Table II. Negative Charge Associated with Methyl Groups

N	2	3	4	5	6
ϵ'	0.046	0.072	0.086	0.096	0.104

electron density ϵ', Table II gives the values of ϵ' for several ions in the series. The trend of the negative charge, ϵ', increasing with n would result in the positive charge in this region decreasing with n, supporting Sorensen's observation.

Acknowledgment. The authors wish to thank Dr. T. S. Sorensen for bringing this problem to their attention and for discussion of the results. The support of the National Research Council of Canada and the award of a University of Calgary Research Assistantship (to R. B. F.) is gratefully acknowledged.

Electron Spin Resonance of Radical Intermediates in the Thermal Decomposition of Diazo Compounds[1]

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Abstract: Electron spin resonance (esr) spectra have been obtained for the stable free-radical intermediates formed during the thermal decomposition of a number of aliphatic diazo compounds. Analyses of the esr hyperfine spectra determined for pyrolyzed diphenyldiazomethanes, diazofluorene, azibenzil, diazoacenaphthenone, and diazophenanthrone show that these intermediates are biradicals or biradical polymers resulting from the secondary reaction of an initially formed carbene. The formation of stable biradicals from these diazo compounds is evidence for the triplet-state nature of their carbene intermediates.

Electron spin resonance (esr) is proving to be an extremely useful technique for detecting and identifying free-radical intermediates in chemical reactions. From a knowledge of the starting materials, reaction products, and analyses of hyperfine spectra, one can infer chemical structures for the radical intermediates. This approach has been successfully applied to mechanism studies of a number of chemical reactions including olefin additions,[2a] the pyrolysis of diazonium salts,[2b] and the photolysis of alcohols and ketones.[3] In this paper we describe the application of esr to the study of the radical intermediates formed during the thermal decomposition of aliphatic diazo compounds.

The pyrolysis of diazo compounds is known to produce divalent carbon (carbene) intermediates, the nature and reactivity of which have been the subject of a large number of investigations.[4–10] Much of the interest has centered on the distinction between the two possible electronic ground-state configurations of divalent carbon species, the singlet and the triplet state. Esr experiments on several diazo compounds photolyzed at low temperatures have proven the existence of stable triplet-state carbenes,[11,12] which would be expected to undergo radical or biradical reactions.[13,14] The radical-like behavior of carbenes has been proposed for addition,[5,15,16] insertion,[17] and rearrangement[18] reactions.

We have studied the esr of the doublet-state radical intermediates formed during the thermal decomposition of a number of diazo compounds in inert liquid solvents. The compounds selected were those for which aromatic substituents would tend to stabilize any radical intermediates. The results of our studies for diphenyldiazomethanes, diazofluorene, azibenzil, diazoacenaphthenone, and diazophenanthrone show that in all cases, stable free-radical intermediates are produced in the decomposition process. The structures of these radical intermediates have been inferred by analysis of the esr spectra and related, where possible, to the final products of decomposition.

Experimental Procedure

Preparation of Diazo Compounds. Diphenyldiazomethane, diazofluorene, azibenzil, and substituted diphenyldiazomethanes were prepared by oxidation of the corresponding hydrazones with HgO.[19] The hydrazones were prepared from the respective ketones

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(1) This research was sponsored in part by the Research and Technology Division, Air Force Systems Command, U. S. Air Force.

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(11) R. W. Brandon, G. L. Closs, and C. A. Hutchison, *J. Chem. Phys.*, 37, 1878 (1962).

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(18) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 45.

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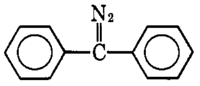
and hydrazine hydrate.[20] Deuterated benzophenone hydrazone, obtained from Merck, Sharp and Dohme, was converted to the diazo compound by the same oxidation procedure. The 2-diazo-1-acenaphthenone and the 10-diazo-9(10H)-phenanthrone were prepared from the corresponding *p*-toluenesulfonylhydrazones.[21]

The esr spectra were measured at 9.3 GHz using superheterodyne detection at a microwave power of 100 μW. No saturation was observed in any of the samples at this power level. Since the microwave frequency was stabilized on the sample cavity, only the pure absorption mode was observed. For the first derivative curves, 1-kHz field modulation was employed. Second derivative spectra were obtained by modulating at 500 Hz and detecting the 1-kHz component of the signal.

Experimental Results

Diphenyldiazomethane. An intense esr spectrum is observed when diphenyldiazomethane $(C_6H_5)_2CN_2$ is heated above 110°, either in the pure state or dissolved in biphenyl. The esr of thermally decomposed $(C_6H_5)_2CN_2$ is quite complex, and the appearance of the spectrum is critically dependent upon reaction conditions. We have observed at least three kinds of esr spectra: spectrum 1, which contains partially resolved hyperfine structure with an alternating intensity distribution; spectrum 2, which consists of partially resolved structure with a uniform intensity distribution; and spectrum 3, which shows more highly resolved hyperfine splittings. Each of these spectra is discussed in the following paragraphs.



