The Radical Cation of Bicyclo[2.2.2]octa-2,5,7-triene (Barrelene). An E.S.R. and ENDOR Study†

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The radical cation of bicyclo[2.2.2]octa-2,5,7-triene (barrelene) in a non-degenerate A_2' ground-state has been characterized by its hyperfine data with the use of e.s.r. and ENDOR spectroscopy (coupling constants: 0.603 mT for the six alkenic and 0.115 mT for the two bridgehead protons).

Bicyclo[2.2.2]octa-2,5,7-triene (barrelene; **1**)[2] is an intriguing molecule of D_{3h} symmetry and of a Möbius-type.[2b,3] It has been the subject of a photoelectron spectroscopic study,[4] as well as of many other experimental and theoretical investigations.[2,5,6] The electronic structure of (**1**) has usually been discussed in terms of through-space and through-bond interactions.[3—5,7] The prediction that the radical cation should exist in a non-degenerate A_2' ground state[4—6] has not yet been verified by e.s.r. spectroscopy which is the most powerful tool for exploring the structure of paramagnetic species. To our knowledge, only the radical cations of some derivatives of (**1**), in which the symmetry is lowered from D_{3h} to C_{2v}, have been investigated so far by this method. Thus, a few years ago, Davies and co-workers[8] reported on the e.s.r. spectra of the radical cations of two methyl-substituted benzobarrelenes, (**2**) and (**3**), in fluid solution and, more recently, an e.s.r. and ENDOR study has been performed on the radical cation of bicyclo[2.2.2]octa-2,5-diene (dihydrobarrelene; **4**) in Freon matrices.[1] As will be specified, the electronic structures of (**2**)·+, (**3**)·+, and (**4**)·+ greatly differ from that of the parent radical cation (**1**)·+ which is characterized here by its hyperfine data with the use of both e.s.r. and ENDOR spectroscopy.

Hydrocarbon (**1**) was synthesized according to a procedure described elsewhere.[9] γ-Irradiation of (**1**) in a $CF_2ClCFCl_2$ matrix at 77 K yielded (**1**)·+, the e.s.r. spectrum of which, taken at 114 K, is shown at the top of Figure 1. The septet spaced by 0.6 mT is clearly diagnostic of a hyperfine interaction with the six alkenic (al) protons. Owing to the large line-width (0.3 mT), hyperfine splittings from the two bridgehead (bh) protons remained unresolved. The corresponding proton ENDOR spectrum, displayed at the bottom of Figure 1, exhibits isotropic features. The signals from the two bh-protons appear at 12.95 and 16.17 MHz, *i.e.*, they are centred at the frequency, ν_H 14.56 MHz, of the free proton.[10] A coupling constant $a(H_{bh})$ 0.115 ± 0.002 mT is associated with these signals. For the six al-protons only the high-

frequency signal at 23.01 MHz could be observed, because its low-frequency counterpart (at *ca.* 6 MHz) was too weak to be detected. A coupling constant $a(H_{al})$ 0.603 ± 0.008 mT has been derived from ν_H and the position of the high-frequency signal. In addition to the protons of (**1**)·+, ^{19}F nuclei of the matrix give rise to two ENDOR signals centred at 13.70 MHz. From the positions of these signals at 13.29 and 14.11 MHz, a ^{19}F coupling constant of 0.029 ± 0.001 mT has been obtained.

The e.s.r. hyperfine components of (**1**)·+ can readily be saturated (this is a prerequisite for the observation of the ENDOR spectrum[10]), and the ENDOR signals are relatively narrow like those found for freely rotating radicals in fluid solution. These findings indicate that the electron spin relaxation time is not shortened by spin–orbit coupling, as would be the case for radical cations subject to the Jahn–Teller distortion.[11] Thus, the saturation behaviour of (**1**)·+ confirms the prediction[4—6] that the ground-state of this radical cation ought to be non-degenerate. Theory requires that the singly occupied orbital of (**1**)·+ should be represented by a MO a_2' which is of 'pure' π-character and which can be regarded as an antisymmetric combination of three bonding ethene π-MO's
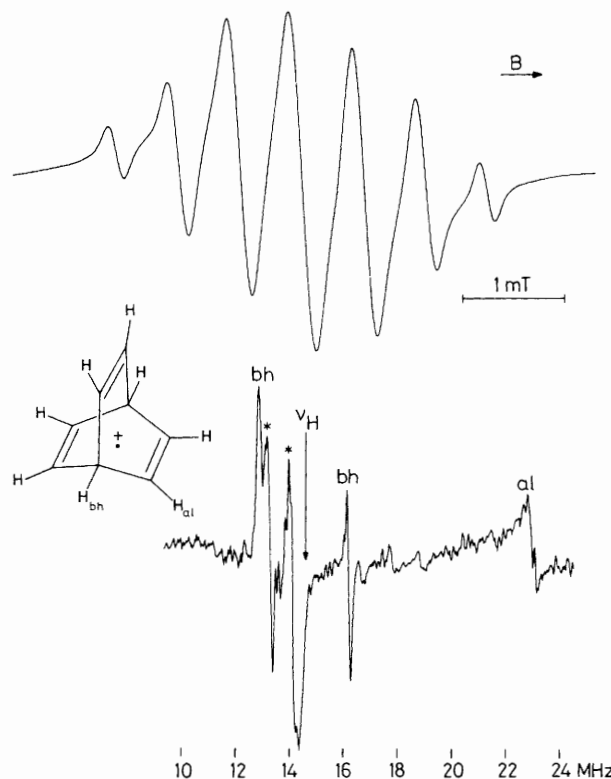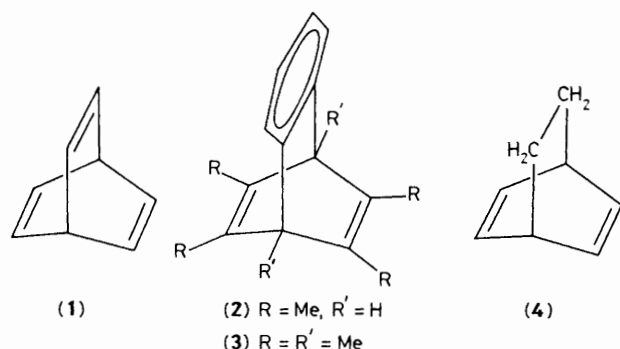

