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This value is comparable to the axial I–F stretching force constant. The higher force constant could be taken as indicating a shorter equatorial I–F bond distance and, indeed, the equatorial and axial I–F bond lengths may be nearly the same. The strengthening, and or shortening, of the equatorial I–F bond may be related to the increased positive charge or valence of the central I atom when an additional oxygen atom is added to IF_5.

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Electron Paramagnetic Resonance Spectra of the Ground-State Triplet Diphenylmethylene and Fluorenylidene Molecules in Single Crystals*†‡

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The paramagnetic resonance spectra of the triplet ground states of diphenylmethylene and fluorenylidene molecules, oriented in single crystals, have been investigated. The fine structures and ^{13}C hyperfine structures of these spectra have been studied and the parameters for best fit by a spin Hamiltonian have been determined. The implications of these results with respect to electron spin distribution and molecular structures have been examined.

1. INTRODUCTION

THE electron paramagnetic resonance spectra of the ground-state triplet diphenylmethylene and fluorenylidene molecules have been previously described for the case of randomly oriented molecules by Murray, Trozzolo, Wasserman, and Yager[1]; by Trozzolo, Murray and Wasserman[2]; by Yager, Wasserman, and Cramer[3]; by Wasserman, Barash, Trozzolo, Murray, and Yager[4]; and by Wasserman, Snyder, and Yager.[5] The diphenylmethylene spectrum has been briefly described by Brandon, Closs, and Hutchison[6] for the case of molecules oriented in single crystals.

The zero field splittings and spin–spin interactions in these molecules have been discussed by Higuchi.[7–9]

In the present paper we present the results of detailed studies of the electron magnetic resonance spectra of ground-state triplet diphenylmethylene molecules oriented in benzophenone single crystals and of ground-state triplet fluorenylidene molecules oriented in diazofluorene single crystals.

2. PREPARATION OF THE SINGLE CRYSTALS

2.1. Benzophenone Host Containing Diphenylmethylene Guest

Diphenyldiazomethane[10] (0.012 g) in *n*-pentane (1 ml) was added to a saturated solution (10 ml) of benzophenone (reagent grade, twice recrystallized from *n*-pentane) in *n*-pentane at 25°C. The resulting solution was allowed to cool in a closed Erlenmeyer flask to 15°C over a period of 48 h. The slow cooling was achieved by placing the flask in a 10-liter well-insulated water bath with an initial water temperature of 25°. The bath was located in a cold room held at 10°C. A large number of fairly well formed crystals was usually obtained without seeding the solution. The crystals were harvested by decanting the solution. Crystals with edge lengths of several millimeters, which were suitable for the electron magnetic resonance experiments, were obtained by this method. Analysis of the resulting crystals by measuring the absorbance of the 512-mμ band of a *n*-pentane solution of the crystals, showed that the diphenyldiazomethane content was between 0.12 and 0.14 mole %.

Crystals of diphenyldiazomethane enriched in ^{13}C in the center position in benzophenone were obtained

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[7] J. Higuchi, J. Chem. Phys. **38**, 1237 (1963).
[8] J. Higuchi, J. Chem. Phys. **39**, 1339 (1963).
[9] J. Higuchi, J. Chem. Phys. **39**, 1847 (1963).
[10] Org. Syntheses, Collective Vol. **2**, 496 (1943), describes the synthesis of phenylbenzoyldiazomethane from benzilhydrazone. Our diphenydiazomethane and diazofluorene were prepared in a similar manner using benzophenonehydrazone and fluorenonehydrazone. The benzophenonehydrazone was prepared according to Org. Syntheses, Collective Vol. **3**, 352, Note 1 (1955) and the fluorenone hydrazone was prepared in a similar manner.

by the same procedure. The diphenyldiazomethane-1-^{13}C was prepared from benzophenone-^{13}C [10] supplied by Merck, Sharp and Dohme of Canada Limited.

The crystals of benzophenone containing diphenyldiazomethane were mounted in the microwave resonant cavity on polystyrene wedges as described in previous investigations of photoexcited triplets,[11,12] or on polystyrene V blocks in some cases as described below. The polystyrene was mounted on a lucalox (high-density finely divided sapphire) post which provided thermal contact with the brass end plate of the cavity. The samples were cooled, in the cavity, to the boiling point of N_2. At that temperature they were irradiated by means of an A-H6 high-pressure Hg arc in a manner similar to that described previously[11,12] but for only a time sufficient to develop a suitable concentration of oriented ground-state triplet diphenylmethylene molecules in the benzophenone crystal.

2.2. Diazofluorene Host Containing Fluorenylidene Guest

A saturated solution at 29°C of diazofluorene[10] (~0.3 g) in n-pentane (10 ml) was diluted with n-pentane (0.5 ml) and placed in a closed Erlenmeyer flask. The crystals were grown in a manner similar to that described above by allowing the solution to cool to ~0°C over a period of 48 h. The crystals were removed by decanting the solution and were needles or long prisms with a rhombus cross section normal to the needle axis. The largest were ~3 cm in length. Their large faces were ~0.1 cm wide measured normal to the long edges. These crystals were mounted and the ground triplet-state species, fluorenylidene, was generated at the boiling point of N_2 in a manner similar to that described in 2.1. Crystals of diazofluorene containing ^{13}C in the center position were prepared in a manner similar to that described for ^{13}C-labeled diphenyldiazomethane in 2.1.

3. STRUCTURES OF THE CRYSTAL HOSTS

3.1. Benzophenone

The detailed structure of the benzophenone crystal is unknown. Groth[13] has described the crystal as orthorhombic. Banerjee and Haque[14] have determined the space group to be $P2_12_12_1$ with four molecules per unit cell and have measured the unit-cell dimensions. Fleischer[15] has confirmed by x-ray diffraction that the crystals prepared by us as described in 2.1. are the same modification as studied by Groth[13] and by Banerjee and Haque[14] and he has measured the unit-cell dimensions. The measurements of the unit-cell dimensions are summarized in Table I.

TABLE I. Benzophenone unit-cell dimensions.

Reference	a	b	c
Groth[13]	0.8511 b	1.0000 b	0.6644 b
Banerjee and Haque[14]	10.17 Å 0.8433 b	12.06 Å 1.0000 b	7.98 Å 0.6617 b
Fleischer[15]	10.30 Å $\sigma\{a\}=0.03$ Å 0.8477 b	12.15 Å $\sigma\{b\}=0.03$ Å 1.0000 b	8.00 Å $\sigma\{c\}=0.02$ Å 0.6584 b

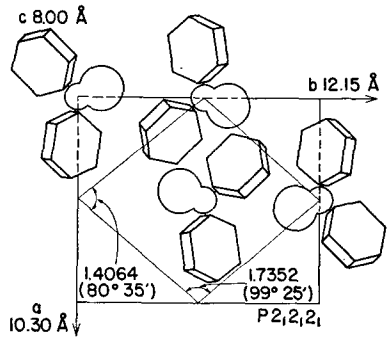

FIG. 1. Schematic diagram of proposed crystal structure of benzophenone which is consistent with available information on diamagnetic susceptibilities, absorption spectra, and magnetic resonance studies on diphenylmethylene in benzophenone.