Spectrum 1. The first esr spectrum obtained for $(C_6H_5)_2CN_2$ thermally decomposed between 110 and 180° has the general appearance shown in Figure 1a. The particular spectrum in Figure 1a was obtained at 140° for a 5% solution of $(C_6H_5)_2CN_2$ in biphenyl. This incompletely resolved spectrum consists of approximately 39 hyperfine lines extending over 40 G. The most striking feature of the hyperfine pattern is the central portion containing 19 equally spaced lines 0.7 G apart which appear to alternate in intensity. The lines in the wings of the spectrum are not equally spaced. The appearance of this spectrum suggests that it consists of at least two superimposed hyperfine patterns, a central group of evenly spaced lines, and a more complex pattern extending over a wider range of magnetic field. This "alternating spectrum" is symmetrical near the center and has an apparent *g* value of 2.0028 ± 0.0001.

Spectrum 2. When a solution of thermally decomposed $(C_6H_5)_2CN_2$ in biphenyl is held at temperatures between 110 and 180° for more than 15 min, the spectrum transforms irreversibly from that in Figure 1a to that in Figure 1b, spectrum 2. This second spectrum contains approximately 33 equally spaced lines of line width 0.33 G. The lines show a uniform fall-off in amplitude from the center toward the wings and are spaced 0.7 G apart. The *g* value for spectrum 2 was found to be the same as that for spectrum 1. The second spectrum is fairly stable at temperatures below 170°.

We have examined the temperature dependence of the signal amplitude for spectrum 2. As the decomposition temperature for $(C_6H_5)_2CN_2$ is raised from 110 to 170°, the radical concentration increases. The maximum signal is obtained at approximately 170°. The change in amplitude is only partially reversible with temperature.

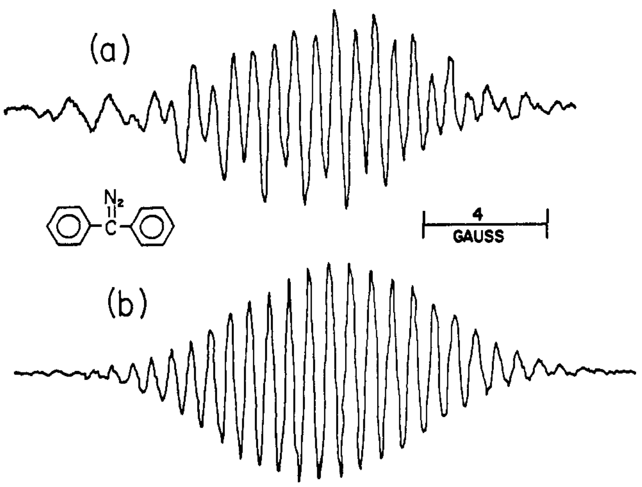


Figure 1. Esr spectra for a 5% solution of $(C_6H_5)_2CN_2$ in biphenyl at 140°: (a) spectrum 1, the "alternating spectrum," (b) spectrum 2, the transformed spectrum after 15 min.

Although the radicals which give rise to spectrum 2 are stable to 170° in the absence of air, they are extremely reactive to both oxygen and uv irradiation. When $(C_6H_5)_2CN_2$ was decomposed in the presence of oxygen, no esr signal was observed. When oxygen was admitted at room temperature to an evacuated sample which had been heated to 170°, the signal disappeared and could be only partially restored by deoxygenating and reheating to the same temperature. Similarly, uv irradiation destroyed the radicals associated with spectrum 2. However, after the radicals formed thermally had been destroyed by irradiation, new radicals could be generated by reheating the sample to high temperatures.

Spectrum 3. Under conditions of high resolution (low microwave power, low modulation, and dilute radical concentration), spectrum 2 could be resolved further to yield a spectrum consisting of sharp hyperfine lines, 0.12 G wide, superimposed on the broad lines (spectrum 3). The relative amplitudes of the sharp and broad-line portions of the spectrum depended on both concentration and temperature. Figure 2d shows the resolved spectrum for a 1% solution of $(C_6H_5)_2CN_2$ in biphenyl at 170°. In this spectrum, the amplitudes of the sharp and broad-line portions of the curve are approximately equal. In no case were we able to obtain a greater proportion of the sharp-line portion of the spectrum.

Although no unique coupling constants could be assigned for the poorly resolved spectra 1 and 2, an analysis was made of the sharp-line portion of spectrum 3. Since there are at least 100 sharp hyperfine lines in this pattern (more than would be expected for the ten protons in a $(C_6H_5)_2C\cdot$ fragment), the presence of nitrogen in the radical seems likely.

