

field methyl resonance has the larger area it appears that the N-methyl group lying close to the benzene ring, as in IVa, is more shielded than the one *syn* to the carbonyl, as in IVb. Consequently it is possible to assign the methyl resonances in *o*-fluoro-N,N-dimethylbenzamide by analogy: the methyl group closer to the benzene ring must be the more shielded of the two.

The number of bonds between the two N-methyl groups and the fluorine nucleus is the same: four single bonds and two "partial" double bonds (one aromatic and one C-N bond). However, the proximity and geometrical relationship of the two methyl groups to the fluorine are different and this undoubtedly accounts for the fact that H-F spin-spin splitting with only one of the groups is observed. Interestingly enough it is, as has been noted above, the high field methyl resonance, arising from the methyl group lying closer to the fluorine, which is split. This splitting is field invariant<sup>11</sup> ( $J = 1.2$  c.p.s.) and is consequently ascribed to H-F coupling.

The magnitude of the six-bond H-F coupling observed in this system is comparable to that of the five-bond *gauche* H-F coupling observed by Roberts,<sup>5</sup> raising, once more, the question whether, perhaps, such long-range couplings are not taking place through space instead of through the bonds.

**Acknowledgment.**—The author wishes to acknowledge the helpful assistance of Dr. Theodore Cohen and to thank Jonathan Lipowitz for a sample of *o*-fluoro-N,N-dimethylbenzamide.

(11) The spectra were recorded at 60 Mc. on a Varian A-60 spectrometer and at 100 Mc. on a Varian HR-100.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF PITTSBURGH  
PITTSBURGH 13, PENNSYLVANIA

ANITA H. LEWIN

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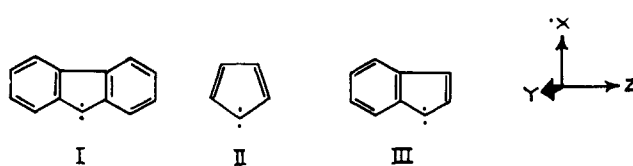
### Election Spin Resonance of Triplet Cyclopentadienylidene and Indenylidene

Sir:

Previously we reported the e.s.r. of the ground state triplet fluorenylidene (biphenylenemethylene)<sup>1,2</sup> (I) which may be regarded as dibenzocyclopentadienylidene. We have now observed the e.s.r. of the parent cyclopentadienylidene (II) and the monobenzo derivative, indenylidene (III). The observations indicate that these species have one  $\sigma$ - and one  $\pi$ -unpaired electron. The interaction between the two electrons stabilizes one of the degenerate  $\pi$ -orbitals in II so that the formula II represents the dominant resonance form. The bonds to the divalent carbon atoms (C-1) in these cyclic methylenes appear to be "bent."

(1) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

(2) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).



The precursors, diazocyclopentadiene<sup>3</sup> and diazoindene,<sup>3</sup> were photolyzed in hexafluorobenzene or hexachlorobutadiene at 77 or 4°K. The spectra were obtained with a Varian V-4500 spectrometer with 100-kc. modulation and were characteristic of randomly oriented triplets of low symmetry.<sup>4</sup> The spectra persisted for hours after irradiation ceased indicating that the observed species were the ground states or were thermally excited above the ground states by not more than  $\sim 10$  cm.<sup>-1</sup>.

The spectra may be described by the Hamiltonian<sup>5</sup>

$$3\mathcal{C} = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$$

With I  $D = 0.4078$  and  $E = 0.0283$ ,<sup>1,2</sup> and we find for II  $D = 0.4089$  and  $E = 0.0120$  while for III  $D = 0.3777$  cm.<sup>-1</sup> and  $E = 0.0160$  cm.<sup>-1</sup>. The zero-field parameters,  $D$  and  $E$ , are proportional to the averages of  $(1/r^3) - (3z^2/r^5)$  and  $(y^2 - x^2)/r^5$ , respectively, where  $r$  and its components refer to the distance between the two unpaired electrons.<sup>6</sup> A possible assignment of the principal magnetic axes, analogous to I,<sup>2</sup> accompanies the formulas; the  $y$ -axes are perpendicular to the molecular planes.

If the nonbonding  $\sigma$ -orbital at C-1 in II contained two paired electrons, the triplet would have two unpaired  $\pi$ -electrons. In such  $\pi$ -triplets with one  $2p\pi$  atomic orbital available at each carbon atom, the Pauli exclusion principle requires the vanishing of any interactions due to the unpaired electrons residing on the same carbon atom. This limitation upon the closest approach of the spins places an upper limit on  $D$  of  $\sim 0.2$  cm.<sup>-1</sup>.<sup>7</sup> The larger value observed requires a significant one-center interaction, and indicates that one unpaired electron lies in a C-1  $\sigma$ -orbital.

