EPR OF CH_2: A SUBSTANTIALLY BENT AND PARTIALLY ROTATING GROUND STATE TRIPLET

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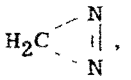
EPR spectra assignable to ground state triplet CH_2 have been observed on photolysis of diazomethane and diazirene at 4°K. Two different systems ascribable to two different crystalline sites are observed with each precursor. Analysis of the spectra shows that the long axis of the molecule is largely fixed while rotation about that axis is almost free. The most probable value of the HCH angle is 136°, in good agreement with most theoretical calculations and smaller than some values compatible with the electronic spectrum.

Previous EPR studies of a variety of aliphatic [1] and aromatic methylenes [2,4]* have shown that the resonance spectrum can yield detailed information on the distribution of the unpaired electrons and on the molecular geometry. We now wish to report the observation of the EPR of the parent methylene, CH_2, and the geometrical implications of the spectra. Methylene was first observed, in the gaseous state, by Herzberg [6]. From the electronic absorption spectra he deduced that the molecule is linear or nearly linear, and most probably a ground state triplet. The EPR observations and analyses provide the first experimental evidence indicating a substantial deviation from linearity while confirming the ground state as a triplet. One of the systems which we discuss here has been observed recently by Bernheim et al. [7]**.

Gaseous mixtures of diazomethane, H_2CN_2, or the cyclic isomer, diazirene,



were condensed with xenon at 77° or 4°K. The samples were irradiated in the diazo or diazirene bands to yield methylene and nitrogen. Both irradiation and the X-band EPR measurements were performed with the sample at 4°K. The resonance spectra were independent of precursor and temperature of condensation. The signals obtained from diazirene were stronger and most of the discussion below is based on them. One variable which appears to be of significance is the concentration of precursor. At high concentrations the dominant feature was a single broad line near 6000 G similar to but skewed from that typical of a species with 3-fold or higher symmetry [8,9]. At low concentrations two lines were seen characteristic of a system with lower symmetry. At intermediate concentrations both were visible (fig. 1). The zero-field parameters for the two forms were $D = 0.6636\ \mathrm{cm}^{-1}$, $E < 0.002\ \mathrm{cm}^{-1}$ (high concentration) and $D = 0.6881\ \mathrm{cm}^{-1}$, $E = 0.00346$ (low concentration), both assuming the g-factor of a free electron [8,9].

The assignment of the spectrum to methylene is supported by the known efficiency of each of the two precursors as a source of CH_2 [10]. However, other processes can occur. Diazome-

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[*] A summary of the data available for aromatic methylenes is given in ref. [3]. Bernheim et al. [5] discuss methylenes which are conjugated with groups containing triple bonds.

[**] We are grateful to Dr. Bernheim for making a preprint of ref. [7] available. Their report provides the first published confirmation of the triplet ground state.

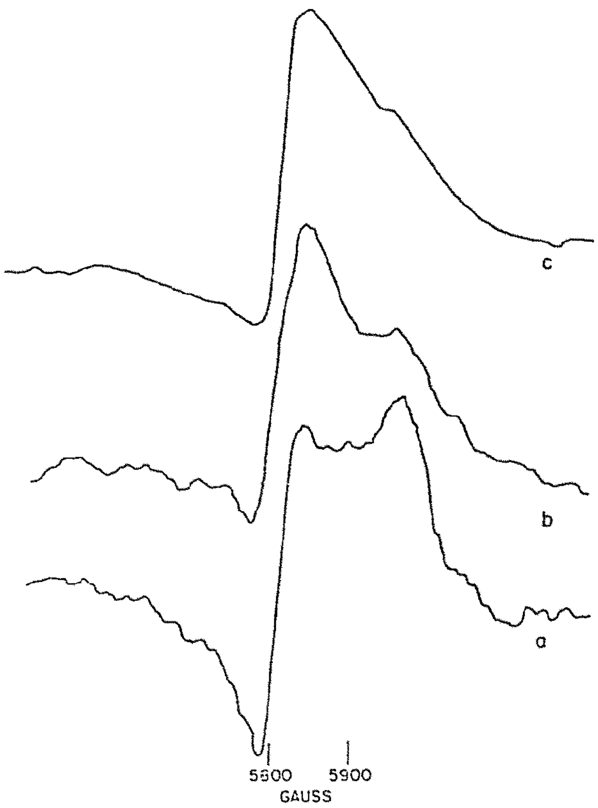
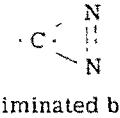


Fig. 1. X-band EPR spectra of methylene. Signal/noise increases from a) to c) and is associated with increased concentration.

thane forms triplet NCN on gas phase photolysis [10]. Cleavage of hydrogen can also occur on irradiation of diazirene as we observe the EPR characteristic of hydrogen atoms (two lines about $g = 2$ with a separation of 508 G [12] as well as the methylene signals. Of the ground state triplets which could arise from a CH_2N_2 system, NCN and CNN have been previously observed by EPR. Their zero-field parameters are clearly different from those above [13]. The cyclic methylene



is eliminated by the observation that a substantial change in the zero-field parameters occurs on deuteration of the diazirene precursor (D = 0.7563 cm^{-1}, E = 0.00443 cm^{-1} [14]); hydrogen must be present in the triplet observed.

