Electron Spin Resonance Study of Radicals in γ-Irradiated Mono- and Poly-cyclic Olefins: Substituted Cyclopentadienes

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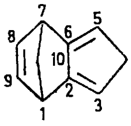
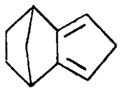
The matrix isolation technique coupled with e.s.r. spectroscopy has been used to obtain information regarding the nature and the reactions of free radical intermediates from the radiolysis of some substituted cyclopentadienes. The mechanisms of radiolysis are mainly concerned with changes in the cyclopentadienyl part of the molecules and predominantly involve the breakage of the weakest bisallylic C–H bonds and [1,4] opening of the conjugated system. An ionic mechanism has been attributed to the latter process by comparisons with u.v. irradiation experiments. Interesting e.s.r. properties of new cyclopentadienyl-type radicals have also been observed.

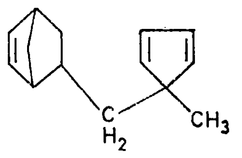
THIS paper reports the e.s.r. spectra obtained following irradiation at 77 K of tricyclo[5.2.1.0^{3,6}]-deca-2,5,8-triene (DDCP), -deca-2,5-diene (IDCP), and norborn-5-en-2-yl-(1-methylcyclopentadienyl)methane (NMCM). The aim of the investigation was to gain information on the nature and relative stabilities of free radical intermediates from the radiolysis of conjugated polyenes with strained ring structures; furthermore, it was felt that IDCP and DDCP might allow the study of the effect of alkyl substituents on the orbital degeneracy of the cyclopentadienyl radical.



DDCP



IDCP



NMCM

EXPERIMENTAL

DDCP, IDCP, and NMCM were prepared following the methods described.[1-3] NMCM (97% pure) was isolated from the other isomers by repeated fractional distillation *in vacuo* and its thiourea adduct was obtained by precipitation at 273 K from a nearly saturated propan-2-ol solution of thiourea.

Irradiations were performed at 77 K using a ^{60}Co γ source with total doses of *ca.* 10 Mrad. After irradiation the samples were placed in the rectangular cavity of a 4500 Varian X band spectrometer and their e.s.r. spectra recorded at various temperatures with the aid of an automatic temperature control accessory. Single crystals of DDCP for preliminary e.s.r. measurements were obtained by slow sublimation under vacuum. U.v. irradiations were performed at 77 K with a 100 W high pressure mercury lamp. For computer simulations of e.s.r. spectra, a program originally made available by Snyder[4] was used. Preliminary M.O. calculations have been performed by using INDO QCPE 141 and HMO computer programs.

RESULTS

DDCP.—γ Irradiation at 77 K of polycrystalline samples of DDCP yields a spectrum dominated by a singlet with a line width at maximum slope of *ca.* 25 G (Figure 1A). The presence of a second minor hyperfine component with an overall splitting of *ca.* 70 G is also inferred from the

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[1] K. Alder, F. M. Flock, and P. Janssen, *Chem. Ber.*, 1956, **89**, 2689.

[2] S. Cesca, M. L. Santostasi, W. Marconi, and M. Greco, *Ann. Chim.* (*Italy*), 1965, **55**, 682.

[3] S. Cesca, F. Arrighetti, A. Priola, P. V. Duranti, and M. Bruzzone, *Makromol. Chem.*, 1974, **175**, in the press.

[4] L. C. Snyder, Proceedings Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, 1960.

weakly resolved peaks on each side of the main signal. Upon warming to 298 K the larger splitting component disappears gradually without showing resolved couplings; the main signal is stable for weeks at 298 K and, because of the improvement in resolution, shows a 1 : 1 : 1 : 1 four-line structure with an average peak–peak separation of 6·3 G (Figure 1B). These hyperfine features are characteristic of a species having two non-equivalent protons with splitting constants of *ca.* 12 and 6 G respectively; furthermore the size of the average splitting is diagnostic of unpaired electrons delocalized over more than three carbon atoms. From the results of INDO MO calculations,[5] these properties are best accounted for in terms of the substituted cyclopentadienyl radical (IA) formed by loss of a secondary bisallylic hydrogen atom from positions 4. In fact the INDO method shows that radical (IA) has only two couplings larger than the experimental line width (4 G), associated with the H_σ and H_γ; furthermore a_{H_σ} is nearly twice as large as a_{H_γ} and close to 12 G, in agreement with the experimental observations. Further support for this interpretation has been obtained from preliminary single crystal measurements which indicate that the coupling of 12 G is strongly anisotropic whilst the other is nearly isotropic as expected for σ- and γ-protons, respectively. The larger splitting component contributing to the spectrum of Figure 1a is overshadowed by the signal from radical (IA) in the whole range of temperature explored; as a consequence it could not be positively identified. However, by analogy with IDCP, where the larger splitting component can be isolated in a nearly pure form because of its greater relative stability in the glassy matrix, it might tentatively be assigned to a telomeric radical of type (II).

