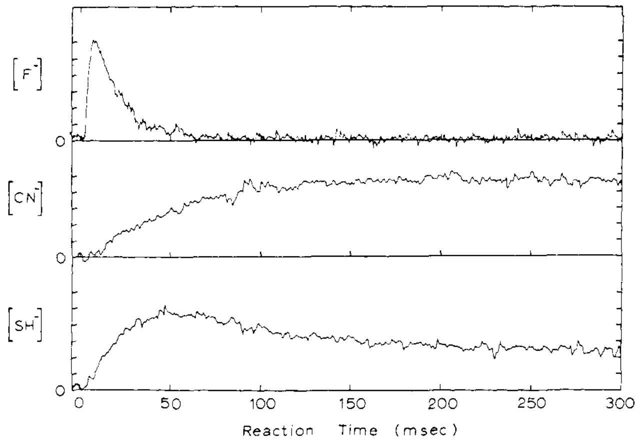

Figure 1. Pulsed icr spectra showing the concentration of F^- (upper trace), CN^- (middle trace), and SH^- (lower trace) as a function of reaction time for a 3.98:1.00 mixture of H_2S:HCN.

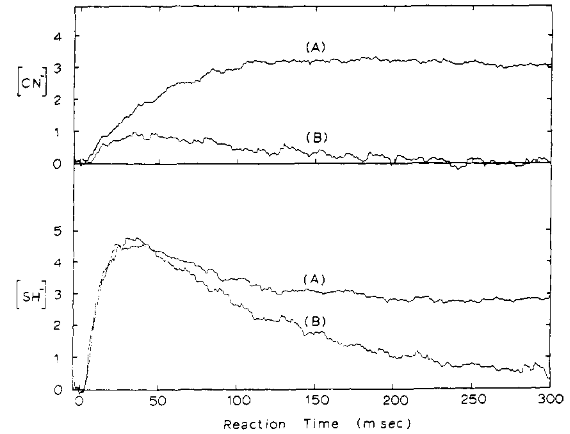

Figure 2. Pulsed icr spectra for a 10.41:1.00 mixture of H_2S and HCN. Upper half: (A) concentration of CN^- *vs.* reaction time, (B) concentration of CN^- *vs.* reaction time when SH^- is ejected from the cell. Lower half: (A) concentration of SH^- *vs.* reaction time, (B) concentration of SH^- *vs.* reaction time when CN^- is ejected from the cell.

the icr analyzer cell, and trace B in the lower half of Figure 2 shows the analogous situation when the concentration of SH^- is monitored and CN^- is ejected continuously. If CN^- and SH^- were not chemically coupled, then ejection of one of them would have no effect on the other. A more detailed kinetic analysis[9] shows that this method for measuring the rate of the forward and reverse reactions gives $K = k_1/k_2 = 8.9 \pm 0.5$.

NF_3 was used in the experiments described above because it is a convenient and efficient source of negative ions in the gas phase. However, experiments have also been performed with binary mixtures of H_2S and HCN. SH^- formed directly at 6 eV (uncorrected) by dissociative electron attachment to H_2S serves as the source of negative ions. Formation of the negative ions by a different primary mechanism is another means of testing whether thermal equilibrium is being attained. These experiments are more difficult than the ones using NF_3, but still $K = 10.1 \pm 1.8$ was obtained. The two different modes of negative ion formation are likely to give rise to different initial internal energies in the ions studied, yet values of K are obtained which agree within experimental error.

The excellent agreement among equilibrium constants obtained by three different methods supports our contention that thermal equilibrium is closely approached in the pulsed icr experiments. Furthermore, using the average value $K = 9.5 \pm 1.5$ for reaction 1, a value of $\Delta H_f^{298}(CN^-) = 15.5 \pm 1.3$ kcal/mol can be calculated from existing thermochemical data.[10] This is in quite good agreement with $\Delta H_f^{298}(CN^-) = 15 \pm 1.5$ kcal/mol which can be derived from the photoionization measurements of Berkowitz, Chupka, and Walter.[11]

The ability to measure gas-phase ionic equilibria shows great promise for the determination of accurate relative stabilities of positive and negative gaseous ions. The measurement of equilibrium constants for proton transfer reactions such as reaction 1 will permit establishment of an absolute gas phase acidity scale. Such a scale is not only of inherent interest, but also will allow determination or reconfirmation of many bond strengths and electron affinities.[12]

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(10) Obtained using $\Delta G = -RT \ln K$, $\Delta H = \Delta G + T\Delta S$; $T = 298°K$; $\Delta S = 2.7$ eu calculated from S_0^{298} values for HCN, H_2S, and the *radicals* SH· and CN· in S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 196–198; $\Delta H_f^{298}(H_2S) = 4.9$ kcal/mol, $\Delta H_f^{298}(HCN) = 32.3$ kcal/mol from D. D. Wagman, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards (U. S.) Technical Note No. 270-3, 1968; the $D_0(HS\text{–}H) = 89.3 \pm 0.7$ kcal/mol value from V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, **49**, 482 (1968); and the electron affinity of HS· = 53.5 kcal/mol from B. Steiner, *ibid.*, **49**, 5097 (1968).