Some information concerning the arrangement of the molecules in the unit cell is obtainable from the work of Krishnan, Guha, and Banerjee[16] on the anisotropy of the diamagnetic susceptibility of the benzophenone crystal and from the investigations of the triplet–triplet optical absorption spectrum of the crystal by McClure and Hanst.[17] The measured values of the anisotropic magnetic susceptibilities upon comparison with the known anisotropic susceptibilities of the diphenyl molecule show that both the a and b axes of the crystal are close to being parallel to the planes of all the aromatic rings of all the benzophenone molecules. For example, the measured susceptibility along the a axis is accounted for if this axis makes an angle, 0.39 (22°), with its projections in all the benzene planes. The susceptibility along the b axis is nearly equal to that along the a axis. The susceptibility along the c axis is very large, showing that the aromatic planes are nearly normal to the c axis.

The polarization of the triplet–triplet optical absorption of benzophenone[17] shows that the CO bond lies nearly in the ab plane of the crystal. An arrangement of the molecules such as that described in Fig. 1 is consistent with the available information on the benzophenone crystal.

The crystals prepared as described in 2.1. were frequently in the form of rods or prisms with rhombus cross sections, the prism axis being the c axis of Fig. 1

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[17] D. S. McClure and P. L. Hanst, J. Chem. Phys. **23**, 1772 (1955).

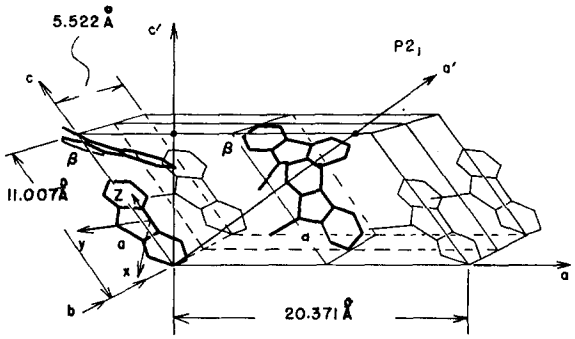

FIG. 2. Schematic diagram of proposed crystal structure of diazofluorene which is consistent with magnetic resonance studies on fluorenylidene in diazofluorene.

and the well-developed faces being the 110 and $1\bar{1}0$ faces.

3.2. Diazofluorene

The structure of the diazofluorene crystal is unknown. Fleischer[15] has determined by x-ray diffraction that the crystal is monoclinic with space group either $P2_1$ or $P2_1/m$. He has found the unit-cell dimensions to be $a=20.19$ Å, $b=5.53$ Å and $c=11.09$ Å with the monoclinic angle, $\beta=2.208$ (126.5°). He showed that the needle axis of the crystals prepared as described in 2.2. was the b axis. The initial magnetic measurements, described below, showed that the space group did not contain a center of symmetry. Ibers[18] and co-workers subsequently redetermined the unit-cell dimensions to be $a=20.371$ Å, $b=5.522$ Å, and $c=11.007$ Å with $\beta=2.205$ (126.3°) and reported piezoelectric measurements by Post[18] which showed that the crystals were not centrosymmetric and hence that they have the space-group symmetry $P2_1$. An arrangement of molecules such as that described in Fig. 2 is consistent with the available information on the diazofluorene crystal. The crystals prepared as described in 2.2. were in the form of needles. The needle axis was the b axis of Fig. 2. The cross section of the needles was usually hexagonal in shape, the 100, 001, and $20\bar{1}$ planes being the well-developed faces of the crystals.

4. MAGNETIC RESONANCE EXPERIMENTS

4.1. General Remarks

The experimental investigations of the electron magnetic resonance spectra of the irradiated single crystals described above were made in a manner similar to that used in the studies of the photoexcited triplet state of naphthalene in durene single crystals described by Hutchison and Mangum[11] and of the photoexcited triplet state of phenanthrene in diphenyl single crystals described by Brandon, Gerkin, and Hutchison.[12]

All the measurements were made with the crystals at the boiling point of N_2 using apparatus similar to that described previously.[11] The carrier frequencies were all determined by means of a frequency counter which was locked to the output of a stable oscillator whose harmonics were beat against the carrier. The magnetic fields were measured as described previously.[11] The microwave radiation was polarized perpendicular to the static magnetic field for all orientations of **H** with respect to the crystal. The crystals were mounted as described in 2. and after irradiation and generation of the paramagnetic species the magnetic field **H** was rotated with respect to the crystal in order to study the anisotropy of the spectra. The directions of the principal planes of the fine-structure tensors were located by the surveys described below.

For the measurements on diphenylmethylene at high magnetic fields the microwave carrier frequency was in the range from 2.32×10^{10} to 2.37×10^{10} cycle sec^{-1}. After determination of the orientation of the principal axes of the fine structure tensor, 32 measurements of the stationary values for the variation of $|\mathbf{H}|$ required for resonance with angle in the principal planes were made together with measurements of the microwave carrier frequency, 10 along the z axis, 12 along the x axis, 10 along the y axis of the fine-structure tensor.

For the measurements on fluorenylidene at high magnetic fields the microwave carrier frequency was in the range from 2.37×10^{10} to 2.41×10^{10} cycle sec^{-1}. Sixty measurements of the stationary values for the variation of $|\mathbf{H}|$ required for resonance with angle in the principal planes were made together with measurements of the microwave carrier frequency, 26 along the z axis, 20 along the x axis, 14 along the y axis of the fine-structure tensor.

Measurements were made on fluorenylidene in the earth's magnetic field where the resonance frequency was found to be 1.68528×10^9 cycle sec^{-1} for the absorption observed with the microwave magnetic field polarized perpendicular to the crystal needle axis. This measurement was made using a frequency-scanning paramagnetic resonance spectrometer which does not employ a laboratory magnetic field and which will be described in a future publication.

4.2. Fine Structure of the Diphenylmethylene Spectrum

Preliminary examination, at high field, of the $|\mathbf{H}|$ required for magnetic resonance as a function of the angle which **H** made with the crystallographic axes revealed that there were four differently oriented sets of principal axes for fine-structure tensors. Absorptions at three different $|\mathbf{H}|$'s were observed for each of the four molecules per unit cell at a general arbitrary angle of **H** with respect to crystal axes.

