119. Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices

Part 1

The Radical Cation of s-*trans*-Buta-1,3-diene

by **Fabian Gerson*** and **Xue-Zhi Qin**

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

(6.VI.88)

Precise values of the proton coupling constants have been determined from the ENDOR spectra of the radical cation of s-*trans*-buta-1,3-diene generated from the neutral compound by γ irradiation in a $CFCl_3$ matrix at 77 K. These values are 1.119 and 1.050 mT for the pairs of *exo*- and *endo*-protons in the 1,4-positions, respectively, and 0.283 mT for the pair of protons in the 2,3-positions. A general TRIPLE resonance spectrum proves that all coupling constants have the same sign which should be negative by theory. Evidence by experiment and theory indicate that the s-*trans*-configuration of the neutral compound is retained upon ionization.

Introduction. – To our knowledge, ENDOR and TRIPLE resonance spectroscopy [1] have not yet been applied to organic radical cations in freon matrices [2]. Use of the ENDOR technique in this field of research can lead to an enormous improvement in the spectral resolution and in the accuracy of the hyperfine data. This effect is demonstrated by the present report on an application of ENDOR and TRIPLE resonance spectroscopy to the radical cation of s-*trans*-buta-1,3-diene (**1**).

The radical cation $\mathbf{1}^{+}$, a 4-centre, 3π-electron system, is one of the simplest paramagnetic organic species. ESR signals attributed to $\mathbf{1}^{+}$ were first detected in 1971 for **1** absorbed on silica gel and irradiated by γ rays at liquid N_2 temperature [3]. Almost ten years later, *Shida et al.* [4] observed an ESR spectrum of $\mathbf{1}^{+}$ upon γ irradiation of **1** in a $CFCl_3$ matrix at 77 K. Because of the poor resolution achieved under the above-mentioned conditions [3] [4], only approximate values could be determined for the proton coupling constants. By contrast, ENDOR spectroscopy has enabled us to characterize $\mathbf{1}^{+}$ by its hyperfine data with high precision. Moreover, the relative signs of the coupling constants have been derived from a general TRIPLE resonance experiment.

Results. – The radical cation $\mathbf{1}^{+}$ was generated from the neutral compound by γ rays (^{60}Co source) in a $CFCl_3$ matrix at 77 K, as described in [4]. The *Figure* shows the ESR spectrum of $\mathbf{1}^{+}$ taken at 130 K. It consists of five broad components spaced by *ca.* 1.1 mT, characteristic of a hyperfine interaction with four equivalent or nearly-equivalent protons ($g = 2.0029 \pm 0.0002$). The corresponding proton ENDOR spectrum is reproduced at the bottom of the *Figure*. The observed isotropic ENDOR signals, one at 10.59 MHz (*i.e.* below the free-proton frequency ν_H of 14.55 MHz) and three at 18.51, 29.26, and 30.22 MHz (*i.e.* above ν_H), are relatively narrow for α-protons at π-centres of high-spin