(11) Obtained using an estimated threshold of 819 ± 2 Å at 298°K for the process $h\nu + HCN \rightarrow H^+ + CN^-$ from J. Berkowitz, W. A. Chupka, and T. A. Walter, *ibid.*, **50**, 1497 (1969); $\Delta H_f^{298}(H^+) = 365.7$ kcal/mol; and $\Delta H_f^{298}(HCN) = 32.3$ kcal/mol as in ref 10.

(12) For a discussion of the interrelation between bond strength, electron affinity, and acidity, see J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *J. Amer. Chem. Soc.*, in press.

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Electron Paramagnetic Resonance of 9,9′-Dianthrylmethylene. A Linear Aromatic Ground-State Triplet Methylene

Sir:

An aromatic ring adjacent to a divalent carbon usually does not affect the angle at that site. Methylene,[1,2] phenylmethylene,[3] diphenylmethylene,[3–5] 1- and 2-naphthylmethylenes,[6] and 9-anthrylmethylene[6] have ap-

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(1) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, 7, 409 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).

(2) G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971); R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *ibid.*, **54**, 3223 (1971).

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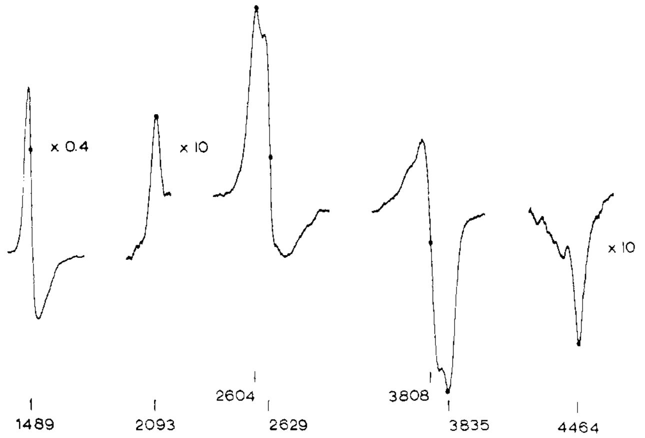


Figure 1. Epr spectrum of 9,9′-dianthrylmethylene in 9,9′-dianthryl ketone at 140°K with $h\nu/g\beta$ = 3273.5 G.

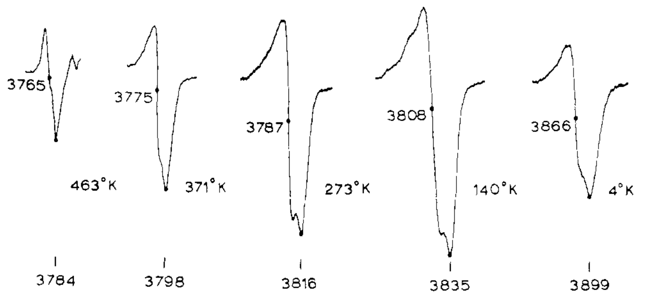
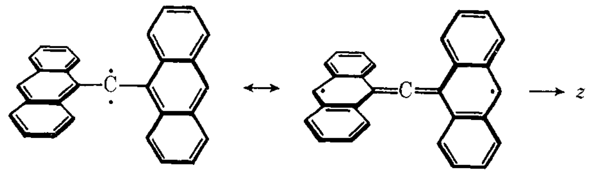


Figure 2. The high-field xy line of I in II, with fields given in gauss. D is proportional to the separation of the average of the two lines from 3273.5 G. The measurement at 4°K was made with an experimental arrangement different from that used for obtaining the higher temperature spectra. Saturation was a severe problem at 4° (and to a lesser degree at 77°), and may partly account for the increase in line width.

proximately the same angle, *viz.*, ~135–140°. We have now observed the epr spectrum of the ground-state triplet 9,9′-dianthrylmethylene (I). The observations are consistent with the structure shown below; the bonds to the divalent carbon are collinear and the two ring planes are perpendicular. In one host, spectra have been obtained from 4 to 480°K, thus demonstrating the most stable methylene system yet observed. This stability has allowed the triplet to be prepared by thermal decomposition of the precursor, 9,9′-dianthryldiazomethane (II), as well as by the more common photodecomposition.



