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ELECTRON SPIN RESONANCE STUDIES ON NEUTRAL AROMATIC HYDROCARBON RADICALS

SUBSTITUENT AND ISOTOPE EFFECTS

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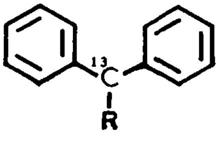
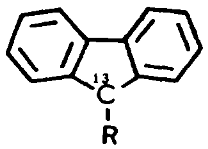
Abstract—The neutral, ^{13}C bearing, radicals diphenylmethyl and 9-fluorenyl have been generated in solution and the hyperfine coupling between ^{13}C and the free electron obtained. On the basis of this information, the nonplanarity assigned to these radicals is seen to lie not in the hybridization of $C_{central}$, which is sp^2, but rather in the "propellor" type disposition of the phenyl rings. Some substituted neutral diphenylmethyl radicals have also been examined and no simple correlation between the usual sigma σ substituent parameters and the hyperfine (a_H) splitting constants of the hydrogen at $C_{central}$ is apparent.

INTRODUCTION

THE preparation and properties of the parent odd-alternant unsubstituted diphenylmethyl and non-alternant 9-fluorenyl neutral radicals have recently been reported.[1] These radicals were generated in a suitable hydrogen donating solvent (decalin or bicyclohexane) by thermolysis of the corresponding diazo compound or phosphazine precursor.[1d] Of particular importance with regard to these systems were the observations: (a) that ring substituents appeared to affect the spin distribution within the system; as reflected in the hyperfine coupling constant, a_H, of the hydrogen at the central C atom, $C_{central}$, and (b) that there was unexpectedly high spin density at $C_{central}$ for what was presumbly a planar system. This high spin density was accounted for by assuming that the systems were nonplanar.[1c]



I: R = H
II: R = D



III: R_1 = H
IV: R = D

On the basis of these results, therefore, we have examined additional substituted diphenylmethyl radicals in hopes of observing significant correlations between spin density and substitution and, since there are, *a priori*, two ways in which such a system could be nonplanar, i.e. the plane defined by the hydrogen attached to $C_{central}$ and the C atom of each of the benzene rings attached to $C_{central}$ could (sp^2) or could not (sp^3) contain $C_{central}$, we have examined the interaction of the odd electron with the suitably substituted ^{13}C compounds.

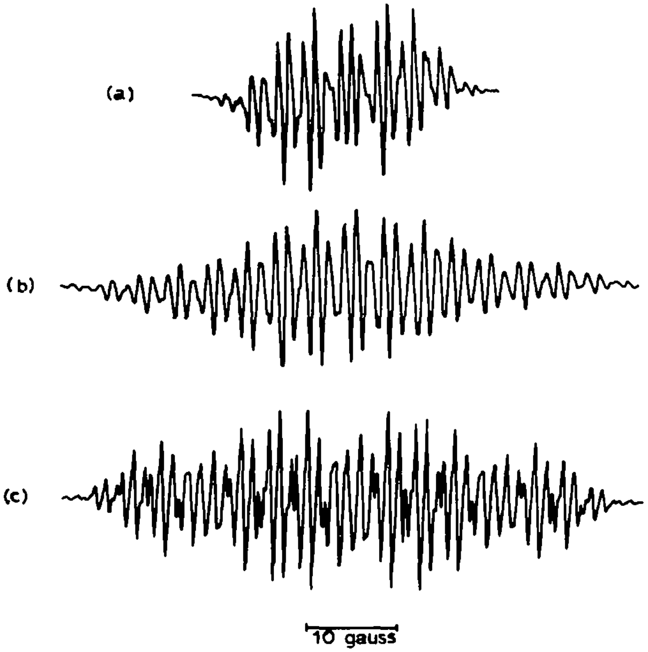


FIG 1. (a) Experimental spectrum, the diphenylmethyl radical, $[(C_6H_5)_2{}^{12}CH\cdot]$ in bicyclohexane at 180°; 1H = 8·36 gauss, 6H = 3·05 gauss, 4H = 1·22 gauss, line width = 0·4 gauss; (b) Experimental spectrum, the diphenylmethyl radical, $[(C_6H_5)_2{}^{12}CH\cdot]$ and $[(C_6H_5)_2{}^{13}CH\cdot]$ in bicyclohexane at 180°. (c) Computed spectrum, the diphenylmethyl radical, $[(C_6H_5)_2{}^{12}CH\cdot]$ and $[(C_6H_5)_2{}^{13}CH\cdot]$, ratio ^{13}C:^{12}C = 42:58. For ^{12}C, 1H = 8·80 gauss, 6H = 3·05 gauss, 4H = 1·22 gauss, line width = 0·4 gauss and for ^{13}C, 1 ^{13}C = 32·0 gauss, 1H = 8·80 gauss, 6H = 3·05 gauss and 4H = 1·22 gauss.