A crystal of benzophenone containing diphenyldiazomethane was mounted in a polystyrene V block designed to fit the 1.4064 (80°35′) edge of the prism (see Fig. 1). The base of the V block was parallel to the ac crystal plane. This V block was mounted in the microwave cavity in such a way that **H** could be rotated in a plane which contained the c axis of the crystal and which made a known dihedral angle with

[18] J. A. Ibers, private communication.

the *ac* plane of the crystal. When **H** was rotated in the *ac* plane, a plot of the fields at which resonance was observed versus angle gave patterns very similar to that shown for the α molecule in Fig. 3. A succession of such experiments was performed in which the plane of rotation of **H** made various dihedral angles with the *ac* plane. The absorptions were displayed oscillographically and it was possible to locate that plane of rotation of **H** which gave, for some angle of **H**, the largest separation in magnetic field (similar to the *A–C* separation of Fig. 3 for fluorenylidene) for two absorptions from the same molecule that was ever seen for any mounting of the crystal. This plane was found to make the dihedral angle, 0.3595 (20.6°), with the *ac* plane. Measurement of that angle of **H**, in the plane so determined, at which the maximum peak separation was observed, fixed the direction of

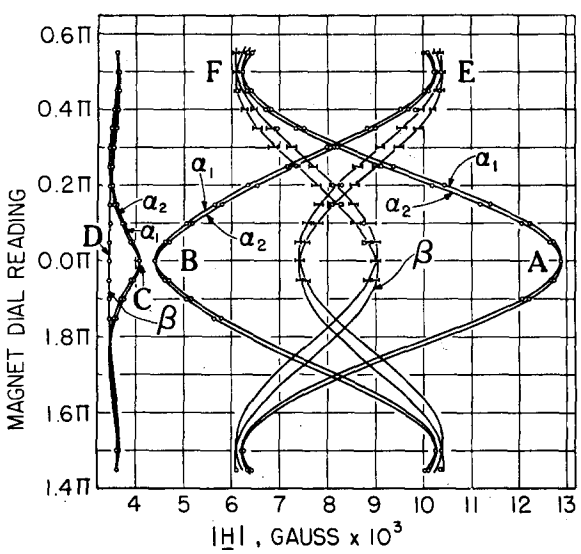

FIG. 3. $|\mathbf{H}|$ for electron magnetic resonance absorption vs angle of **H** in *bc* plane of diazofluorene crystal. 0.0π denotes a direction $\parallel c$ axis.

one of the principal axes of one of the fine-structure tensors. This axis was arbitrarily called the *z* axis. In Fig. 1, the benzophenone molecule at the origin is drawn so that the line between the centers of its benzene rings is in the direction of this experimentally determined *z* axis of the magnetic species. The direcion cosines of the *z* axis in the crystallographic axis system are given in Table II.

The crystal was then held in a second *V* block, designed to fit the 1.7352 (99°25′) edge of the prism, which held the crystal in such a position that **H** could be rotated in a plane perpendicular to the previously determined *z* axis. The patterns observed in this case were very similar to those shown for fluorenylidene in Fig. 4. Observation of the stationary values of $|\mathbf{H}|$ required for resonance, versus angle of rotation of **H**, fixed the other two principal axes. All of the direction cosines are given in Table II. Subsequent rotations of

TABLE II. Direction cosines, in the benzophenone crystallographic system, of the *x*, *y*, *z* axes of the fine-structure tensor of triplet-state species produced by irradiation of a single-crystal dilute solution of diphenyldiazomethane in benzophenone.

Fine-structure axis	Crystal axis		
	a	*b*	*c*
x	+0.1172	+0.1814	−0.9764
y	−0.3699	+0.9204	+0.1266
z	+0.9216	+0.3464	+0.1750

H in planes normal to the *x* axis and normal to the *y* axis, both these axes having been determined as described above, confirmed the correctness of the determinations of the principal axes of the fine-structure tensors. It was always found that, for rotations of **H** in planes containing a principal axis, one of the three absorptions which were observed for each molecule per unit cell disappeared when **H** was parallel to a principal axis. For example, Fig. 3 shows the $|\mathbf{H}|$ for absorption versus angle of **H** in a plane which passes quite near a principal magnetic axis at the angle of *A*, *B*, *C*. When the crystal was tilted slightly so that **H** could be made to be parallel to a principal axis the pattern was very similar and the peak labeled *B* disappeared just at its stationary value of $|\mathbf{H}|$ with respect to angle in accordance with the expected selection rules.

The 32 measurements of the stationary values for resonance $|\mathbf{H}|$ versus angle of **H** in principal axis planes, mentioned in 4.1., were fitted by the spin Hamiltonian

$$\mathcal{H}=\mathbf{H}\cdot g\cdot|\beta|\,\mathbf{S}+DS_z^2+E(S_x^2-S_y^2);\qquad S=1. \quad (1)$$

Those values of the parameters which gave a least-squares fit of the computed $|\mathbf{H}|$'s, for the microwave carrier frequency which was used, to the 32 experimental $|\mathbf{H}|$'s were obtained and are given in Table III.

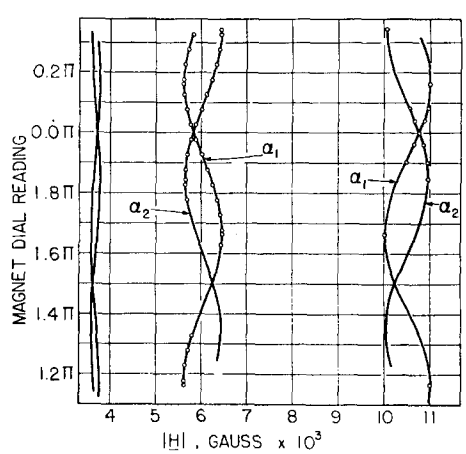

FIG. 4. $|\mathbf{H}|$ for electron magnetic resonance vs angle of **H** in *xy* plane of fluorenylidene molecule. 0.0π denotes a direction $\perp b$ axis of diazofluorene crystal.

TABLE III. Best values of D, E, g_{zz}, g_{xx}, g_{yy} in the spin Hamiltonian (1) and their standard deviations for diphenylmethylene in benzophenone at the boiling point of N_2. (The signs of D and E are opposite.)

Parameter	Value	σ {Parameter}
D/hc	± 0.40505 cm^{-1}	0.00016 cm^{-1}
E/hc	∓ 0.01918 cm^{-1}	0.00010 cm^{-1}
g_{zz}	2.00251	0.00048
g_{xx}	2.00451	0.00048
g_{yy}	2.00432	0.00053

4.3. Fine Structure of the Fluorenylidene Spectrum

As previously stated in 3.2., the crystals of diazofluorene were needles, the needle axis being the b axis. (See Fig. 2.) By microscopic examination the ab bc pair of faces could be determined but of course it could not be so decided which was which. Characteristic magnetic resonance patterns ($|\mathbf{H}|$ for resonance versus angle in the plane), after they had been correlated with the x-ray results, served to identify the faces. The bc face was found to be almost always the best developed face. Both it and the ab face served as mounting faces for direct mounting on the plane end of the lucalox post. Thus $\mathbf{H}$ could conveniently be rotated in the ab or bc plane. The needles could also be held conveniently in a small hole drilled in the lucalox post parallel to its axis. In this way $\mathbf{H}$ could conveniently be rotated in the ac plane. During preliminary explorations of these three planes, (i.e., the ab plane, the bc plane, the ac plane) the following three observations were made:

(1) a pattern very similar in general features to the patterns designated by α in Fig. 3 (Fig. 3 presents the values of $|\mathbf{H}|$ for resonance versus angle between $\mathbf{H}$ and the b axis when $\mathbf{H}$ is rotated in the bc plane) was observed in all three orientations;

(2) there were four differently oriented sets of principal axes of fine-structure tensors;

(3) there were two pairs of fine-structure axis sets, related within either one of the pairs by a twofold rotation about the b axis, but without such symmetry relations between two sets of axes chosen from different pairs. The two different pairs are designated by α and by β in Fig. 3.