Additional support for the methylene assignment is given by the proximity of D to those observed with perfluoroalkyl methylenes [1]. The alkyl groups are thought to be inefficient in delocalizing the unpaired electrons. The spin distribution about the divalent carbon should be similar in the substituted and parent methylenes leading to similar D's. However, the agreement may be fortuitous. The substantial change for methylene on deuteration indicates significant zero-point motion. D increases with the reduced movement of the more massive CD_2. Extrapolation yields $D = 0.93$ cm^{-1} for an immobile methylene [14]. Comparison of CH_2 and CD_2 also indicates that the mean square deviations of the long axes from their equilibrium position are 24° and 20°, respectively [14]. We do not have similar information for the perfluoroalkyl methylenes, and are unable to judge the importance of zero-point motion in their D's.

Geometry

A major question remaining from Herzberg's classic study is the value of the HCH angle in the ground triplet state. He found no evidence requiring a deviation from 180° although small variations from linearity might be undetectable [6]. In contrast, the alkyl and aromatic methylenes are bent at the divalent carbons [1,2,4]. Theoretical calculations by a variety of workers have indicated a bent ground state for methylene with an angle of 130-150° *. Where calculations have been made for substituted methylenes as well as for the parent molecule similar angles are predicted **. This experimental-theoretical argument leans towards a conclusion of a substantially bent CH_2; a conclusion which has not been supported by the previously available experimental evidence.

In the deduction of geometry from EPR, the discussion is dominated by the motive possibilities of the small, light methylene. The first application is in the two spectra seen with CH_2. These we ascribe to two slightly different sites in the crystal. The site with the lower D is believed to allow greater motion so that larger deviations of the long axis from its equilibrium position are possible. The greater motive freedom is consistent with the smaller E as well: a bent molecule which rotates freely about the

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* Harrison et al. [15] give an extensive review of the theoretical literature. See also ref. [16].

** Hoffman et al. [17] use extended Hückel theory. Z. Wasserman, in unpublished work using "polyatom", comes to a similar conclusion.

long axis will have $E = 0$. The observation that the dominant site depends on the concentration of the methylene precursor has precendent in the studies of Meyer [18]. He found that the most stable structure of pure argon is face-centered cubic, but impurities stabilize the hexagonal close packed form. Similar behavior may well occur with xenon, as we find that if argon is an added impurity only $E = 0$ is observed.

The preferred structure of methylene could be linear with a face-centered cubic xenon lattice distorting the free molecule geometry to yield $E \neq 0$. However, a variety of environments have been found to be without influence on the divalent carbon angle of substituted methylenes [2,19,20]. Also, calculations of the variation of D with angle indicate that deviations from linearity should decrease D [21]*, while here the "linear" form has the lower D. The above assignment of the "linear" ~~t~~riplet to increased motion of the bent form seems more appropriate. A major argument against the linear structure for free methylene is given in the discussion below. There we show that the observed E in the bent form is the residue of a much larger E associated with a substantially bent triplet. An angular distortion by the matrix would then have to be of the order of 40°, an unreasonably large value [20].

In the model the HCH angle is taken as 2θ (fig. 2). The angle bisector is the x axis, y is perpendicular to the molecular plane and z is the long axis of the molecule. These molecular axes, with the origin at the center of gravity, are complemented by a set of space-fixed axes in which x' is the direction of lowest potential energy in the matrix for the x axis of methylene. The z and z' axes remain parallel as we neglect any wobble of the long axis. Rotation about z is designated by φ, the angle between the x and x' axes. Such rotation will be hindered by intermolecular forces. Neglecting these forces for the moment the system is a free rigid rotator in a plane [23], with energy levels $W_j = Bj^2$. For CH_2 with arbitrary θ,

$$B = \frac{9.11\ \mathrm{cm}^{-1}}{\cos^2\theta} .$$

The barrier to rotation may be expressed as

$$\sum_n V_n(1 - \cos n\varphi) ,$$

in which $2V_n$ designates the barrier with a periodicity of $360°/n$. The barrier will mix the states of the free rotator.

If $\theta = 70°$; $B = 79.3\ \mathrm{cm}^{-1}$. At 4°K, with $kT = 3\ \mathrm{cm}^{-1}$, only the lowest rotational state will be populated. The ground state of the free rotator, $\psi_0 = (2\pi)^{-1/2}$, is cylindrically symmetric and will not contribute to E as E measures the difference in the spin-spin interaction along two perpendicular directions in the x, y plane. A first-order calculation of the lowest state shows that the nth state of the free rotator is coupled to the ground state by V_n. A zero-field parameter transforms as a second-order spherical harmonic and will only be influenced by that part of the perturbed wave function with similar transformation properties, namely $\psi_2 = \pi^{-1/2} \cos 2\varphi$ with energy W_2. We find that the observed

$$E = E_{\parallel}(V_2/W_2) , \tag{1}$$

where $E_{\parallel}$ is the value of E expected for a triplet state which is not rotating about the z axis, but fixed in space. D is not altered by rotation about z.