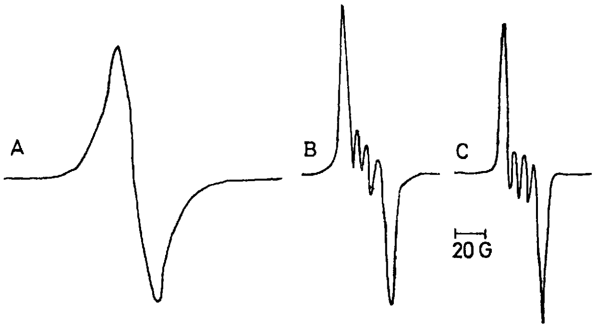
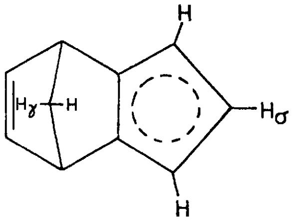


FIGURE 1 E.s.r. spectra of polycrystalline DDCP irradiated at 77 K: A recorded at 89 K; B recorded at 298 K; C computer simulation of spectrum B obtained by using a line width at maximum slope of 2·5 G and a_{H} = 6·3 and 12·6 G



(IA)

IDCP.—γ Irradiation. This compound can be obtained in either glassy or polycrystalline form by respectively quenching or slow cooling at 77 K. After irradiation at 77 K, both phases yield e.s.r. spectra (Figure 2A) nearly identical with that obtained from polycrystalline DDCP and showing the presence of the two hyperfine components. This first is a broad singlet, probably corresponding to the unresolved signal of radical (IB) [the spectrum of Figure 3B which was obtained by u.v. irradiation of glassy IDCP, and its computer simulation, clearly show that the radical (IB) has the same e.s.r. as (IA)]. The second is a larger splitting structure extending over *ca,* ±35 G. On warming above 77 K, these two hyperfine components show a decay behaviour strongly influenced by the phase state of the trapping matrix. In polycrystalline IDCP the e.s.r. spectrum changes observed as a function of the temperature are substantially the same as those observed in polycrystalline DDCP, *i.e.*, the larger splitting component decays at a faster rate, without showing resolved couplings, thus representing a progressive increase of the relative intensity of the signal from radical (IB). This signal, however, is not obtained in pure form because at 243 K (which is the highest temperature used for IDCP) the decay of the larger splitting structure is very slow.

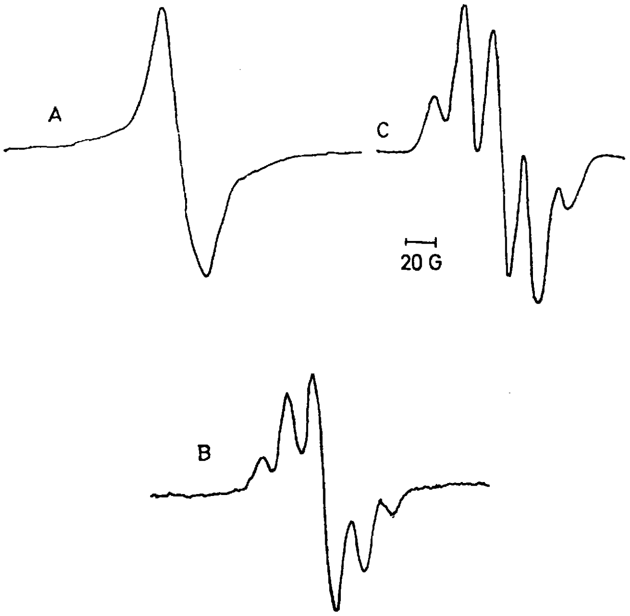
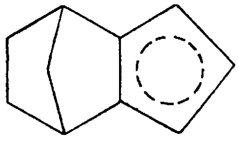