From the x-ray studies of Fleischer,[15] it was known that the space group was either $P2_1$ with two general points or $P2_1/m$ with four general points. These two space groups differ only by a center of symmetry. Inasmuch as Fig. 3 shows the occurrence of four differently oriented fine-structure tensors, each with essentially the same parameter values but without any symmetry relations between the two different pairs, there can be no more than two general points per unit cell if the symmetry of the host is determining for the orientation of the produced magnetic species. Thus the host cannot have a center of symmetry and belongs to space group $P2_1$.

When $\mathbf{H}$ was rotated in the ac plane, two patterns similar in general features to the α patterns of Fig. 3 were observed, one with the A, B, C stationary points $+0.044\pi$ ($\sigma=0.010\pi$) from the a axis and the other with the A, B, C stationary points -0.023π ($\sigma=0.006\pi$) from the c axis. Only two fine-structure patterns were observed in this plane because it was the symmetry plane. When $\mathbf{H}$ was rotated in the bc plane, the four fine-structure patterns shown in Fig. 3 were observed. The angle 0.0π denotes that $\mathbf{H}$ was perpendicular to the symmetry axis (b axis). When $\mathbf{H}$ was rotated in the ab plane, four fine-structure patterns were observed, and the observations were very nearly the same as those seen in Fig. 3.

All of these observations are simply interpretable on the assumptions that (a) one pair of symmetry-related molecules (called here the α pair) is situated so that the particular principal magnetic axis (called here the z axis) which is associated with the largest principal value (called here D) of the fine-structure tensor is very close to the mirror plane (i.e., the ac plane) as well as being close to the c axis; and (b) that the other pair of symmetry related molecules (called here the β pair) has its z axis (defined the same as for the α molecule) also very close to the symmetry plane but near the a axis. Thus rotation of $\mathbf{H}$ in any of the 3 principal crystallographic planes produces a magnetic resonance pattern similar to the α pattern of Fig. 3 in that the stationary point A, B, C corresponding very nearly to $\mathbf{H} \parallel z$ axis is observed in each case.

This model was confirmed by construction of a polystyrene wedge similar to the center one ($xz-1$) of Fig. 6 of a previous paper[11] but without the skewed rulings. The crystal was thus held so that $\mathbf{H}$ rotated in a plane whose dihedral angle with the bc plane was approximately equal to that angle, namely -0.023π, which had been observed in the ac plane (i.e., when $\mathbf{H}$ was rotated in the ac plane) between the direction of the A, B, C set of stationary points and the c axis. This wedge therefore held the crystal so that $\mathbf{H}$ rotated in the bz plane. In this way the angle between the two z axes of the α molecules (i.e., the molecules with z axes near the c axis) was directly measured and found to be 0.0134π ($\sigma=0.0022\pi$). This angle was of course observed to be bisected by the normal to the b axis whose position is very precisely fixed by the crossover of the two α patterns (e.g., the points A, B, C in Fig. 3).

Having thus fixed the two z-axis directions of the α molecules a second wedge was constructed which held the crystal in such a position that $\mathbf{H}$ could be rotated in a plane normal to the z axis of one of the α molecules. As previously stated the most developed face was usually the bc face, and this fact could easily be confirmed by preliminary rotation of $\mathbf{H}$ in the plane of the crystal face and observation of the spacing in magnetic field of points such as A, B, C in Fig. 3, because the α molecules lay closer to the bc plane than did the β molecules to the ab plane. The rotations of

TABLE IV. Direction cosines and their standard deviations in the diazofluorene crystallographic axis a', b, c system, of the x, y, z axes of the α and β fine-structure tensors of the triplet-state species produced by irradiation of a pure diazofluorene crystal.

Fine-structure axis		Crystal axis a' cos	a' $\sigma\{\cos\}$	b cos	b $\sigma\{\cos\}$	c cos	c $\sigma\{\cos\}$
α	x	+0.868	0.022	−0.494	0.039	+0.051	0.016
	y	+0.492	0.039	+0.869	0.022	+0.053	0.011
	z	−0.071	0.018	−0.021	0.007	+0.997	0.001
β	x	+0.554	0.025	−0.627	0.028	+0.548	0.025
	y	+0.424	0.025	+0.779	0.023	+0.463	0.026
	z	−0.717	0.023	−0.024	0.012	+0.697	0.023

H in the plane normal to the z axis fixed the directions of the other two principal magnetic axes (called here the x and y axes). The values of $|\mathbf{H}|$ for resonance for the α molecule versus magnet dial reading are shown in Fig. 4. Similar studies fixed the directions of x, y, and z principal axes of the fine-structure tensors of the β molecules.

The results of the determination of the direction cosines of the principal fine-structure axes of the α and β molecules with respect to the crystallographic a', b, c axes are given in Table IV. The a' axis is a crystallographic axis which is perpendicular to both the b and c axes (see Fig. 2). The standard deviations, $\sigma\{\cos\}$, of the measured direction cosines are also given in Table IV.

Sixty measurements of field strengths at which resonance absorption occurred at measured microwave frequency, when **H** was parallel to one of the fine-structure axes of the α molecules whose directions are given in Table IV, were least squares fitted by the spin Hamiltonian (1). Along each principal axis the high-field peaks and low-field peaks corresponding to $|\bar{1}\rangle\rightarrow|0\rangle$ and $|0\rangle\rightarrow|1\rangle$ transition were measured. These measurements were subdivided into six groups as follows: in the bz plane, along the z axis, 13 high field and 13 low field; in the xy plane, along the x axis, 10 high field and 10 low field; along the y axis, seven high field and seven low field. These 60 measurements were made on 11 different crystals. It was assumed that within each of these six groups of measurements the angles of the deviations from the desired directions were Gaussian and that the distribution in field strength, $H\equiv|\mathbf{H}|$, was given by $P(H)dH=(\sqrt{2}/\sigma)\exp\{-[(H^\circ-H)/\sigma]\sqrt{2}\}dH$. For each of the six groups a best estimate of H° was made by the method of moments, proper corrections having been made for small frequency differences within the measurements of a single group. These six best estimates of H° were then fitted by a least-squares adjustment of the values of D, E, g_{zz}, g_{xx}, g_{yy} in the spin Hamiltonian (1). The results of this fitting procedure are given in Table V.

