Experimental Section

Nmr Measurements. The pmr spectra were taken with a Varian HA-100 and an A-60A (or A-60) spectrometers in about 10% solutions in D_2O containing DSS as an internal reference at various temperatures. The $^1H,^1H$ double-resonance experiments were carried out by using the HA-100 spectrometer operating at 100 MHz in the frequency-swept and DSS-locked mode with a Hewlett-Packard HP-200ABR audiooscillator. The peak positions were calibrated by direct readings of frequencies using a Hewlett-Packard HP-5212A electronic counter with accuracies to ±0.1 Hz. The spectra taken with the A-60A (or A-60) spectrometer were calibrated by the usual side-band method.

The $^1H,^{14}N$ double-resonance spectra of I and III at 100 MHz were recorded on the Varian HA-100 spectrometer equipped with an NMR Specialties HD-60B heteronuclear $^1H,^{14}N$ spin decoupler operating at about 7.224 MHz. All the spectra were taken in the frequency-swept and DSS-locked mode. The modulation frequencies were directly read by using the HP-5212A electronic counter.

The $^1H,^{14}N$ double-resonance spectrum of I at 60 MHz was measured with the Varian A-60 spectrometer equipped with an NMR Specialties HD-60A heteronuclear $^1H,^{14}N$ spin decoupler operating at about 4.33 MHz.

The ^{14}N nmr spectrum of I was determined with a Spectrospin AG (Zürich) HX-3 spectrometer at a frequency of 6.50 MHz (a field of about 21 kG) with simultaneous field-frequency locking on the $N^+(CH_3)_3$ proton resonance and $^1H,^{14}N$ decoupling of the CH_3 protons. The spectrometer was operated in the frequency-swept mode. The solution used was 30% in D_2O; the sample tube has 13 mm o.d. Referencing was achieved by inserting a tube containing an acidified aqueous ammonium nitrate solution.

Materials. Trimethylvinylammonium bromide (I) was commercially available.

Trimethyl-(*trans*-β-phenylvinyl)ammonium bromide (II) was prepared according to Truce and Simms.[51]

Trimethyl-(α-bromovinyl)ammonium bromide (III) was prepared according to Klages and Drerup;[27] ν_{max}^{KBr} 3000 (m), 1650 (m), 1625 (m), 1470 (m), 1410 (m), 1235 (m), 1145 (m), 1090 (m), 940 (s), 920 (s), and 875 (s) cm^{-1}.

Anal. Calcd for $C_5H_{11}NBr_2$: C, 24.50; H, 4.49. Found: C, 24.52; H, 4.44.

Trimethyl-(α,β-dichloroethyl)ammonium Bromide. Chlorine gas was bubbled during 3 hr through a solution of I (4.85 g) in chloroform (200 ml). The dichloro addition compound precipitates out during the reaction. After removal of the solvent, the crystals are washed with small quantities of absolute ethanol to obtain 5.49 g of the dichloro product (yield 80%); ν_{max}^{KBr} 3020–2900 (s), 1450–1490 (s), 1420 (m), 1320 (m), 1285 (s), 1240 (m), 1195 (m), 1140 (w), 1055 (w), 965 (s), 955 (s), 935 (m), 880 (s), 790 (s), and 740 (s) cm^{-1}.

Anal. Calcd for $C_5H_{12}NBrCl_2$: C, 25.40; H, 5.10. Found: C, 25.57; H, 5.24.

Trimethyl-(α-chlorovinyl)ammonium Bromide (IV). Trimethyl-(α,β-dichloroethyl)ammonium bromide was treated with the equivalent quantity of potassium ethoxide in absolute ethanol at room temperature. Potassium chloride precipitates out. After standing 3 hr at room temperature the solution was filtered and concentrated under reduced pressure. The product (IV) was precipitated by an addition of ether and recrystallized from absolute ethanol (yield *ca.* 30%). The infrared spectrum (KBr) is nearly identical with that of III.

Anal. Calcd for $C_5H_{11}NBrCl$: C, 29.95; H, 5.53; N, 6.98. Found: C, 29.92; H, 6.42; N, 6.36.

Trimethyl-(α-ethoxyvinyl)ammonium bromide (V) was obtained by the procedure described by Arens, Bouman, and Koerts.[26]

Acknowledgments. M. O. and K. T. thank Dr. T. Maeda (Shionogi and Co., Ltd., Osaka) for preparation of the compound II. J. M. L. and R. S. thank Mr. Keller (Spectrospin A.G., Zürich) and J. P. Kintzinger (Institut de Chimie, Strasbourg) for measuring the ^{14}N nmr spectrum.

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(51) W. E. Truce and J. A. Simms, *J. Org. Chem.*, 22, 762 (1957).