FIGURE 2 E.s.r. spectra of glassy IDCP γ-irradiated at 77 K: A recorded at 89 K; B recorded at 153 K; C computer simulation of spectrum B obtained by using a line width at maximum slope of 8 G, and $a_{3\cdot\mathrm{H}} = a_{4\cdot\mathrm{H}} = 21$ and $a_{5\cdot\mathrm{H}} = 14$ G



(IB)

In glassy IDCP, the diffusion of radicals becomes appreciable near 100 K and leads to the complete disappearance of e.s.r. signals above 153 K; within this temperature range radical (IB) disappears at a faster rate with respect to the

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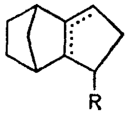
[5] A. Faucitano, R. Fantechi, G. A. Helcke', S. Cesca, and F. Faucitano Martinotti, in preparation.

larger splitting component which can thus be isolated in nearly pure form and which can be seen to consist of a quintet (*ca.* 1 : 4 : 8 : 4 : 1) with average peak–peak separation of 16—18 G (Figure 2C).

This peculiar phase effect which is similar to that observed in γ-irradiated cyclopentadiene[6] might reasonably be explained by assuming that the quintet of Figure 2B is generated by a telomeric radical which is more stable than (IB) in the glassy matrix because of its greater molecular size which results in a slower rate of diffusion, but less stable than (IB) in the crystalline matrix, where the diffusion of radicals is hindered and higher temperatures can be reached, because of the tendency to abstract hydrogen atoms from parent IDCP molecules to form the new radical (IB). Valid support for this interpretation arises from the fact that oligomers have indeed been found among the radiolysis products of liquid IDCP and that the hyperfine features of the quintet are consistent with the substituted cyclopentenyl radical (II) formally generated by [1,4] addition of a radical precursor R• to the diene system. This radical has one α and five β allyl protons; however, under the experimental conditions employed (line width *ca.* 8 G), the two bridgehead protons are not expected to give rise to resolved structures since one of them is bound to the carbon located in the centre of the allyl triad whilst the other lies close to the nodal plane of the π-allyl orbital. The remaining three β protons are equally oriented above and below the planar conjugated system, as a consequence of which the magnitude of their splitting should be *ca.* 20—21 G.[7-9] The coupling of the α proton should not exceed a value of 13—14 G. The simulated pattern resulting from the use of these constants is shown for comparison in Figure 2C; the similarity with the experimental spectrum is satisfactory provided allowance is made for the superimposition of a residue of the signal of radical (IB) which enhances the intensity of the central peak of the quintet.



(II)

U.v. irradiation. If it is assumed, as is reasonable, that the ionization potential of IDCP does not differ too much from that of cyclopentadiene (*ca.* 198 kcal mol^{-1}[10]) then under u.v. irradiation radicals arising from an ionic mechanism should not be observed [u.v. irradiation from a high pressure mercury lamp has energy in the range 66—113 kcal mol^{-1} with a negligible component (irradiations were performed in air) of 150 kcal mol^{-1} (λ 185·9 nm)]. On the other hand, radicals arising from excitation processes should be observed. It follows that comparative u.v. irradiation experiments might yield information on the role played by ionization and excitation in radical-forming processes under γ irradiation.

U.v. irradiation at 77 K of glassy samples of IDCP yields a spectrum consisting mostly of a singlet from radical (IB) (Figure 3A); on warming above 77 K this signal becomes partially resolved (Figure 3B) (see the computed pattern of Figure 3C) and also gradually disappears without revealing the presence of the quintet. This indicates that the telomeric radical (II) is not formed when low energy irradiation is used.

