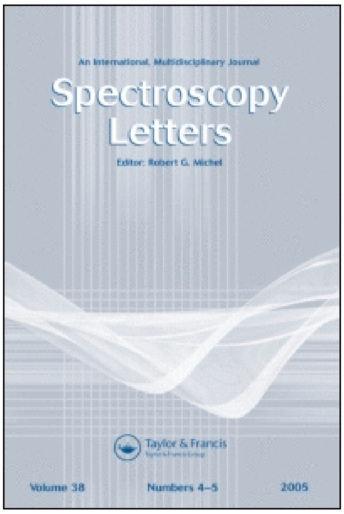

**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Electron Spin Resonance Spectra and Indo Calculation of the Cyclooctatrienyl Radical

A. R. McIntosh[a]; D. R. Gee[a]; J. K. S. Wan[a]
[a] Department of Chemistry, Queen's University, Kingston, Ontario, Canada

**To cite this Article** McIntosh, A. R. , Gee, D. R. and Wan, J. K. S.(1971) 'Electron Spin Resonance Spectra and Indo Calculation of the Cyclooctatrienyl Radical', Spectroscopy Letters, 4: 7, 217 — 225
**To link to this Article: DOI:** 10.1080/00387017108064642
**URL:** http://dx.doi.org/10.1080/00387017108064642

SPECTROSCOPY LETTERS, 4(7), 217-225 (1971)

# ELECTRON SPIN RESONANCE SPECTRA AND INDO CALCULATION OF THE CYCLOOCTATRIENYL RADICAL

A.R. McIntosh, D.R. Gee, and J.K.S. Wan

Department of Chemistry, Queen's University
Kingston, Ontario, Canada

Cyclooctatetraene $C_8H_8$, although a very reactive compound, is remarkably resistant to gamma irradiation[1]. Liquid phase radiolysis at high dose[1,2], 30-50 Mrad, yields hydrogen, acetylene, benzene and some polymeric material. Such radiation resistance is rather surprising since gaseous $C_8H_8$ readily undergoes photoisomerisation to styrene and photodecomposition to give benzene and acetylene[3,4]. More recent photochemical studies at lower temperatures also report bicyclo-4.2.0-octa-2,4,7-triene[5] and semibullvalene[6] as reaction products.

E.s.r. spectra assigned to the $C_8H_8^-$ radical anion have been reported when $C_8H_8$ is reduced in alkali metal tetrahydrofuran solutions at 173°K[7]. The distribution of the unpaired electron is symmetrical and the spectra consist of nine lines each separated by 3.209 G, suggesting a planar configuration[7]. Parallel studies on alkyl substituted $C_8H_8$[8] and cyclooctatetraene-1-d[9] have also been reported.

Recently Wood and Lloyd[10] have found that specifically incorporated additives in an adamantane solid matrix can be selectively damaged by ionizing radiation to yield paramagnetic species with isotropic e.s.r. spectra. Using this technique, we have observed[11] the isotropic e.s.r. spectra of a variety of alkyl substituted cycloalkenyl radicals by γ-irradiation of the parent olefins doped in an adamantane matrix. This investigation reports the analysis of the complex e.s.r. spectra which are due to the trapped cyclooctatetraene anion radical $C_8H_8^-$ and the neutral cyclooctatrienyl radical $C_8\dot{H}_9$, when cyclooctatetraene doped in an adamantane matrix is γ-irradiated. Spectral parameters for $C_8\dot{H}_9$ are obtained by computer simulation and the assignment of a planar structure to the radical is substantiated by an INDO calculation. The radiolysis of this system thus appears quite different from those with cyclomonoolefins. While the cyclomonoolefins do not trap electrons to give radical anions in the matrix[11], cyclooctatetraene is found to be an efficient electron scavenger in the solid matrix.

A typical e.s.r. spectrum observed after $C_8H_8$ doped into an adamantane matrix was irradiated is shown in Fig. 1. The spectrum was obtained at room temperature at a microwave attenuation of 20 db. The difference in the intensities and line widths between the central and outer lines of the spectrum led us to the conclusion that there were at least two different paramagnetic species. Increasing the microwave power by decreasing the attenuation of the klystron to 3 db changed the spectrum to the one shown in Fig. 2a, in which one of the paramagnetic species has apparently been saturated.

