

ionic reaction since no cyclic product was observed in the free-radical addition of hydrogen bromide to allene,¹⁶ while the presence of an inhibitor did not prevent the formation of I.

Experiments are under way to examine the reaction mechanism in more detail and to define the scope of this novel cyclization with regard to other electrophilic reagents, other unsaturates, and possible crossover experiments between different unsaturates. The results of these investigations and the chemistry of the 1,3-dihalocyclobutanes obtained will be discussed in forthcoming papers.

Acknowledgment.—The author is indebted to Dr. G. G. Wanless for providing the mass spectrometric data and Mr. A. M. Palmer for valuable technical help.

(16) K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, in press.

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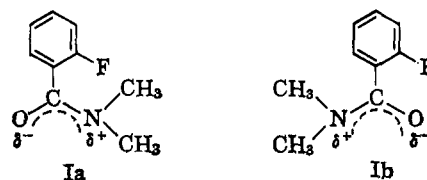
The Question of Long/Range Spin-Spin Coupling through Space: H-F Splitting over Six Bonds¹

Sir:

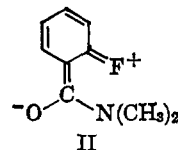
It has been noted that long-range spin-spin couplings, namely over more than three consecutive bonds, are not necessarily negligibly small.² Special geometries are required in order for the splitting to be observable,³ but proximity of the nuclei is not always required. Thus, four-bond H-H coupling has been observed by Meinwald⁴ between an *endo*-2-proton and the 7-proton *anti* to it, which are further apart than the corresponding *exo*-2-proton and the 7-proton *syn* to it in a bicyclo-[2.2.1]heptane skeleton; the geometry, however, is such as to favor four-bond H-H coupling.³ On the other hand, Roberts, who has reported a number of cases of H-F spin-spin coupling over four and five bonds,^{5,6} has suggested that possibly the five-bond H-F couplings observed by him may take place through space rather than through the bonds. Spin-spin coupling between H and F nuclei over more than five bonds seems to be unknown.

The proton n.m.r. spectrum of *o*-fluoro-N,N-dimethylbenzamide shows the following signals: an aromatic multiplet centered at τ 2.75 p.p.m. (area = 4), a methyl singlet at τ 6.97 p.p.m. (area = 3), and a methyl doublet at τ 7.22 p.p.m. (area = 3). The nonequivalence of the two N-methyl groups arises from restricted rotation around the C-N bond, of which many examples are known.⁷

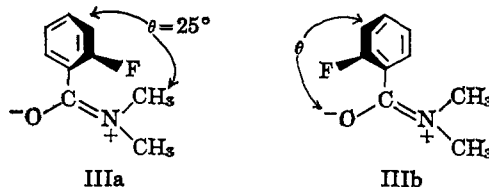
The conformations of this amide which maximize resonance interactions could be flat, all the atoms (except the methyl hydrogens) being coplanar as in Ia and Ib. Although these forms would be consistent



with the observed n.m.r. spectrum, it seems more reasonable to assume that, due to nonbonded and electrostatic repulsive forces, the dimethylamido group is flat but turned out of the plane of the benzene ring.⁸ In order to estimate the interplanar angle θ (between the benzene ring and the dimethylamido group) acetophenone derivatives were used as models. Application of the method of Braude and Nachod⁹ to the values of the extinction coefficients reported by Horton and Robertson¹⁰ for the primary absorption bands of *o*- and *p*-fluoroacetophenone indicates that the angle θ is *ca.* 25°. Consequently contributions from the resonance form II must be small and the system can be considered as rotating sufficiently fast between



the limiting structures IIIa and IIIb, at room temperature, to result in a n.m.r. spectrum which is the average of the two forms. On the average, then, one methyl



group is closer to the π -electron cloud of the aromatic ring and to the *o*-fluorine than the other one, and is constrained by the *ortho* substituent to lie above (or below) the plane of the phenyl ring.