In order to ascertain the existence of nitrogen in the radical responsible for spectrum 3, we have also measured the esr of thermally decomposed $(C_6D_5)_2CN_2$ in biphenyl. The spectrum obtained for a 5% solution of $(C_6D_5)_2CN_2$ in biphenyl at 150° is shown in Figure 3.

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(20) O. Grummitt and A. Jenkins, *J. Am. Chem. Soc.*, **68**, 914 (1946).
(21) M. P. Cava, R. L. Litle, and D. R. Napier, *ibid.*, 80, 2257 (1958).

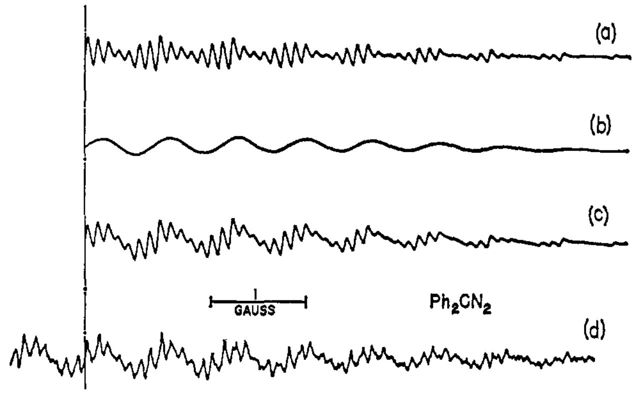


Figure 2. Spectrum 3 for $(C_6H_5)_2CN_2$; comparison of simulated curves with experimental curve d. Curve a, sharp-line spectrum (0.12 G line widths) simulated from coupling constants 1N (a_1 = 1.54 G), 2H (a_2 = 1.43 G), 4H (a_3 = 1.32 G), and 4H (a_4 = 0.77 G). Curve b, broad-line spectrum simulated from same coupling constants as (a) with 0.33-G line widths. Curve c, a 1:1 combination of curves a and b.

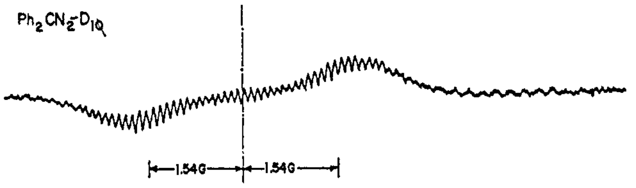


Figure 3. Esr spectrum for a 5% solution of $(C_6D_5)_2CN_2$ in biphenyl at 150°.

The central region of the spectrum exhibits three very similar groups of sharp lines 0.05 G wide with a separation between groups of 1.54 G. The large 1.54-G separation must be assigned to the splitting by one nitrogen. In order to eliminate the possibility of proton–deuterium exchange with the biphenyl solvent in the formation of the radicals, spectra were also obtained for $(C_6H_5)_2CN_2$ decomposed in biphenyl-d_{10}. These spectra were identical with those obtained in the protonated solvent.

It was not possible to obtain a complete analysis of the $(C_6H_5)_2CN_2$ spectrum since, presumably, more than one radical was present. However, the determination of the presence of a single 1.54-G nitrogen splitting made it possible to deduce the following coupling constants (gauss) for the sharp-line portion of spectrum 3 (see Figure 2d): 1N, a_1 = 1.54; 2H, a_2 = 1.43; 4H, a_3 = 1.32; and 4H, a_4 = 0.77. Figure 2a shows the spectrum simulated from these constants to be in good agreement with the sharp-line portion of spectrum 3.

One can reconstruct spectrum 3 completely, by assuming the presence of a second radical with a broader line spectrum. The periodicity of the broad bumps in Figure 2d suggested that the second radical had the same hyperfine splittings as those above but exhibited broader lines. If one constructs a spectrum from these values using a line width of 0.33 gauss, the spectrum in Figure 2b is obtained. Figure 2c shows a composite spectrum simulated by adding equal contributions of the spectra in Figures 2a and 2b.

Substituted Diphenyldiazomethanes. Some esr spectra were also obtained for thermally decomposed methyl- and halogen-substituted diphenyldiazomethanes. These signals disappeared in a matter of a few minutes, suggesting that the radicals were reacting with methyl hydrogens. The only stable spectra were obtained from mono-*p*-bromodiphenyldiazomethane, mono-*p*-chlorodiphenyldiazomethane, and di-*p*-chlorodiphenyldiazomethane. The spectra of all three compounds contained broad lines 0.35 G wide with the same 0.7-G spacing observed in unsubstituted Ph_2CN_2.