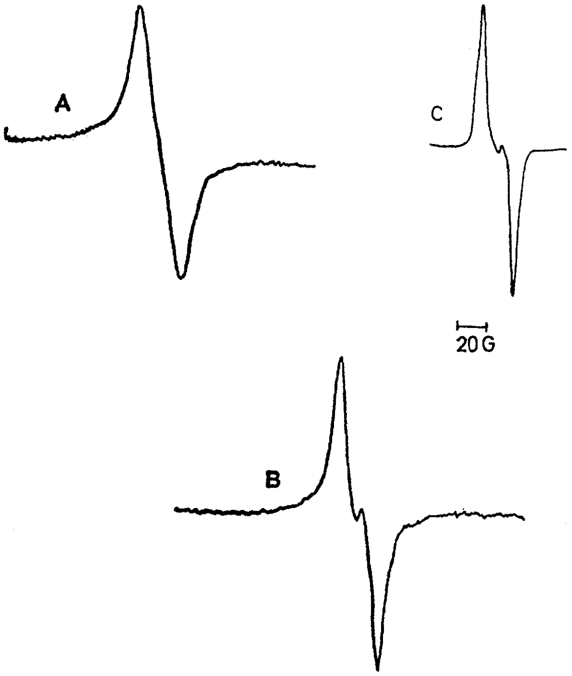
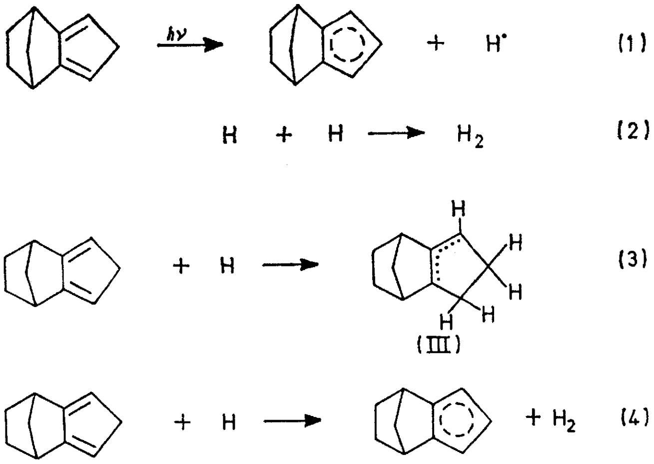


FIGURE 3 E.s.r. spectra of glassy IDCP u.v.-irradiated at 77 K: A recorded at 89 K; B recorded at 153 K; C computer simulation of B obtained by using a line width at maximum slope of 7 G and a_H = 6·3 and 12·6 G

The results suggest that, in γ-irradiated IDCP, the telomeric radical is likely to have an ionic origin, whereas for radical (IB) either ionic or excited precursors may be involved.



The photolytic formation of radical (IA) may be attributed to direct C–H bond homolysis in position 4 following the absorption of a photon with energy >88 kcal mol^{-1}

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[6] A. Faucitano and F. Faucitano Martinotti, *European Polymer J.*, 1974, **10**, 489.

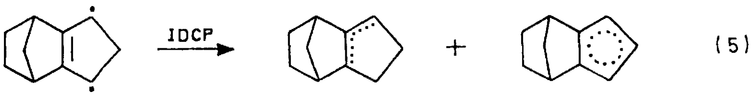
[7] R. W. Fessenden, *J. Chem. Phys.*, 1964, **61**, 1570.

[8] D. R. Gee and J. K. S. Wan, *Canad. J. Chem.*, 1971, **49**, 20.

[9] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **37**, 1326.

[10] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, 'Bond Energies, Ionization Potentials and Electron Affinities,' Edward Arnold, London, 1966.

(the C–H bond energy) [reaction (1)]. The hydrogen atoms resulting from this process may decay by the bimolecular recombination (2) or react with IDCP by addition to the double bonds or hydrogen abstraction [reactions (3) and (4)]. The product of reaction (3) is an allyl-substituted cyclopentenyl radical which under the experimental conditions employed is expected to yield a sextet with an overall splitting of *ca.* 94 G; as this structure is not present in the spectra of Figure 3, it may be inferred that radical (III), if present, is capable of abstracting hydrogen from parent IDCP molecules at 89 K or alternatively that reaction (3) is of minor importance. The latter hypothesis seems more reasonable on the basis that the closely related telomeric radicals (II) do not show a tendency to react at temperatures <200 K.



(5)

The failure to observe radical (III) also suggests that alternative mechanisms of formation of radical (IB), based on triplet state intermediates, for instance reaction (5), are likely to play a minor role.

NMCM.—Attempts to take e.s.r. measurements of crystalline or glassy samples of NMCM did not yield satisfactory results. However, sufficiently resolved spectra have been obtained by using the thiourea adduct. Blank experiments with pure thiourea samples had shown that the interference by thiourea radical was negligible. Both spectra, at 89 K and after annealing at 298 K, consist mostly of a quartet (15—16 G) with a nearly binomial intensity ratio (Figure 4); this structure is superimposed on a minor component with larger splitting, presumably due to radicals of the other positional isomers of NMCM [3] present in total concentration of *ca.* 3%.