Electron Spin Resonance Studies on Neutral Aromatic Hydrocarbon Radicals

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Contribution from the Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122. *Received September 20, 1968*

Abstract: Electron spin resonance (esr) spectra have been obtained for the diphenylmethyl, fluorenyl, and perinaphthenyl neutral free radicals. These radicals were generated *via* thermolysis of phosphazine and/or diazo precursors in solvents capable of hydrogen donation and investigated as a function of temperature. The spectra obtained compared favorably with computer-simulated spectra generated from the experimentally determined hyperfine coupling constants. The geometry of these systems is discussed in light of previously developed semiempirical relationships.

The generation of radical species *via* the thermolysis of certain phosphazines and their diazo precursors, in solvents capable of hydrogen donation, has been demonstrated.[1] Analysis of the products obtained on thermolytic decomposition of diphenylmethylenetriphenylphosphazine was in concert with initial fragmentation to triphenylphosphine and the corresponding diaryldiazomethane; the latter undergoing further fragmentation to the carbenic species and subsequent hydrogen abstraction.[2]

When the diazo precursor, as well as azobisdiphenylmethane[3] (a known free-radical precursor) were decomposed, respectively, in decalin, bicyclohexyl, or diphenylmethane solvents, the corresponding free radical was detected.

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(1) D. R. Dalton, S. A. Liebman, H. Waldman, and R. S. Sheinson, *Tetrahedron Lett.*, 145 (1968).

(2) To be published at a later date.

(3) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, 77, 2457 (1955).

Computer-simulated spectra,[4] utilizing experimentally determined hyperfine splitting constants, are in good agreement with the observed spectra. Significant spectral variations, which could also be simulated, were noted as the esr patterns were monitored at various temperatures.

Based on the results reported and previously developed semiempirical relationships[5] inferences as to the geometry of this radical is possible.

Experimental Section

First derivative esr spectra were obtained on a Varian 4500-10A, X-band spectrometer with 12-in. rotating magnet, 100-kHz field modulation, variable-temperature insert dewar, V-4540 controller, and V-4533 cylindrical cavity. Reported temperatures are considered accurate to ±5°. Samples were decomposed in sealed esr tubes (degassed solvents and He atmosphere) within the cavity. Control samples in which open tubes and undegassed solvents were utilized resulted in the same spectral patterns.[6] For all recorded spectra, g values were determined[7] to be 2.0030 ± 0.0003 using a Hewlett-Packard 5245L frequency counter, 5253B frequency converter, a 2590B (microwave) frequency converter, and an nmr precision gaussmeter, G-502, Ventron Instruments Corp., Burlington, Mass.

Pmr spectra were obtained on a Varian A60-A spectrometer; ir spectra on a Beckman IR5A spectrophotometer,[8] and uv spectra on a Perkin-Elmer 237 spectrophotometer. Melting points were determined with a Fisher-Johns block and are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del. Gas-liquid partition chromatography (glpc) was performed with an Aerograph A90-P3 chromatograph with thermal conductivity detector using columns of 5% SE-30 on acid-washed DMCS Chromosorb G, 3% OV-17 on Gas Chrom Q, and/or 5% polyphenyl ether (six rings) on Diaport S. Helium was used as a carrier gas throughout.

Benzophenone, 9-fluorenone, their corresponding hydrazones, tetraphenylethylene, benzopinacole, 1-perinaphthenone hydrazone, 9,9′-bifluorene, and 4-methoxybenzophenone were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis. and used as received. Hydrazine hydrate, 95%, was obtained from Eastman Organic Chemicals, Distillation Products Industries, Rochester, N. Y.; HgO (yellow) powder, from Mallinckrodt Chemical Works, St. Louis, Mo.; and MnO_2, fine powder from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Triphenylphosphine was obtained through the courtesy of the Carlisle Chemical Works, Inc., Reading, Ohio. *o*-, *m*-, and *p*-methylbenzophenones were purchased from K & K Laboratories, Inc., Plainview, N. Y., and were used as received. Bicyclohexyl and *cis*- and *trans*-decalins were obtained from Chemical Samples, Co., Columbus, Ohio and determined to be at least 99.8% pure by glpc. Decalin-d_{18} was purchased from Merck Sharp and Dohme of Canada, Ltd., Montreal, Canada and analyzed to be at least 99.5% pure by glpc, ir, and pmr.

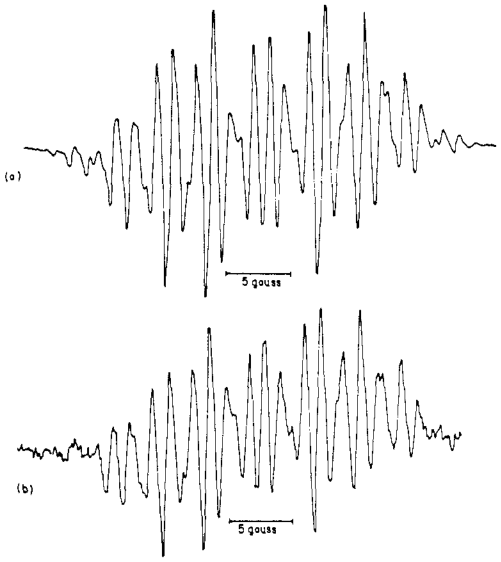

Figure 1. The diphenylmethyl radical, $(C_6H_5)_2CH\cdot$, generated from diphenyldiazomethane at 150° in (a) decalin and (b) in bicyclohexyl.