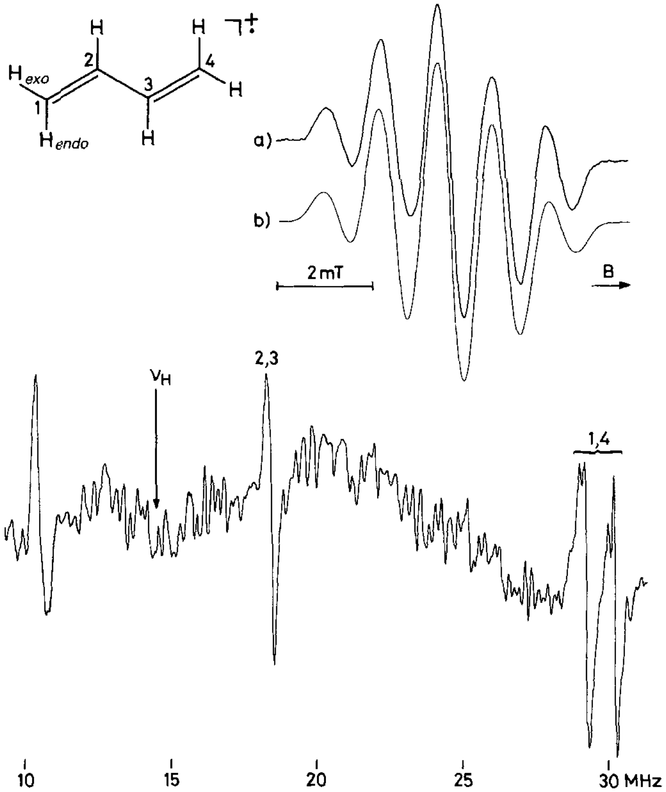

Figure. Top: *ESR spectra of* $\mathbf{1}^{+}$ (*a*) experimental, taken on a *Varian-E9* spectrometer; *b*) simulated with the coupling constants given in the text and in the *Table;* line-width, 0.5 mT; line-shape, *Gaussian*). Bottom: *Proton ENDOR spectrum of* $\mathbf{1}^{+}$ (taken on a *Bruker-ESP-300* spectrometer system).

population in a radical held in rigid solution. These signals yield coupling constants of 0.283 ± 0.002, 1.050 ± 0.005, and 1.119 ± 0.005 mT, each for a pair of equivalent protons. Moreover, a general TRIPLE resonance experiment performed on the ENDOR spectrum [1] indicates that all these values have the same sign. Since the two larger coupling constants (1.050 and 1.119 mT), due to the two pairs of protons in the 1,4-positions are undoubtedly negative, this sign must also be allotted to the smaller coupling constant (0.283 mT) arising from the pair of protons in the 2,3-positions. By analogy with the hyperfine data for the allyl radical [5] and guided by an INDO calculation [6], 1.119 mT is assigned to the two equivalent *exo*-protons, leaving 1.050 mT for their *endo*-counterparts.

Discussion. – In the presentation of the experimental results, we have tacitly assumed that the radical cation of **1** has the same configuration as the neutral compound, *i.e.* s-*trans*→s-*cis* isomerization does not occur upon the ionization process $\mathbf{1}\rightarrow\mathbf{1}^{+}$. This assumption is supported by both INDO [6] and UHF/AM1 [7] calculations which predict that the s-*trans*-configurated radical cation $\mathbf{1}^{+}$ should be lower in energy by 7–8 kJ/mol than its s-*cis*-isomer. Considering the relatively small energy difference and the approximate nature of the semiempirical methods, one may argue that $\mathbf{1}^{+}$ can exist as an equilibrium mixture of s-*trans*- and s-*cis*-isomers. The existence of such an equilibrium at 130 K must, however, be disregarded for the following reasons.

i) The ENDOR spectrum of $\mathbf{1}^{+}$ reveals the presence of only one coupling constant for the pair of protons in the 2,3-positions. This value can be due to only one configuration, unless the two protons have equal coupling constants in the s-*trans*- and s-*cis*-configurated species. Such an equality should be excluded by INDO calculations which yield a substantially larger value for the s-*cis*- than for the s-*trans*-configuration. Also, a coupling constant of 0.42 mT, as compared to 0.283 mT for $\mathbf{1}^{+}$, is exhibited by the analogous pair of protons in the 2,3-positions of the radical cation of cyclohexa-1,3-diene [4] which contains a butadiene-π-system in a s-*cis*-configuration.

ii) The ENDOR signals attributed to the pairs of *exo*- and *endo*-protons in the 1,4-positions have practically equal intensities *(Figure)*. Alternatively, it is possible to associate these signals with two different configurations, each giving rise to one coupling constant of four equivalent or nearly-equivalent protons in the 1,4-positions. However, in view of the equal intensities of the pertinent signals, such an interpretation would mean that the s-*trans*- and s-*cis*-configurations are almost equally populated in $\mathbf{1}^{+}$. In turn, this equality would require that the two configurations are near-degenerate with respect to their free energies, which is highly improbable.

In conclusion, the exclusive occurrence of the s-*trans*-configuration of $\mathbf{1}^{+}$ appears to be well established by both theory and experiment.