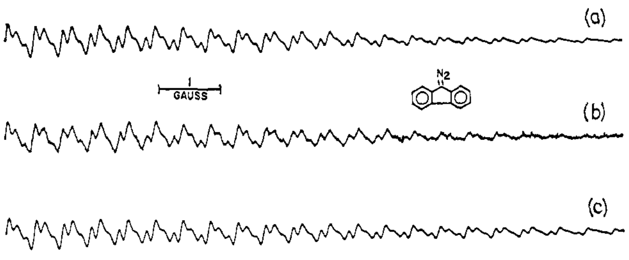
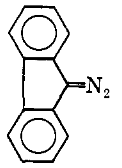


Figure 4. Comparison of simulated esr spectra with experimental curve b for a 10% solution of 9-diazofluorene in biphenyl at 190°. Curve a, simulated from the coupling constants 4H (a_1 = 3.44 G), 4H (a_2 = 1.37 G), 4H (a_3 = 0.83), and 4H (a_4 = 0.42 G). Curve c, simulated with the 4H (a_1 = 3.44 G) replaced by 2N (a_1 = 3.44 G).

9-Diazofluorene. When a solution of 9-diazofluorene in biphenyl was heated above 130°, a stable esr spectrum was observed. The intensity increased reversibly with increasing temperature, although the resolution deteriorated above 200°. The optimum signal was recorded at 190° for a 10% solution of 9-diazofluorene in biphenyl. This spectrum is reproduced in Figure 4b. The partially resolved hyperfine spectrum shows approximately 90 lines with a line width of 0.085 G and a total spectrum spread of approximately 22 G. The *g* value for the spectrum was found to be 2.0027 ± 0.0001.

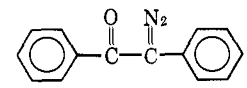


We have found two chemically reasonable coupling constant assignments which are in approximate agreement with experiment. The first assignment involves 16 protons: 4H, a_1 = 3.44; 4H, a_2 = 1.37; 4H, a_3 = 0.83; 4H, a_4 = 0.42 G. The spectrum simulated from this assignment is shown in Figure 4a.

The second assignment attributes the large 3.44-G splitting to two equivalent nitrogens rather than to four protons. The spectrum simulated for this assignment is shown in Figure 4c.

The agreement of Figure 4a with experiment is somewhat better than that of 4c. Furthermore, the measured *g* value is not as high as would be expected for a nitrogen-containing free radical. The 16-proton assignment (Figure 4a) was, therefore, selected for the esr spectrum of the radical from diazofluorene.

Azibenzil. A well-resolved esr signal was obtained when a biphenyl solution of azibenzil was heated above 130°. The signal intensity increased with temperature and showed stability to approximately 265°. Figure 5a shows the esr spectrum obtained for a 10% solution of azibenzil in biphenyl at 180°. Seventy-two hyperfine



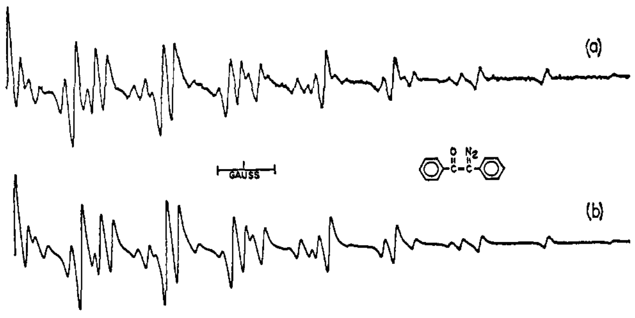
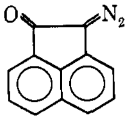


Figure 5. Comparison of simulated and experimental esr spectra for a 10% solution of azibenzil in biphenyl at 130°: (a) experimental spectrum; (b) spectrum simulated from the assignment, 2H (a_1 = 2.88 G), 4H (a_2 = 2.67 G), 4H (a_3 = 1.17 G).

lines with a line width of 0.085 G were recorded. The g value was determined to be 2.0032 ± 0.0001. The spectrum in Figure 5a was readily reduced to the following coupling constants: 2H, a_1 = 2.88; 4H, a_2 = 2.67; and 4H, a_3 = 1.17 G. A spectrum simulated from this assignment is shown in Figure 5b.

1-Diazo-2-acenaphthenone. Our esr study of the

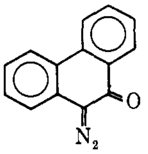


thermal decomposition of 1-diazo-2-acenaphthenone indicated the presence of two discrete radical species. When a biphenyl solution of this diazo compound was heated between 135 and 190°, a complex esr spectrum containing over 100 lines 0.15 G wide was obtained. The g value was 2.0028 ± 0.0001.

When the sample was heated above 190°, a second more stable esr spectrum was obtained. This spectrum had a much simpler hyperfine pattern and contained only 38 lines with a line width of 0.28 G and a g value of 2.0026 ± 0.0001. Because of the poor resolution, second derivative presentation was employed. The spectrum at 200° is shown in Figure 6a. An examination of this spectrum shows the presence of five major groups of hyperfine lines spaced approximately 6.1 G apart. Although there is considerable overlap within the central groups, the outer-most group exhibits a completely resolved triplet of doublets. The triplet spacing is 1.78 G and the doublet separation is 0.34 G.