Phosphazines were prepared by a minimum of two independent procedures.[9] Diphenylmethylenetriphenylphosphazine, mp 170° dec (lit.[9,10] 165 and 173° dec); 9-fluorenylidenetriphenylphosphazine, mp 210° dec (lit.[9,10] 203 and 210° dec); benzylidenetriphenylphosphazine, mp 135° (lit.[9,10] 65 and 130°); 1,1-diphenyl-2-propylidenetriphenylphosphazine, mp 123° (*Anal.* Calcd for $C_{33}H_{29}N_2$: C, 81.72; H, 6.04. Found: C, 81.42; H, 6.10). Benzophenone azine, mp 161° (lit.[11] 163°) and fluorenone azine, mp 275° (*Anal.* Calcd for $C_{26}H_{16}N_2$: C, 87.60; H, 4.41; N, 7.80. Found: C, 87.64; H, 4.30; N, 7.49) were prepared from their corresponding ketones and hydrazones. Azobisdiphenylmethane, mp 110° dec (lit.[3] 114° dec) produces 1,1,2,2-tetraphenylethane, mp 209° (lit.[3] 205–209°). All diazo compounds were prepared as previously noted[12] and exhibited characteristic strong diazo absorption at *ca.* 2040 cm^{-1} and were free of hydrazone absorption in the 3400-cm^{-1} region.

Results and Discussion

I. Identification of Species. The alternate radical species which we report as diphenylmethyl (I) was generated from three different precursors, *viz.*, diphenyldiazomethane, diphenylmethylenetriphenylphosphazine, and azobisdiphenylmethane, in three different solvents, *i.e.*, decalin, bicyclohexyl, and diphenylmethane, in the absence and presence of known thermolysis products.

Figure 1 compares the spectra obtained when the radical was generated from diphenyldiazomethane in decalin and bicyclohexyl solvents, respectively. Figure 2 records the spectra from phosphazine and azo precursors, respectively, in decalin. The dimer of the presumed radical, tetraphenylethane, was identified (glpc) in the thermolytic mixture in *ca.* 20% yields (uncorrected area per cent). A trace of benzophenone or added benzophenone azine did not change the spectral pattern. However, added tetraphenylethylene or the use of diphenylmethane as solvent resulted in some

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(4) We gratefully acknowledge the able assistance of Mr. H. Eto, JEOLCO, Inc., Nutley, N. J. for simulation of the spectra with the JRA-1 spectrum accumulator.

(5) (a) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958); (b) A. D. McLachlan, *ibid.*, **32**, 1488 (1960); (c) C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960); (d) H. M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961); (e) E. W. Stone and A. Maki, *ibid.*, **37**, 1326 (1962); (f) I. Bernal, P. H. Reiger, and G. K. Fraenkel, *ibid.*, **37**, 1489 (1962); R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963); (h) K. Morokuma and K. Fukui, *Bull. Chem. Soc., Jap.*, **36**, 534 (1964); (i) K. Mobius, *Z. Naturforsch.*, *A*, **20**, 1102 (1965); (j) G. A. Russell and K. Y. Chang, *J. Amer. Chem. Soc.*, **87**, 4381 (1965).

(6) This presumably indicates that the hydrogen atom abstraction step is dominant with respect to the competing carbene–oxygen reaction.

(7) Technical assistance in the determination of this value was provided by Mr. G. E. Kemmerer, Jr., Department of Physics, Temple University, to whom we are grateful.

(8) The spectrophotomer was purchased from funds provided by a grant (CA 08841) from the National Cancer Institute, National Institute of Health. We gratefully acknowledge this financial aid.

(9) (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); (b) H. J. Bestman and H. Fritzche, *Ber.*, **94**, 2477 (1961); (c) C. C. Walker and H. Shechter, *Tetrahedron Lett.*, 1447 (1965).

(10) G. Singh and H. Zimmer, *J. Org. Chem.*, 30, 417 (1965).

(11) W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, **76**, 935 (1954).

(12) L. I. Smith and H. L. Howard in "Organic Synthesis," Coll. Vol. III, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1955, p 315.