I

The diazo compound II[7] was prepared by the method outlined in Scheme I.

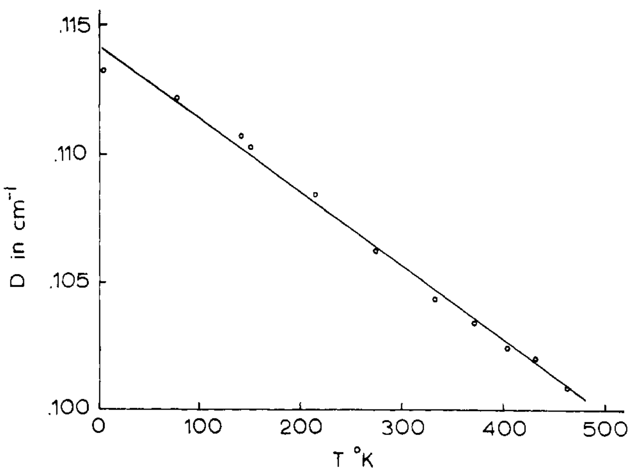
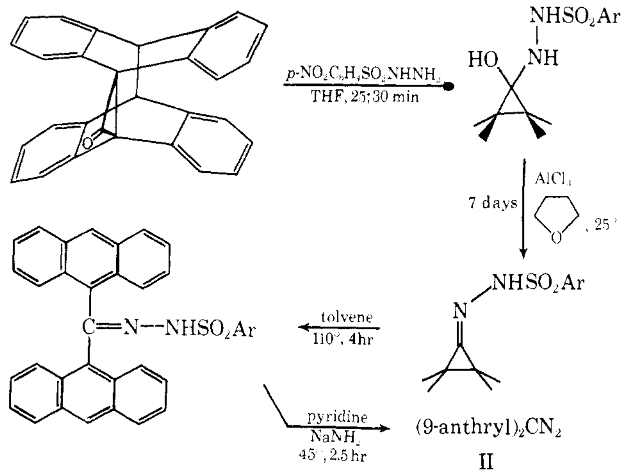


Figure 3. D *vs.* T for 9,9′-dianthrylmethylene in 9,9′-dianthryl ketone. Except for irreversible decreases in intensity at temperature >120° C, the spectra did not depend on the previous thermal history of the sample.

Powdered samples of a "solid solution" of 9,9′-dianthryldiazomethane (II) in 9,9′-dianthryl ketone (III) were irradiated with 3500–4500-Å light. The epr spectrum of the methylene I at 140°K is given in Figure 1. A portion is shown as a function of temperature in Figure 2. On warming to 60–80°C, a substantial increase in signal was observed due to the thermal decomposition of the diazo precursor II remaining after irradiation. The spectra from thermal and photodecomposition were indistinguishable. Observations were made to 210°C; the half-life at 200°C was 7 min. The zero-field parameter D, obtained from the randomly oriented samples,[8,9] is plotted as a function of temperature in Figure 3. E varied from 0.0011 at 4°K to 0.0005 cm^{-1} at 190°C.

Scheme I



D measures the average distance beteen electrons, E the deviation of the molecule from threefold or higher symmetry weighted by this distance. The ratio E/D then provides a measure of the deviation from a structure of high symmetry. The E's observed are essentially zero, as their small magnitudes are typical of the shifts of

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[7] The initial adduct of cyclopropanone and p-nitrophenylsulfonylhydrazone decomposes at 158–160°; the dehydration product (the cyclopropanone sulfonylhydrazone) turns yellow at ~100° and decomposes at 229–230° (the decomposition point of the ring-opened product 9,9′-dianthryl ketone p-nitrophenylsulfonylhydrazone). 9,9′-Dianthryldiazomethane, recrystallized from tetrahydrofuran–acetone as dark red needles, changes to a yellow solid at ~100°, which decomposes above 280°: ir 2035 cm^{-1}; uv (THF) λ_{max} (log ϵ), 250 (5.11), 369 (3.87), 388 (4.00), 413 (3.94), 431 (3.93) trailing to 580 nm. For preparation of the cyclopropanone of Scheme I, see N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968). Satisfactory combustion analyses have been obtained for all new compounds.