Figure 6b shows a spectrum computed from the following assignment (values in gauss): 1H, a_1 = 6.26; 1H, a_2 = 6.16; 1H, a_3 = 6.04; 1H, a_4 = 5.76; 2H, a_5 = 1.78; and 1H, a_6 = 0.34. Although this computed spectrum agrees with experiment, it includes hyperfine interactions by seven protons, which is one more than the starting molecule contains. The additional proton could arise from hydrogen abstraction by carbene intermediates; however, experiments in deuterated solvent resulted in the identical spectrum.

10-Diazo-9(10H)-phenanthrone. A resolved esr spec-



trum was obtained when solutions of diazophenanthrone in biphenyl were heated above 200°. At this temperature, however, there was visible evidence of rapid polymerization, and spectra sufficiently stable for analysis could not be obtained.

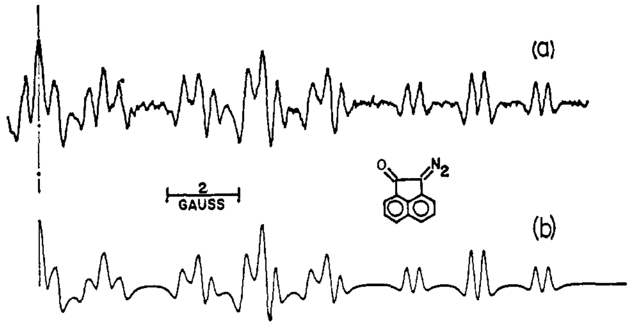
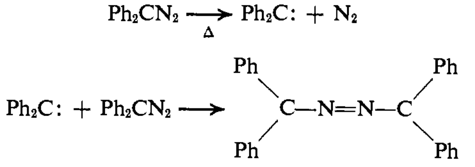


Figure 6. Comparison of experimental and simulated esr second-derivative curves for 1-diazo-2-acenaphthenone. Curve a, experimental spectrum for a 10% solution of 1-diazo-2-acenaphthenone in biphenyl at 200°. Curve b, spectrum simulated from the assignment, 1H (a_1 = 6.26 G), 1H (a_2 = 6.16 G), 1H (a_4 = 5.76 G), 2H (a_5 = 1.78 G), and 1H (a_6 = 0.34 G).

Discussion

Free-radical intermediates have been observed during the thermal decomposition of all the diazo compounds which we have examined. These radical intermediates could arise from the reaction of carbenes with unreacted starting material, with other carbenes, or with the reaction products of decomposition. In this section, the esr spectra are discussed, chemical structures of the radicals are proposed, and the relation of these intermediates to the over-all reactions of carbenes is discussed.

Diphenyldiazomethane. The pyrolysis reactions of Ph_2CN_2 have been extensively investigated.[22–25] In oxygen-free solution, the dominant reaction leads to benzophenone azine, as shown in eq 1. Dimerization of the carbene to tetraphenylethylene does not occur.



$$Ph_2CN_2 \xrightarrow[\Delta]{} Ph_2C\colon + N_2$$

$$Ph_2C\colon + Ph_2CN_2 \longrightarrow (Ph)_2C{=}N{-}N{=}C(Ph)_2 \qquad (1)$$

Our esr results show that there are at least two kinds of radical intermediates observable in the thermal decomposition of Ph_2CN_2. The experiments on deuterated Ph_2CN_2 prove that these radicals contain nitrogen. Our analysis of the most highly resolved spectrum in Figure 3 is consistent with that for a $Ph_2\dot{C}{-}N{<}$ radical fragment. In Table I, our experimental coupling constants for this radical are compared with those found for other related diphenyl-substituted free radicals.

The phenyl ring proton splittings are in good agreement with those determined for the other radicals in Table I, with $a_{H,para} \cong a_{H,ortho} \cong 2a_{H,meta}$. The small nitrogen splitting suggests that there is a high unpaired electron density on the central carbon atom.

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(22) H. Reimlinger, *Chem. Ber.*, **97**, 339 (1964).

(23) D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 2466 (1965).

(24) W. Fielding and H. O. Pritchard, *J. Phys. Chem.*, **64**, 278 (1960).

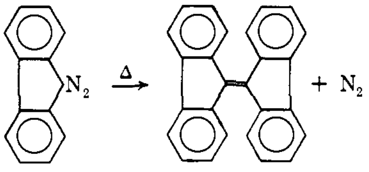
(25) F. O. Rice and J. D. Michaelsen, *ibid.*, **66**, 1535 (1962).

Table I. Esr Coupling Constants for Diphenyl-Substituted Radicals

	$\mathrm{Ph_2CN<}$	$\mathrm{Ph_2\dot{N}O}$[a]	$\mathrm{Ph_2\dot{N}}$[b]	$\mathrm{Ph_2\dot{C}O}$[c]
$a_{\mathrm{H},para}$	1.43	1.50	1.81	3.50
$a_{\mathrm{H},ortho}$	1.32	1.50	1.81	2.52
$a_{\mathrm{H},meta}$	0.77	0.83	0.74	0.82
a_{N}	1.54	9.3	9.4	...

[a] K. Mobius and F. Schneider, *Z. Naturforsch.*, **18a**, 428 (1963). [b] J. Pannell, *Mol. Phys.*, **5**, 291 (1962). [c] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

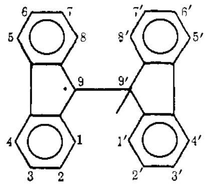
9-Diazofluorene. Only a single esr spectrum was observed during the pyrolysis of 9-diazofluorene. Its pyrolysis, eq 2, has been shown to produce the unsaturated dimer, $\Delta^{9,9'}$-bifluorene as the major product,[4] presumably *via* a carbene intermediate. The fluorenylidene carbene has been observed at low temperatures by esr.[26]



(2)

9-diazofluorene $\Delta^{9,9'}$-bifluorene

The discussion in the previous section has shown that the best assignment for the esr spectrum from pyrolyzed diazofluorene consists of four sets of four equivalent protons. The 16 protons indicate that the unpaired electron is delocalized over two fluorene fragments. A reasonable structure consistent with the above reaction is a bifluorenyl radical fragment (II).

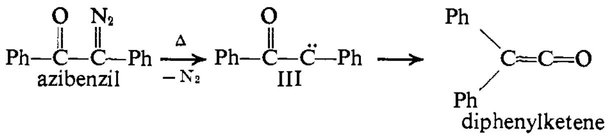


II

The esr coupling constants have been determined for a number of aromatic free radicals which incorporate the fluorene ring system. These include the radical anion and cation of $\Delta^{9,9'}$-bifluorene[27] and the anion of fluorenone.[28] All these esr studies, as well as HMO calculations, show that the 1, 3, 6, and 8 positions in an aromatic fluorene radical are positions of high spin density; low spin densities are observed at the 2, 4, 5, and 7 positions. On the basis of these considerations, we can assign the 3.44-G coupling constant to positions 1, 3, 6, and 8. The small 0.42-G coupling constant can most likely be attributed to the 2′, 4′, 5′, and 7′ positions.

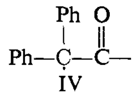
The observation of hyperfine interaction from the protons in the "primed" fluorene group of II is not surprising since similar effects have been observed for the radical anion of the related molecule biphenylenemethane.[29]

Azibenzil. The pyrolysis of azibenzil has been shown to yield diphenylketene, presumably *via* a Wolff rearrangement involving the carbene III in eq 3.[30,31]



(3)

The coupling constant assignment and the g value of the esr spectrum from decomposed azibenzil are consistent with a radical fragment having structure IV.



$\mathrm{Ph{-}\overset{Ph}{\underset{\cdot}{C}}{-}\overset{O}{\overset{\|}{C}}{-}}$

IV

In Table II, the coupling constants obtained for radical IV are compared with those reported for the benzil anion radical[28] and the triphenylmethyl radical.[32]

Table II. Coupling Constants in Gauss for Radical IV, Triphenylmethyl Radical,[32] and Benzil Anion Radical[28]

	Radical IV	$\mathrm{Ph_3C\cdot}$	$\mathrm{PhC({=}O)\dot{C}(O^-)Ph}$
$a_{\mathrm{H},para}$	2.88	2.77	1.22
$a_{\mathrm{H},ortho}$	2.67	2.53	0.99
$a_{\mathrm{H},meta}$	1.17	1.11	0.36

The magnitudes of the coupling constants for radical IV are virtually identical with those for the triphenylmethyl radical. The actual esr spectra are, of course, quite different since radical IV contains a carbonyl substituent in place of the third phenyl substituent in triphenylmethyl. The close similarity of the two sets of coupling constants is further evidence for structure IV and indicates that a C=O group is as effective as a phenyl group in electron delocalization. The coupling constants for benzil anion, although in the same relative ratios as for IV, are considerably smaller due to electron delocalization over two carbonyl oxygens.

2-Diazo-1-acenaphthenone. The thermal decomposition of diazoacenaphthenone is known to yield a mixture of biacenaphthylidenedione and acenaphthenoneketazine as reaction products, eq 4.[33]

The esr results discussed previously show that there are two distinct radical intermediates formed in the process. The first, observable at lower temperatures, gave a complex spectrum which we were unable to analyze. The second, more stable radical, which was observed at higher temperatures, had the simpler spectrum shown in Figure 6. Since the final reaction products of decomposition include both nitrogenated and nonnitrogenated species, it is expected that radical intermediates of both types could be observed. The higher g value obtained for the first radical suggests that it contains nitrogen.

The esr spectrum obtained for the second radical from the decomposition of diazoacenaphthenone definitely exhibits a hyperfine interaction by more than

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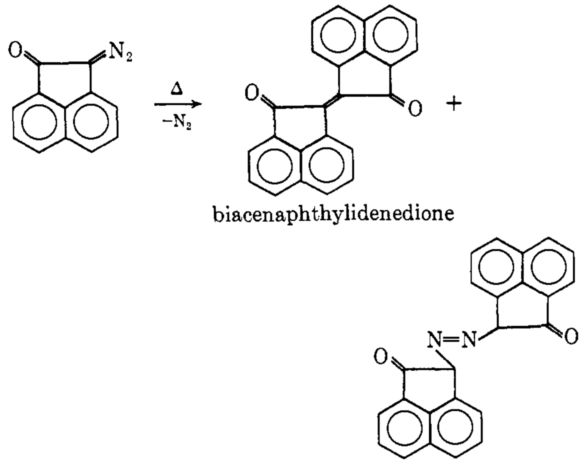


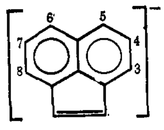
biacenaphthylidenedione

acenaphthenone ketazine

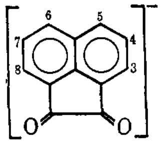
(4)

six protons. The assignment of these coupling constants to a definite chemical structure can be facilitated by examining the hyperfine splittings of other aromatic radicals related to acenaphthene.

The coupling constants for two such radicals, the anions of acenaphthylene[34] (a) and acenaphthenequinone[35] (b), are listed in Table III.



a



b

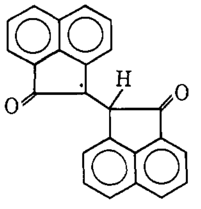
Table III. Coupling Constants for Acenaphthylene and Acenaphthenequinone Anions

Position	a_H, G a	 b
3,8	4.51	1.17
4,7	0.46	0.27
5,6	5.60	1.27

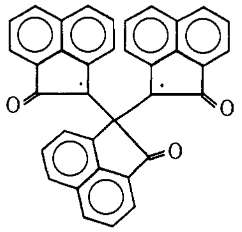
Both radicals show four large and two small ring-proton splittings. The splittings for acenaphthenequinone anion are smaller because of localization of the unpaired electron on the two oxygen atoms.

The second radical from diazoacenaphthenone also exhibits a large hyperfine splitting by four protons and a smaller splitting by two equivalent protons. If one now takes into account the additional small single proton splitting of 0.34 G, a structure such as V can be proposed for the radical. The formation of this radical requires hydrogen abstraction. The observation of the same spectrum in completely deuterated solvents shows that this additional proton could not arise from the solvent.

Since the additional single proton splitting of 0.34 G is unexpected, a second interpretation of the spectrum in Figure 6 is that it arises from a mixture of two 6-proton radical fragments which differ only in the magnitude of a single proton splitting. A spectrum identical with that in Figure 6b is obtained from the assignments given in Table IV. This assignment suggests a biradical structure (VI) where the two radical ends exhibit slightly different coupling constants for one proton only. Such a biradical can form by the polymerization of acenaphthenone carbenes. For steric reasons, the two radical ends would have different conformations with respect to the connecting molecule. This configurational inequivalence could lead to a slight alteration of one of the coupling constants. Pronounced conformational effects on proton splittings have been observed for other radical systems.[36]



V



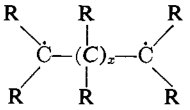
VI

Table IV

Assignment, G Fragment 1	 Fragment 2
1H a_1 = 6.26	1H a_1 = 6.26
1H a_2 = 6.16	1H a_2 = 6.16
1H a_3 = 6.10	1H a_3 = 5.42
1H a_4 = 6.04	1H a_4 = 6.04
2H a_5 = 1.78	2H a_5 = 1.78

Nature of the Radical Intermediates

The results of our esr experiments for diazoacenaphthenone suggest the formation of biradicals during the thermal decomposition process. It is likely that all the observed intermediate radical fragments exist as biradicals with the general structure VII, in which the unpaired spins are separated by one or more interspersed carbene units. Stable biradicals have been observed in other chemical processes[37–39] and have been previously suggested as intermediates in carbene reactions.[13] Recently, biradicals have been shown to occur during the reaction of triplet methylene with olefins.[40] Biradicals have also been suggested as intermediates in the pyrolysis of aromatic diazonium compounds.[2b]



$$R_2\dot{C}-(CR_2)_x-\dot{C}R_2$$

VII

Our experimental results from Ph_2CN_2 provide further evidence for biradical intermediates. The reversible temperature dependence of radical concentration observed for $(C_6H_5)_2CN_2$ is similar to that found by Waring and Sloan for the biradical polymers of Chichibabin's hydrocarbon.[39] The line-width behavior of

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the esr spectra of the $(C_6H_5)_2CN_2$ intermediates suggest that biradical polymers of different chain lengths coexist. Biradical polymers are known to exhibit esr spectra in which the line width depends on the length of the polymer chain.[38]

It is evident that the radical intermediates bear a direct structural relationship to both the initially formed carbenes and the final decomposition products of the diazo compounds. Furthermore, the observation of radical products formed from the particular diazo compounds included in this study is direct evidence for the triplet-state nature of their carbene intermediates.