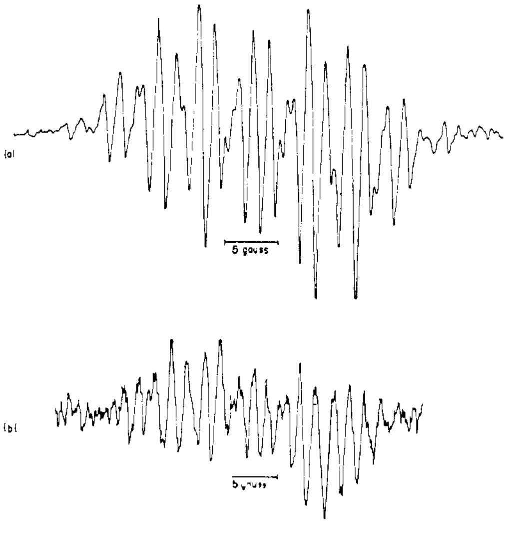

Figure 2. The diphenylmethyl radical, $(C_6H_5)_2$ CH·, generated in decalin solvent (a) from diphenylmethylenetriphenylphosphazine at 180°; (b) from azobisdiphenylmethane at 170°.

spectral complications, while radical traps such as thiophenol or cyclohexene immediately quenched the esr signal. Reference spectra of diphenylhydroxymethyl radical[13] and the diphenyl ketyl species[14] (which are possible oxidation products) were distinctly different from the observed spectrum of I.

Finally, with respect to this species, it has been pointed out[15] that the esr spectra of a number of heavily substituted diphenylmethyl radicals are, except for the C–H doublet in the former, strikingly similar to the spectra of the corresponding ketyl series. The similarity detected for these other cases is also evident in this system.[14,16]

The neutral nonalternant fluorenyl radical (II) was generated from 9-diazofluorene and 9-fluorenylidenetriphenylphosphazine in decalin and bicyclohexyl solvents. The diazo parent decomposed readily at about 125° to generate a relatively stable species with a well-resolved pattern. The spectrum from the phosphazine decomposition at 220° was poorly resolved and short lived. A mixture of the diazo precursor and phosphazine gave the same poorly resolved pattern, which indicated that the presence of secondary products in the thermolysis were responsible for the loss of esr signal due to II. Utilizing the diazo precursor, II was generated in the presence of its azine, 9-fluorenone, 9-fluorenone hydrazone, and its radical dimer, 9,9′-bifluorene, with no change in pattern. Figure 3 presents the spectrum of the neutral fluorenyl radical at *ca.* 60°.

The previously reported spectrum of the perinaphthenyl radical (III)[17] could also be obtained by thermolysis of its diazo precursor. The spectrum, Figure 4, is fully resolved and is in accord with that published.

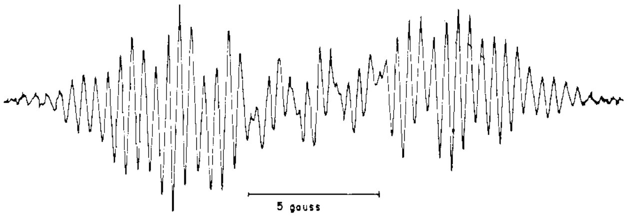

Figure 3. The fluorenyl radical generated from 9-diazofluorene in decalin at 140° and cooled to *ca.* 60°.

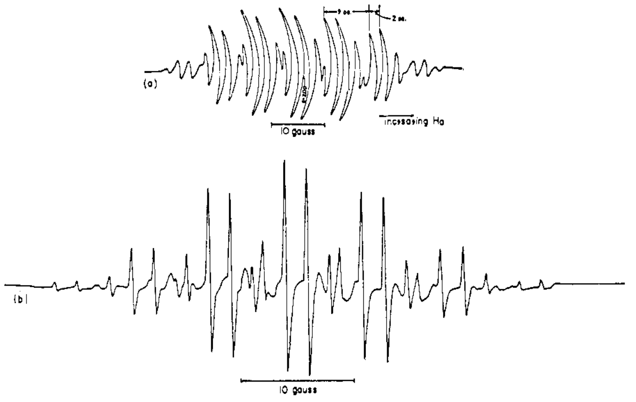

Figure 4. (a) The reported[17] spectrum of the perinaphthenyl radical. (b) The observed spectrum of the perinaphthenyl radical generated from 1-diazoperinaphthene in decalin at 60° and the solution cooled to room temperature.

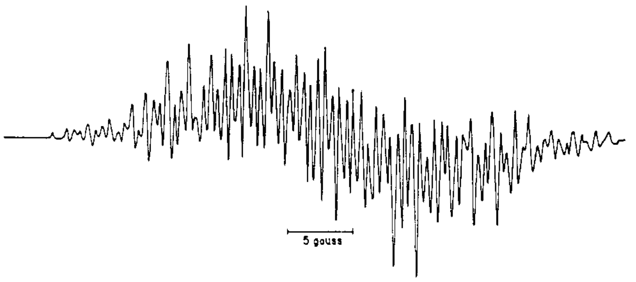

Figure 5. The perinaphthenyl-1-*d* radical generated from 1-diazoperinaphthene in decalin-d_{18} at 60° and the solution cooled to room temperature.

