

Figure 1. ^{19}F nmr spectra of solid C_6F_{12} at 200°K : (a) normal spectrum, from Fourier transformation of Bloch decay, showing restricted molecular rotation *in situ*; (b) multiple-pulse spectrum under the same conditions, showing lack of ring inversion.

sults that could not always be obtained by high resolution or wide-line methods, separately or together.

As an example, we consider perfluorocyclohexane. From a previous high resolution study³ it is known that the spectrum of C_6F_{12} in solution at low temperatures consists approximately of an AB quartet, reflecting the presence of distinguishable interacting axial and equatorial fluorines (δ 18.2 ppm, $J = 284$ Hz). As the temperature is raised, a characteristic collapse to a single line occurs, indicating a rapid interconversion of conformers.

In Figure 1a we show the wide-line ^{19}F spectrum of solid C_6F_{12} , obtained at $\sim 200^\circ\text{K}$ by Fourier transformation of the Bloch decay, using a pulse spectrometer operating at 54.0 MHz. A barely resolved Pake doublet⁴ is seen. While a detailed analysis of such a spectrum is difficult, the splitting appears to be consistent with a dominant dipolar interaction between geminal ^{19}F nuclei in a molecule which is rapidly rotating or reorienting about its "sixfold" axis. (Just below this temperature the spectrum rapidly broadens to a width consistent with a rigid lattice.)

We guessed that the mechanism of such a reorientation might involve a jump through 60° , accompanied by a chair-chair conformational flip to restore the molecule to harmonious packing with its neighbors. This is apparently *not* the case: the molecule rotates (through 120°) as a rigid entity. That this is so is evident from Figure 1b, which shows the spectrum obtained by Fourier transformation of the envelope of a multiple-pulse decay (WAHUA spectrum) in solid C_6F_{12} at the same temperature. (This experiment employed a four-pulse cycle described elsewhere,⁵ with a cycle time of 21 μsec and a 90° pulse width of 1.1 μsec .) Suppression of the dipolar broadening reveals the same AB quartet observed by Tiers³ (δ 17.5 ± 1.5 ppm, $J = 310 \pm 40$ Hz). This shows that the molecule, as it rotates more rapidly than $6 \times 10^4 \text{ sec}^{-1}$, is undergoing axial-equatorial interchange *less* rapidly than $1 \times 10^3 \text{ sec}^{-1}$.

At higher temperatures the AB structure collapses: at 0° one sees a single line of ~ 300 Hz width. This is greater than our experimental resolution, indicating that AB collapse is not yet complete: the barrier to axial-

equatorial interconversion may be very slightly greater in the solid than in solution.

No convincing evidence of a ^{19}F chemical shift anisotropy appears in any of our spectra, a situation which we find puzzling.

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Oxidation by Metal Salts. VI. A New Chemical Method for the Generation of Aromatic Radical Cations

Sir:

Aromatic radical cations have been prepared by various techniques, but these have generally been limited to polynuclear aromatics having very low oxidation potentials.^{1,2} Attempts to prepare the less stable radical cations of simple alkyl-substituted benzenes in solution by chemical oxidations have been relatively unsuccessful. It is the structure of these radical cations as determined by electron spin resonance spectroscopy that is most crucial in testing the various theoretical treatments of aromatic radical ions.

We now wish to report a new chemical oxidation method which, combined with a rapid mixing flow technique, permits the detection and characterization of aromatic radical cations. The chemical reaction involves the oxidation of the aromatic hydrocarbon by cobaltic ion, a process postulated to involve radical cation intermediates.³ Pure trifluoroacetic acid was used as the solvent and ligand in order to increase the oxidation rate and stabilize the radical cation intermediate. In a typical procedure, $10^{-3} M$ solutions of the hydrocarbon in trifluoroacetic acid and cobaltic acetate in trifluoroacetic acid were rapidly mixed in a flow cell at room temperature. The total flow rate was usually in the range of 15–50 ml/min. By this technique, the esr spectra of hexamethylbenzene, pentamethylbenzene, and the various tetramethylbenzene radical cations were obtained. Radical cations derived from less alkylated aromatics such as 1,3,5-tri-*t*-butylbenzene and *p*-di-*t*-butylbenzene were also observed successfully.

The esr spectrum of the hexamethylbenzene radical cation in trifluoroacetic acid was similar to that reported for the radical cation prepared in sulfuric acid.^{4,5} The spectrum consisted of at least 13 evenly spaced lines, with a hyperfine splitting constant of 6.45 G.⁶ One carbon-13 splitting of 2.2 G was also observed. The average line width (measured between points of maxi-

(1) