

$\text{Ar}_2^+$  production will be more important at short reaction times (short delay times) because of the exponential term. As reaction time (or delay time) is increased, however, eq. 4 indicates that the relative contributions of states with larger  $\tau$  will increase. In other words, the excited states with large  $\tau$ , having not yet radiated, will make more collisions in the longer time available for reaction. This is, in fact, observed in Fig. 1 and 2 in the growth of the peak at 18 e.v. with respect to that at 28 e.v., and the growth of both of these with respect to the broad peak at 60–70 e.v. In fact, the ratio of the 18-e.v. peak to the 65-e.v. peak increases approximately linearly with delay time. This would be expected from (4) if the peak at 18 e.v. is due to a state long-lived with respect to delay time, while the 65-e.v. peak is due to a state short-lived with respect to delay time. We, therefore, assign the peaks at 18, 28, and 60–70 e.v. to the excitation functions for those states observed by Kaul<sup>3</sup> to have lifetimes of  $1.9 \times 10^{-5}$ ,  $2.0 \times 10^{-6}$ , and  $5.4 \times 10^{-7}$  sec., respectively. We suggest that the first two peaks represent excitation to optically forbidden states and the latter to an optically allowed state with the observed ionization efficiency curve being a superposition of the three excitation functions. As Kaul<sup>3</sup> has pointed out, a specific assignment of these states to known argon terms is not now possible.

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### Pentachlorocyclopentadienyl Cation, a Ground-State Triplet

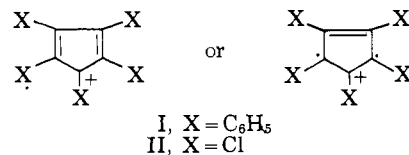
Sir:

In cyclic conjugated systems with  $4n$   $\pi$ -electrons and  $C_3$  or greater symmetry, it is predicted that the ground state may be a triplet (*i.e.*, have two unpaired electrons). As has been reported elsewhere,<sup>1</sup> pentaphenylcyclopentadienyl cation (I), a symmetrical derivative of the 4  $\pi$ -electron cyclopentadienyl cation, has a low-lying ( $E_a = +550$  cal./mole) triplet state, although its ground state is a singlet.<sup>2</sup> It seems likely that the singlet is favored in I because the large  $\pi$ -system decreases electron correlation and the complex structure allows easy distortion of symmetry. Such factors are found to an even greater extent in heptaphenylcycloheptatrienyl anion, in which a low-lying triplet state was not detected.<sup>3</sup> Accordingly, the possibility remains that in simpler derivatives of 4  $\pi$ -electron systems the ground state will be a triplet. We wish to report that pentachlorocyclopentadienyl cation (II) is apparently such a case.

(1) R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963).

(2) Bulk susceptibility measurements indicate  $<10\%$  triplet at 4°K. and  $<6\%$  at 213°K.

(3) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962), and subsequent e.s.r. studies.



Mixing hexachlorocyclopentadiene and  $\text{SbF}_5$  (10 moles excess) at room temperature produced a dark green viscous oil which, when quickly transferred to a sample tube and cooled to 77°K., exhibited an electron spin resonance spectrum typical of a triplet species (Fig. 1), along with evidence of an ordinary radical at  $g = 2$ . The signal for a  $\Delta m = 2$  transition at 1362

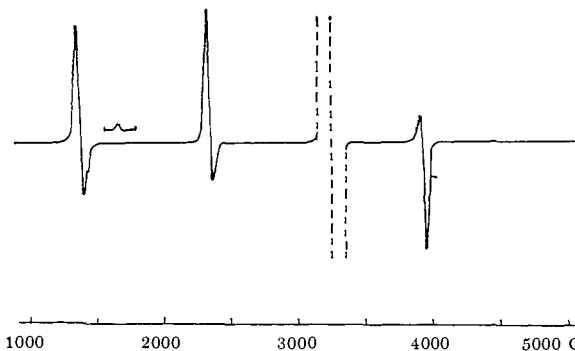


Fig. 1.—E.s.r. spectrum of  $\text{C}_5\text{Cl}_5^+$ . This spectrum shows all the reproducible features of several runs; the very weak  $z$ -lines are shown at the fields at which they appear with much greater amplification.

