a) consists of a four-proton *quintet* spaced by ca. 0.8 mT and split into two-proton  *triplets*  by ca. 0.3 mT. The *quintet* arises undoubtedly from an interaction with the four olefinic protons ( $\text{H}_{\text{ol}}$ ), while the *triplet* splitting is attributed to the pair of methano-bridge protons ( $\text{H}_{\text{mb}}$ ; see Discussion). The hyperfine splitting from the two bridgehead protons ( $\text{H}_{\text{bh}}$ ) is too small to be resolved in the ESR spectrum (line-width 0.2mT). All these coupling constants,  $a(\text{H}_{\text{ol}})$ ,  $a(\text{H}_{\text{mb}})$ , and  $a(\text{H}_{\text{bh}})$ , could be accurately determined from the corresponding proton ENDOR spectrum (Fig. 1, bottom) which exhibits essentially isotropic features. The two pairs of signals, at 10.30 and 18.82 MHz, and at 13.87 and 15.25 MHz, centred at the frequency of the free proton ( $\nu_{\text{H}} = 14.56$  MHz), yielded  $a(\text{H}_{\text{mb}}) = 0.304 \pm 0.002$  mT and  $a(\text{H}_{\text{bh}}) = 0.049 \pm 0.002$  mT, respectively [5a]. The largest coupling constant,  $a(\text{H}_{\text{ol}}) = 0.780 \pm 0.005$  mT, was derived from  $\nu_{\text{H}}$  and the position of the high-frequency signal at 25.48 MHz, because its low-frequency counterpart (at ca. 3.6 MHz), was too weak to be detected. Simulation of the ESR spectrum with the use of these hyperfine data led to an excellent fit of the computed derivative curve (Fig. 1b) to the experimental one (Fig. 1a). The general TRIPLE-resonance technique [5a] indicated that the coupling constant 0.304 mT has a sign opposite to that of 0.049 mT. Considerations of geometry as well as evidence by experiment and theory (see Discussion) require a positive sign for  $a(\text{H}_{\text{mb}}) = 0.304$  mT, whereas  $a(\text{H}_{\text{bh}}) = 0.049$  should be negative. Since large coupling constants of protons attached directly to the  $\pi$  system are generally negative [6a], this sign must also be allotted to  $a(\text{H}_{\text{ol}}) = 0.780$  mT.

Bicycloheptadiene **1** in  $\text{CF}_3\text{CCl}_3$ . In  $\text{CFCl}_3$  and  $\text{CF}_3\text{CCl}_3$  matrices, the ESR spectra of  $\mathbf{1}^\ddagger$  remained anisotropic up to the softening points of the glassy solutions. They are exemplified by a spectrum of  $\mathbf{1}^\ddagger$  in  $\text{CF}_3\text{CCl}_3$  at 135 K (Fig. 2a). The analysis of its intricate hyperfine pattern relied on the corresponding proton ENDOR spectrum (Fig. 2, bottom). The high-frequency signal of the  $\text{H}_{\text{bh}}$  is isotropic and appears at the same position (15.25 mT) as in a  $\text{CF}_2\text{ClCFCl}_2$  matrix (the low-frequency counter-signal is obscured by the strong matrix absorption at 13.70 MHz due to  $^{19}\text{F}$  nuclei). The  $\text{H}_{\text{mb}}$  give rise to two pairs of anisotropic signals centred at  $\nu_{\text{H}}$  (14.56 MHz). The inner pair, at 10.88 and 18.24 MHz, has a shape characteristic of a perpendicular feature [1][5b][7], while the outer one, at 9.16 and 19.96 MHz, represents the corresponding parallel feature. The two pairs of signals are associated with the anisotropic coupling constants  $A_{\perp} = 0.263 \pm 0.002$  and  $A_{\parallel} = 0.386 \pm 0.002$  mT. Their

isotropic average,  $a_{\text{iso}} = 1/3(2A_{\perp} + A_{\parallel})$ , agrees with the coupling constant  $a(\text{H}_{\text{mb}})$  observed for  $\text{I}^{\ddagger}$  in the  $\text{CF}_2\text{ClCFCl}_2$  matrix. Both  $A_{\perp}$  and  $A_{\parallel}$  must have the same sign which should be positive, as has been specified above for  $a(\text{H}_{\text{mb}})$  and as is consistent with  $|A_{\perp}| < |A_{\parallel}|$  [1]. The group of three signals at the highest frequencies, 22.88, 26.23, and 27.34 MHz, is attributed to anisotropic features from the  $\text{H}_{\text{ol}}$ . The three signals are assigned to the  $x$ ,  $z$ , and  $y$  components of the hyperfine tensor in the order of the increasing frequency. Therein,  $x$  and  $y$  represent the directions in the  $\pi$  plane parallel and perpendicular to the C-H bond, respectively, while  $z$  is the direction of the  $2p_{\pi}$  axis at the  $\pi$  centre (see Discussion). The anisotropic coupling constants  $A_x = 0.594 \pm 0.005$ ,  $A_z = 0.834 \pm 0.005$ , and  $A_y = 0.913 \pm 0.005$  mT were readily derived from  $\nu_{\text{H}}$  and the positions of these signals (their low-frequency counterparts in the range of 1.7 to 6.3 MHz are again too weak to be detected). They yielded the value  $a_{\text{iso}} = 1/3(A_x + A_y + A_z) = 0.780 \pm 0.005$  mT which is equal to the coupling constant  $a(\text{H}_{\text{ol}})$  determined for  $\text{I}^{\ddagger}$  in the  $\text{CF}_2\text{ClCFCl}_2$  matrix. This result indicates that  $A_x$ ,  $A_y$ , and  $A_z$  have the same negative sign as  $a(\text{H}_{\text{ol}})$  (see above).

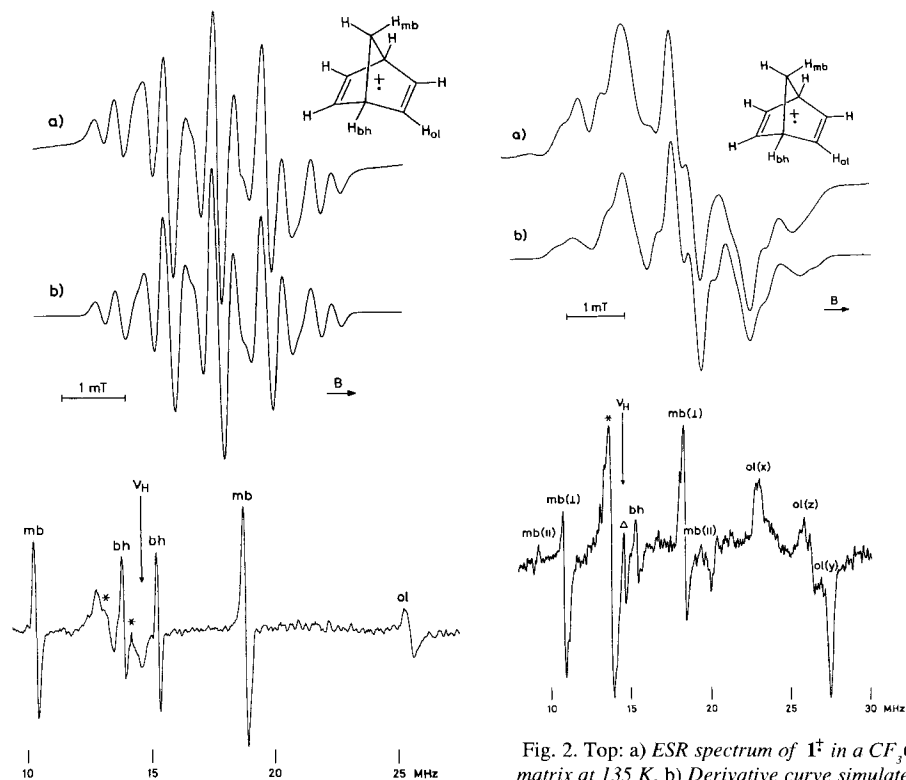
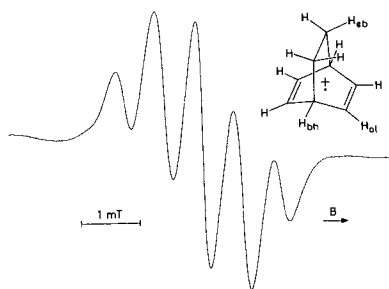


Fig. 1. Top: a) ESR spectrum of  $\text{I}^{\ddagger}$  in a  $\text{CF}_2\text{ClCFCl}_2$  matrix at 115 K. b) Derivative curve simulated with the use of isotropic coupling constants given in the text and the Table (line-shape: Gaussian; line-width: 0.2 mT). Bottom: proton ENDOR spectrum taken under the same conditions.  $^{19}\text{F}$  signals are marked by asterisks.