Diphenyldiazomethane, 9-diazofluorene, and 1-diazoperinaphthene were thermolyzed in deuterated decalin ($C_{10}D_{18}$) to produce esr spectra of the corresponding presumed $(C_6H_5)_2CD\cdot$, fluorenyl-9-*d* and perinaphthenyl-1-*d* species. For the first two systems, complete spectral interpretation is not yet possible because of complicating factors inherent at the central carbon position, *i.e.*, using the expected relation $a_D = 0.15a_H$[18a] leads to generation of computer spectra which are inexact comparisons with the experimentally determined spectra. Deviations of this sort have been noted previously with regard to deuterium substitution.[18] For the perinaphthenyl-1-*d* radical, the complex spectrum seen, Figure 5, apparently arises from loss of the respective proton equivalencies.

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(13) R. Wilson, *J. Chem. Soc., B*, 84 (1968).

(14) P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen and Co., Ltd., London, England, 1967, p 274.

(15) H. R. Falle and F. C. Adam, *Can. J. Chem.*, **44**, 1387, 1397 (1966).

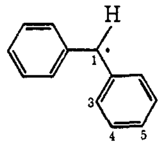
(16) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

(17) P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957).

(18) (a) R. G. Lawler, J. R. Bolton, M. Karplus, and G. K. Fraenkel, *J. Chem. Phys.*, **47**, 2149 (1967); (b) D. M. Schrader and M. Karplus, *ibid.*, **40**, 1593 (1964); (c) I. A. Zlochower, W. R. Miller, Jr., and G. K. Fraenkel, *ibid.*, **42**, 3339 (1965); (d) D. M. Schrader, *ibid.*, **46**, 3895 (1967); (e) M. K. Carter and G. Vincow, *ibid.*, **47**, 292 (1967); (f) T. R. Tuttle, Jr., *J. Amer. Chem. Soc.*, **84**, 1492 (1962).

II. Spectral Interpretation. HMO–SCF computer calculated McLachlan spin densities are presented for three reasonable β values for the diphenylmethyl radical in Table I. Table II presents the observed hyperfine splitting constants, a_H, and spin densities, ρ, calculated for various values of $|Q|$. It is to be noted, as already discussed,[1] that reasonable correlation is attained only if an abnormal (-14) value obtains at the $C_{central}$. This result implies relatively little simultaneous delocalization into both rings.

Table I. HMO-SCF Computed McLachlan Spin Densities, ρ, for the Diphenylmethyl Radical



I

Resonance integral	Position 1	3	4	5
β = 1.00 for all bonds (planar)	0.574	0.130	−0.051	0.131
$\beta_{1,2}$ = 0.90	0.691	0.109	−0.046	0.105
$\beta_{1,2}$ = 0.85	0.754	0.098	−0.043	0.091

Table II. Hyperfine Splitting Constants, a_H, and Spin Densities, ρ, for Various Values of $|Q|$ for the Diphenylmethyl Radical, $(C_6H_5)_2CH\cdot$

Value of $\lvert Q\rvert$	Experimental spin densities[1] 3,5[a]	4[b]	1[c]
23[d]	0.133	−0.053	0.363
23[e]	0.133	−0.053	0.514[f]
27[e]	0.113	−0.045	0.602[g]

[a] a_H = 3.05 G. [b] a_H = 1.22 G. [c] a_H = 8.36 G. [d] This value of Q used for all positions. [e] This value of Q used for ring positions only. [f] Calculated spin density, 1.00 − Σ of spin densities in rings; $|Q|_{central}$ = 16.2. [g] Calculated spin density, 1.00 − Σ of spin densities in rings; $|Q|_{central}$ = 13.8.

Previous work[5c] has dealt with the variation of $|Q|$ as a function of hybridization and bond angle. Thus, it is possible to infer that for I the angle θ, Figure 6, is approximately 127°. In addition, consideration of the angles ψ and ψ', and their possible values obtainable from cos² approximations based on spectral parameters, results in the conclusion that I is nonplanar (ψ' is *ca.* 50°). Experimental support for this contention was obtained by noting the effect of temperature of the observed spectrum and comparing the resultant patterns to computer-simulated spectra, one of which is seen in Figure 7, where only the central a_H coupling constant was permitted to vary. With regard to this, out-of-plane twisting (ψ' = *ca.* 45°) has been predicted[19a] for the carbenic precursor, diphenylmethylene. In addition, it would seem that a nonplanar minimum energy configuration for this radical at these temperatures is necessary in order to produce four equal *ortho* spin density values, since in a planar situation two of the *o*-hydrogens should exist in a considerably different spin locality relative to the other two. Finally, valence bond calculations predict equality of *ortho* and *para* spin densities for this nonplanar system.[15] Computer variation of our reported *ortho* and *para* splitting constants resulted in an optimized pattern only when all four $a_{H_{ortho}}$ were equal and $a_{H_{ortho}} = a_{H_{para}}$ (±5%).

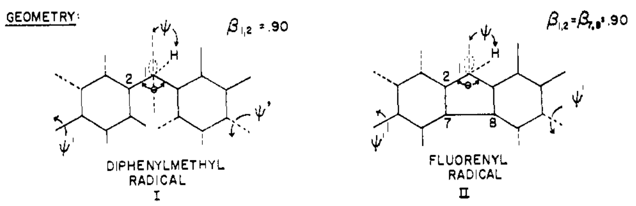


Figure 6.

