The following techniques were employed for analyzing the cmr spectrum[6] of pristimerin: (i) proton noise decoupling, (ii) off-resonance ^{1}H decoupling, (iii) single frequency decoupling of previously assigned ^{1}H peaks, (iv) partially relaxed Fourier transform (PRFT) (Figure 1).

The T_1 relaxation times of ^{13}C contained in alicyclic molecules, e.g., cholesteryl chloride[7] or gibberellins,[8] usually increase in the sequence of CH_2, CH, CH_3, and C with no protons.[7] As shown in Figure 1a for pristimerin at an interval time, τ, of 0.6 sec, PRFT is especially useful for assigning ^{13}C peaks in congested spectra. As τ is increased the negative peaks invert to positive peaks in the general sequence shown above; thus, in Figure 1a, quaternary and carbonyl carbons are still negative, all methylene and methine peaks are positive, while the methyl ^{13}C peaks are weakly negative, nulled, or weakly positive. A typical simplification is seen in the 40–50 ppm region of Figure 1b.

The peaks thus assigned to pristimerin were as follows: seven Me groups, 10.2 (C-23), 18.3 (C-27), 21.5 (C-26), 30.8 (C-30)[9] and 31.5 (C-28),[9] 38.2 (C-25), 51.4 (C-31); seven CH_2 groups, 28.6, 29.6, 29.8, 30.4, 33.5, 34.8, 36.3; four CH groups 44.2 (C-18), 118.0 (C-7), 119.5 (C-1), 133.8 (C-6); ten quaternary carbons, 30.5 (C-20), 38.3, 39.3, 40.3, 44.9, 117.1, 127.2, 146.0, 164.0, 169.8; two carbonyl groups, 178.1, 178.4 ppm (Figure 1a).

Tingenin A 2 has a secondary methyl (pmr, 1.00 ppm, br, d 6), which was assigned to C-20, and a carbonyl group (ir, 1715 cm^{-1}) at C-19 or C-21, both assignments based on biogenetic arguments. The cmr spectrum (Figure 1b) fully supports this and, moreover, places the carbonyl at C-21. Namely, the 30.5 ppm quat-C signal (C-20) in pristimerin (Figure 1a) is replaced by a 41.8 ppm methine, a methyl (C-30) is shifted upfield to 15.1 ppm (because it is attached to sec-C),[10] and a methylene (C-22) is shifted downfield to 52.4 ppm. Finally, the 20-Me at 1.00 ppm (pmr) is equatorial because of its W-type coupling between the 2.9 ppm 22-eq-H signal (br d, $J = 14$ Hz) and the large $W_{1/2}$ (18 Hz) of the 20-H (ax) at 2.4 ppm; the 20-Me is also β from the observation of an NOE between 20-H and 13-Me.

In tingenin B 3 (Figure 1c) containing a sec-hydroxyl group (3.67 ppm; d, in pmr; disappears with D_2O addition), a new methine (C-22) appears in the cmr at 76.4 ppm instead of the C-22 methylene in tingenin A. Hence the hydroxyl is attached to C-22. In addition, there is seen a high-field shift of a methyl group, which is either 27 or 28. In the pmr spectrum, there was observed a W-type coupling between the 4.55 ppm carbinyl proton (22-H) and a methyl at 0.86 (hence 28), and a 19% NOE between 22-H and a 0.99 ppm methyl (hence 27). It follows that the 22-OH is equatorial (β) and that the methyl which moves upfield from 32.5 to 25.0 ppm in the cmr is C-28. Finally, the 20-H is

α and axial because a small (3%) but distinct NOE was observed on 22-H upon irradiation of 20-H.[11,12]
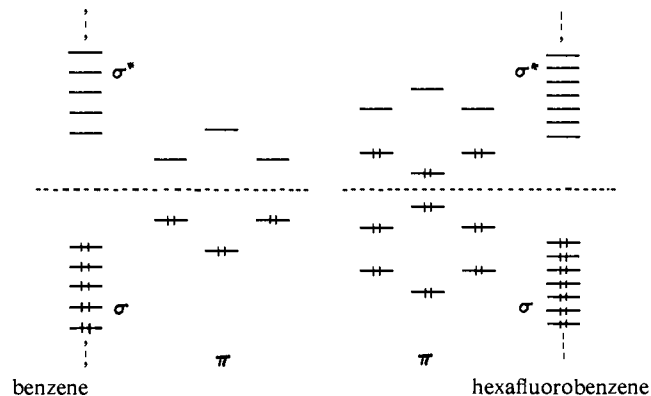
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Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. VI.[1] The Hexafluorobenzene Anion Radical