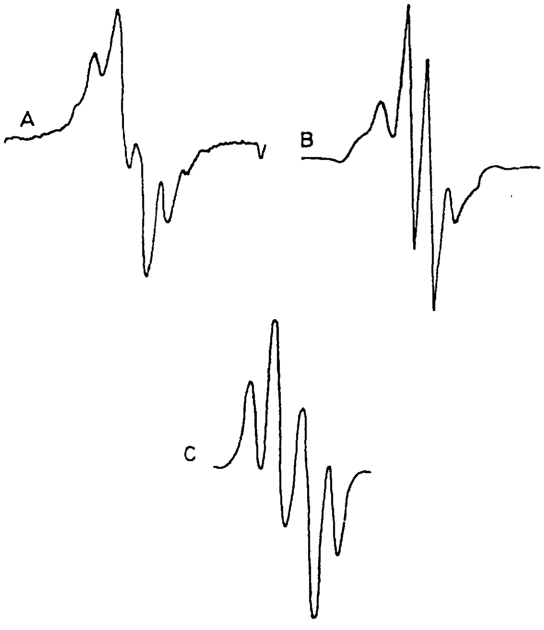
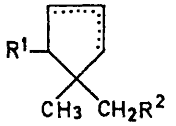


FIGURE 4 E.s.r. spectra of the thiourea adduct of NMCN γ-irradiated at 77 K; A recorded at 89 K; B recorded at 298 K; C computer simulation by using $a_{2'\cdot H} = a_{4'\cdot H} = 14$, $a_{3'\cdot H} = 3$, and $a_{5'\cdot H} = 21$ G

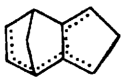
The quartet has hyperfine features characteristic of an allyl type radical with three 'equivalent' protons interacting with constants larger than the experimental line width (*ca.* 7 G). This is diagnostic of species (IV) which arises from [1,4] opening of the conjugated bonds.



(IV)

DISCUSSION

The predominant species trapped at 77 K in γ-irradiated DDCP and IDCP can formally be accounted for by the loss of a secondary bisallylic hydrogen atom in position 4 and by [1,4] opening of the conjugated double bonds following, probably, a telomerization reaction. In NMCM, which does not contain bisallylic C–H bonds, only radicals from the latter process are identified. Thus the radical-forming processes in the radiolysis of these olefins occur mainly in the conjugated section of the molecules whereas the norbornyl and norbornenyl substituents play only a minor role. The inertness of these groups may, in part, be explained with the inability of the bridgehead sites readily to adjust their structures to accommodate a planar or near planar free radical; thus, for instance, in DDCP, the delocalized radical (V) is expected to be formed in competition with radical (IA); nevertheless, their hyperfine structure is not observed, presumably because the increase of strain which would inevitably accompany a change from sp^3 to sp^2 hybridization of the bridgehead atoms C-1 and -7 [11,12] would reduce tendency to form by hindering the delocalization of the unpaired electron in the pentadienyl system. In the case of radical (IA) the restrictions imposed by strain effects are likely to be much less important since the two bridgehead carbon atoms involved in the pentadienyl system are already in a planar sp^2 state in the parent molecule so that very little change in bond angles and distances is required in the radical-forming process.


(V)

As far as the origin of IDCP radicals is concerned, the evidence from the experimental results can be rationalized by reactions (6)—(9) together with (2) and (4).

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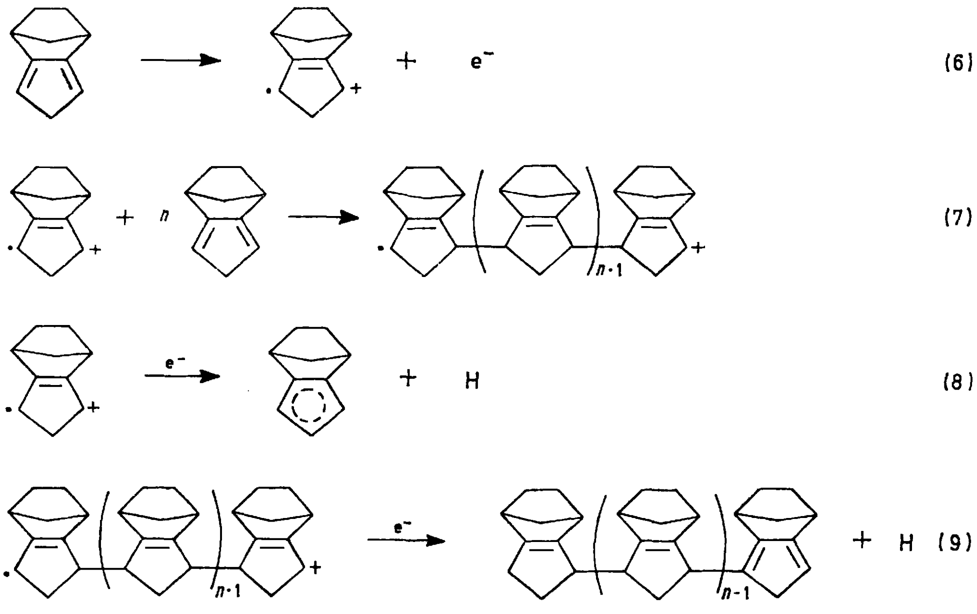
[11] V. R. Koch and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1971, **93**, 1657.