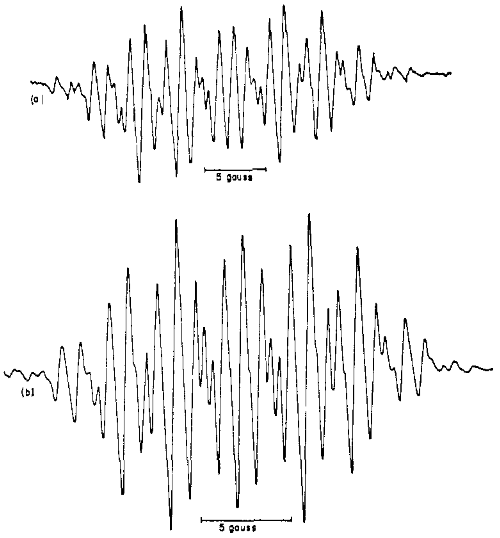


Figure 7. (a) Experimental spectrum; the diphenylmethyl radical, $(C_6H_5)_2CH\cdot$, generated from diphenyldiazomethane in decalin at 140° and the solution heated to 190°. (b) Computer-simulated spectrum; 1 H = 8.50 G, 6 H = 3.05 G, 4 H = 1.22 G; line width = 0.8 G.

It must be pointed out that an alternative explanation is also possible[20] based on the assumption that the radical is planar and, therefore, the spin density at $C_{central}$ is 0.36 and $Q = -23$. This assumption does not, however (1) correlate as well with the HMO–SCF McLachlan spin densities reported nor (2) account for the variation in $a_{H_{central}}$ with temperature.

McLachlan spin densities (HMO–SCF) for the fluorenyl radical (II) are presented, Table III, for three reasonable β values. Utilization of $Q = -27$ for all positions results in calculated spectral widths of (a) 27 G (β = 1.00); (b) 29 G ($\beta_{1,2} = \beta_{7,8} = 0.95$); and (c) 31 G ($\beta_{1,2} = \beta_{7,8} = 0.90$). The observed spectral width is 22 G.

Utilization of $Q = -27$ at all positions except $C_{central}$ (Table IV) and calculation of the resultant $Q_{central}$ yields, as in the case of I, significant deviation from that expected for sp² hybridization. The experimentally determined $a_{H_{central}}$ = 7.0 G requires $Q_{central} = -11$ which in turn corresponds, Figure 6, to θ = *ca.* 133°. The carbenic precursor has been examined[19b-d] and there, θ has been estimated to be >135°.

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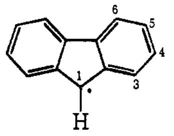
(19) (a) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (b) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 40, 2408 (1964); (c) C. A. Hutchinson, Jr., and G. A. Pearson, *ibid.*, **43**, 2545 (1965); (d) *ibid.*, 47, 521 (1967).

(20) G. A. Russell, *Science*, **161**, 423 (1968).

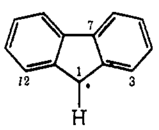
Table III. HMO–SCF Computed McLachlan Spin Densities, ρ, for the Fluorenyl Radical



II

Resonance integral	Position 1	3	4	5	6
β = 1.00 for all bonds (planar)	0.492	0.111	−0.019	0.119	+0.003
$\beta_{1,2} = \beta_{7,8} = 0.95$	0.566	0.110	−0.025	0.112	−0.007
$\beta_{1,2} = \beta_{7,8} = 0.90$	0.648	0.107	−0.030	0.102	−0.015

Table IV. Hyperfine Splitting Constants, a_H, and Spin Densities, ρ, for Various Values of $|Q|$ for the Neutral Fluorenyl Radical



Value of $\lvert Q \rvert$	Position 3,12[a]	4,6,11,9[b]	5,10[c]	1 (central)[d]
	Experimental spin densities			
27[e]	0.139	−0.018	0.070	0.259
27[f]	0.139	−0.018	0.070	0.654[g]

[a] a_H = 3.75 G. [b] a_H = 0.49 G. [c] a_H = 1.89 G. [d] a_H = 7.0 G. [e] This value of Q used for all positions. [f] This value of Q used for ring positions only. [g] Calculated spin density, 1.00 − Σ of spin densities in rings; $|Q|_{\text{central}}$ = 11.0.

Figure 8 presents the reversible variation of spectral pattern observed with changes in temperature. Since the fluorenyl species is more constrained relative to diphenylmethyl, less ring twisting is possible (*i.e.*, ψ' is smaller). The spectral variation, therefore, is probably due to the anisotropy of the H_{central} in temperature-dependent radical conformations. Variations of $a_{H_{\text{central}}}$ *only* from 6.90 to 7.10 G resulted in computer simulated patterns close to the experimentally observed spectra, Figure 9.