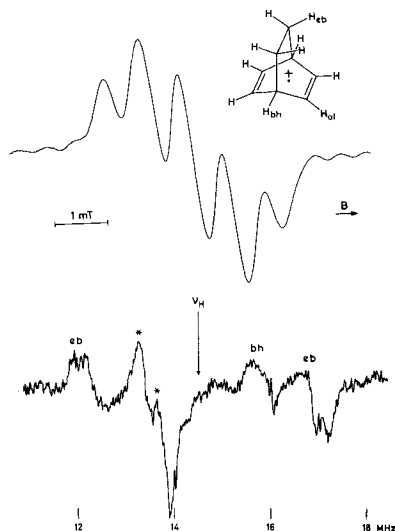
Fig. 2. Top: a) ESR spectrum of  $\text{I}^{\ddagger}$  in a  $\text{CF}_2\text{ClCFCl}_2$  matrix at 135 K. b) Derivative curve simulated with the use of the anisotropic coupling constants given in the text and the Table, along with a doublet hyperfine splitting of 0.29 mT (line-shape: Gaussian; line-width: 0.3 mT). Bottom: proton ENDOR spectrum taken under the same conditions.  $^{19}\text{F}$  matrix signal and a proton impurity signal are marked by an asterisk and a triangle, respectively.

It is noteworthy that the centre of the ESR spectrum (*Fig. 2a*) shows a hyperfine splitting which cannot arise from the three sets with an even number of equivalent protons. Computer simulation (*Fig. 2b*), thus, requires the use of an additional coupling constant of *ca.* 0.3 mT from a set with an odd number of nuclei having the spin quantum number  $l = 1/2$  or  $3/2$ . Obvious candidates are  $^{19}\text{F}$  or  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$  nuclei in  $\text{CF}_3\text{CCl}_3$ . The corresponding ENDOR signals must be broadened beyond recognition ( $^{35}\text{Cl}$ -,  $^{37}\text{Cl}$ -ENDOR spectra have not yet been observed [5c]).

*Bicyclooctadiene 2 in  $\text{CFCl}_3$ .* The ESR spectrum of  $2^\ddagger$  in a  $\text{CFCl}_3$  matrix at 155 K (*Fig. 3*) consists of a *quintet* spaced by  $0.676 \pm 0.008$  mT which is identified as  $a(\text{H}_{\text{ol}})$  of the four olefinic protons by analogy with the hyperfine data for  $1^\ddagger$ . Because of the large line-width (0.3 mT), the hyperfine splittings from the four ethano-bridge protons ( $\text{H}_{\text{eb}}$ ) and the two bridgehead protons ( $\text{H}_{\text{bh}}$ ) are unresolved. The corresponding ENDOR spectra, which could not be reliably analyzed, have not provided the pertinent information.



*Fig. 3.* ESR spectrum of  $2^\ddagger$  in a  $\text{CFCl}_3$  matrix at 155 K



*Fig. 4.* Top: ESR spectrum of  $2^\ddagger$  in a  $\text{CF}_3\text{CCl}_3$  matrix at 135 K. Bottom: corresponding proton ENDOR spectrum.  $^{19}\text{F}$  signals are marked by asterisks.