[12] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 1958, **4**, 382.

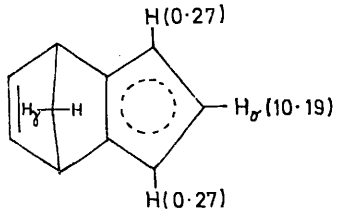


This mechanism implies that the primary ionizations involve the ejection of electrons from the delocalized π-molecular orbitals and that the resulting radical ions are capable of initiating the cationic polymerization of the parent monomer molecules. The latter assumption is consistent with the observation of oligomers among the radiolysis products of IDCP and with the fact that this compound is readily polymerized by using cationic catalysts, whilst being relatively inert toward radical initiators.[13]

The mechanism proposed for IDCP may apply also to DDCP and to NMCM; in the latter case however no definite hypothesis can be made about reactions (4) and (8) since no other species, beside the telomeric radical, have been identified.

The e.s.r. properties of radicals (II) and (III) are diagnostic of an electronic structure similar to that of other previously studied alkyl-substituted cyclopentenyl radicals. Of greater theoretical interest is the e.s.r. spectrum of radical (IA) since it provides evidence of the effect of alkyl-substituents on the electronic degeneracy of an odd, non-alternant, cyclic polyenyl radical. HMO Calculations for the cyclopentadienyl radical, having D_{5h} symmetry, show that the orbital of the unpaired electron has two-fold degeneracy; as a consequence the spin density distribution is averaged over the two orbitals and the hyperfine structure arises from the interaction of five equivalent protons.[14] If this electronic structure could also be applied to radical (IA) the three σ ring protons would be magnetically equivalent and the spectrum would consist of a binomial quartet. The experimentally observed intensity ratio therefore suggests that the norbornenyl substituent lifts the orbital degeneracy of the radical (IA) so that the hyperfine constants reflect either the spin density distribution in one of the orbitals or a weighted average of the distribution in both orbitals depending whether the energy gap is large compared to KT or of the same order of magnitude, respectively. The former hypothesis seems more likely on the basis of the lack of temperature effects in the range 245—273 K.

The lifting of the orbital degeneracy in cyclic, odd non-alternant radical anions has been successfully treated as a purely inductive perturbation of the substituent.[15-17] In our case the application of the HMO method (inductive model), and considering the norbornenyl substituent as electron repelling, confirms conclusions about the removal of orbital degeneracy and gives a satisfactory value for the π-spin density distribution over the cyclopentadienyl section and for the σ proton splitting of 12 G. However the more sophisticated INDO method is also needed to account for the smaller long range coupling of 6 G. Further work is in progress in order to elucidate fully the structure of this and related radicals.[5]



We thank ENI, Italy, for support.

[3/2163 *Received*, 22*nd October*, 1973]

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[13] S. Cesca and A. Priola, to be published

[14] S. Ohnishi and I. Nitta, *J. Chem. Phys.*, 1963, **39**, 2848. According to the Jahn–Teller theorem, the pentagonally symmetrical structure of cyclopentadienyl is not stable, therefore the equivalence of the five ring protons is more rigorously explained by rapid interconversion between two distorted configurations (see for instance L. C. Snyder, *J. Chem. Phys.*, 1960, **33**, 619).

[15] K. Möbius, H. V. Willigen, and A. H. Maki, *Mol. Phys.*, 1971, **20**, 289.

[16] S. P. Solodovnikov and A. P. Prokof'ev, *Russ. Chem. Rev.*, 1970, **39**, 591.

[17] K. Möbius and M. Plato, *Z. Naturforsch.*, 1967, **22**, 929.