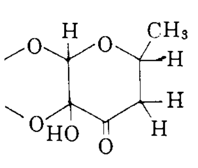
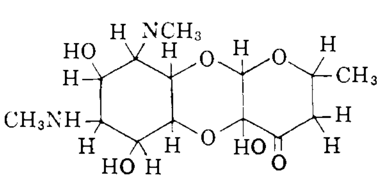
amine either as in I or as in V, explains these products.

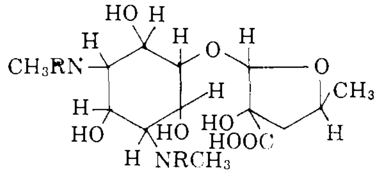


IV

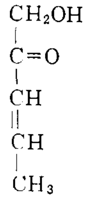


V

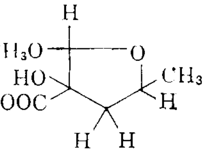
Mild base hydrolysis rearranges actinospectacin to actinospectinoic acid, $C_{14}H_{26}N_2O_8$ (VIa), melting 230–235°, pK_a 3.30 (acidic), and 7.37, 9.33 (basic), and reducing four moles of periodate. Acid cleaves VIa to actinamine, carbon dioxide, and a five-carbon, optically active compound which was isolated as a 1,2-bis-2,4-dinitrophenylhydrazone, $C_{17}H_{16}N_8O_9$, suggesting a 1,2-dicarbonyl or an α-hydroxy carbonyl compound. More vigorous hydrolysis yielded the five-carbon fragment as the unsaturated compound VII, isolated and characterized as its 1,2-bis-2,4-dinitrophenylhydrazone. After borohydride reduction of VII to produce the glycol (not isolated) periodate oxidation gave formaldehyde[9] and crotonaldehyde.[9] Methanolysis of VIa afforded actinamine and neutral, optically active VIII ($C_8H_{14}O_5$), which contains two methoxyls, consumes no periodate, and exhibits infrared absorption in the ester carbonyl region. The formation of VI must be due to a special example of the tertiary ketol rearrangement[10] involving cleavage of the actinamine–actinospectose bond adjacent to the carbonyl. The isolation and behavior of VIII confirm the presence of a six-carbon moiety in actinospectacin. The alternate structure V would rearrange to IXa.



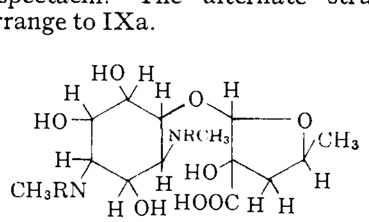
VIa, R = H
b, R = ethylcarbamoyl



VII



VIII



IXa, R = H
b, R = ethylcarbamoyl

The choice between pairs I and V, and VI and IX remains to be made. Base converts N,N′-bis-(ethylcarbamoyl)-actinospectacin, Ie, to the corresponding actinospectinoic acid derivative, VIb, α_D −63° (*c*, 1, water). Since VIb consumes no periodate, the alternate structure IXb is excluded. Consequently the choice of VIa is required for actinospectinoic acid, eliminating V, and establishing I as the structure of actinospectacin.

We gratefully acknowledge the contributions toward this work of Dr. R. W. Rinehart and associates and Mr. J. F. W. Keana.

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(10) For a review on this subject see S. Selman and J. F. Eastham, *Quarterly Reviews*, **14**, 221 (1960).

E.P.R. OF DIPHENYLMETHYLENE, A GROUND-STATE TRIPLET

Sir:

Electron resonance (e.p.r.) due to a triplet state of an organic molecule was first observed by Hutchison and Mangum.[1] The triplet state of naphthalene was detected in this elegant method by measuring the spin resonance of ultraviolet-irradiated single crystals of solid solutions of this compound in durene. These resonance absorptions were attributed to transitions between neighboring sublevels of the triplet ($|\Delta m| = 1$ transitions). Van der Waals and de Groot[2] observed the e.p.r. due to the $|\Delta m| = 2$ transition of the triplet state of a number of polynuclear aromatic hydrocarbons in irradiated rigid glass solutions at 77°K.

Recently, Yager, Wasserman and Cramer[3] have observed the $|\Delta m| = 1$ transition in ultraviolet-irradiated rigid glass solutions of several aromatic hydrocarbons. The detection of these lines in randomly oriented molecules is possible when the magnetic field is approximately parallel to a molecular axis. This is a simple and fruitful method for the examination of triplet states.

All of the above experiments have been concerned with resonance absorption due to an excited state of a molecule. We now wish to report the detection of e.p.r. absorptions due to both $|\Delta m| = 1$ transitions and $\Delta m = 2$ transitions in a chemical species, diphenylmethylene, which is presumably in its ground state. This constitutes the first physical evidence for the triplet nature of diphenylmethylene, a species of considerable interest in the chemistry of divalent carbon intermediates.

In a typical experiment[4] a dilute solution (*ca.* 10^{-3} *M*) of diphenyldiazomethane in polychlorotrifluoroethylene[5] was irradiated with a Hanovia 140-w. mercury arc at 77°K. in the quartz Dewar insert of a Varian 100-kc. modulation e.p.r. spectrometer

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(1) C. A. Hutchison, Jr. and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961).

(2) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 233 (1959); **3**, 191 (1960).

(3) W. A. Yager, E. Wasserman and R. M. R. Cramer, *J. Chem. Phys.*, in press.

(4) The authors wish to acknowledge the assistance of Mr. Richard M. R. Cramer in these experiments.