*Bicyclooctadiene 2* in  $CF_3CCl_3$ . The ESR spectrum of  $2^\ddagger$  in a  $CF_3CCl_3$  matrix at 135 K (Fig. 4, top) resembles that observed for  $2^\ddagger$  in glassy  $CFCl_3$ . This time, however, the poor resolution has been compensated by the information obtained from the corresponding proton ENDOR spectrum which clearly exhibits essentially isotropic signals for  $H_{eb}$  and  $H_{bh}$  (Fig. 4, bottom). The pair of more intense signals at 12.29 and 16.83 MHz, centred at  $\nu_H$  (14.56 MHz) is associated with  $a(H_{eb}) = 0.162 \pm 0.005$  mT (see *Discussion*). Only the high-frequency signal at 16.07 MHz can be observed for the  $H_{bh}$ , because the low-frequency counterpart is once more obscured by  $^{19}F$  signals (at ca. 13.9 and 13.5 MHz,  $a(^{19}F) = 0.14$  mT). From  $\nu_H$  and the position of the high frequency signal,  $a(H_{bh}) = 0.108 \pm 0.005$  mT was obtained. A weak signal representing one anisotropic feature of the four  $H_{oi}$  appeared at 25.1 MHz (not shown in Fig. 4). The pertinent isotropic coupling constant  $a(H_{oi}) = 0.69 \pm 0.01$  mT was determined by the simulation of the ESR spectrum (Fig. 4, top).

The hyperfine data for  $1^\ddagger$  and  $2^\ddagger$  in the various freon matrices are collected in the *Table*. By analogy to  $1^\ddagger$  and in accordance with the results of calculations (see below), the coupling constants  $a(H_{oi})$  and  $a(H_{bh})$  for  $2^\ddagger$  are assumed to be negative, while  $a(H_{eb})$  is given a positive sign. The g-factor of  $1^\ddagger$  and  $2^\ddagger$  is  $2.0030 \pm 0.0003$  throughout.

Table. Anisotropic and Isotropic Proton-Coupling Constants [mT] for the Radical Cations of Bicyclo[2.2.1]hepta-2,5-diene (**1**) and Bicyclo[2.2.2]octa-2,5-diene (**2**)

$1^\ddagger$			$2^\ddagger$	
	$CF_2ClCFCl_2$	$CF_3CCl_3$	$CF_3CCl_3$	$CFCl_3$
$H_{oi}$ (4 H)	-0.780 (0.80 <sup>a</sup> )	-0.594(x) -0.913(y) -0.834(z)	$H_{oi}$ (4 H)	-0.69 -0.676
$H_{mb}$ (2 H)	+0.304 (0.33 <sup>a</sup> )	+0.386(l) +0.263(l)	$H_{eb}$ (4 H)	+0.162 <sup>b</sup> )
$H_{bh}$ (2 H)	-0.049	-0.049	$H_{bh}$ (2 H)	-0.108 <sup>b</sup> )

<sup>a</sup>) [2]; Absolute value. <sup>b</sup>) Not determined.

**Discussion.** – *Spin Distribution.* Following an early PE-spectroscopic study of **1** [8a], the electronic structure of this diene has been a favourite research subject of theorists [8-13], because the two ethene  $\pi$  systems in **1** provide a typical example for through-space interaction [8b,c][9]. Due to such an interaction, the antisymmetric combination,  $b_2(\pi_-)$ , of the bonding ethene  $\pi$  orbitals lies above the symmetric one,  $a_2(\pi_+)$  [8-13]. This ‘natural’ MO sequence implies that  $b_2(\pi_-)$  should be regarded as the HOMO of **1** (Fig. 5). An analogous statement, based on PE spectroscopy and theory, holds for **2** [8a,c][14]. The HOMO of **2** is, thus, likewise considered as  $b_2(\pi_-)$  (Fig. 5), albeit the through-space interaction of the two ethene  $\pi$  systems ought to be less dominant in **2** than in **1** [15].

A single occupancy of the HOMO  $b_2(\pi_-)$  in  $1^\ddagger$  and  $2^\ddagger$  is tantamount to the unpaired electron residing at the four C  $\pi$  centres of the two double bonds, so that each centre bears a  $\pi$ -spin population of 0.25. The relatively large  $a(H_{oi})$  (the  $H_{oi}$  directly attached to the  $\pi$  centres are  $\alpha$ -protons), comply with such a spin population [6a][16]. As pointed out in the

