1070. *Electron Spin Resonance Studies of γ-Irradiated Single Crystals of Aromatic Compounds. Part I. Diphenylmethane.*

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The electron spin resonance spectra of γ-irradiated single crystals of diphenylmethane show a proton hyperfine doublet which is believed to arise from the α-protons in diphenylmethyl radicals. The coupling tensor is discussed in relation to the electronic structure and conformation of the radicals and their orientation in the crystal.

Electron spin resonance (e.s.r.) spectroscopy is a powerful technique for studying radiation damage. Most information can be gained by working with single crystals because radicals trapped in these have orientations simply related to those of the parent molecules so that the anisotropies of the hyperfine interactions and the g-value can be determined.[1] This approach

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[1] D. H. Whiffen, in "Free Radicals in Biological Systems," ed. M. S. Blois, Academic Press, New York, 1961; M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 283.

has been extensively used but virtually all the organic compounds studied have been aliphatic. In this series we will present some results for radicals derived from aromatic compounds.

There are several features which make such studies interesting. First, it should be possible to obtain information about the electronic structure of radicals which are too unstable to be studied in solution. Secondly, there is interest in the mechanism of radiation damage, which is generally held to be inefficient for aromatic molecules. Thirdly, there is the prospect of comparing the radiation chemistry of molecules with their photochemistry: studies of the latter are far more numerous than of the former.

We now describe results for the diphenylmethyl radical produced by γ-irradiation of diphenylmethane. This radical does not seem to have been previously studied by e.s.r., although dimesitylmethyl has been known for some time.[2]

EXPERIMENTAL

Single crystals of diphenylmethane were grown from solutions in light petroleum, or other hydrocarbons, by slow evaporation. They were irradiated in a 300curie ^{60}Co γ-ray source, in air at room temperature, with doses of up to 0·47 megarads.

The crystals are monoclinic, with four molecules per unit cell, space group $P2_1/c$ or $P2/c$, and tend to be elongated along the direction of the *b* axis.[3] For e.s.r. measurement a crystal was mounted on a Perspex post which could be rotated about an axis perpendicular to the applied magnetic field. Spectra were taken at 10° intervals during rotation about each of the *a*, *b*, *c** set of orthogonal right-handed axes. Comparison of results for different crystals showed that the crystal alignment was accurate to ± 2°. *g*-Values were measured by comparing the position of the radical spectrum with that of diphenylpicrylhydrazyl (DPPH), for which $g = 2{\cdot}0036$.[4] A Varian 100 kc./sec. *X*-band spectrometer was used.

RESULTS

For all directions during rotation about any of the axes the spectrum is a symmetrical doublet, indicating hyperfine coupling to only one proton. The crystal structure is such that there should be two magnetically distinguishable radicals in the unit cell, so the lack of a site splitting indicates that the coupling tensors for differently sited molecules must have their principal axes parallel, and that the *b* axis must be one of the principal axes.

Figure 1(*a*) shows the spectrum for the magnetic field parallel to (0, 0·342, 0·940) and represents the best resolution of the doublet that was obtained. At the other extreme of resolution the spectrum is almost a single line. Fig. 1(*b*) shows the spectrum for H_0 parallel to $(-\sqrt{3}/2, 0, 1/2)$ and shows extra hyperfine splitting on the main lines. This spectrum represents the best resolution of this hyperfine splitting that was obtained, and shows that each line of the principal doublet is in fact an envelope of many hyperfine lines. This is to be expected as the radical is derived from a molecule containing many protons. The doublet splitting was measured on the assumption that the breadth of the components of the doublet was independent of orientation. This was

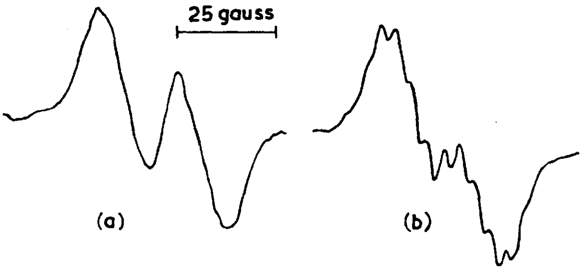

FIG. 1. Derivative spectra of a γ-irradiated diphenylmethane crystal. (*a*) H_0 parallel to (0, 0·342, 0·940), (*b*) H_0 parallel to $(-\sqrt{3}/2, 0, 1/2)$.