Table. *Proton Coupling Constants* [mT] *for the Radical Ions of* s-trans-*Buta-1,3-diene* (**1**)

Position	$\mathbf{1}^{+}$ a)	$\mathbf{1}^{+}$ b)	$\mathbf{1}^{+}$ c)	$\mathbf{1}^{\bar{\cdot}}$ d)
1,4	1.14 (4 H)	1.22 (4 H)	1.119 (2 H_{exo}) 1.050 (2 H_{endo})	0.762 (4 H)
2,3	0.32 (2 H)	0.20 (2 H)	0.283 (2 H)	0.279 (2 H)

a) [3]. b) [4]. c) This work. d) [8].

In the *Table*, the coupling constants we measured are compared with those given in [3] [4] as well as with the analogous values found for the radical anion $\mathbf{1}^{\bar{\cdot}}$ in fluid solution [8]. The hyperfine data for $\mathbf{1}^{+}$ and $\mathbf{1}^{\bar{\cdot}}$ bear out the expectation that the α-proton coupling constants for the two radical ions of the same alternant hydrocarbon should be of similar size. The finding that the value for the protons in the 1,4-positions increases as much as by a factor of 1.4 on going from $\mathbf{1}^{\bar{\cdot}}$ (0.762 mT) to $\mathbf{1}^{+}$ (average 1.085 mT) is remarkable, although it is in line with the general behaviour of such radical ions; a marked increase in the largest coupling constant is usually observed, when one passes from the anion to the corresponding cation [9]. There is also a consistency of our values for $\mathbf{1}^{+}$ in a rigid matrix and those reported for the radical cations of highly alkyl-substituted buta-1,3-dienes in fluid solution [10].

It is noteworthy that the coupling constants of *exo*- and *endo*-protons in the 1,4-positions of $\mathbf{1}^{+}$ differ by 0.07 mT, whereas the analogous difference for $\mathbf{1}^{\bar{\cdot}}$ must be smaller than the line-width of 0.03 mT [8]. The two pairs of protons can hardly be considered as effectively equivalent in the ESR spectrum of $\mathbf{1}^{\bar{\cdot}}$, because rotation about the C(1)–C(2) and C(3)–C(4) bonds (*Hückel* π-bond order 0.671) is unlikely to be fast on the hyperfine time-scale at 195 K [8].

We are obliged to Prof. *E. Haselbach*, Université de Fribourg, for the permission to use their ^{60}Co source of γ rays. This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Financial assistance by *Ciba-Geigy AG, Sandoz AG*, and *F. Hoffmann-La Roche & Co. AG*, Basel, is acknowledged.

REFERENCES

[1] H. Kurreck, B. Kirste, W. Lubitz, *Angew. Chem.* **1984,** *96*, 171; *ibid. Int. Ed.* **1984,** *23*, 173.
[2] T. Shida, E. Haselbach, T. Bally, *Acc. Chem. Res.* **1984,** *17*, 180; M. C. R. Symons, *Chem. Soc. Rev.* **1984,** *13*, 412.
[3] T. Shiga, A. Lund, P. O. Kinell, *Acta Chem. Scand.* **1971,** *25*, 1508.
[4] T. Shida, Y. Egawa, H. Kubodera, *J. Chem. Phys.* **1980,** *73*, 5963.
[5] J. K. Kochi, P. J. Krusic, *J. Am. Chem. Soc.* **1968,** *90*, 7157.
[6] J. A. Pople, D. L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970.
[7] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985,** *107*, 3902.
[8] D. H. Levy, R. L. Myers, *J. Chem. Phys.* **1964,** *41*, 1062.
[9] See, *e.g.*, F. Gerson, 'High Resolution ESR Spectroscopy', Wiley, New York, and Verlag Chemie, Weinheim, 1970, Chapt. 2.1.
[10] J. L. Courtneidge, A. G. Davies, *J. Chem. Soc., Chem. Commun.* **1984,** 136; *Acc. Chem. Res.* **1987,** *20*, 90.