Acknowledgments. We thank Mrs. S. B. Wallon for the synthesis of the diazo compounds and Mr. A. R. Cherry for his assistance in analyzing the esr spectra.

Electron Spin Resonance of Oxygen-17 Enriched Pentamethylnitrobenzene and *p*-Dinitrobenzene Anion Radicals

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Abstract: Synthesis of ^{17}O-enriched pentamethylnitrobenzene (PMNB) and *p*-dinitrobenzene (DNB) has been accomplished. Electrochemical reduction of these compounds has permitted observation of the isotropic ^{17}O coupling constants for the resulting anion radicals in several different solvents. The oxygen coupling constant, a_O, for $PMNB^-$ in dimethylformamide was -11.54 G. a_O increased on addition of water to -10.80 G when the water content reached a mole fraction of 0.788. a_O for DNB^- was -3.82 G in dimethylformamide and decreased to -4.36 G on addition of 0.147 mole fraction of water. In addition, $PMNB^-$ was observed in a rigid glass, and anisotropic parameters for both ^{14}N and ^{17}O were obtained. The solvent dependence of a_O suggests that steric interactions are involved in the solvent effect. The ^{17}O data are discussed in relation to previous models for solvent effects and in relation to previous spin-density estimates for nitro aromatic radicals.

It is well known that the magnitude of the isotropic nitrogen coupling constant, a_N, in the electron spin resonance (esr) spectra of nitro aromatic anion radicals is strongly dependent upon the detailed nature of the medium containing the radicals. a_N increases as the solvent is made progressively more polar, say by addition of water to acetonitrile. These observations were explained by Rieger and Fraenkel[2] on the basis of the model proposed by Gendell, Freed, and Fraenkel,[3] that of rapidly exchanging solvent–radical complexes which cause a redistribution of unpaired spin density, primarily at the oxygen atoms of the nitro group. This shift in spin density was approximated in Hückel molecular orbital calculations by making the oxygen atoms more electronegative, *i.e.*, by using larger absolute values of α_O, the oxygen Coulomb integral. This results in progressively larger predicted values of $\rho_N{}^\pi$, the π-spin density on nitrogen, but progressively smaller values of $\rho_O{}^\pi$. In a study[4] of ^{17}O-enriched nitrobenzene anion we found that as the solvent was made more polar a_N increased, but so did $|a_O|$. This observation is explicable within the framework of the model outlined above if a_O can be represented by an equation of the form

$$a_O = Q_1\rho_O{}^\pi + Q_2\rho_N{}^\pi \qquad (1)$$

in which the Q's are of comparable magnitude and have the same sign. (The results for nitrobenzene anion could be accommodated with Q's of opposite sign if the dominate contribution to a_O came from the term containing $\rho_N{}^\pi$; it appears that this is not so.) However, if analogy to the theory of Karplus and Fraenkel[5] is applicable, then the contribution to a_O from polarization due to spin on nitrogen may be expected to be of opposite sign to the contribution from spin on ^{17}O itself.

Ling and Gendell,[6] as an outgrowth of a study of the effects of alkali cations on a_N in nitro aromatic anions, pointed out that calculated values of both $\rho_O{}^\pi$ and $\rho_N{}^\pi$ can be made to increase if α_N is increased, as well as α_O, to simulate increasing solvation or electrostatic interaction with a gegenion.

Thus, an increase in the magnitude of a_O can be predicted from the term $Q_1\rho_O{}^\pi$ alone and Q_2 in eq 1 could be zero. Data presented in this report, however, show that in pentamethylnitrobenzene anion the magnitude of a_O *decreases* with increasing solvent polarity, a result correctly predicted by increasing only α_O in the MO calculations and not predicted by the method suggested by Ling and Gendell.[6] Our data indicate that changes in a_O with variation in solvent polarity (and presumably also with ion pair formation) are distinctly different for a radical containing a sterically crowded nitro group than for those containing unhindered nitro groups.

The importance of steric considerations has been suggested previously in a slightly different context. In fact, the entire correlation of a_N values with HMO calculations, as exemplified by the work of Rieger and

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(1) (a) Author to whom communications should be addressed. (b) Deceased, Dec 4, 1967.

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