(5) Obtained from the Hooker Chemical Company as "Fluorolube." No resonance absorption was observed when this material was irradiated alone. Nujol glasses gave similiar resonances.

employing a frequency of 9080 Mc./sec. Resonance absorptions were observed at these magnetic fields[6]: 1227, 1619, 1978, 4588, 5272, and 7522 gauss. A broad line at the free spin value (3239 gauss; $g = 2.0027$) also was observed. (This latter line presumably is due to doublet radicals resulting from further reaction). The intensities of the absorptions were not diminished appreciably when irradiation ceased,[7] as long as the temperature of the sample did not rise above −150°. However, warming to −130° caused the lines to disappear rapidly. Measurements also were carried out at a series of temperatures by using the Varian variable-temperature insert instead of the Dewar insert. The intensity of the various lines decreased at essentially the same rate when the temperature of the sample was raised from −186 to −133°, with the exception that the line at 1619 gauss may decay more slowly and the broad line at $g \approx 2$ did not diminish appreciably. Some difficulty was experienced in observing the spin resonance absorptions when less viscous matrices such as ethyl ether–isopentane or methylcyclohexane–isopentane were used.[8]

The absorption lines can be grouped in the following manner: (1) the line at 1619 gauss corresponds to a $|\Delta m|$ equal to transition, occurring at one-half the free-spin value; and (2) the lines at 1227, 1978, 4588, 5272, and 7522 gauss are associated with $|\Delta m| = 1$ transition. The line 4 has a much larger deviation from the free spin value than any known for a phosphorescent triplet.[1,2,3] Much larger interactions occur here, as the divalent carbon has two orbitals with unpaired spins with a concomitant smaller average distance between the magnetic dipoles.

Diphenylmethylene has been described by Skell as a triplet species because it adds to olefins in a non-stereospecific manner.[9] Also diphenylmethylene reacts with oxygen to give benzophenone,[10] unlike singlet, electrophilic carbenes which do not react with oxygen. In addition, diphenylmethylene is apparently able to abstract hydrogen atoms from a variety of substrates.[10,11] Herzberg[12] has shown that the ground state of CH_2 (obtained from photolysis of diazomethane) is a triplet which has an approximately linear structure. Our results indicate that the ground state of diphenylmethylene is a triplet which is stable in rigid media. The position and number of the absorption lines indicate that we are not observing a *single* species having D_{2d} symmetry[13] such as the one proposed by Skell.[9]

Recently, we have learned that Brandon, Closs and Hutchison have observed e.p.r. absorptions in an irradiated dilute single crystal solid solution of diphenyldiazomethane. Their observations indicate the presence of an oriented ground state triplet molecule.[14]

Further work with isotopically substituted samples is in progress to obtain more information on the number and structure of the species which are present in diphenylmethylene and other carbenes.

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[6] Magnetic fields were determined from proton resonance frequencies. Treatment of absorption curves is that given in ref. 3.

[7] Overnight storage at 77°K caused no substantial change in the intensities of the absorption lines.

[8] Recent experiments involving the photolysis of diphenyldiazomethane in fluorocarbon glasses at 77°K. indicate that the diphenylmethylene which is produced can undergo diffusion readily in the matrices used. See W. B. DeMore, H. O. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959). However, when we irradiated benzophenone azine, which might be formed by such a process, in the quartz Dewar, no absorptions were detected.

[9] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[10] W. Kirmse, L. Horner and H. Hoffmann, *Ann. Chem.*, **614**, 19 (1958).

[11] (a) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954); (b) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).

[12] G. Herzberg, *Proc. Roy. Soc.* (London), **Ser. A.**, **262**, 291 (1961).

[13] The spin Hamiltonian (see K. W. H. Stevens, *Proc. Roy. Soc.* (London), **Ser. A.**, **214**, 237 (1952) and Hutchison[1]) which is appropriate in this case would require only two pairs of lines for a single species having D_{2d} symmetry.

[14] The authors wish to thank Professor Hutchison for communicating his observations prior to publication.

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RECEIVED JUNE 21, 1962

PHOTOLYSIS OF CARBON-2-$^{14}C_1$-SUBOXIDE IN ETHYLENE[1]

Sir:

In a recent communication, Bayes[2] reported on the photolysis of mixtures of C_3O_2 and ethylene, propylene and other hydrocarbons. The considerable yield of allene from ethylene and methylallene from propylene suggested to Bayes that atomic carbon might be the intermediate responsible for these products, although ketocarbene was not excluded.

Since one might expect some discrimination between double bond addition and carbon hydrogen insertion, if indeed a carbene-like species is involved, we felt it of value to investigate this discrimination ratio in ethylene. To this end carbon-2-$^{14}C_1$-suboxide (I) was photolyzed in the presence of ethylene. The allene-$^{14}C_1$ (II) produced was degraded.

A preparation of I in 15% yield was achieved by the P_2O_5 dehydration[3] of commercially available malonic acid-2-$^{14}C_1$. Decarboxylation of the malonic acid-2-$^{14}C_1$ proved it to be a minimum of 99.95% 2-labeled. The I was purified by gas-liquid chromatography (g.l.c.) using a silicone (GE-SF 96) column. Its identity was established by infrared analysis. Mixtures of I (pressure 0.5–0.8 mm.) and ethylene (pressure $\cong$ 50 mm.) were photolyzed in a quartz reactor using an unfiltered medium pressure mercury lamp. The two major products were allene-$^{14}C_1$ ($\sim$80%) and methylacetylene-$^{14}C_1$ ($\sim$20%).[4] Small amounts of acetylene-$^{14}C_1$ were also observed (1–2%).

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

[3] O. Diels and G. Meyerheim, *Ber.*, **40**, 355 (1907).

[4] These yields refer only to a 47% conversion photolysis; there is evidence that the allene to methylacetylene ratio decreases with increasing conversion. The discrepancy between our results and those of Bayes (ref. 2), who observed no methylacetylene or acetylene, may