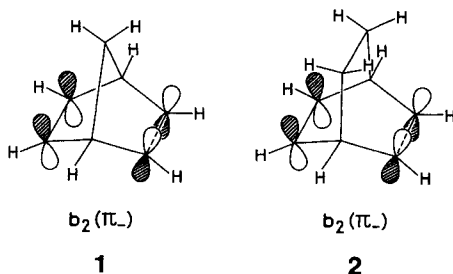


Fig. 5. Orbital diagrams of the HOMOs for bicyclo[2.2.1]hepta-2,5-diene (**1**; left) and bicyclo[2.2.2]octa-2,5-diene (**2**; right)

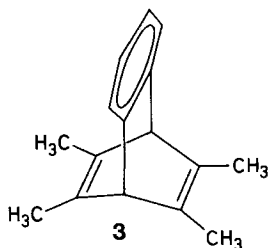
*Results*,  $a(H_{oi})$  should be negative; this sign is due to the mechanism of  $\pi$ - $\sigma$  spin polarization effective for  $\alpha$ -protons [6b]. A negative sign is also expected for the small coupling constants,  $a(H_{bh})$ , each of the ( $H_{bh}$ ) being separated in **1**<sup>+</sup> and **2**<sup>+</sup> from the  $\pi$  centres by one  $sp^3$ -hybridized C-atom ( $\beta$ -protons). These protons lie in the molecular mirror plane passing through the C-atoms of the bridgehead and the alkanone bridging groups. Since this plane is nodal for  $b_2(\pi_-)$ ,  $\pi$ - $\sigma$  spin delocalization (hyperconjugation), which is by far the most important mechanism of spin transfer to  $\beta$ -protons [6a][17], is ineffective in **1**<sup>+</sup> and **2**<sup>+</sup>. Consequently,  $\pi$ - $\sigma$  spin polarization, a mechanism usually neglected for  $\beta$ -protons, becomes prominent in this case, giving rise to the small and negative coupling constants  $a(H_{bh})$ . On the other hand, although each of the  $H_{mb}$  in **1**<sup>+</sup> and  $H_{eb}$  in **2**<sup>+</sup> is separated from the  $\pi$  centres by two  $sp^3$ -hybridized C-atoms ( $\gamma$ -protons), it is not surprising that the  $a(H_{mb})$  for **1**<sup>+</sup> and  $a(H_{eb})$  for **2**<sup>+</sup> are larger than  $a(H_{bh})$ . The magnitude and the positive sign of  $a(H_{mb})$  and  $a(H_{eb})$  can be accounted for by a long-range mechanism of  $\pi$ - $\sigma$  spin delocalization which is favoured by an approximate W arrangement of C- $H_{mb}$  and C- $H_{eb}$  bonds with respect to the  $2p_\pi$  axes at the olefinic  $\pi$  centres [19].

For **1**<sup>+</sup>, the allotment of a negative sign to  $a(H_{oi})$  and  $a(H_{bh})$  and a positive one to  $a(H_{mb})$  is justified by the results of CIDNP experiments [20]. Moreover, these signs as well as the relative absolute values of the three coupling constants are in agreement with *ab initio* calculation on **1**<sup>+</sup> (6-31 G\* basis set) [13]. For both, **1**<sup>+</sup> and **2**<sup>+</sup>, assignments and signs of the coupling constants have been corroborated by AM1 [21] and INDO [22] calculations performed in the present work. In the case of **2**<sup>+</sup>, these calculations support the assignment of the larger (positive) value of 0.162 mT to the  $H_{eb}$ , leaving the smaller (negative) one of 0.108 mT for the  $H_{bh}$ .

An antisymmetric combination,  $b_2(\pi_-)$ , of the two bonding ethene  $\pi$ -MOs also represents the singly occupied orbital of the radical cation **3**<sup>+</sup> which has been generated from the benzo derivative **3** of bicyclo[2.2.2]octa-2,5,7-triene (barrelene) with  $AlCl_3$  in fluid solution [23]. The prominent hyperfine feature of **3**<sup>+</sup> is the large coupling constant of 0.858 mT from the 12 protons of the four Me groups. This finding provides a further piece of evidence confirming the assignment of 0.676 mT to the four  $H_{oi}$  in **2**<sup>+</sup>, since a comparable relative