Accurate values for V_2 are usually not available. One value we may consider, $40\ \mathrm{cm}^{-1}$, arises from the shift in the A ← X spectrum of NH_2 on going from the vapor phase to xenon [24]. This transition involves the bent ground state (∠HNH = 102°) going to a linear excited state. The changes in the atomic positions are undoubtedly larger than those involved in a rotation of CH_2 about the z axis; $40\ \mathrm{cm}^{-1}$ is then an upper

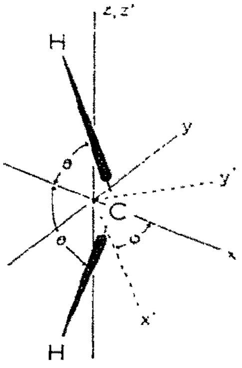

Fig. 2. Structure of methylene together with the axes used in the analysis. The unprimed axes are fixed in the molecule with the origin at the center of gravity and x the bisector of the HCH angle. The primed axes are fixed in the lattice.

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* Eq. (3) summarizes the calculations reported here. See also ref. [22].

limit to V_2 for methylene. We are here neglecting any differences in dipolar or dispersion forces. Another barrier, that for rotation of a hydrogen molecule in solid hydrogen, has been estimated to be $\approx$3-5 cm^{-1} [25]. Finally, from a comparison of CH_2 and CD_2 in xenon we can show that for end-over-end rotation (about the x or y axis) $V_2 = 122\ cm^{-1}$ [14]. For our present purposes we assume that the barrier for rotation about z has the same form as that about x and y. The only difference is taken to be in the magnitude of atomic displacements. Expanding about a potential minimum which we represent by a parabola, the barrier will be proportional to the square of the hydrogen displacement on rotation.

$$V_2 = 122(6/7)^2 \cot^2\theta = 89.6 \cot^2\theta\ cm^{-1}\ . \quad (2)$$

For stationary methylenes E_η/D directly measures the angle at the divalent carbon. Using a simple s-p hybrid model we have [2,21]

$$E_\eta/D = -\frac{\cos^2\theta}{2 - 3\cos^2\theta}\ . \quad (3)$$

If methylene were slightly bent and fixed in xenon the observed $E/D = E_\eta/D = 5.04 \times 10^{-3}$ would correspond to $\theta = 86^\circ$. However, for such a geometry $B = 1874\ cm^{-1}$. From (1), even with $V_2 = 40\ cm^{-1}$, $E = E_\eta(40/1874 \times 2^2) = 1.8 \times 10^{-5}\ cm^{-1}$ well below our limit of resolution. Clearly, θ and B must be smaller and E_η larger to yield the observed $E = 0.0034\ cm^{-1}$.

Combining (1) and (3)

$$E/D = (V_2/9.11 \times 4) \cos^4\theta/(2 - 3\cos^2\theta)\ . \quad (4)$$

Using (2) and the observed E/D then yields $\theta = 68^\circ$. This calculation involves no adjustable parameters but does depend on the assumptions inherent in (2) and (3). (3) is supported by the studies on aromatic methylenes [2,4]. The uncertainty in V_2 is a substantial source of error. Fortunately, (4) indicates that $\cos\theta \propto V_2^{-1/4}$. For $\theta = 68^\circ$, (2) yields $V_2 \approx 14.5\ cm^{-1}$. Variations from this value by a factor of 2, (V_2 = 7-29 cm^{-1}) correspond to θ = 64-71.5°. Arbitrarily, we set these values as the limit of error. The HCH angle is then taken as 128-143° with 136° the most probable value. The agreement with quantum mechanical calculations is satisfactory [15].

Additional support for the assignment of $2\theta = 136^\circ$ follows from the lack of hyperfine interaction in CH_2. There is no detectable narrowing of the EPR spectrum on deuteration [14]. A hyperfine coupling of -95 MHz has been predicted for a linear CH_2 [26]. On bending, the coupling with the in-plane, s-p hybrid will become more positive, eventually cancelling out the negative contribution of the largely unchanged p-orbital. Calculations, originally performed for the vinyl radical, indicate that this cancellation should occur for an angle of 135-140°; in agreement with the angle assigned above [24]. Such an explanation has been previously employed to explain the small hyperfine coupling of phenylmethylene [2].

The analysis of the methylene spectra given in this report has possible implications for monosubstituted methylenes. The monoperfluoroalkyl methylenes [1] and HC̣CN [5] could have low E's due to motion of the hydrogen. Angles at the divalent carbons would then be less than originally assigned. However, the attempts we have made to examine HC̣CN in a variety of matrices at 4°K have only given spectra corresponding to $E = 0$ thus supporting the linear form.

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