gauss,  $xy$ -component  $\Delta m = 1$  satellites at 2340 and 3944 gauss, and very weak  $z$ -component  $\Delta m = 1$  satellites at 1675 and 4865 gauss, indicates that a triplet is present with  $D = 0.1495$   $\text{cm}^{-1}$  and  $E < 0.002$   $\text{cm}^{-1}$ .<sup>4</sup> Similar values were obtained at 4°K.<sup>5</sup> There the  $\Delta m = 2$  and  $xy$  lines were observed at the low microwave power levels needed to minimize saturation. The value of  $D$ , which measures the interaction of the two unpaired electrons, is as expected larger than the 0.1050  $\text{cm}^{-1}$  for I, but smaller than values for carbenes<sup>6</sup> or nitrenes<sup>7</sup> in which the two electrons are largely localized on the same atom (*e.g.*, cyclopentadienylidene,<sup>6b</sup>  $D = 0.4089$   $\text{cm}^{-1}$ ). The zero value of  $E$  indicates that the triplet is isotropic in the  $xy$  molecular plane; this is expected for a species with pentagonal symmetry, and was also observed for I, but nonzero values of  $E$  are easily detected for triplets<sup>6,7</sup> which lack such symmetry. The vanishing of  $E$  at 4°K. as well indicates that the symmetry is inherent in the triplet and not due to rotation in the  $xy$ -plane. Thus the triplet species being observed here must almost certainly be II.<sup>8</sup>

When the  $\text{SbF}_5$  solution is quenched in methanol, the major products (total 92%) are four dimeric perchlorocyclopentenones<sup>9</sup> (analysis, infrared, ultraviolet)

(4) Cf. E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(5) We would like to thank Mr. W. A. Yager and Mr. R. M. R. Cramer for their aid in the liquid helium measurements.

(6) (a) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962); (b) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *ibid.*, **86**, 2304 (1964).

(7) E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166, (1964); **84**, 3213 (1962).

(8) The possibility that it is instead a cyclopentadienyl cation with some or all of the chlorines replaced by fluorines is excluded by the observation that no fluorine is present in any of the products from methanol quenching.

(9) The structures of these compounds will be discussed in the full publication.

together with 5% of volatile material. The bulk of this is  $C_6Cl_6$ , but about 20% has been identified as 1,1-dimethoxytetrachlorocyclopentadiene, by comparison of v.p.c. retention time, n.m.r. spectrum, and mass spectrum with those of an authentic sample.<sup>10</sup> Thus only 1% of the product seemingly derived from II can be found; the major reaction of  $C_6Cl_6$  is Lewis acid catalyzed dimerization<sup>11</sup> and subsequent changes. With  $AlCl_3$ ,  $BF_3$ ,  $SbCl_5$ , or  $SbF_5$  in  $SO_2$ ,  $C_6Cl_6$  gives no detectable triplet signal,<sup>12</sup> although all give the strong doublet radical signal at  $g = 2$ .

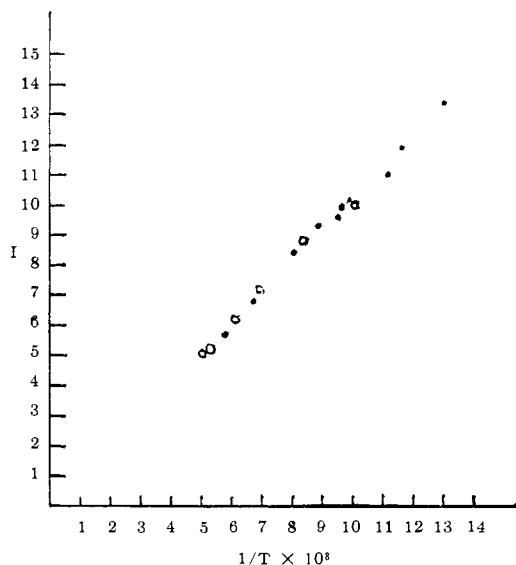


Fig. 2.—Amplitude of  $\Delta m = 2$  signal vs. reciprocal temperature: O, run A (Columbia); ●, run B (Bell Labs).

