Electron Spin Resonance Study of Radicals in γ-Irradiated Mono- and Poly-cyclic Olefins. Part III.[1] Allyl and Pentadienyl Radicals from Dienes and Trienes with Strained Ring Structures

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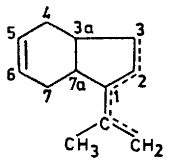
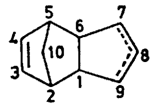
An e.s.r. study of the radicals produced by low temperature γ-irradiation of dicyclopentadiene and 1-isopropylidenetetrahydroindene in an adamantane–thiourea matrix leads to the identification of the species dicyclopentadien-9-yl (II) and 1-(tetrahydroinden-1-ylidene)ethyl (I) respectively. The origin, structure, and e.s.r. properties of these radicals are discussed on the basis of the results of progressive thermal annealing experiments and of SCF MO calculations performed to the INDO and HMO (McLachlan) levels of approximation.

PURSUING our investigation on free radical intermediates produced by radiolysis of cyclic polyenes,[1,2] we report the e.s.r. spectra of the radicals (I) and (II) from 1-isopropylidenetetrahydroindene (IPTI) and dicyclopentadiene (DCP), respectively. Interest in these compounds derives from the possibility of obtaining new neutral odd alternant radicals belonging to the class of allyls and pentadienyls. Furthermore these compounds are of interest also from the point of view of free radical chemistry since their radical reactivity is expected to be influenced by the molecular geometry. As conjugated radicals are characterized by small hyperfine couplings a matrix is needed which, whilst restricting the translational diffusion of the radicals, permits considerable rotational motion of the molecules so that e.s.r. lines have as little anisotropic broadening as possible. The thiourea[3] and adamantane[4] matrices seem to be suitable in this respect; accordingly the e.s.r. experiments have been performed on the thiourea adduct of IPTI and on the adamantane adduct of DCP.



(I)



(II)

EXPERIMENTAL

IPTI Was prepared according to Cesca.[5] DCP Was a commercial product purified by repeated vacuum distillation. Adamantane (Aldrich) was purified prior to use by the method of Wood.[4] Adamantane–DCP samples were obtained by vacuum evaporation of ether solutions containing *ca.* 5% adamantane and <0.01% DCP. Attempts to obtain IPTI–adamantane samples which could be used for e.s.r. experiments failed, and only the thiourea clathrate was used in this case. The IPTI–thiourea clathrate was precipitated as needles by adding *ca.* 10% olefin to a nearly saturated propan-2-ol solution of thiourea.

The samples were irradiated at 77 K in a ^{60}Co source and e.s.r. spectra recorded at various temperatures with a Varian 4500 X band spectrometer as described elsewhere.[1,2] Computer simulations of first-order isotropic spectra were performed by using a Fortran IV program originally made available by Snyder;[6] a gaussian shape of the absorption lines and variable line widths and couplings up to best fit were assumed.

SCF MO Calculations to the INDO level of approximation developed by Pople *et al.*[7] have been made on a Honeywell 6030 computer using a QCPE 141 program. In the case of radical (I) the simple HMO and HMO SCF (McLachlan)[8] methods have been employed for the sake of comparison. The INDO method was employed within both the open shell (o.s.) and closed shell (c.s.) frameworks; the latter approximation, though incapable of predicting negative spin densities, proved to be more suitable for the radical investigated. The INDO (o.s.) hyperfine splittings have

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[1] F. Faucitano Martinotti and S. Cesca, *J.C.S. Perkin II*, 1974, 1694 is regarded as Part II.

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

[3] G. A. Helckè and R. Fantechi, *Mol. Phys.*, 1970, **18**, 1.

[4] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 1970, **53**, 3932.

[5] S. Cesca, W. Marconi, and A. Ruggero, *Chimica e Industria*, 1967, **49**, 1160.

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

[7] A. Pople and O. L. Beveridge, 'Approximate Molecular Orbital Calculations,' McGraw-Hill, New York, 1970.