In trying to assign the methyl resonances the anisotropy of both the phenyl ring and the carbonyl group must be considered and assignment on theoretical grounds becomes questionable. It seemed that an unsymmetrically N,N-disubstituted benzamide, in which one of the methyl groups had been replaced by a bulkier group, might exist in a preferred conformation. Such a system would, then, enable unequivocal assignment of the methyl resonances in *o*-fluoro-N,N-dimethylbenzamide. The compound prepared for this purpose was *o*-fluoro-N-cyclohexyl-N-methylbenzamide. Its proton n.m.r. spectrum shows, in addition to the aromatic and cyclohexyl multiplets, two discrete methyl resonances, 0.2 p.p.m. apart, the high field one being a doublet with $J = 1.3$ c.p.s. The integrated areas, in this case, are in the ratio of 3:2, the high field resonance having the larger area. This can be interpreted as being due to the rotational isomers IVa and IVb; it seems reasonable to assume that IVa will be the energetically preferred form. Since the high

(8) This argument is strengthened by current studies in ring-substituted benzamides to be published separately.

(9) E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, pp. 173-174.

(10) W. J. Horton and D. E. Robertson, *J. Org. Chem.*, **25**, 1016 (1960).

(1) Work supported by grant G-23705 from the National Science Foundation.

(2) Only the most pertinent references will be given.

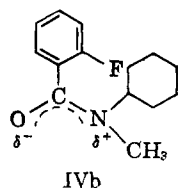
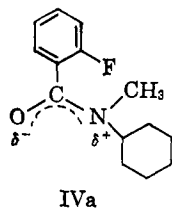
(3) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, No. 5, 233 (1964).

(4) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(5) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961).

(6) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962).

(7) (a) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); (b) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962); (c) The magnitude of the barrier to rotation in this system and related ones will be discussed separately.



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 invariant¹¹ ($J = 1.2$ 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,⁵ 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.

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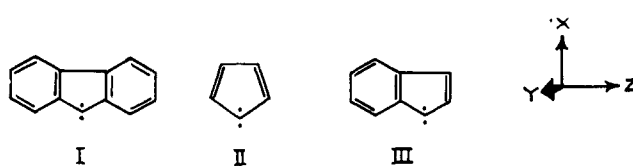
Electron Spin Resonance of Triplet Cyclopentadienylidene and Indenylidene

Sir:

Previously we reported the e.s.r. of the ground state triplet fluorenylidene (biphenylenemethylene)^{1,2} (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 σ - and one π -unpaired electron. The interaction between the two electrons stabilizes one of the degenerate π -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, diazocyclopentadiene³ and diazoindene,³ 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.⁴ 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 ~ 10 cm.⁻¹.

The spectra may be described by the Hamiltonian⁵

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

With I $D = 0.4078$ and $E = 0.0283$,^{1,2} and we find for II $D = 0.4089$ and $E = 0.0120$ while for III $D = 0.3777$ cm.⁻¹ and $E = 0.0160$ cm.⁻¹. 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.⁶ A possible assignment of the principal magnetic axes, analogous to I,² accompanies the formulas; the y -axes are perpendicular to the molecular planes.

If the nonbonding σ -orbital at C-1 in II contained two paired electrons, the triplet would have two unpaired π -electrons. In such π -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 ~ 0.2 cm.⁻¹.⁷ The larger value observed requires a significant one-center interaction, and indicates that one unpaired electron lies in a C-1 σ -orbital.

A symmetrical distribution of the unpaired π -electron in II, in which each of the lower pair of degenerate orbitals is equally populated, would have a π -spin density at C-1, ρ_1 , of 0.20. Because of the dominance of the one-center interaction,⁸ for a given geometry about C-1, D should be approximately proportional to ρ_1 . The similar values of D for I, II, and III imply similar values of ρ_1 . An SCF-MO calculation for the fluorenyl radical yields $\rho_1 = 0.55$; for the indenyl radical $\rho_1 = 0.41$.⁹ With II ρ_1 should be ≥ 0.4 . A mechanism for the increase in ρ_1 in II above 0.20 arises from the presence of the orbital degeneracy in the π -system. One of the degenerate pair of orbitals has a Hückel $\rho_1 = 0.40$. An exchange interaction with the unpaired σ -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.⁻¹ 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.