The 60 different fields for resonance, computed from the spin Hamiltonian (1), using these parameters for the conditions of the measurements, show a weighted root-mean-square deviation from the 60 measured fields equal to 0.695 G.

In Fig. 3 the circles represent the values of $|\mathbf{H}|$ for resonance when **H** was rotated in the bc crystallographic plane. The solid line is computed from the spin Hamiltonian (1) using the parameters of Table V and assuming the orientations of fine-structure tensors given in Table IV and assuming **H** to be rotating in the bc crystallographic plane. The brackets on the curves for the β molecules represent the variations in $|\mathbf{H}|$ for resonance corresponding to a change of 0.011π in orientation about the b axis. The same change in orientation produces a change in $|\mathbf{H}|$ for resonance of the α molecules which lies within the diameter of the circles used to represent the experimentally obtained points.

4.4. Hyperfine Structure of the Diphenylmethylene Spectrum

Substitution of ^{13}C in the central position of the diazo compound as described in 2.1. produced hyperfine structure in the spectra. ^{13}C peak separations were measured along all three principal axes of the fine-structure tensor by superpositions of the proton absorption line from a sample of H_2O near the microwave cavity onto the ^{13}C electron resonance peaks on an oscilloscope while sweeping the field at 60 cycle sec^{-1}. Six measurements along the z axis, 10 measurements along the x axis, and eight measurements along the y axis gave the proton frequency differences for the two ^{13}C lines in each of these directions. Along the z axis the hyperfine splitting was measured only for the low-

TABLE V. Best values of D, E, g_{zz}, g_{xx}, g_{yy}, in the spin Hamiltonian (1) and their standard deviations for the α molecule of fluorenylidene in diazofluorene at the boiling point of N_2.[a]

Parameter	Value	σ {Parameter}
D/hc	±0.40923 cm^{-1}	0.00020 cm^{-1}
E/hc	∓0.02828 cm^{-1}	0.00009 cm^{-1}
g_{zz}	2.00512	0.00037
g_{xx}	2.00234	0.00067
g_{yy}	2.00272	0.00026

[a] From almost zero-field measurements, $E/hc=0.0281074$ cm^{-1}, $\sigma\{E/hc\}=0.0000015$ cm^{-1}.

TABLE VI. ^{13}C hyperfine interaction frequencies A_{zz}/h, A_{xx}/h, A_{yy}/h for the spin Hamiltonian $\mathbf{I}\cdot A\cdot\mathbf{S}$ for diphenylmethylene in a single-crystal solution in benzophenone.

	$i=z$	$i=x$	$i=y$
A_{ii}/h, 10^6 sec^{-1}	115.4	189.6	214.8
$\sigma\{A_{ii}/h\}$, 10^6 sec^{-1}	1.3	0.7	0.4
Isotropic component $(1/3h)\sum_{i=x,y,z} A_{ii}$, 10^6 sec^{-1}		173.3	
σ\{isotropic component\}, 10^6 sec^{-1}		0.5	
Anisotropic component $(1/h)A_{ii}-1/3h\sum_{i=x,y,z} A_{ii}$, 10^6 sec^{-1}	−57.8	+16.3	+41.5
σ\{anisotropic component\}, 10^6 sec^{-1}	1.4	0.9	0.6

field $|0\rangle\rightarrow|1\rangle$ transition, but for the x and y axes it was determined for both the $|0\rangle\rightarrow|1\rangle$ and the $|\bar{1}\rangle\rightarrow|0\rangle$ transitions. It was assumed that the principal axes of A in the hyperfine interaction term $\mathbf{I}\cdot A\cdot\mathbf{S}$ in the spin Hamiltonian are coincident with the principal axes of the fine-structure term. It was assumed that the ^{13}C hyperfine interaction energies were equal to $A_{ii}=h\times 328.73\times\Delta\nu_p\times g_{ii}$, where $\Delta\nu_p$ was the proton frequency difference mentioned above. The results are summarized in Table VI.

4.5. Hyperfine Structure of the Fluorenylidene Spectrum

Substitution of ^{13}C in the central position of the diazo compound as described in 2.2. produced hyperfine structure in the spectra. ^{13}C peak separations were measured as described in 4.4. Measurements were made for the α molecule only. Three measurements were made along the z axis, seven measurements along the x axis, and seven measurements along the y axis. The results are summarized in Table VII.

5. DISCUSSION OF EXPERIMENTAL RESULTS

5.1. Fine Structure

The most salient feature of the fine structures of the electron magnetic resonance spectra of the paramagnetic species produced by irradiation of diphenyldiazomethane and diazofluorene in single crystals is the very large anisotropy and the very large value of the zero-field splittings. For the photoexcited triplet states of aromatic molecules previously investigated in this laboratory, the zero-field energy splittings arise from magnetic-dipole–dipole interaction between the two parallel spin electrons and are in the neighborhood of 0.10 cm$^{-1}\times hc$. They cannot exceed approximately this value because of the Pauli principle, which in the usual π orbital approximation restricts the closest approach of the two parallel spin electrons to one aromatic ring C–C distance. The much larger observed values of D in the cases discussed in this paper show that the two electrons are on the same C atom a large fraction of the time. This very large value of the zero-field splitting thus points to the existence of a divalent C atom with two available orthogonal orbitals. In the simplest model with the divalent C atom on the line of centers of the two phenyl groups these two orthogonal orbitals might be expected to approximate p orbitals, the situation being similar to that of the ground triplet state of the O_2 molecule in which the two parallel spin electrons can both be on the same atom at the same time.

For two electrons in the two orthogonal p orbitals, $2^{\frac{1}{2}}b^{\frac{5}{2}}\pi^{-\frac{3}{4}}(x\pm iy)\exp(-br^2)$, on the same C atom, with Gaussian radial dependence, the magnetic-dipole–dipole interaction energy

$$\frac{-g^2\beta^2}{2}\left[\frac{3z_{12}^2-r_{12}^2}{r_{12}^5}\right]\left[2s_{z1}s_{z2}-\frac{s_{1+}s_{2-}+s_{1-}s_{2+}}{2}\right],$$

was estimated[6] by adjusting b to maximize the overlap between these p functions and a Slater p orbital on the same C atom. This yielded 1.35 cm^{-1} for the value of D/hc, in the spin Hamiltonian (1) taking the z axis to be the axis normal to the plane of the two orthogonal p orbitals. This interaction energy was calculated by Sharma[19] using Slater p orbitals and was found to be 1.1 cm$^{-1}\times hc$. Higuchi[7] obtained the value 0.9055 cm^{-1} for D/hc using Löwdin's[20] expansion of the radial part of the C self-consistent-field p function as a sum of exponential functions.

