

ESR DETECTION OF THE DIPHENYLMETHYL RADICAL

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Electron spin resonance (esr) spectroscopic (1) examination of diphenylmethylenetriphenylphosphazine (2), azobisdiphenylmethane (3) or diphenyldiazomethane (4) during thermolysis, in solvents capable of hydrogen donation, e.g. decalin and diphenylmethane, unequivocally demonstrates the presence of a radical species.

Figure 1 records the derivative of the esr spectrum of the hitherto unobserved diphenylmethyl radical, $(C_6H_5)_2CH\cdot$, $g \cong 2.0030$. This radical is presumably generated via the corresponding diphenylmethylene produced on fragmentation of the above compounds.

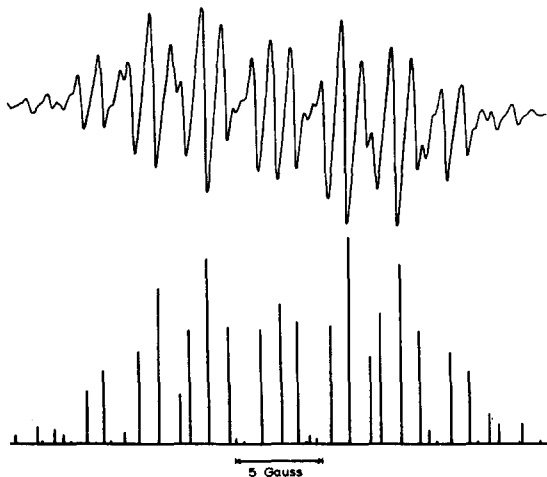


Figure 1. The derivative of the resonance absorption spectrum of a solution of the diphenylmethyl radical $(C_6H_5)_2CH\cdot$ in decalin at 140°

In general, in contrast to Figure 1, ortho alkylated diarylmethyl radicals reported (5) do not show complications due to overlapping of the doublet halves and the relative hyperfine splittings of the ortho, meta and para hydrogens.

The computer-simulated spectrum (Figure 2) (6) utilizing the experimental hyperfine splitting constants presented in Table 1, served to confirm our conclusions regarding the validity of these values.

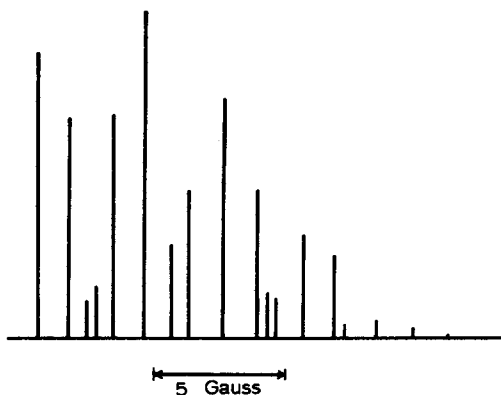


Figure 2. The computed resonance absorption spectrum of the diphenylmethyl radical $(C_6H_5)_2CH\cdot$ (Half spectrum shown.)

Table 1.- Hyperfine splitting constants, a_H , and spin densities, ρ , for various (9,10,11, 12) values of Q.

	SPIN DENSITIES			
	<u>ortho, para</u> $a_H = 3.05$	<u>meta</u> $a_H = 1.22$	<u>central</u> $a_H = 8.36$	<u>adjacent</u>
<u>Value of Q (ref.)</u>				
23 ^a (2b, 12)	0.133	-0.053	0.363	-0.05
27 ^b (11)	0.113	-0.045	0.602 ^c	-0.05
23 ^b (2b,12)	0.133	-0.053	0.514 ^d	-0.05

a. This value of Q used for all positions.

b. This value of Q used for ring positions only.

c. Calculated spin density, $1.00 - \Sigma$ of spin densities in rings; $Q_{center} = 13.8$

d. Calculated spin density, $1.00 - \Sigma$ of spin densities in rings; $Q_{center} = 16.2$

Table 1 also presents spin densities for various values of Q (7) calculated from the experimentally determined hyperfine splittings (9).

It has been noted that introduction of phenyl groups onto a carbon atom bearing an unpaired electron results in a lower electron density at that carbon and a prediction of $P_{\text{center}} = 0.66$ has been made for the radical reported (13). Our experimentally observed a_{H} and $P_{\text{center}} = 0.60$ tends to confirm the original prediction.

Finally, since the ratio of the exchange integral between the rings and the central carbon atom (K) and the exchange integral between the ring atoms (J) is directly related to the angle subtended by the odd-electron p_z orbital and the pi cloud of the aromatic rings (14) it is possible to infer that the angle of twist in the unsubstituted diphenylmethyl radical is 50-60° for both rings. This relationship is, in part, substantiated by examination of models, which also demonstrate that both rings in ortho-substituted diaryl radicals (5) need not participate to the same extent.

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6. We gratefully acknowledge the able assistance of the Computation Center, Massachusetts Institute of Technology, Cambridge, Massachusetts, for their help in obtaining the simulated spectrum. It is to be noted that a greater than 5% variation in the experimental a_H values given in Table 1 for the ortho and para hydrogens was not acceptable. HMO-SCF calculations give spin densities: central = +0.63016; ortho = + 0.1198; meta = - 0.0458 para = + 0.1189.
7. a_H and ρ , the spin density, are related through the equation $a_H = Q\rho$, where Q is a semi-empirical constant (8)
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9. It has been pointed out that the various semi-empirical relationships between a_H and the spin density, ρ , become equivalent for neutral odd-alternate hydrocarbon radicals (10). Nevertheless, there are numerous (10, 11, 12) suggestions relating to the absolute value of Q in these systems. Utilizing $|Q| = 23$ (2b, 11), for all positions results in an unusually low ρ at the central carbon atom, whereas, if it is used for the ring positions only, ρ at the central carbon atom becomes 0.514 and $|Q|$ assumes a value of 16.2. If $|Q|$ is assigned the value of 27 (10) for the ring positions only, then $\rho_{\text{center}} = 0.602$ and $|Q|_{\text{center}} = 13.8$. Adjustment of $|Q|$ has been treated elsewhere (12).
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