Figure 1. Top: e.s.r. spectrum ($g = 2.0025 \pm 0.0002$) of (**1**)·+ in a $CF_2ClCFCl_2$ matrix at 114 K. Bottom: corresponding ENDOR spectrum. ^{19}F signals are marked by asterisks.

(**1**)

(**2**) R = Me, R' = H
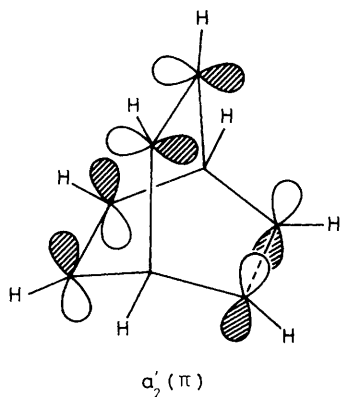(**3**) R = R' = Me

(**4**)

$a'_2 (\pi)$

Figure 2. Schematic representation of the MO a'_2.

(Figure 2). Such an occupancy implies that each of the six equivalent alkenic carbon atoms bears a π-spin population ρ^π of 1/6. The observed coupling constant, $a(H_{al})$ 0.603 mT, is compatible with such a spin population, although the ratio $a(H_{al})/\rho^\pi$ 3.6 mT seems higher than usually found for protons directly attached to π-centres (α-protons).[12] Owing to the mechanism for π–σ spin polarization relevant to such protons, $a(H_{al})$ should be negative. In general, π–σ spin delocalization (hyperconjugation) is by far the most important mechanism of spin transfer to β-protons which, like the bh-protons in (1)$^{\cdot+}$, are separated by one sp^3-hybridized carbon atom from the π-centres.[12,13] However, since the bh-protons lie in the three nodal planes of a'_2, π–σ spin delocalization is ineffective in this case. As a consequence, π–σ spin polarization, which is in most cases negligible for β-protons,[13] becomes prominent, and gives rise to the small (and expectedly negative) coupling constant $a(H_{bh})$ 0.115 mT. It is noteworthy that the relative values and the negative sign of both $a(H_{al})$ and $a(H_{bh})$ are reproduced by INDO calculations[14] for (1)$^{\cdot+}$, which have been based on the geometry determined for this radical cation by the MNDO method.[15]

On going from the parent radical cation (1)$^{\cdot+}$ to (2)$^{\cdot+}$, (3)$^{\cdot+}$, and (4)$^{\cdot+}$, one of the alkenic π-systems is replaced by a benzene moiety or by an ethano bridging group. The singly occupied orbital is then transformed from a'_2 in D_{3h} to b_2 in C_{2v}, and the π-spin population becomes essentially restricted to the two remaining ethene π-systems.[1,8] In fact, while the coupling constants $a(H_{bh})$ are almost equal for (4)$^{\cdot+}$ (0.108

mT)[1] and (1)$^{\cdot+}$ (0.115 mT), the observed absolute value of $a(H_{al})$ is larger for (4)$^{\cdot+}$ (0.676 mT)[1] than for (1)$^{\cdot+}$ (0.603 mT). However, this $a(H_{al})$ value for (4)$^{\cdot+}$ is considerably smaller than that expected (0.603 mT $\times$ 6/4 = 0.905 mT) for the π-spin population being distributed among four instead of six alkenic carbon atoms. The discrepancy may be traced back to the character of the singly occupied orbitals. Whereas a'_2 in (1)$^{\cdot+}$ is a 'pure' π-MO with no π –σ spin delocalization, the corresponding MO b_2 in (4)$^{\cdot+}$ can 'mix' with some σ-orbitals by through-bond interaction.

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