A symmetrical distribution of the unpaired  $\pi$ -electron in II, in which each of the lower pair of degenerate orbitals is equally populated, would have a  $\pi$ -spin density at C-1,  $\rho_1$ , of 0.20. Because of the dominance of the one-center interaction,<sup>8</sup> for a given geometry about C-1,  $D$  should be approximately proportional to  $\rho_1$ . The similar values of  $D$  for I, II, and III imply similar values of  $\rho_1$ . An SCF-MO calculation for the fluorenyl radical yields  $\rho_1 = 0.55$ ; for the indenyl radical  $\rho_1 = 0.41$ .<sup>9</sup> With II  $\rho_1$  should be  $\geq 0.4$ . A mechanism for the increase in  $\rho_1$  in II above 0.20 arises from the presence of the orbital degeneracy in the  $\pi$ -system. One of the degenerate pair of orbitals has a Hückel  $\rho_1 = 0.40$ . An exchange interaction with the unpaired  $\sigma$ -electron, analogous to Hund's rule, and

(3) T. Weil and M. Cais, *J. Org. Chem.*, **28**, 2472 (1963). Ethylenediamine was found to be the most effective base.

(4) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

(5) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A214**, 235 (1952).

(6) (a) M. Gouterman and W. Moffitt, *J. Chem. Phys.*, **30**, 1107 (1959); (b) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959).

(7) B. Smaller, *J. Chem. Phys.*, **37**, 1578 (1962), and M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963), find  $D < 0.2$  cm.<sup>-1</sup> for the lowest triplet state of benzene.

(8) J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

(9) Obtained by the method of L. C. Snyder and A. T. Amos, *J. Am. Chem. Soc.*, **86**, 1647 (1964). We thank Dr. Snyder for making these spin density calculations available.

a Jahn-Teller distortion<sup>10</sup> should stabilize the configuration where this orbital contains the unpaired electrons;  $\rho_1$  may then be somewhat above 0.40.

Another feature of the electronic distribution at C-1 appears in an examination of the values of  $|E|/|D|$ . To a fair approximation, this ratio should equal the fractional s-character in the unfilled in-plane  $\sigma$ -orbital at C-1.<sup>11</sup> If the axes of the C-1 hybrids involved in bonding form an angle  $\theta$  of  $180^\circ$ ,  $|E|/|D| \sim 0$ , while for  $\theta \approx 120^\circ$  ( $sp^2$ )  $|E|/|D| \sim 1/3$ . The observed ratio makes it likely that  $\theta > 135^\circ$  in I, a value significantly greater than any reasonable internuclear angle at C-1. We suggest that the bonds to C-1 in I, II, and III are "bent" bonds. The angle formed by the axes of the hybrids at C-1 is greater than the internuclear angle. The interpretation is supported by an examination of the variation of the C<sup>13</sup> hyperfine splittings and zero-field parameters,  $D$  and  $E$ , in I, phenylmethylene, and diphenylmethylene.<sup>2</sup> The latter two appear to be approximately planar and bent with  $\theta \sim 140$ - $155^\circ$ .<sup>2</sup>

To explain the smaller  $E$  for II and III in comparison with I we note that  $\rho_3 = \rho_4 = 0.26$  for the stabilized Hückel orbital of II and  $\rho_3 = 0.41$  in III. With respect to the unpaired  $\sigma$ -orbital at C-1 these spin densities have larger  $x$ -components than  $y$ -components so that they yield a negative contribution to an originally positive  $E$  and reduce its magnitude. The spin densities at atoms other than C-1 in I do not have as large an effect.

**Acknowledgment.**—We wish to thank Mr. R. M. R. Cramer for his assistance in obtaining the e.s.r. spectra.

(10) L. C. Snyder, *J. Chem. Phys.*, **33**, 619 (1960).

(11) Such an approximate relation is implied in the treatment of J. Higuchi [*ibid.*, **39**, 1339 (1963)] when two-center terms are included. See also H. Sternlicht, *ibid.*, **39**, 2316 (1963).