Further interpretation of these spectra for inferences concerning the geometry of these systems would be, we feel, inappropriate until totally optimized computer treatments are performed and more exact fundamental relationships between splitting constants and structural parameters become available.

Finally, recent refinement in spin density calculations[21] for the perinaphthenyl radical give calculated $a_{H_1} = -7.5$ and $a_{H_2} = 4.3$ G (lit.[17] (exptl) $a_{H_1} = -7.3$ and $a_{H_2} = 2.2$; this work, $a_{H_1} = -7.0$ and $a_{H_2} = 2.0$ G). If $Q = -27$ then $\rho_1 = 0.26$ and $\rho_2 = 0.07$ (*i.e.*, $a_H = Q\rho$) and the ratio $\rho_1:\rho_2$ = *ca.* 3.7:1. A 1.8:1 ratio for densities $\rho_1:\rho_2$ has been predicted[22] from valence bond theory. Refined MO–SCF (INDO) estimates[21] a 1.7:1 ratio. It appears, therefore, that only the relative magnitudes of the spin densities can be predicted by either calculation.

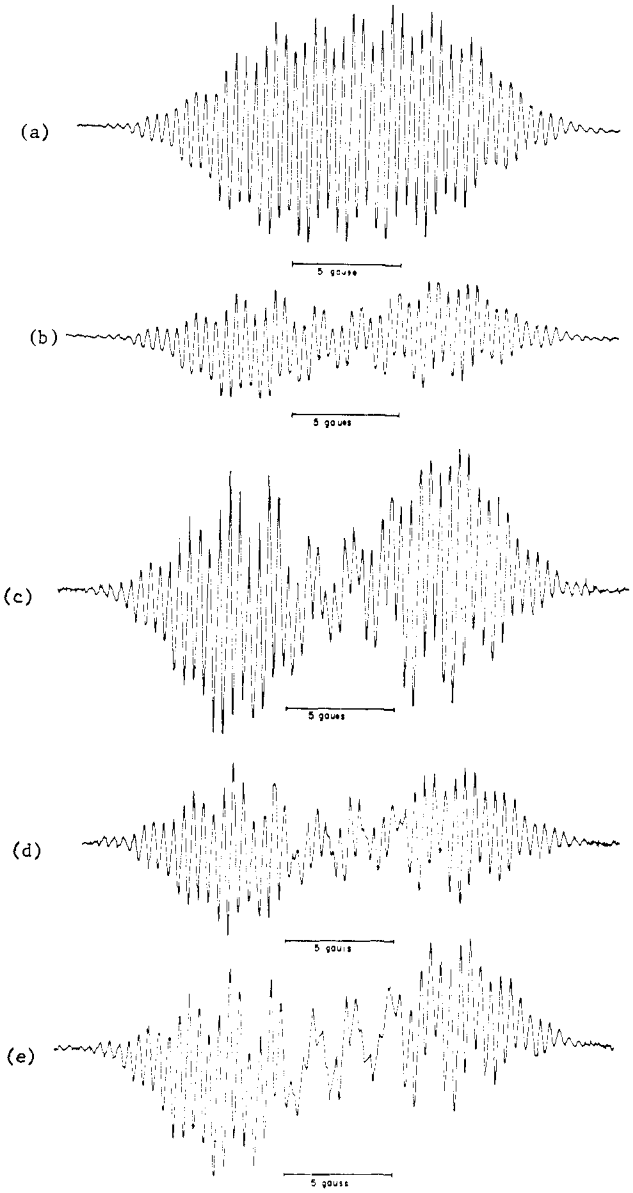


Figure 8. Experimentally determined spectra for the fluorenyl radical generated from 9-diazofluorene in decalin at 140° and the spectrum observed reversibly at (a) 170°, (b) 120°, (c) 100°, (d) 80°, (e) 60°.

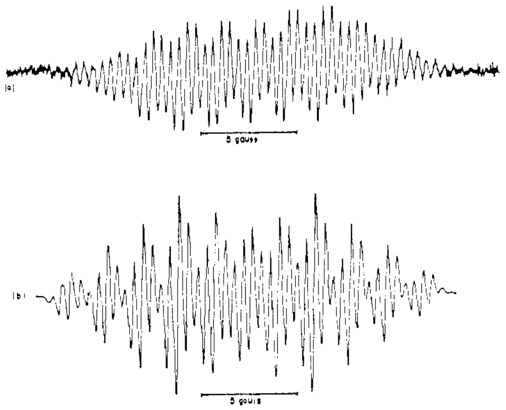


Figure 9. (a) Experimental spectrum; the fluorenyl radical generated from 9-diazofluorene in decalin at 140° and the solution heated to 160°. (b) Computer-simulated spectrum; 1 H = 7.10 G, 2 H = 3.75 G, 2 H = 1.89 G, 4 H = 0.49 G; line width = 0.4 G.