Sir:

The epr spectrum of hexafluorobenzene anion radical in an adamantane matrix at 218°K is shown in Figure 1. It was prepared by 50 kV X-irradiation at 77°K of an adamantane matrix containing ~0.5% hexafluorobenzene and a somewhat larger amount of trimethylamine–borane (TMAB). The smaller lines in the center of the spectrum are due to the anisotropically broadened epr spectrum of a cyclohexadienyl type of radical caused by hydrogen atom addition to hexafluorobenzene. Data on this type of radical together with information on the use of TMAB to stabilize anion radicals will be published later. The $C_6F_6^-$ radical has six equivalent fluorine nuclei with $a_F = 137$ G and $g = 2.0015$ as can be seen from the placement of the second-order components[2] in the stick diagram. These fluorine hyperfine splitting constants (hfs) are about ten times larger than would be expected for a π radical based upon all previous results for fluorinated benzyl radicals, fluorinated aromatic cation radicals, and fluorinated aromatic anion radicals.[3] This strongly suggests that the electronic structure of $C_6F_6^-$ is better described as a σ radical than as a π radical. This novel suggestion can be easily understood by consideration of the LCAO–MO diagrams for the valence-electron orbitals of benzene and hexafluorobenzene schematically shown below.

benzene   hexafluorobenzene

(6) A JEOLCO PH-100 instrument was used.
(7) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 55, 189 (1971).
(8) Unpublished data.
(9) These two assignments could be interchanged.
(10) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, Chapter 3; J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York and London, 1972, pp 55–69.

(1) Part V: D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, 94, 9278 (1972).
(2) R. W. Fessenden, *J. Chem. Phys.*, 37, 747 (1962).
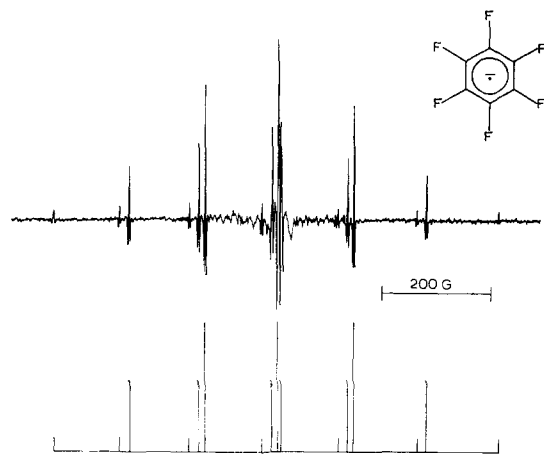(3) A. Hudson and K. D. Root, *Advan. Magn. Resonance*, 5, 1 (1971).

Figure 1. Second derivative epr spectrum of hexafluorobenzene anion radical in an adamantane matrix at 218°K. The stick diagram shows the location of the expected second-order components. Extra lines near the center belong to the anisotropically broadened hydrogen addition radical of hexafluorobenzene, $C_6F_6H\cdot$.

The six benzene π orbitals occur in degenerate pairs except for the highest and the lowest. Hexafluorobenzene has two sets of π orbitals, one of C–F π-bonding and the other of C–F π-antibonding nature. The latter set differs from the former and from the benzene π orbitals only by having a nodal cylinder, which bisects all of the C–F bonds, perpendicular to the ring. This set is above the orbital center of gravity (dotted line) and the C–F π bonding set is below it. For benzene, the conventional wisdom places the σ orbitals well below and the σ^* orbitals well above the highest occupied and lowest unoccupied π orbitals, respectively. This belief seems reasonable on the basis of the observations that benzene anion and cation are π radicals, that the lower-energy electronic transitions of benzene are $\pi-\pi^*$, and that π electron approximations are relatively successful for molecules of this type.