A reasonable model would therefore be one in which the main contribution to the fine-structure interactions arises from the one center interaction on the divalent

TABLE VII. ^{13}C hyperfine interaction frequencies, A_{zz}/h, A_{xx}/h A_{yy}/h, for the spin Hamiltonian $\mathbf{I}\cdot A\cdot\mathbf{S}$ for fluorenylidene in a single-crystal solution in diazofluorene.

	$i=z$	$i=x$	$i=y$
A_{ii}/h, 10^6 sec^{-1}	203.4	280.0	307.3
$\sigma\{A_{ii}/h\}$, 10^6 sec^{-1}	0.5	1.4	4.4
Isotropic component $(1/3h)\sum_{i=x,y,z} A_{ii}$, 10^6 sec^{-1}		263.6	
σ\{isotropic component\}, 10^6 sec^{-1}		1.55	
Anisotropic component $(1/h)A_{ii}-1/3h\sum_{i=x,y,z} A_{ii}$, 10^6 sec^{-1}	−60.2	+16.4	+43.8
σ\{anisotropic component\}, 10^6 sec^{-1}	1.6	2.1	4.7

[19] R. D. Sharma, J. Chem. Phys. **38**, 2350 (1963).
[20] P.-O. Löwdin, Phys. Rev. **90**, 120 (1953).

C atom, the z axis of the spin Hamiltonian (1) being the direction normal to the plane of the $x \pm iy$ orbitals.

The measured values of D are considerably lower than these values which have been estimated for the dipole–dipole interaction on a single C atom. But of course delocalization of these electrons over the associated aromatic ring system in each of the species described here would reduce the interaction. The z axis, being normal to the plane of the two orthogonal p orbitals, lies in the direction of the line of aromatic ring centers. Thus the delocalization results in a more prolate spin distribution. The two center contributions to D therefore lower its value still further below the reduced value for the one center dipole–dipole interaction assuming that the effects of +spin densities predominate over those of −spin densities.

The observed value of D hence seems to point clearly to a divalent C atom with two available orthogonal orbitals as the source of the paramagnetism of these crystals. This indicates that well-oriented substituted methylenes have been prepared by loss of N_2 from the diazo molecules in these crystals.

The second interesting feature of the fine structure is the fact that E in the spin Hamiltonian (1) is not zero. For two orthogonal p orbitals on a single center, each containing one electron, E is of course zero. In models of the diphenylmethylene molecule such as that proposed originally by Etter, Skovronek, and Skell,[21] in which the divalent C lies on the line of centers of the two phenyl groups and the phenyl planes are perpendicular to each other, E would necessarily vanish by symmetry. For a model in which the divalent C still lies on the line of ring centers and the rings are not perpendicular, the one center interactions for the central C atom still lead to zero contribution to E even with different extents of delocalization for the two different orthogonal p orbitals. The two center interactions in this case, however, lead to not zero E.

The delocalization of the parallel spin electrons to be expected on the basis of the most naive LCAO–MO considerations may be mentioned. For a molecule with coplanar rings and with the divalent C on the line of ring centers, we see that the spin density in the p orbital which is normal to the ring plane is $\frac{4}{10}$ and in the p orbital which lies in the plane is 1 (neglecting any delocalization involving the σ system). Thus the value calculated for D/hc with one spin in each of the two p orbitals of the central C, say 0.9055 cm^{-1}, should be reduced to 0.36 cm^{-1}. When the two rings are perpendicular to each other (as in the previously mentioned Skell model) the molecule is essentially two overlapping benzyl radicals and the spin density in each of the two p orbitals is $\frac{4}{7}$ giving $\frac{16}{49}$ of the unattenuated D/hc mentioned above, i.e., 0.30 cm^{-1}. These values are much too small and would of course be still smaller because of the two center contributions to D by the spin on the rings.

McLachlan[22,23] has shown, in connection with a discussion of spin densities in dimesitylmethyl radical and benzyl radical, that we may consider the actual spin densities to be the superposition of the spin densities of an electron in a normal self-consistent field or Hückel orbital and the induced spin densities which result from the exchange interactions of the "odd" electrons with the closed shells, these interactions being different for closed-shell electrons of spins α or β. By a perturbation method based on Hückel theory, he found for benzyl radical, including the induced spin, the value of the spin density on the out of ring C to be 0.7696. For a model of perpendicular ring diphenylmethylene consisting of two overlapping benzyl radicals, this would give the value +0.54 cm^{-1} for the one center contribution to D/hc based on the 0.9055-cm^{-1} unattenuated interaction. For dimesitylmethyl with coplanar rings McLachlan has shown that whereas simple Hückel theory gives a spin density, $+\frac{4}{10}$, on the central C, the induced spin density changes this to +0.5525 and that a simple valence bond calculation gives +0.605 for this value. These two calculations applied to our molecules in coplanar ring form correspond to one center contributions 0.500 and 0.548 cm^{-1}, respectively, based on the 0.9055-cm^{-1} figure.

We thus see that these considerations, all of which result in the occurrence of negative spin densities on the rings, lead to spin densities on the central C which give one center contributions to D/hc which are some 25%–30% larger than the observed values for either the parallel or perpendicular ring plane model. This one center contribution would of course be increased by the presence of the negative spin densities in the rings and lowered by the positive spin densities. For the planar dimesitymethyl model in the case of the Hückel plus induced spin densities, the +spin densities in the 2, 4, 6 positions have a larger effect than the −spin contributions. In the case of the planar dimesitylmethyl model the valence bond calculation gives −densities which are much larger than for the case just mentioned but puts a very large +density, +0.25, on the extreme 4, 4′ positions. For the benzyl model of the perpendicular plane structure, the −densities in the rings are considerably smaller than the +densities and of course there is a relatively large +density in the extreme positions. All of these considerations lead us to expect D/hc values very close to the observed ones. Higuchi[8] had mentioned that Snyder, in unpublished work, has given an unrestricted self-consistent-field treatment which gives higher spin densities on the divalent C atom but has presented no numerical results for the molecules discussed in this paper.

Higuchi[7] had computed the D/hc which results, on the basis of simple Hückel molecular orbital considera-

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

[22] A. D. McLachlan, thesis, Trinity College and Department of Theoretical Chemistry, University of Cambridge, 1959; benzyl, p. 157; dimesitylmethyl, pp. 161–165.

[23] A. D. McLachlan, J. Chem. Phys. **32**, 1488 (1960).

tions, for all dihedral angles between the rings (central C on line of ring centers), from both the one center central C contribution and the all +densities on the rings, obtaining values in the range from 0.315 cm^{-1} in the parallel ring plane case to 0.254 for the perpendicular ring case. Such considerations are clearly inadequate to account for the observations.

Another factor affecting the value to be expected for D/hc is the degree of sp hybridization to be expected for the central C orbitals. sp hybridization results in a smaller one center contribution, per unit spin density, to D/hc than considered above. Higuchi[7] has computed the one center dipole–dipole interaction for one electron in a $2s$ and another in a $2p$ state on the same C atom using the Löwdin[20] expansions. The value obtained for D/hc was 0.4803 cm^{-1}. As the angle, θ, between the two bonds from the central C to the phenyl rings changes from π to smaller angles, $2s$ character is admixed with the $2p$ orbital in the plane defined by the two bonds. This orbital, ϕ_y, is described by

$$\phi_y=[(1+\cos\theta)/(1-\cos\theta)]^{\frac{1}{2}}\phi_{2s}+[-2\cos\theta/(1-\cos\theta)]^{\frac{1}{2}}\phi_{2py}, \quad (2)$$

while the other orbital ϕ_x is given by

$$\phi_x=\phi_{2px}.$$

Thus the bond angle determines the one center contribution to the dipole–dipole interactions and deviation of the angle from π reduces the size of D/hc from the values given above.

In the case of such ground-state triplet molecules as we are considering here the spin–orbit interaction must also be taken to be a factor which has an effect on the value to be expected for D/hc. This situation may be different from that for photoexcited triplet-state molecules where the spin–orbit effects on the values of D/hc are small and negligible. Glarum[24] and Fogel and Hameka[25] have computed this contribution to D/hc for CH_2 and have found ratios of this contribution to that of the electron magnetic-dipole–dipole interaction in the linear molecule to be 0.12 and 0.030, respectively. Glarum[24] found this ratio to be also 0.030 for a molecule with –C– angle equal to 0.83π. The spin–orbit effects will, of course, also be seriously affected by the delocalization of spin onto the rings of the molecules which we have investigated. As mentioned in 5.3. the finer details of the implication of our measurements with respect to the spin distributions in these molecules are subject to considerable uncertainty because of the large number of unknown parameters. We therefore find that the spin–orbit effects which are probably as small or smaller than those mentioned above do not influence the clear general conclusions that have been drawn.

[24] S. H. Glarum, J. Chem. Phys. **39**, 3141 (1963).
[25] S. J. Fogel and H. F. Hameka, J. Chem. Phys. **42**, 132 (1965).

5.2. Hyperfine Structure

The measurements, by ^{13}C labeling, of the hyperfine interactions between the triplet-state electrons and the divalent C atom's nucleus afford further detailed information on the distribution of spin angular momentum in the molecules discussed in this paper. The traceless part of this interaction is the magnetic-dipole–dipole interaction between the two parallel spin electrons in the two orthogonal p orbitals on the divalent C atom and the C nucleus, and it affords an accurate measure of the spin density in these orbitals. The isotropic component of the hyperfine interaction measures the s character admixed with these p orbitals and thus affords information on the angle of the –C– bond.

The dipole–dipole interaction energy between an electron in a C $2p$ orbital and the C nucleus when both spins are well quantized in the direction of a very strong magnetic field and the magnetic field is in the direction of the cylindrically symmetric axis of the p orbital is given by

$$2\,|\beta|\,|\beta_N|\,g_N\tfrac{4}{5}\langle 1/r^3\rangle_{2p}M_SM_I.$$

Smith, Sorokin, Gelles, and Lasher[26] have used the Hartree solutions, given by Brown, Bartlett and Dunn[27] and by Torrance[28] for the free atoms to evaluate $\langle 1/r^3\rangle$ and have found the value 1.20 a.u. This gives 128×10^6 $sec^{-1}\times hM_SM_I$ as the hyperfine energy. On the other hand Adam and Weissman[29] also using the Hartree function given by Torrance[28] have found 1.45 a.u. for $\langle 1/r^3\rangle$, which gives 156×10^6 $sec^{-1}\times hM_SM_I$ as the energy.

We have used the expansions of the C $2p$ orbital given by Löwdin[20] (the same one as used by Higuchi for calculating the 0.9055 $cm^{-1}\times hc$ figure for the zero-field splitting) and this gives for $\langle 1/r^3\rangle$ the value 1.66 a.u. and yields 178×10^6 $sec^{-1}\times hM_SM_I$ as the hyperfine interaction energy. With **H** in the plane perpendicular to this direction the hyperfine interaction energy is of course -89.0×10^6 $sec^{-1}\times h$.

When we consider the hyperfine interaction between two parallel spin electrons in two orthogonal p orbitals on the same C atom and the nucleus of the C atom, we therefore find for A_{zz}/h (using the 178×10^6-sec^{-1} figure) the value $\frac{1}{2}\{-89.0-89.0\}=-89.0\times10^6$ sec^{-1} (where the z axis is normal to the plane of the $2p$ $x\pm iy$ orbitals) and $\frac{1}{2}\{178-89.0\}=+44.5\times10^6$ sec^{-1} for $A_{xx}/h=A_{yy}/h$. (The factor $\frac{1}{2}$ occurs in these expressions because it is required that the spin density be normalized to 1, not 2.)

The previously mentioned delocalization of the electrons from the p orbitals on the central divalent C atom onto the rings will of course reduce this hyperfine interaction. If we use the measured values for the

[26] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).
[27] F. W. Brown, J. H. Bartlett, Jr., and C. G. Dunn, Phys. Rev. **44**, 296 (1933).
[28] C. C. Torrance, Phys. Rev. **46**, 388 (1934).
[29] F. C. Adam and S. I. Weissman, J. Am. Chem. Soc. **80**, 2057 (1958).

anisotropic component of the hyperfine interaction for diphenylmethylene from Table VI we can uniquely determine the separate extents of the delocalizations from the p_x and p_y orbitals. This yields, in the diphenylmethylene case, a spin density 0.56 in the p_x orbital and 0.74 in the p_y. For the fluorenylidene data of Table VII the corresponding figures are 0.57 and 0.78. If we reduce the Higuchi[7] value, 0.9055 cm^{-1}, for D/hc by the corresponding factors we obtain the values 0.374 and 0.405 cm^{-1} for the D/hc values for diphenylmethylene and fluorenylidene, respectively.

These values for D/hc are of course very close to those determined experimentally for the molecules discussed in this paper which are given in Tables III and V, and there is thus excellent consistency between the measurements of the fine structure and of the hyperfine structure. As pointed out in 5.1., however, this one center contribution to the value of D will be altered by the delocalization onto the rings and this will be expected to have the effect of reducing D because the increased prolateness of spin distribution arising from the +spin densities will probably predominate over the effects of the −spin densities. The 178×10^6-sec^{-1} figure used above is probably too large and the value 156×10^6 sec^{-1} given by Adam and Weissman[29] may be a better estimate inasmuch as it seems to be very reasonable from the standpoint of their free-radical results. Using this value for the diphenylmethylene case one obtains 0.63 and 0.85 for the p_x and p_y spin densities, respectively. In a similar manner to that discussed previously this leads to the value 0.658 cm^{-1} for D/hc. The Smith, Sorokin, Gelles, and Lasher[26] value, 128×10^6 sec^{-1}, gives for diphenylmethylene the values 0.77 and 1.03 for the p_x and p_y spin densities, respectively, and 0.718 cm^{-1} for D/hc. This value of the ^{13}C hyperfine interaction has been used by Cole and Heller[30] to discuss the ^{13}C hyperfine interactions in irradiated malonic acid but seems to be too small for our case in that it gives a too large value of D/hc.