[8] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

been derived from equation (1) where the quantity in square brackets is a constant equal to 539.8 G [7] and ρ_{SNSN} is the

$$a^{H} = [(4/3\pi)g\beta\gamma_{H}\hbar\langle S_z\rangle^{-1}|\phi_{SN}(O)^2|]\rho_{SNSN} \qquad (1)$$

proton *s* orbital unpaired spin density obtained from the spin density matrix. The derivation of INDO (c.s.) β-couplings was performed by replacing ρ_{SNSN} with the squares of proton 1*s* orbital coefficients in the unpaired electron molecular orbital; for INDO (c.s.) α-coupling the usual McConnell relationship with Q_α 29 G was used. The McConnell [9] relationships for both α- and β-couplings were used in connection with the HMO and HMO SCF (McLachlan) methods. In the McLachlan method, ρ^{π} is corrected for electron correlation effects through equation (2) where π_{Rt} is

$$\rho_t = c_{mt}^{2} + \lambda \sum_{R\rightarrow 1}^{n} \pi_{Rt}c_{mR}^{2} \qquad (2)$$

the atom–atom polarizability and c_{Rt} the coefficient of atom *t* in the *m*th molecular orbital. π_{Rt} and c_{mt} are obtained from the HMO method. The HMO method was employed within the framework of the inductive model by adopting coulomb integrals $\alpha_C = \alpha_0 - 0.5\ \beta$ for sp^2 carbon atoms with alkyl substituents; in the other cases $\alpha_C = \alpha_0$ and $\beta_{C-C} = \beta_0$, where α_0 and β_0 are the coulomb and exchange integrals for benzene, were used.

RESULTS AND DISCUSSION

E.s.r. Spectra and Nature of the Radicals trapped at Room Temperature.—Dicyclopentadiene (*DCP*). The room temperature spectrum of DCP–adamantane is shown by examination of the computer simulation (Figures 1A, B) to consist of a triplet of 20.2, a doublet of 3.4, and a triplet of 14.3 G. These hyperfine features are most reasonably accounted for in terms of the substituted cyclopentenyl radical (II) formed by loss of secondary hydrogen at C-9. The proton hyperfine splitting assignments (Table 1) are based on the reasonable assumptions that the unpaired electron occupies a molecular orbital of the allyl type and that the two β-protons, as suggested by comparison with framework molecular models, make dihedral angles of *ca.* 30° with the symmetry axis of the π orbital. These conclusions are entirely consistent with the results of INDO MO calculations performed within the open and closed shell scheme.

TABLE 1

Experimental and calculated proton hyperfine splitting (G) of radical (II)

	Experimental	INDO (o.s.)	INDO (c.s.)
a^{H}_{8}	3.4	7.1	0
a^{H}_{7}	14.3	−14.6	−12.2
a^{H}_{6}	20.2	27.1	19.1
a^{H}_{1}	20.2	27.1	19.1
a^{H}_{9}	14.3	−14.6	−12.2
Others		<0.8	

Isopropylidenetetrahydroindene (*IPTI*). Following γ-irradiation at 77 K and annealing to room temperature IPTI–thiourea clathrate yield a seven line pattern with 9.1 G average peak to peak separations and 1 : 4 : 7 : 8 : 7 : 4 : 1 intensity distribution (Figure 2A). These hyperfine features have been satisfactorily reproduced by assuming two doublets of 12 and 19 G, a 1 : 3 : 3 : 1 quartet of 9 G, and a 1 : 4 : 6 : 4 : 1 quintet of 3 G (Figure 2B). The size of the average splitting is suggestive of a conjugated radical having the unpaired electron orbital