<sup>2)</sup> An  $sp^3$ -hybridized bridgehead C-atom, bearing a  $H_{bh}$  in **1**<sup>+</sup> and **2**<sup>+</sup> is linked to *two*  $\pi$  centres. According to Whiffen [18], the hyperconjugative contribution to the coupling constant of such a  $\beta$ -proton is proportional to  $(c_1 + c_2)^2$ , where  $c_1$  and  $c_2$  are the LCAO coefficients of the two centres in the singly occupied orbital. For a  $H_{bh}$  and the MO  $b_2(\pi_-)$  in **1**<sup>+</sup> and **2**<sup>+</sup>,  $c_1 = -c_2$ , and hence, this contribution is zero.

increase in the absolute value of the coupling constant is usually found for radical cations, when an  $\alpha$ -proton at a  $\pi$  centre bearing high spin population is replaced by a Me substituent with three  $\beta$ -protons<sup>3</sup>).



*Hyperfine Anisotropy.* A few remarks on the anisotropic hyperfine features observed in the ESR and ENDOR spectra of  $\mathbf{1}^\ddagger$  in the  $\text{CF}_3\text{CCl}_3$  matrix (*Fig. 2*) are required here.

i) As expected, the hyperfine anisotropy is particularly large for the four  $\alpha$ -protons  $\text{H}_{\text{ol}}$ . The contributions by anisotropy to the hyperfine tensor for these protons,  $T_x = A_x - a_{\text{iso}}$ ,  $T_y = A_y - a_{\text{iso}}$ , and  $T_z = A_z - a_{\text{iso}}$ , can be related to the analogous values for the  $\alpha$ -protons in the  $\cdot\text{CH}(\text{COOH})_2$  radical:  $T_x = +1.12 \pm 0.07$  mT,  $T_y = -1.09 \pm 0.07$  mT, and  $T_z \approx 0$  [25] (the directions of  $x$ ,  $y$ , and  $z$  have been specified, see *Results*; their notation differs from the one used previously [25] in that  $x$  and  $z$  have been interchanged). The relation between the two sets of values  $T_x$ ,  $T_y$ , and  $T_z$  has served for the assignment of the coupling constants,  $A_x$ ,  $A_y$ , and  $A_z$  of the  $\text{H}_{\text{ol}}$  in  $\mathbf{1}^\ddagger$ , so that the corresponding contributions by anisotropy to the hyperfine tensor of these protons are:

$$T_x = -0.594\text{mT} - (-0.780\text{mT}) = +0.186 \text{ mT},$$

$$T_y = -0.913\text{mT} - (-0.780\text{mT}) = -0.133 \text{ mT}, \text{ and}$$

$$T_z = -0.834\text{mT} - (-0.780\text{mT}) = -0.054 \text{ mT}.$$

ii) The hyperfine anisotropy tensor of the two  $\text{H}_{\text{mb}}$  is apparently axial with

$$\begin{aligned} a_{\text{iso}} - A_{\perp} &= +0.304\text{mT} - (+0.263\text{mT}) = +0.041 \text{ mT} \\ &= 1/2(A_{\parallel} - a_{\text{iso}}) = 1/2[+0.386\text{mT} - (+0.304\text{mT})]. \end{aligned}$$

The direction of the principal axis relevant to  $A_{\parallel}$  cannot be given without further experimental and/or theoretical evidence. It may tentatively be identified with the molecular symmetry axis  $C_2$  which bisects the H-C-H angle in the methano bridging group. Rotation of the molecule about this axis would then lead to an averaging of the tensor components in the plane perpendicular to  $C_2$ , thus, yielding  $A_{\perp}$ .

iii) The anisotropy contributions to the coupling constant of the  $\text{H}_{\text{bb}}$  in  $\mathbf{1}^\ddagger$  must be less than 0.01 mT, since the pertinent ENDOR signal (*Fig. 2*) does not exhibit measurable deviations from an isotropic shape. Considering the small magnitude (0.049 mT) of  $a(\text{H}_{\text{bb}})$ , this finding is not unexpected.

<sup>3</sup>) For instance, the coupling constant of the 12  $\beta$ -protons in the radical cation of 9,10-dimethylanthracene is 0.800 mT, as compared with the absolute value of 0.653 mT for the two  $\alpha$ -protons in the 9,10-positions of the unsubstituted species [24].

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