Inspection of Fig. 2a reveals a pattern of nine lines with a splitting of 3.21 gauss and their intensities are

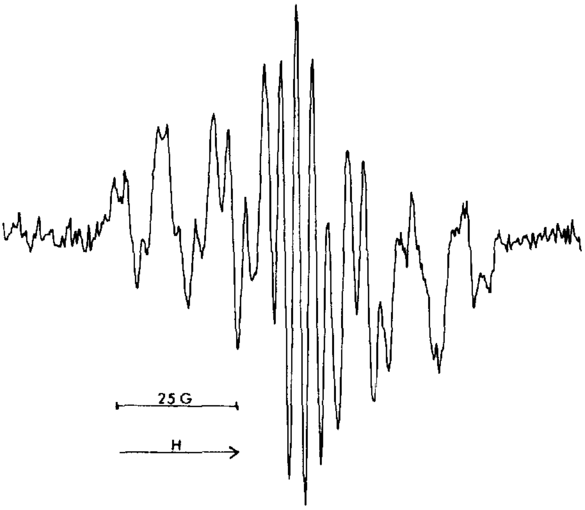

FIG. 1

The e.s.r. spectrum of radicals from γ-irradiation in adamantane of cyclooctatetraene, recorded at room temperature and low microwave power.

approximately binomial. The saturation properties of this species must be such that the spin-lattice relaxation time is relatively short. Such properties are found in anion or cation radicals with orbitally degenerate ground state[12]. The observed splitting constant of 3.21 gauss agrees with the literature assignment of the radical anion $C_8H_8^-$ [7]. The radical cation $C_8H_8^+$ has been recently reported to exhibit eight equivalent protons with a splitting constant of 1.5 G[13].

While the planar structure of $C_8H_8^-$ has been established[7], Dessau[13] proposed a nonplanar structure for $C_8H_8^+$ based on the theoretical prediction by Dewar et al[14]. To determine whether a nonplanar $C_8H_8^+$ could lead to eight incidentally equivalent protons in hyperfine splitting, we carried out here an INDO calculation of the proton splittings using the bond lengths

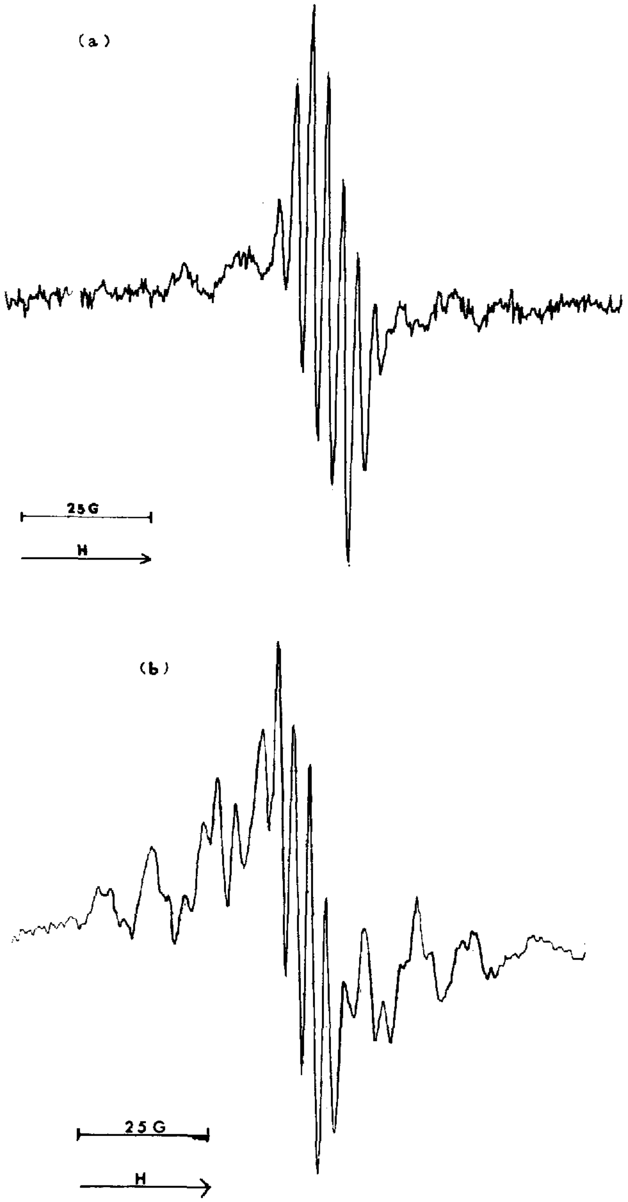

FIG. 2

The e.s.r. spectra of radicals from γ-irradiation in adamantane of cyclooctatetraene; (a) recorded at room temperature and high microwave power; (b) recorded at 85°C and low microwave power.

and angles reported by Traetteberg[15]. Assuming $D_{2d}$ symmetry for the nonplanar $C_8H_8^+$ with opposite carbon-carbon double bonds taken as parallel, the proton hyperfine splitting was +2.1 G for all eight protons. This value compares favourably with the experimental value of 1.5 G[13]. It appears reasonable that the nonplanar $C_8H_8^+$ could exhibit a nine-line pattern spectrum but with splitting less than that of the planar anion. The experimental spectrum in Fig. 2a is therefore assigned to $C_8H_8$.