BELL TELEPHONE LABORATORIES,  
INCORPORATED  
MURRAY HILL, NEW JERSEY

E. WASSERMAN  
L. BARASH  
A. M. TROZZOLO  
R. W. MURRAY  
W. A. YAGER

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## Stable Dianion Radicals and Trianions in Substituted Pentadienyl Systems

Sir:

Not a few organic molecules have vacant MO's of sufficiently low energy to accept extra electrons forming anion radicals and dianions. Some of these are thermally stable even at room temperature and above. The naphthalene,<sup>1</sup> cyclooctatetraene,<sup>2</sup> semiquinone,<sup>3</sup> benzophenone,<sup>4</sup> and benzil<sup>5</sup> anion radicals are some more familiar examples. Stable dianions are also formed in several of these same systems. More often, however, only the anion radical is formed and found to be unstable at room temperature. Recent work shows that even such non- $\pi$ -electronic systems as cyclopropane<sup>6</sup> and adamantane<sup>7</sup> form unstable anion radicals. Both stable and unstable anion radicals are of considerable interest since they permit an easy check

(1) S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953).

(2) T. J. Katz and H. L. Strauss, *ibid.*, **32**, 1873 (1960).

(3) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *J. Am. Chem. Soc.*, **60**, 1678 (1938).

(4) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

(5) H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

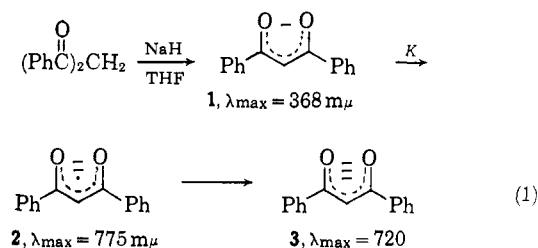
(6) K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

(7) K. W. Bowers, G. J. Nofi, and F. D. Greene, *ibid.*, **85**, 3707 (1963).

on the accuracy of trial eigenfunctions (e.s.r.) and eigenvalues (polarographic reduction potentials) of the lowest vacant MO's of these molecules.<sup>8</sup>

HMO calculations made in our laboratories indicate that a surprising number of organic anions have low-lying vacant MO's and could be expected to form dianion radicals and trianions. This report describes several such species which are formed with astounding ease in relatively simple systems and which possess remarkable stability. Some precedent for dianion radicals of unspecified stability already exists in the tetra- and pentacyanoallyl dianion radicals, the e.s.r. spectra of which have been obtained.<sup>9</sup>

Dibenzoylmethane, in THF solvent under nitrogen, reacts with excess sodium hydride to form the enolate, 2,4-diphenyl-1,5-dioxapentadienyl anion (1). This, in turn, reacts readily with either one or two atoms of potassium or sodium at temperatures from  $-78$  to  $66^\circ$  to form, respectively, the deep green dianion radical 2 or the blue trianion 3, according to eq. 1. The structures of 2 and 3 are unequivocally established by



the following evidence. Aliquots of solutions of 1, 2, and 3 were filtered (to remove excess sodium hydride and any unreacted potassium) into quenching aqueous solutions and titrated to a phenolphthalein end point with 0.100  $N$  sulfuric acid; 1 required 0.93, 0.93, 2 required 1.95, 1.87, and 3 required 2.75, 2.67 equiv. of acid to neutralize 1 mole of diketone, thus showing them to be mono-, di-, and triacidic bases, respectively. Control runs established that potassium in THF generates no appreciable acid titer under any of our conditions. Secondly, both 2 and 3 could be oxidized back to dibenzoylmethane in  $>90\%$  yield by adding anhydrous nickel chloride and then acidifying the nickel chelate. Degradation is therefore excluded. Finally, whereas the enolate and trianion are both diamagnetic, the dianion radical is paramagnetic, as shown by their e.s.r. spectra.<sup>10</sup>

Solutions of 2 and 3 are stable for months at room temperature under nitrogen, and at least weeks even in refluxing THF ( $66^\circ$ ).

HMO calculations accord with the ease of the reaction, the relevant MO having  $E = \alpha - 0.49\beta$ .<sup>11,12</sup> The 2-phenyl-4-methyl-1,5-dioxapentadienyl system has a corresponding MO at  $-0.57\beta$  and it too forms a dianion radical (4) which is stable at room temperature but decomposes during an hour's refluxing in THF. The parent 1,5-dioxapentadienyl system has its lowest

(8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., Chapters 6 and 7.

(9) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(10) We wish to thank Professor Allen J. Bard, of this department, for e.s.r. spectra. These extremely interesting spectra will soon be discussed elsewhere.

(11) Using parameters as follows<sup>12</sup>:  $\alpha_0 = \alpha + 2\beta$ ;  $\beta_0 = \beta\sqrt{2}$ ;  $\beta$  for phenyl to benzylic carbon overlap, 0.8.

(12) J. D. Roberts, "Notes on Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1962, p. 78.