The e.s.r. spectrum of the  $\Delta m = 2$  transition was observed as a function of temperature (Fig. 2). For a triplet excited state lying  $E_a$  above the ground singlet state the intensity of the signal should be related to the temperature by

$$\text{intensity } (I) = k/T \left( \frac{3e^{-E_a/(RT)}}{1 + 3e^{-E_a/(RT)}} \right)$$

As Fig. 2 shows, experimentally we see essentially no variation from the Curie Law ( $I = k/T$ ) down to 77°K. With an  $E_a$  of 30 cal./mole the lowest temperature point would deviate from the straight line, because of the exponential term, by 5%, while an 8% deviation would result from  $E_a = 46$  cal./mole. From the plot in Fig. 2 the triplet is thus either the ground state or very close to it. Additional evidence on this point is found in the fact that the corrected intensity of the  $\Delta m = 2$  signal at 4.2°K. is 22 times that of the same sample at 77°K., as expected if  $E_a$  is zero. The observed ratio of 22 has an uncertainty of perhaps 30–40%.<sup>13</sup> We conclude that the triplet is either the

(10) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 948 (1949).

(11) J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 952 (1949); E. T. McBee, J. D. Idol, and C. W. Roberts, *ibid.*, **77**, 4375 (1955).

(12) See also H. P. Fritz and L. Schäfer, *J. Organometallic Chem.*, **1**, 318 (1964).

(13) Variations in  $Q$  and in the filling factor and some residual saturation at liquid helium are expected to be significant contributors to this uncertainty.

ground state of the system or at most 6–8 cal./mole from it.<sup>14</sup>

(14) Support of this work by the National Science Foundation is gratefully acknowledged.

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### Electroluminescence in Solutions of Aromatic Hydrocarbons

Sir:

We have studied an unusual type of electroluminescent cell which operates on alternating current (a.c.) at applied voltages  $\geq 3.5$  v. and produces bright chemiluminescence from the reaction between positive and negative radical ions derived from aromatic hydrocarbons.

Hoijsink has observed chemiluminescence upon mixing solutions of electrogenerated anthracene positive and negative ions.<sup>1</sup> We were able to perform a similar experiment in a single vessel but decomposition occurs rapidly. We hoped to improve the efficiency of this experiment by using a.c. electrolysis and by choosing compounds having greater chemical stability and higher fluorescence efficiency than anthracene. A.c. electrolysis provides a means of generating both radical ions at the same electrode by diffusion-controlled electrochemical reactions on alternate half-cycles. It is then possible for these species to undergo the chemiluminescent reaction in the Nernst diffusion layer rather than to require mechanical transport of the reactants with concomitant opportunity for side reactions. The surface concentration of R is virtually zero during the entire voltage cycle, and a continued diffusion of starting material is ensured. The disadvantages that the highly colored radical ions ( $R^+$  and  $R^-$ ) react readily with traces of oxygen and water and that these ions in general undergo other undesirable side reactions, leading to discoloration of the solution, appear to be greatly reduced by the use of a.c.

The electrochemical processes associated with anthracene and its derivatives have been studied previously.<sup>2–5</sup> Reduction yields the stable anion radical. It has been reported that electrochemical oxidation of anthracene gives the dipositive cation  $R^{2+}$ , but some substituted anthracenes appear to give  $R^+$  and/or  $R^{2+}$ . We have investigated the behavior of 9,10-diphenylanthracene (DPA) as a model system. Solutions (DMF) of anthracene, perylene, rubrene, quaterphenyl, and 1,1,4,4-tetra-phenylbutadiene were also found to luminesce under our conditions.<sup>6</sup> The working electrodes

(1) Professor G. J. Hoijsink (Amsterdam) mentioned these results during a visit in the summer of 1963.

(2) P. H. Given, *J. Chem. Soc.*, 2684 (1958).

(3) G. J. Hoijsink, J. von Schooten, E. de Boer, and W. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

(4) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(5) J. D. Voorhies and N. H. Furman, *Anal. Chem.*, **31**, 381 (1959).

(6) The solvents employed were Spectrograde N,N-dimethylformamide (DMF), Spectrograde acetonitrile (AN), N-methylpyrrolidone, acetone, or glyme. Solvents used for detailed electrochemical studies were further purified by commonly used procedures: J. F. Coetzee, *et al.*, *Anal. Chem.*, **34**, 1139 (1964); S. Wawzonek, *et al.*, *J. Electrochem. Soc.*, **102**, 235 (1955). Tetraalkylammonium perchlorates were supporting electrolytes; alkali perchlorates or chlorides can also be used. Oxygen was excluded by passing dry  $N_2$  through or over the solution.