Finally, since deuterium substitution often gives an independent check of spin density assignments, thermolysis of the appropriate precursors in perdeuteriodecalin was also examined.[2]

RESULTS

Fig 1 presents for comparison the spectrum of the unlabelled (^{12}C) diphenylmethyl radical, the spectrum of a mixture of $^{12}C_{central}$ and $^{13}C_{central}$ diphenylmethyl radical (experimental) and the spectrum of a mixture of $^{12}C_{central}$ and $^{13}C_{central}$ diphenylmethyl radical (calculated).* Comparison of the observed spectral widths ($^{12}C_{central}$, ca. 29 gauss; $^{13}C_{central}$, ca. 63 gauss) indicates the $^{13}C_{central}$ splitting constant, $a_{^{13}C}$ = ca. 32 gauss. The simulated spectrum, using a ^{13}C:^{12}C ratio of 42:58, assigns $a_{^{13}C}$ = 32·0 gauss, $a_{H_{central}}$ = 8·80 gauss, $a_{H_{ortho}} = a_{H_{para}}$ = 3·05 gauss (6H) and $a_{H_{meta}}$ = 1·22 gauss (4H). The hyperfine splitting constants for hydrogen given above are the same as those assigned to the ^{12}C spectrum.[1c] Further optimization of the computed spectrum was not attempted since over ten (10) independent variables are involved and more exact analysis appeared unwarranted at this time.

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* We gratefully acknowledge the able assistance of Mr. R. Sheinson, Chemistry Department, Massachusetts Institute of Technology, Cambridge, Mass. for the computer simulated spectra, which were carried out with the WESRP-1 program on a GE-360 computer equipped with a CalComp plotter.

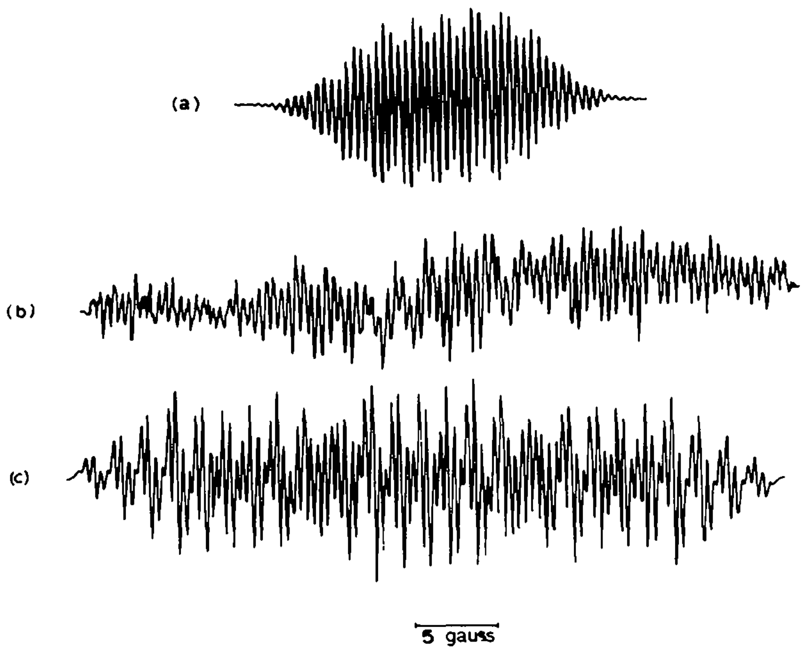

FIG 2. (a) Experimental spectrum, the 9-fluorenyl radical-^{12}C in bicyclohexane at 180°; 1H = 7·0 gauss, 2H = 3·75 gauss, 2H = 1·89 gauss and 4H = 0·49 gauss. (b) Experimental spectrum, the 9-^{12}C-fluorenyl radical and the 9-^{13}C-fluorenyl radical in bicyclohexane at 180°. (c) Computed spectrum, the 9-^{12}C-fluorenyl radical and the 9-^{13}C-fluorenyl radical, ratio $^{13}C:^{12}C$ = 45:55. For ^{12}C, 1H = 7·0 gauss, 2H = 3·75 gauss, 2H = 1·89 gauss and 4H = 0·49 gauss, line width = 0·3 gauss. For ^{13}C, 1 ^{13}C = 27·0 gauss with other values as in ^{12}C case.

Fig 2 presents, for comparison, the spectrum of the unlabelled (^{12}C) 9-fluorenyl radical, the spectrum of a mixture of ^{12}C-9-fluorenyl radical and ^{13}C-9-fluorenyl radical (experimental) and the spectrum of ^{12}C-9-fluorenyl and ^{13}C-9-fluorenyl radicals (calculated). For the parent species, the spectral width is ca. 21 gauss[1c] while for the ^{13}C species, the spectral width is ca. 48 gauss. The computer simulated spectrum presented assigns $a_{^{13}C}$ = ca. 27·0 gauss and $a_{H_{central}}$ = 7·0 gauss and 2H = 3·75 gauss, 2H = 1·89 gauss and 4H = 0·49 gauss.[1c] The $^{13}C:^{12}C$ ratio used is 45:55.

Fig 3 presents for comparison the spectra obtained when $^{12}C_{central}$ diphenyldiazomethane and enriched $^{13}C_{central}$ diphenyldiazomethane were thermolyzed, respectively, in perdeuteriodecalin.* The first spectrum is assigned to the neutral ^{12}C-7-deuteriodiphenylmethyl radical and the second to the ^{13}C-7-deuteriodiphenylmethylradical (II), each formed by abstraction of a deuterium atom from the solvent by the carbene generated in the thermolysis process.[1d] The latter spectrum is assigned $a_{^{13}C}$ = ca. 33 gauss and a_D = 0·9 gauss with the remainder of the proton splittings as previously mentioned. For the ^{12}C-deuterated species, we assign a_D = ca. 1·2 gauss as based on the experimentally determined spectra. As previously noted[1c] computer

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* Qualitatively, slightly higher temperatures were needed for the thermolysis in this solvent.

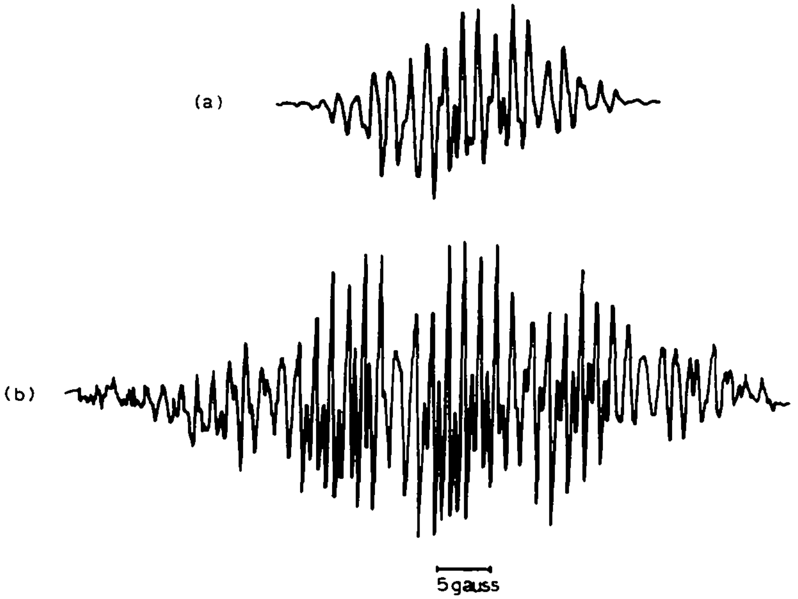

FIG 3. (a) Experimental spectrum, the 7-deuteriodiphenylmethyl radical $[(C_6H_5)_2{}^{12}CD\cdot]$ in decalin-d_{18} at 180° (b) Experimental spectrum, the 7-deuteriodiphenylmethyl radical $[(C_6H_5)_2{}^{12}CD\cdot]$ and $[(C_6H_5)_2{}^{13}CD\cdot]$ in decalin-d_{18} at 180°

simulated spectra generated as above for these deuterated species remain unsatisfactory. Meaningful spectra from ^{12}C and ^{13}C-9-diazofluorene were not obtained when these compounds were thermolyzed in perdeuteriodecalin.

DISCUSSION

Table 1 presents the collected data for these systems. The ^{13}C hyperfine splitting constants are those experimentally determined and the resultant $|Q|$ values were obtained from the modified McConnell equation[3] $[a_{^{13}C} = Q_1\rho_1 + Q_2(\rho_2 + \rho_3)]$. The ^{13}C-methyl radical ($a_{^{13}C}$ = 41 gauss) has been assigned a planar configuration[4] on the basis of the calculation that the hyperfine coupling for an electron in a carbon 2s orbital should be 1130 gauss;[5] there is, thus, a very small (~3%) s contribution to the p orbital or the observed coupling arises from spin polarization.[6] For the neutral

TABLE 1

Radical	$a^{13}C_{central}$ (gauss)	$\|Q\|_{^{13}C}$
Diphenylmethyl, ^{13}C—H	31·0	50
Diphenylmethyl, ^{13}C—D	33·0	51
9-Fluorenyl, 9-^{13}C—H	27·5	40
9-Fluorenyl, 9-^{13}C—D	—	—
		$\|Q\|_{^{12}C}$
Diphenylmethyl, ^{12}C—H	—	14
9-Fluorenyl, 9-^{12}C—H	—	11

trifluoromethyl radical, however the ^{13}C hyperfine splitting constant, $a_{^{13}C}$, is ca. 271 gauss[7] from which it can be argued that the unpaired electron has ca. 25% s character and that the hybridization around carbon is sp^3 with a pyramidal structure prevailing.