When the sample temperature was progressively raised within the microwave cavity, the intensity of the spectrum in Fig. 2a recorded at high microwave power gradually decreased and had diminished markedly at 85°C. At that point reduction of the microwave power to the high klystron attenuation of 15 db gave a new spectrum shown in Fig. 2b. An identical spectrum was obtained from computer subtraction of that of Fig. 2a from the original spectrum of Fig. 1. It appeared clear however that there was still a minor component due to $C_8H_8^-$ present in Fig. 2b, but the other major radicals were relatively less stable than $C_8H_8^-$ at high temperature.

To identify the major radicals responsible for the spectrum in Fig. 2b, we have considered some of the relatively stable radicals such as $C_8\dot{H}_9$. A series of INDO calculations was performed on various geometrical models for the cyclooctatrienyl ($C_8\dot{H}_9$) radical. The calculated proton hyperfine splittings were then compared with the experimental spectrum. These calculations are summarized in Table 1. A description of the models employed is now given where, for the most part,

TABLE 1

Proton Hyperfine Splittings for $C_8\dot{H}_9$ from INDO Calculations

| | Models | | | Experimental Values |
|---|---|---|---|---|
| | I | II | III | |
| Angle $\theta^{o}$ | 0 | 30 | 60 | -- |
| Proton Splitting (gauss) | | | | |
| $a_{H_1}$ ($CH_2$) | +37.5 | +26.4 | +23.5 | 21.0 |
| $a_{H_2}$ ($CH_2$) | +37.5 | + 7.3 | + 1.1 | 10.5 |
| $a_{H_3}$ | -11.3 | - 7.4 | - 3.0 | 7.4 |
| $a_{H_4}$ | + 5.8 | + 9.3 | +15.5 | 9.3 |
| $a_{H_5}$ | -10.3 | - 9.9 | - 9.0 | 9.9 |
| $a_{H_6}$ | + 6.8 | + 6.5 | + 6.2 | 6.5 |
| $a_{H_7}$ | -10.3 | - 9.9 | - 9.0 | 9.9 |
| $a_{H_8}$ | + 5.8 | + 9.3 | +15.5 | 9.3 |
| $a_{H_9}$ | -11.3 | - 7.4 | - 3.0 | 7.4 |

the $C_8\dot{H}_9$ models are planar. Model I was completely planar with a regular octagon of eight carbon atoms for which the assumed carbon-carbon bond distance was taken as 1.34 Å. For Model I, the two hydrogen atoms bonded to the same carbon atom were perpendicular to the plane of the molecule with the H-C-H angle between them taken as 109.47°. Models II and III were slight variations on a puckered triangle of three carbon atoms inclined at varying angles to the main plane of the molecule. In fact, only the methylene carbon atom in each case was taken out of the plane of the molecule, the other atomic positions in each model being identical with those of Model I. The angle of inclination $\theta$ of the puckered triangle relative to the main molecular plane for Models II and III, was taken respectively as $30^{\circ}$ and $60^{\circ}$. Also the angles between the carbon and hydrogen atoms substituted at the methylene carbon in Models II and III were taken as $109.47^{\circ}$.

Computer simulated spectra as predicted by the theoretical hyperfine splittings listed in Table 1 indicate that Model II could account for most of the features in the experimental spectrum in Fig. 2b. A better fit to the experimental spectrum could be obtained when the methylene proton splittings were adjusted by some averaging to the experimental values.

Since an experimental spectrum of pure $C_8\dot{H}_9$ radicals could not be obtained even at higher temperatures and low microwave power, a computer program was used to simulate composite spectra of a mixture of $\dot{C}_8H_9$ and $C_8H_8^-$ in various proportions. The simulated spectra were given Lorentzian line widths of 1.0 G and 1.7 G for $C_8\dot{H}_9$ and $C_8H_8^-$ respectively, and the centre of the $C_8H_8$ component was shifted 1.0 G to higher field relative to that of the $\dot{C}_8H_9$. The "experimental" hyperfine splittings of $\dot{C}_8H_9$ as listed in Table 1 were used in all simulated spectra. Thus, Fig. 3a is the computed spectrum of pure $\dot{C}_8H_9$ radicals and Fig. 3b gives the simulated composite spectrum of a mixture of $\dot{C}_8H_9$ and $C_8H_8^-$ in a 2 to 1