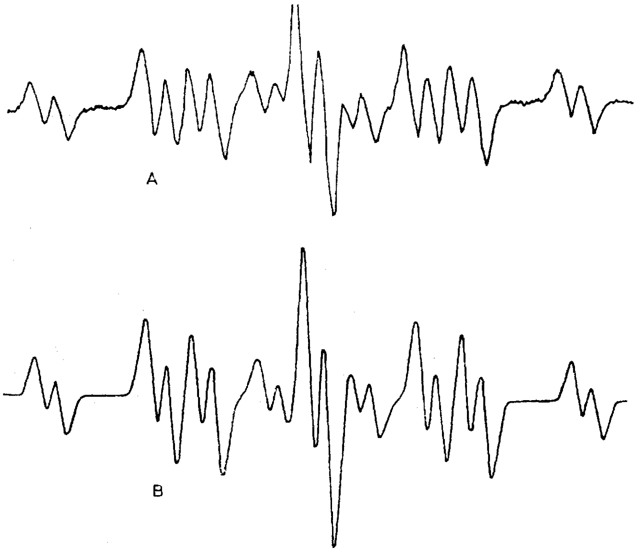

FIGURE 1 E.s.r. spectrum of DCP trapped in an adamantane matrix. A, Recorded at room temperature after γ-irradiation; B, computer simulation based on coupling constants in Table 1

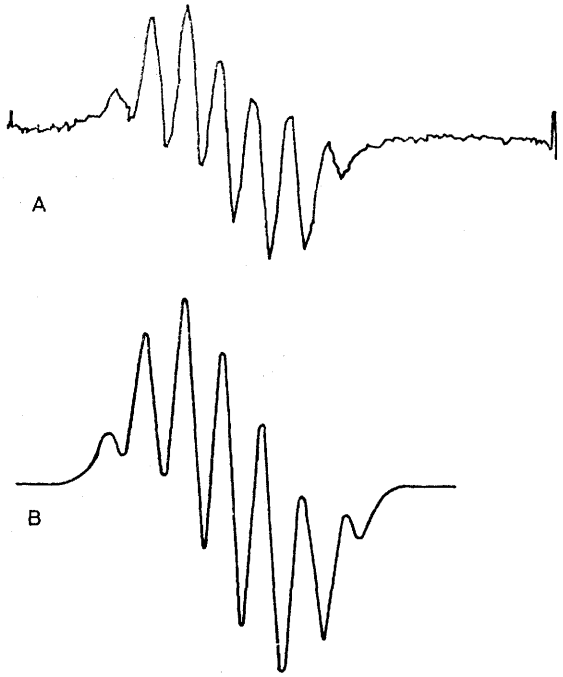

FIGURE 2 E.s.r. spectrum of IPTI trapped in a thiourea matrix. A, Recorded at room temperature after annealing at 373 K; B, computer simulation based on coupling constants in Table 2

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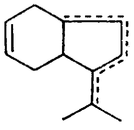
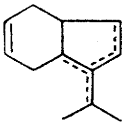
[9] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632; C. Hellor and H. M. McConnell, *ibid.*, 1960, **32**, 1535.

delocalized over more than three carbon atoms. The possibility is thus narrowed to one of the species (I), (III), and (IV) formally arising from the loss of hydrogen atoms at CH_3, C-3a, and C-7a respectively.


(III)


(IV)

The uncertainty has been removed by HMO calculations which clearly show that only radical (I) has the correct number of interacting protons and hyperfine couplings consistent with the experimental results. This conclusion is further supported by the results of INDO calculations performed within the framework of the closed shell approximation which also suggest that hyperfine couplings should be assigned as shown in Table 2.