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[2] H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, 1954, **22**, 1883; A. D. McLachlan, *J. Chem. Phys.*, 1960, **32**, 1488.

[3] M. J. Housty, *Acta Cryst.*, 1961, **14**, 92.

[4] A. N. Holden, C. Kittel, F. R. Merritt, and W. A. Yager, *Phys. Rev.*, 1950, **77**, 147.

true so far as could be determined from spectra showing reasonable resolution, and there is nothing in the results which suggests that it is a bad assumption.

From the measured hyperfine splittings at various orientations the coupling tensor shown in the Table was derived. The variation of hyperfine splitting could be satisfactorily accounted for in terms of a spin Hamiltonian containing only electron Zeeman and hyperfine terms and the curve in Fig. 2, showing the variation in hyperfine splitting during rotation about the *b* axis, is calculated from the tensor and such a Hamiltonian.

Proton coupling tensor (gauss) in *abc** axis system.

Tensor			Anisotropic components	Direction cosines
9·3 ± 0·7	0	−2·0 ± 0·5	(+)0·9 ± 0·4	(0, 1, 0)
0	11·0 ± 0·7	0	(+)3·2 ± 0·35	(0·96, 0, 0·28)
−2·0 ± 0·5	0	15·5 ± 0·7	(−)4·1 ± 0·35	(0·28, 0, −0·96)

The isotropic component is (−) 11·9 ± 0·36 gauss.

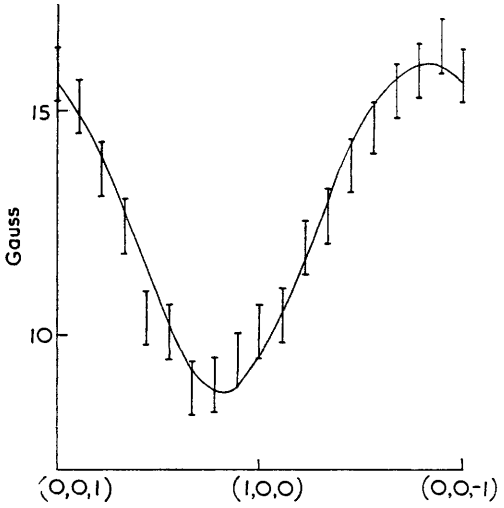

FIG. 2. Variation of hyperfine splitting (gauss) during rotation about *b*; bars are experimental observations, full line is calculated as indicated in text.

Because of the relatively large breadth of the lines it was not possible to measure the *g*-value as a function of orientation sufficiently accurately for the complete tensor to be derived. The *g*-value was always less than that of DPPH and was not markedly anisotropic, extreme measured values not differing by more than 0·0010. From measurements at three perpendicular orientations the isotropic value is estimated to be 2·0024 ± 0·0004.

DISCUSSION

The isotropic hyperfine coupling constant of 11·9 gauss has about the value expected for the proton attached to the α-carbon atom of diphenylmethyl. Hückel theory predicts a π-orbital spin population of 0·4 for the α-carbon atom, which, from the McConnell equation[5] $a_H = Q\rho$, with $Q = 23$ gauss, suggests an isotropic splitting of 9·2 gauss. There are two reasons why the true spin population at the α-carbon in diphenylmethyl should be greater than this crudely estimated value. First, diphenylmethyl is an odd-alternant radical and it is well known that Hückel theory is inadequate for describing spin populations in such radicals. More sophisticated calculations are expected to put negative π-orbital spin populations at the 1, 1′, 3, 3′, 5, and 5′ positions with concomitant increases in the positive spin populations at the remaining carbon atoms. Secondly, there is no reason to suppose

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[5] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

that the radical is planar. The orientation of the rings in the radical is expected to be the same as that in the parent molecule, which the crystal space group suggests is not planar. Turning the rings out of the plane of the radical is expected to increase the spin population on C_α (for a 90° rotation of both rings the unpaired electron should reside wholly in a non-bonding $2p$ orbital on C_α).