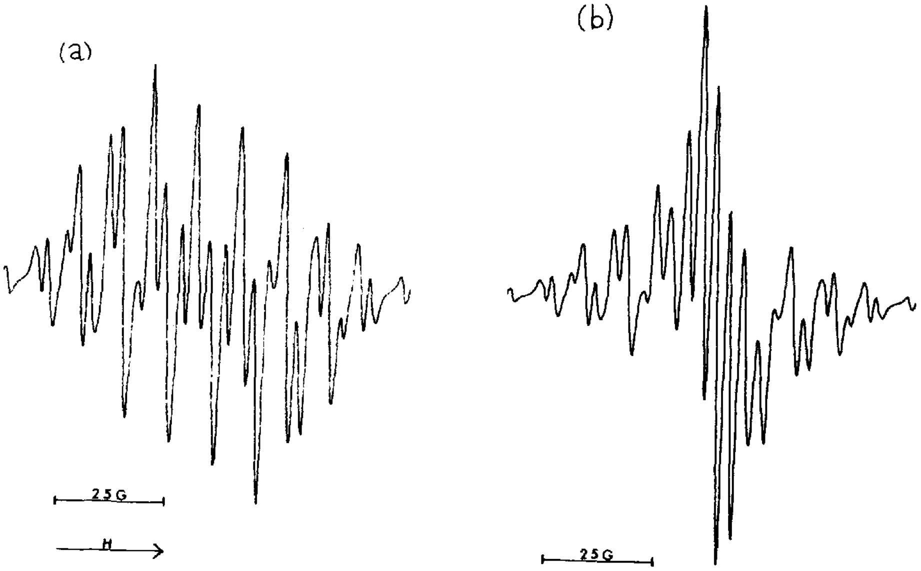

FIG. 3

Computer simulated spectra for: (a) $\dot{C}_8H_9$ radicals; (b) a mixture of 2 to 1 $\dot{C}_8H_9$ and $C_8H_8^-$.

mole ratio. It is observed that Fig. 3b fits reasonably well with the experimental spectrum at 85°C in Fig. 2b. It seems reasonable to conclude that the spectra shown in Fig. 1 and Fig. 2b arise from a mixture of trapped $C_8H_8^-$ radical anions and $\dot{C}_8H_9$ radicals. The conjugated $\dot{C}_8H_9$ radical is found to be planar with the two methylene protons locked in a fixed orientation relative to the remainder of the molecule.

Cyclooctatetraene doped in the adamantane matrix probably serves as an electron scavenger leading to stable $C_8H_8^-$ radical anion:

$$C_{10}H_{16}\text{(adamantane)} \rightsquigarrow C_{10}H_{16}^+ + e^-$$

$$e^- + C_8H_8 \longrightarrow C_8H_8^-$$

It is not certain how the radical $C_8\dot{H}_9$ is produced, as there are a number of possible mechanisms.

## ACKNOWLEDGMENTS

The authors are indebted to Professor J.A. Stone for helpful discussions. Financial support by the National Research Council of Canada and the Defence Research Board is gratefully acknowledged.

## REFERENCES

(1) S. Shida, H. Yamazaki and S. Arai, J. Chem. Phys., 29 245 (1958).
(2) L.P. Ellinger, J. Appl. Chem., 12, 387 (1962).
(3) I. Tanaka and M. Okuda, J. Chem. Phys., 22, 1780 (1954).
(4) H. Yamazaki and S. Shida, J. Chem. Phys., 24, 1278 (1956).
(5a) G.J. Fonken, Chem. Ind. (London), 1625 (1963).
(5b) E. Migirdicyan and S. Leach, Bull. Soc. Chim. Belges, 71, 845 (1962).
(6) H.E. Zimmerman and H. Iwamura, J. Amer. Chem. Soc., 92, 2015 (1970).
(7) T.J. Katz and H.L. Strauss, J. Chem. Phys., 32, 1873 (1960); H.L. Strauss, T.J. Katz and G.K. Fraenkel, J. Amer. Chem. Soc., 85, 2360 (1963); P.I. Kimmel and H.L. Strauss, J. Phys. Chem., 72, 2813 (1968).
(8) A. Carrington and P.F. Flood, Mol. Phys., 7, 533 (1964).
(9) A. Carrington, H.C. Longuet-Higgins, R.E. Moss and P.F. Flood, Mol. Phys., 9, 187 (1965).
(10) D.E. Wood and R.V. Lloyd, J. Chem. Phys., 53, 3932 (1970),
(11) D.R. Gee and J.K.S. Wan, Can. J. Chem., 49, 20 (1971).
(12) M.J. Stephen and G.K. Fraenkel, J. Chem. Phys., 32, 1435 (1960); M.T. Jones, J. Chem. Phys., 42, 4054 (1965); G. Bignol and W. Muller-Warmeith, Phys. Letters, 11, 292 (1964).
(13) R.M. Dessau, J. Amer. Chem. Soc., 92, 6356 (1970).
(14) M.J.S. Dewar, A. Harget, E. Haselbach, J. Amer. Chem. Soc., 91, 7521 (1969).
(15) M. Traetteberg, Acta Chem. Scand., 20, 1724 (1966).