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(21) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

(22) H. M. McConnell and H. H. Dearman, *J. Chem. Phys.*, 28, 51 (1958).

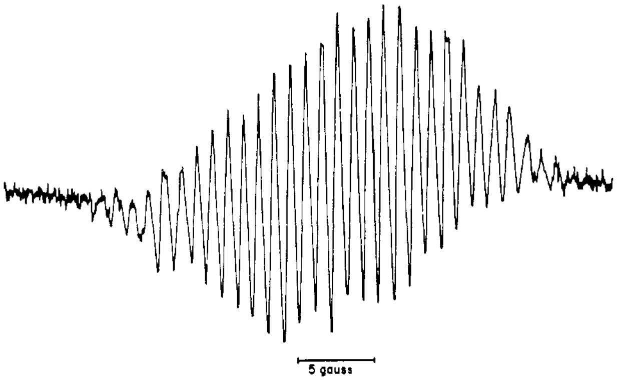

Figure 10. Experimental spectrum of the 3-methyldiphenylmethyl radical, $(3\text{-}CH_3C_6H_4)(C_6H_5)CH\cdot$, generated from 3-methyldiphenyldiazomethane in decalin at 140°.

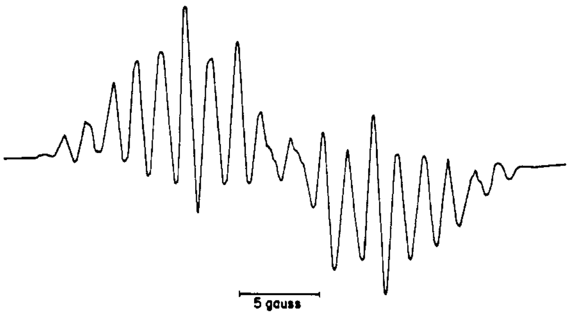

Figure 11. Experimental spectrum of the 4-methoxydiphenylmethyl radical, $(4\text{-}CH_3OC_6H_4)(C_6H_5)CH\cdot$, generated from 4-methoxydiphenyldiazomethane in decalin at 150°.

Conclusion

The generation and observation of radicals obtained *via* hydrogen abstraction from solvent by carbenes has been demonstrated. The carbenes were produced thermally from phosphazines or their diazo precursors.

The utility of these thermolytic methods for the observation of radicals is limited by the following considerations. First, the by-products must be minimized and secondly, a judicious choice of substituents must be exercised so as not to cause lability of the radical.

Demonstration of these factors in the current discussion is provided as follows. (a) The fluorenyl radical, a normally stable species when generated from its diazo precursor, failed to produce a useful spectrum in the presence of its phosphazine (*vide supra*). (b) 2- and 4-methyldiphenyldiazomethanes failed to provide informative spectra, while the *meta* isomer on thermolysis in decalin produced the spectrum shown (Figure 10).[23] In addition, only short-lived signals were obtained from the phosphazines derived from benzaldehyde, benzil, and 1,1-diphenylacetone. Finally, (c) 4-methoxydiphenyldiazomethane on decomposition in decalin resulted in the formation of a paramagnetic species whose spectrum is shown in Figure 11. This species, in which the electron can presumably be delocalized onto the oxygen, is longer lived than the unsubstituted parent in this relatively inert environment, and much longer lived than the corresponding methyl compound.

In the case of the 4-methoxydiphenylmethyl radical (Figure 11) an estimate of increased spin density at the $C_{central}$ can be made. From the obvious doublet pattern ($a_{H_{central}}$ = *ca.* 10.8 G) and the use of $Q = -14$ seen in the unsubstituted parent species, it follows that $\rho_{central} = 0.77$ (rather than 0.60 in the parent). If alternatively, $Q = -23$ then the spin density, ρ, Table I, in the parent species is 0.36 and is 0.47 in the 4-methoxy derivative.[24]

This procedure, therefore, with judicious choice of substituents may provide, regardless which value of Q is used, a way of gauging stabilization provided by delocalization in neutral species.

Summary

For the parent neutral aromatic hydrocarbons studied, the esr spectra infer distorted radical geometry. This conclusion results from utilization of previously developed approximations between hyperfine splitting constants and structural parameters. Temperature dependence studies show complex conformational and/or C–H vibrational variations taking place which are reflected in the sensitive $H_{central}$ splitting constant. Isotope and substituent effects were observed for the neutral radicals. Utilization of this technique for radical generation appears to be applicable only where the criteria of inherent stability and nonreactive environment are met.

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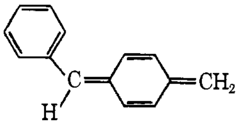
(23) This may be due to the loss of a hydrogen from the methyl group to solvent radical to generate, *e.g.*, i. This mode of decomposition is also available to the 2-methyl derivative but *not* to the 3-methyl. We are seeking evidence for the production of i.



i

(24) We are currently examining further the spectra produced by this and other variously substituted radicals for definitive evidence concerning substituent effects.