The effect of replacing the hydrogen in benzene by fluorine is twofold. Firstly, the number of orbitals is increased which results in a larger total energy spread for each type of orbital. Secondly, the orbitals are filled to a higher level with respect to the center of gravity because each fluorine brings in more electrons per valence orbital than hydrogen. It is easy to see then that a σ^* orbital might be below the lowest unoccupied π orbital of C_6F_6 as depicted in the diagram above with the result that $C_6F_6^-$ would be a σ radical. The lowest σ^* orbital is totally symmetric, yet would possess the nodal cylinder mentioned above, and an electron in this orbital would be expected to have equal and very large fluorine hfs as is observed.

There are several alternative explanations for our observations which did not stand close scrutiny. One of these would be to invoke some sort of reaction with the TMAB to produce an unexpected species. This explanation was shown to be false by our subsequent preparation of the $C_6F_6^-$ by photolysis with visible light of a layered mixture of adamantane–sodium atoms–adamantane–C_6F_6–adamantane. The epr signal of $C_6F_6^-$ appeared at the same time that the epr signal of the sodium atoms and their associated violet color disappeared. Other alternatives would be that the σ state is either being populated thermally or is metastable with respect to the π state. These were

ruled out by the observations that the epr signal strength and hyperfine splitting were essentially unchanged between 240°K, above which the radical irreversibly decayed, and 140°K, below which the spectrum became anisotropic, and that the sample could be stored in this temperature range without loss of signal. A more serious alternative explanation would be that the adamantane matrix has some unexpected effect on anion radicals. This was ruled out by the preparation of benzene anion radical by both the TMAB and the sodium atom method. We found six equivalent hyperfine splittings of 3.69 G and a g value of 2.0028 which are characteristic of benzene anion radical.[4]

We are presently attempting to prepare the entire series of partially fluorinated benzene anion radicals in order to elucidate the nature and extent of this novel $\sigma-\pi$ crossover phenomenon.

INDO[5] energy minimizations which constrained $C_6F_6^-$ to D_{6h} symmetry were performed for both the σ and π states. These calculations yield C–F and C–C bond lengths and a_F and a_c hfs of 1.379 Å, 1.384 Å, 673 G, and 19.8 G for the σ state and 1.360 Å, 1.402 Å, 5.98 G, and 3.53 G for the π state. Adding an electron to the σ^* orbital causes a longer C–F bond and a shorter C–C bond compared to the π-orbital case because of the more effective overlap of σ orbitals and because of the total C–C bonding nature of the σ^* orbital, respectively. The 137 G a_F measured experimentally lies between the values calculated for the two states of $C_6F_6^-$; however, we believe that no particular significance should be attached to this fact because the INDO fluorine hfs were parameterized by consideration of only a few radicals which were mostly π type.[6] The important point about the hfs calculations is that the 2s orbital spin density on fluorine is predicted to be $\sim$100 times larger in the σ state than in the π state. The total energy of the π state is calculated to be 45 kcal below the σ state; however, this result is not particularly surprising because Del Bene and Jaffé[7] pointed out that although geometry and charge densities are well reproduced by INDO/CNDO a reparameterization is necessary in order to give the proper relative ordering of σ and π states. Calculations are in progress to determine how reparameterization and lifting the symmetry restriction modify our theoretical results.

The hexafluoroacetone anion radical[8] likewise has unusually large fluorine hfs which have been explained by interaction of the unpaired electron with low-lying fluorine antibonding orbitals;[9,10] however, a clear distinction between σ and π states can only be made for planar species.

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(6) The multiplication factor for fluorine 2s spin density is 44,829.2 G in INDO but should only be 17,200 G according to a calculation by J. R. Morton, J. R. Rowlands, and D. J. Whiffen, *Nat. Phys. Lab. (U. K.) Circ.*, No. BPR 13.

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Carbon Catalyzed Racemization of 1,1'-Binaphthyl

Sir:

The industrially important carbon blacks and activated carbons are widely used as supports for metal catalysts and, by themselves, are known to catalyze numerous inorganic reactions.[1] However, catalytic reactivity with organic substrates is reported only for some oxidation-reduction reactions[2,3] and for a few polymerizations and cationic isomerizations.[4,5] We report here the high activity of carbon in promoting racemization of optically active 1,1'-binaphthyl.[6] The

$$R(-) \rightleftharpoons S(+)$$
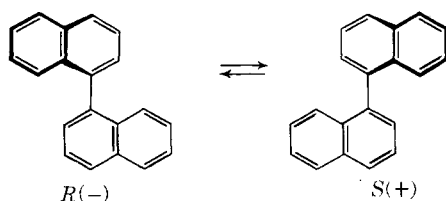
known[7,8] uncatalyzed reaction in solution is a simple nonpolar transformation which involves only rotation around the single bond joining the two naphthalene rings.