For the various models of diphenylmethylene discussed in 5.1. the effects of the delocalization range from +0.55 spin density in the p orbital normal to the plane of a coplanar ring model to +0.77 in each of the $2p$ orbitals in a perpendicular benzyl model. It is to be especially noted that the available information on the crystal structure of benzophenone (see 3.1.) shows that the planes of the phenyl groups, although tilted somewhat, lie approximately parallel to the ab plane of the crystal. From Table II, which gives the orientation of the x, y, z axes of the fine-structure tensor, it is clear that the x axis (which is assumed to lie in the molecular plane perpendicular to the z-axis line of phenyl ring centers) is nearly normal to the ab plane of the crystal and hence nearly normal to the plane of the phenyl groups. Assuming the methylenes to be included substitutionally in the benzophenone structure with orientations and shapes close to those of the benzophenone molecules, it is clear that the x axes of the hyperfine interactions are approximately perpendicular to the planes of the phenyl rings; i.e., if they are tilted slightly with respect to each other the x axis is normal to that plane which bisects the smaller dihedral angle between the two planes. The anisotropic part of the ^{13}C hyperfine interaction has been seen in the immediately preceding part of this paper to demonstrate that the delocalizations from the p_x and p_y orbitals are quite different and to show clearly that the delocalization from the p_x orbital is much larger than from the p_y orbital. Thus these studies of the ^{13}C hyperfine interaction in the oriented diphenylmethylene molecule show that the orbital which can be more readily delocalized over the π systems of the phenyl rings on the basis of molecular shapes and orientations, deduced from crystal properties and fine-structure analyses, is more delocalized and this all supports a model in which the rings are more nearly coplanar than perpendicular. The anisotropic component of the hyperfine structure in the fluorenylidene spectrum is extremely close to being the same as for the case we have just been discussing and in the fluorenylidene case the molecule is most certainly planar.

The isotropic component of the ^{13}C hyperfine interaction measures the s character of the parallel spin electrons' orbitals. If we assume a model in which the two phenyl rings are coplanar and the x orbital is essentially pure p_x, we may estimate the angle of bending, θ, in the plane for diphenylmethylene from the expression

$$[(1+\cos\theta)/(1-\cos\theta)]3342=173.3$$

[see Eq. (2)], where 3342×10^6 sec$^{-1}\times h$ is the ^{13}C hyperfine interaction with a C $2s$ orbital as estimated by Karplus and Fraenkel[31] from the Hartree–Fock orbitals calculated by Jucys[32] and 173.3×10^6 sec$^{-1}\times h$ is the isotropic component of the ^{13}C hyperfine interaction energy from Table VI. This gives 2.694 (154°) as the angle of bending of the –C– link between the phenyl rings. This would give for the orbital in the plane which bisects the smaller dihedral angle between phenyl planes, the value [using (2)]

$$\phi_y=0.228\phi_{2s}+0.974\phi_{2py}.$$

For the fluorenylidene case we obtain

$$\phi_y=0.281\phi_{2s}+0.960\phi_{2py}$$

for the orbital and 2.601 (149°) for the –C– angle.

This amount of s character would of course reduce the one center contribution to the zero-field splitting very slightly from that for the interaction between p_x and p_y orbitals. This has been discussed in 5.1. and

[30] T. Cole and C. Heller, J. Chem. Phys. **34**, 1085 (1961).

[31] M. Karplus and G. K. Fraenkel, J. Chem. Phys. **35**, 1312 (1961).

[32] A. Jucys, Proc. Roy. Soc. (London) **A173**, 59 (1939); J. Phys. USSR **11**, 49 (1947).

alters the situation only slightly from any of our previous discussions.

The case of fluorenylidene is anomalous in the sense pointed out by Wasserman, Trozzolo, and Yager[33] in that the –C– angle in fluorene is much smaller than the value yielded by the isotropic hyperfine interaction as described above. Burns and Iball[34] have found this angle to be 1.83 (105°), and this angle in fluorene would not be expected to be much different from that in the fluorenylidene molecule. This would lead to a much larger isotropic component for the ^{13}C hyperfine interaction than that which is observed. Wasserman *et al.*[31] have proposed the "bent bond" as an explanation.

5.3. General Comments

These fine-structure and hyperfine-structure studies on diphenylmethylene and fluorenylidene oriented in single crystals present a consistent and semiquantitative picture of the spin distribution in these species and of their molecular structures. However, until the details of the spin distribution in the phenyl rings of these molecules is known, it is difficult to make statements concerning these matters which are as precise as would be desired because of the large number of unknown parameters of these problems. For this reason electron–nuclear double-resonance experiments, which may give these spin densities, are presently in progress in our laboratory.

[33] E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, J. Chem. Phys. **40**, 2408 (1964).
[34] D. M. Burns and J. Iball, Proc. Roy. Soc. (London) **A227**, 200 (1955).

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Mobilities of Cesium and Rubidium Ions in Their Parent Vapors

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The mobilities of Rb^+ and Rb_2^+ in rubidium vapor, and of Cs^+ and Cs_2^+ in cesium vapor have been measured. The mobilities of the molecular ions agree well with values calculated from the Langevin theory in its polarization limit. The mobilities of the atomic ions are consistent with the predictions of simple resonant charge transfer theory. Rate constants for the reactions of the atomic ions with diatomic molecules to give diatomic molecular ions have been obtained.

IN a previous paper[1] we described experiments in which the diatomic molecular ions of cesium, rubidium, and potassium were produced by photoexcitation of the gaseous atoms followed by a Horbeck–Molnar ionization process:

$$Cs + h\nu \rightarrow Cs^*(mP),$$

$$Cs^* + Cs \rightarrow Cs_2^+ + e.$$

We noted there that the mobilities of both the atomic and molecular gaseous ions of the alkalis could be obtained from measurements of the phase shift between the chopped exciting light and the current at the ion collector, and we gave preliminary values for the mobilities of Rb^+ and Rb_2^+ in their parent vapor. We also remarked that space-charge effects caused by copious thermal electron emission from the ion-collector electrode could lead to inaccuracy of the measured mobilities. In the present paper we report ion-mobility measurements for the rubidium and cesium systems that have been performed with a refined apparatus designed to eliminate space-charge effects.

EXPERIMENTAL

The materials, optical system, and electronics have been described previously. The photoionization cell was constructed of quartz with plane-parallel platinum electrodes. A 5.0×9.0-cm screen grid of 200-mesh 0.5-mil tungsten wire was located 0.3 cm in front of

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[1] Y. Lee and B. H. Mahan, J. Chem. Phys. **42**, 2893 (1965).