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[9] P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

a zero-field parameter with matrix.[10] The 50% decrease in E with increasing temperature contrasted with the 12% decrease in D also supports the conclusion that nonzero E's arise from environmental perturbations of an $E = 0$ system. At the higher temperatures, lattice expansion should allow the guest methylene to assume its preferred geometry. In anthracene as a host it was observed that $E \cong 0$ for all temperatures ($-196°$ to $+160$°C) with $E < 0.0003$ cm^{-1} in the upper half of the range. Thus the deviation from collinearity at the central carbon atom is not more than 9°.[1]

The one structure which is at all reasonable for $E = 0$ is I. This is the analog of the structure originally postulated for diphenylmethylene by Skell,[11] but which differs from those observed for that species.[3–5] Structure I for 9,9′-dianthrylmethylene may be rationalized by noting that there is extensive delocalization of the unpaired electrons into the anthryl portions. The extensive π bonding converts the methylene carbon into the central atom of a linear allene. The substituents at either end of the central three-carbon-atom group then lie in perpendicular planes.

Evidence for this extensive delocalization of the unpaired electrons is found in the low D's observed with I. Methylene should have $D_{\mathrm{CH_2}} \approx 0.76$ cm^{-1},[12] while 9-anthrylmethylene has $D = 0.3008$.[6] When one electron is delocalized, D should be proportional to the unpaired spin density of that electron remaining at the carbene carbon; $\rho \sim 0.30/0.76$. If each electron is delocalized into one anthryl residue, we should have $D = \rho^2 D_{\mathrm{CH_2}} \approx (0.30/0.76)^2(0.76) = 0.118$ cm^{-1}, as compared to the observed value (at 4°K) of 0.113.

The linear decrease of D with temperature (Figure 3) may be rationalized by considering the molecule to lie in a two-dimensional harmonic oscillator well. The long (z) axis of the molecule wobbles with increasing temperature. Because of the large mass of I, these oscillatory states are closely spaced, and a classical approximation is appropriate. A linear decrease with T is then predicted. The point at 4°K could lie below the line because of zero-point motion.

The stability of I, the free methylene, is due to the rigidity of the environment and not to an intrinsic lack of reactivity. Solid solutions of I when prepared in viscous glass matrices, such as 2-methyltetrahydrofuran and methylcyclohexane, are stable for many hours at 77°K. On warming with a consequent thawing of the matrix, the signals disappeared irreversibly.

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Furan Formation in the Sensitized Photolysis of Methyl Diazomalonate in Acetylenes[1]

Sir:

Although the copper-catalyzed addition of diazo compounds to acetylenes constitutes an important technique for the synthesis of cyclopropenes,[2–4] studies of the reactions of carbenes with acetylenes have focused on the relative contributions of addition and insertion reactions,[5–7] or have dealt with succeeding transformations of the initially formed cyclopropenes.[8] We have recently reported the formation of indenes from the reaction of diphenylcarbene with acetylenes, a reaction characterized by a remarkable steric dependence.[9] It was of considerable interest to ascertain whether or not this closure to an adjacent unsaturation is a characteristic reaction of triplet carbenes. Biscarbomethoxycarbene can be generated in both the singlet and triplet states,[10–12] and thus seemed an excellent test case. Also the products of the desired reaction, alkyl 2-methoxy-3-carbomethoxyfurans, represent a hitherto unreported substitution pattern for the furan nucleus, giving the reaction obvious synthetic appeal.

The direct photolysis of methyl diazomalonate in 2-butyne afforded the expected cyclopropene **2a**, in 36% yield. Only trace amounts of other products, assumed to be insertion products, were detectable by vpc. Similarly 1-hexyne and 4-octyne afforded **2b** and **2c**, respectively, in comparable yields. The cyclopropenes were identified by elemental analysis and spectra, which agreed well with those of known tri- and tetrasubstituted cyclopropenes.[13]

In sharp contrast, sensitization of the photolysis in 2-butyne with an equimolar amount of benzophenone gave as the major product the furan **3a**, in 43% yield, accompanied by only 9% **2a**. Acetylenes **1b–d** gave entirely analogous results, with the slight variations in the relative yields of furans and cyclopropenes noted in Table I.

Table I. Relative Yields of **2** and **3** from Decompositions of Methyl Diazomalonate in **1**

Acetylene	Decomposition mode	% **2**	% **3**
1a	Direct photolysis	>99	<1
1a	Ph_2CO, photolysis	16	84
1b	Direct photolysis	>99	>1
1b	Ph_2CO, photolysis	10	90
1c	Direct photolysis	>99	>1
1c	Ph_2CO, photolysis	25	75
1c	$CuSO_4$, reflux	>99	>1
1d	Ph_2CO, photolysis	<1	<99

(1) Generous support of this work by the National Science Foundation through Grants GP-12759 and GP-30797X is gratefully acknowledged.

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