We have taken account of these effects by standard techniques. We made Hückel calculations where the resonance integral of the $C_{(1)}$–C_α and $C_{(1')}$–C_α bonds was varied according to $\beta' = \beta \cos\theta$, where θ is the angle of twist, out of the radical plane, of the rings.[6] These Hückel orbitals were then used as a basis for an approximate self-consistent field treatment by McLachlan's method.[7] The values of ρ_α, the spin population at C_α, for various angles of twist, are as follows.

θ	0°	10°	20°	30°	60°	90°
ρ_α	0·535	0·543	0·576	0·641	0·969	1·000

These indicate that the rings are turned less than 10° out of the radical plane. In view of the simple nature of the calculation and the error in the observed coupling constant it is unwise to attach too much significance to the absolute value. However, we are confident that we are indeed observing diphenylmethyl radicals.

It is interesting to compare the isotropic hyperfine splitting with that of the α-proton in dimesitylmethyl, where the value is[2] 15·24 gauss. Although a direct comparison is not possible because of the inductive effect of the methyl groups, the two results suggest that the rings in dimesitylmethyl are turned further out of the radical plane than they are in diphenylmethyl. This would be expected for the substituted compound. We have attempted to prepare diphenylmethyl in solution using Dixon and Norman's[8] flow technique, but have been unable to find a sufficiently soluble precursor.

Our identification of the radical as diphenylmethyl is in accord with Chilton and Porter's conclusion that this radical is responsible for the strong absorption at 3365 Å in glassy solutions of diphenylmethane γ-irradiated at 77°K.[9] The radical has also been detected optically as a principal photolysis product in similar solutions.[10]

The anisotropic components of the hyperfine interaction in a C–H "aromatic fragment" are well known from both theory and experiment to be about +10·2 gauss in the C–H bond direction, +0·8 gauss along the axis of the p-orbital, and −10·9 gauss in the third perpendicular direction, for an isotropic component of 20·2 gauss (these figures are the average of 15 experimental results quoted by Symons[1]). The simplest method of allowing for delocalisation of the unpaired electron is to scale these values with the spin population in the $2p$ orbital. If we do this to the above values, taking as the scaling factor the ratio of the isotropic coupling constants, the "expected" anisotropic components for diphenylmethyl come to +6·0, +0·5, and −6·4 gauss, to be compared with the observed values of +3·2, +0·9, and −4·1 gauss. Thus our observed values are rather less anisotropic than expected from the simplest approach. This may be a consequence of the delocalisation in diphenylmethyl.

Drastic effects on the anisotropic hyperfine components have been observed in unsaturated radicals derived from glutaconic acid[11] and from furoic acid.[12] For protons attached to carbon atoms where the spin population is negative, and thus inescapably small, there is a large contribution to the anisotropic coupling from the relatively large positive spin populations on the neighbouring carbon atoms. This has the effect of making the anisotropic component of smallest magnitude parallel to the C–H bond. Such a severe effect is a consequence of the particular distribution of spin populations in these radicals and it is inconceivable that anything comparable should happen at C_α in diphenylmethyl. We therefore assume that the alignment of the anisotropic components of the hyperfine interaction with

[6] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961.
[7] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[8] W. T. Dixon and R. O. C. Norman, *J.*, 1963, 3119.
[9] H. T. J. Chilton and G. Porter, *J. Phys. Chem.*, 1959, **63**, 904.
[10] G. Porter and E. E. Strachan, *Trans. Faraday Soc.*, 1958, **54**, 1595.
[11] C. Heller and T. Cole, *J. Chem. Phys.*, 1962, **37**, 243.
[12] R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, 1964, **7**, 57.

respect to the C–H bond is the normal one for α protons and deduce that the C–H bond in the diphenylmethyl radicals is perpendicular to the *b* axis and makes angles of about 15° and 105° with the *a* and *c* axes of the monoclinic crystal. This direction should correspond closely to the bisector of the $C_{(1)}$–C_{α}–$C_{(1')}$ angle in the original molecules.

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