The triphenylmethyl radical ($a_{^{13}C} = 26$ gauss) which, by the above argument has almost complete sp^2 hybridization is, nevertheless, nonplanar (ca. 30° deviation from the plane)[8] on what is presumably steric grounds. If therefore, the hybridization at C_{central} for the diphenylmethyl radical is close to that of the triphenylmethyl radical and our earlier results bearing on the apparent nonplanarity of the diphenylmethyl radical are correct,[1c] similar twisting must result. The $a_{^{13}C}$ of ca. 31 gauss for the diphenylmethyl radical, lying between methyl and triphenylmethyl, tends to confirm that the hybridization at C_{central} for the diphenylmethyl radical is sp^2 and that the phenyl groups must, therefore, on the basis of the above argument, assume a twisted "propellor" type conformation much the same as in the triphenylmethyl case. We have computed[1c] that the deviation from planarity is, in fact, ca. 50° on the basis of $\cos^2$ approximations. The results expressed here thus tend to confirm the twisting observed since with sp^2 hybridization at C_{central} the steric requirements of the benzene rings can not be accommodated in any other way.

For the 9-fluorenyl radical, the same argument is applied. Here, however, it is necessary to vary the bond integral, β, for the single bond between the benzene rings from a reasonable 0·90–1·00 value in order to accommodate the twist required by the high spin density on C-9.[1c] Curiously, a small amount of twisting is also, from inspection of models, required, in this case, if the C-9 C atom of the neutral fluorenyl radical is to be co-planar with its three immediate substituents.

TABLE 2

Radical	$^{a}H_{\mathrm{central}}$ (gauss)
Diphenylmethyl	8·50
p-Methoxyphenylmethyl[a]	10·8
p-Chlorophenylphenylmethyl	8·7
*p,p'*Dichlorodiphenylmethyl	7·7
p-Pyridylphenylphenylmethyl	7·8

[a] The resolution of the spectrum of this radical[1c] has been improved to yield a_H = ca. 0·4 gauss for the protons of the methoxy group.

With respect to the thermolysis reactions in perdeuteriodecalin, we have previously shown[1c] and we indicate here (*vide supra*) that the expected relationship $a_D = 0{\cdot}15\ a_H$[9] results in assigned a_D values which fail to generate acceptable computer simulated replications of the observed spectra. If the hydridization is sp^2 as indicated, we do not yet understand the reason for this discrepancy although precedent for deviations of this sort does exist.[10]

In this regard, however, it is important to note that significant deviations in the hyperfine coupling constants result *for* ^{13}C depending upon whether a hydrogen or a deuterium is attached to that carbon and, in addition, the a_H and a_D values themselves appear dependent upon whether they are bonded to a ^{12}C or ^{13}C atom.

Finally, with regard to substituents, Table 2 presents the hyperfine coupling constants (a_H) at $C_{central}$ for a small number of substituted diphenylmethyl radicals. Although the number of examples is limited, there does not appear to be a simple correlation between the usual substituent constants[6,11,12] (σ and/or σ^-) and the experimentally determined hyperfine splitting constants. Thus, although σ and/or σ^- substituent constants have successfully been correlated with electron delocalization in some neutral radicals, radical anions and radical cations[6] our results do not show that such a relationship exists for the radicals we describe. We tentatively suggest that such an apparent lack of correlation may be due to (i) the limited number of samples and/or (ii) to the extensive twisting of the rings (*vide supra*) which might, in a qualitative sense, effect some substituents more than others *vis-a-vis* electron delocalization.

Although we continue to seek and examine additional examples of these substituted radicals, it appears that the dictates of natural life times (at the temperatures involved), temperature-dependent radical conformations resulting in overlap variations, and $H_{central}$ anisotropy will limit the applicability of the method.

EXPERIMENTAL

ESR spectra were determined as previously reported.[1c]

^{13}C-Diazodiphenylmethane and 9-^{13}C-diazofluorene were prepared as previously noted[1c] from the corresponding ^{13}C-ketones. The ketones (ca. 50% enrichment) were used as obtained from Merck Sharpe and Dohme of Canada, Ltd.

The substituted diphenyldiazomethanes were prepared from their respective ketones[1d] which were obtained, and used as received, from Aldrich Chemical Co., Milwaukee, Wisc.

Perdeuteriodecalin (99·5% min) was obtained from Merck Sharpe and Dohme of Canada, Ltd. and used as received. Its purity was established as indicated by IR, PMR and GLPC.

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