Decolorizing carbons rapidly racemize solutions of binaphthyl in acetone within a few minutes. For example, 0.015 M binaphthyl is 93% racemized in 10 min at room temperature in the presence of 1.7 mg/ml of Norit SG1. In contrast, the uncatalyzed rate of racemization corresponds to a half-life of 12 hr at 20°. To compare the activity of various carbons the reaction was studied simply by stirring the catalyst at 20° with binaphthyl in acetone. The racemization was quenched by filtering out the catalyst, and solutions were analyzed using normal polarimetric means. The activity of an individual batch of catalyst, with different operators and apparatus and with different rates of stirring, was

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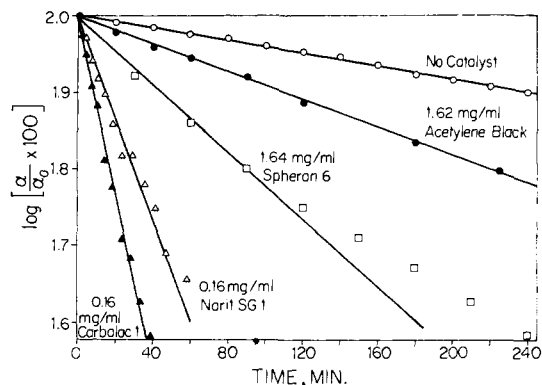(8) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, 68, 651 (1964).

Figure 1. First-order plots for racemization of 0.015 M 1,1'-binaphthyl in acetone at 20° in the presence of various carbon catalysts.

consistent among various runs although different batches of the same commercial carbon gave different rates.[9] Some results, treated as first-order reactions, are shown in Figure 1.

The observed activity (Sterling FT0 < acetylene black < Spheron 6 < Norit < Carbolac 1) parallels the surface/weight ratios of these carbons (15.7, 64, 110, ca. 750, and 1000 m²/g, respectively).[10] Graphitized Spheron 6 (2700°) was less active than Spheron 6 itself, while graphite (grade SP-1) has no observable catalytic properties. Spheron 6, which is a well-characterized carbon black,[10,11] was chosen for more detailed kinetic studies. Kinetic plots showed some deviation from first-order behavior which is apparent after about one half-life (see curve for Spheron 6 in Figure 1). Control experiments showed this was not due to any progressive deactivation of catalyst by standing with binaphthyl in acetone. In any case, initial first-order rate constants were calculated, and representative data are presented in Table I.

The observed first-order rate constants at 20° are proportional to catalyst concentration (at 0.015 M binaphthyl), decrease with increasing binaphthyl concentration (at 1.6 mg/ml catalyst concentration), and are extraordinarily sensitive to small concentrations of compounds with structures similar to binaphthyl. At 0.015 M binaphthyl with 1.6 mg/ml of Spheron 6 only 10⁻⁵ M perylene is sufficient to poison the catalyst. On the other hand, although use of benzene as a solvent prevents catalytic activity, dilute (10^{-3} M) solutions of benzene in acetone have no effect on catalytic activity. Compounds with a greater number of fused aromatic rings are increasingly effective inhibitors (benzene < naphthylene < anthracene < pyrene < perylene). Competitive adsorption by these compounds is no doubt the cause of the inhibition effects. In this regard it should be noted that binaphthyl itself is not noticeably adsorbed (i.e., 0 ± 2% by uv and glc analysis) by Spheron 6 under the conditions of the kinetic runs.

The kinetic results are well correlated by the following

(9) A sample of Spheron 6 from year 1957 was more than twice as active as Spheron 6 supplied in 1970.
(10) Surface areas are determined by nitrogen adsorption; see (a) C. L. Mantell, "Carbon and Graphite Handbook," Interscience, New York, N. Y., 1968, pp 98-103; (b) W. R. Smith and D. C. Bean in "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed, Vol. 4, Interscience, New York, N. Y., 1964, pp 243-282; private communication from American Norit Co., Inc., Jacksonville, Fla.
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Communications to the Editor