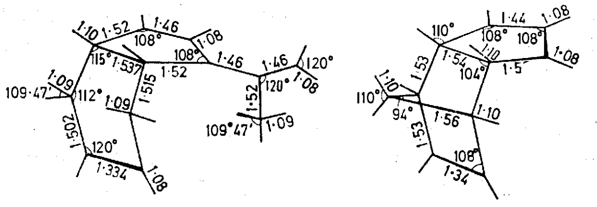
TABLE 2

Experimental and calculated proton hyperfine splitting (6) of radical (I)

	Experimental	HMO (McLachlan)	INDO (c.s)
a_2^H	3	3.4	0.0
a_3^H	9	−11.4	−8.2
a_{3a}^H	12	16.6	13.6
a_{7aH}	19	15.4	16.3
$2a^H{}_{(CH_2)}$	9	−10.4	−7.2
$3a^H{}_{(CH_3)}$	3	3.0	0.35

β- and α-protons, whose couplings depend on π spin densities at alternant carbon atoms are assumed to contribute exclusively to the experimental line width (*ca.* 5 G). The INDO (o.s.) method confirms the gross e.s.r. properties of radical (I) but greatly overestimates β-couplings and negative spin densities; furthermore, the maximum spin density is shifted from the centre to the periphery of the pentadienyl system. In radical (I) this would lead to the erroneous assignment of the largest coupling to the β-proton at C-3. The same type of deviation from the experimental results is observed for the closely related cyclohexadienyl radical whose spin distribution has been determined experimentally;[10,11] it follows that the INDO (o.s.) method may be inadequate for giving a quantitative account of e.s.r. properties of odd alternant pentadienyl radicals. The reason for this inadequacy is perhaps related to the fact that electronic wave functions based on spin unrestricted determinants are not in general eigenfunctions of S^2 because of contamination with states of higher multiplicity. The closed shell approximations (both HMO and INDO) do not suffer from this limitation as a consequence, though as they are incapable of predicting negative spin densities, apparently lead to better agreement with experimental results. In an attempt further to improve the agreement between experimental and calculated results, HMO SCF (McLachlan) calculations were also performed; this method is based on the combination of a restricted single determinant function (with one unpaired and $2n$ paired electrons in n orbitals) with singlet-excited doublet configurations,[8] and is therefore capable of predicting negative densities. The results (Table 2) indicate some improvement in respect to the INDO (o.s.) method but still the maximum spin density is predicted to be at C-3 instead of at C-1. Substantial progress might be obtained within the INDO (o.s.) method, by using spin projected wave functions.[12]

Geometry of the Radicals.—Structural parameters of radicals (I) and (II) giving satisfactory agreement between calculated and experimental coupling constants are summarized in Figure 3. Comparison between calculated and experimental coupling was preferred to the minimum energy criterium because the energy curves did not show minimum values for acceptable geometries. In all cases planar configurations of the conjugated sections of the radicals were assumed with equal C$\cdots$C bond distance of 1.49 Å and $\widehat{CCC}$ angles of 120 or 108° depending on whether the planar centres were enclosed in open-chain or five-membered ring structures, respectively. Other parameters employed were d_{C-C} 1.53, $d_{C=C}$ 1.34, and d_{C-H} 1.09 Å. The geometry of the bicyclo[2.2.1]-heptene ring section of radical (II) was derived from selected data on the structures of the related molecules norbornane, norbornene, and norbornediene.[13] The following assumptions were also made: (a) radicals (I) and (II) retain the *endo*-configuration of the parent hydrocarbon and (b) at tetrahedral carbon atoms the HCH planes bisect the opposing CCC angles.



(I) (II)

FIGURE 3 Geometrical parameters exployed for INDO calculations of proton hyperfine splitting of radicals (I) and (II)

Electronic Structure of the Radicals.—According to the results of INDO calculations (c.s. approximation) the unpaired electron wave function of radical (II) can be described in terms of Hückel formalism as arising from a strong hyperconjugative interaction between the non-bonding combination of the C-7, -8, and -9 p_z orbitals (83.95%) and the $(1s_{H-1}1s_{H-6})$ group orbital (7.1%).

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[10] S. I. Ohnishi and I. Nitta, *J. Chem. Phys.*, 1963, **39**, 2848.

[11] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **38**, 773.

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The remaining 8.95% of the unpaired electron is delocalized in the norbornene section of the molecule, mainly in the C-2 and -5, s, p_x, and p_z orbitals (7.0%).

Of negligible importance is delocalization into the 1s orbital of the γ- and δ-protons. In radical (I), 93.75% of the unpaired electron orbital results from the nonbonding combination of C-1, C-2, C-1, and side-chain carbon, p_z orbitals (88.19%) and the ($1s_{\mathrm{H-3a}}1s_{\mathrm{H-7a}}$) β-proton group orbital (5.56%). The remaining 6.25% is spread over the cyclohexene section of the molecule. Allowance having been made for the loss of symmetry, this structure is similar to that of the cyclohexadienyl radical.[10,11]

Origin of Radicals (I) *and* (II).—In order to elucidate the mechanism of radiation-induced formation of radicals (II) and (I) in the adamantane and thiourea clathrate matrix, the samples were γ-irradiated at 77 K and then submitted to progressive thermal annealing from 77 to 360 K with simultaneous recording of the e.s.r. spectra. At 77 K DCP–adamantane yields an e.s.r. spectrum consisting of a doublet (20—22 G) superimposed on an unidentified singlet. Upon warming for a few minutes at 140 K the singlet decays leaving the doublet in a nearly pure form. The latter signal has been previously detected by Wood in irradiated pure adamantane and attributed to 2-adamantyl radicals on the basis of ENDOR experiments.[14] Further warming of the samples to 200 K causes the doublet to disappear generating the radical (II). Thus 2-adamantyl radical produced on γ-irradiation at 77 K subsequently reacts with DCP to give radical (II). The radiolytic process leading to the formation of 2-adamantyl radicals may involve homolytic scission of C–H bonds, with production of hydrogen atoms, and/or ion–molecule reactions without hydrogen atom production. The latter mechanism seems to be of major importance, judging from the fact that no radical product arising from the reactions of hydrogen atoms with the double bonds of trapped DCP has been observed at 77 K.

Following γ-irradiation at 77 K and annealing for a few minutes at room temperature, the e.s.r. spectrum of the IPTI–thiourea clathrate reveals the presence of the radical (I) which gives a septet superimposed on a decet with an average hyperfine separation of 16—18 G. The latter structure has been isolated in a nearly pure form by submitting to thermal annealing at 153 K glassy samples of pure IPTI γ-irradiated at 77 K. Prolonged storing of the sample at room temperature or warming for a few minutes at 368 K causes the decet to disappear whilst the septet acquires greater pre-eminence. This change is irreversible and therefore suggests that at least part of radical (I) arises from a reaction between radicals $\mathrm{R}^{\bullet}$ (responsible for the decet) and IPTI molecules in the clathrate.

The nature of the radical $\mathrm{R}^{\bullet}$ has not yet been positively ascertained; however the size of the splitting and the number of the lines suggest the presence of allyl type radicals with 8 or 9 interacting protons such as those arising from the loss of a methine hydrogen at 7a or from 1,4-opening of the conjugated double bonds following addition of hydrogen or a polymerization reaction.

The selectivity of hydrogen abstraction reactions leading to the formation of radicals (I) and (II) reflects the influence of geometrical factors on the distribution of reactivity to various positions in the molecules. The lack of reactivity at all bridgehead sites of DCP and IPTI is reasonably explained in terms of strain energy which would inevitably accompany the change of bond angles and distances required for the formation of planar radical centres.* In other words, the strain prevents the delocalization of the unpaired electron into the π system with a consequent loss of resonance stabilization energy (10—15 kcal mol^{-1} for allyl type radicals.[16]) This leads to increase in the tendency of formation of radicals (I) and (II) which are capable of attaining planar π configurations.

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* The lack of reactivity of bridgehead sites toward free radical attack is a widely recognized phenomenon in saturated hydrocarbons with strained ring structures (see, for example, ref. 15).

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[16] P. J. Krusic, P. Meakin, and B. E. Smart, *J. Amer. Chem. Soc.*, 1974, **96**, 6211.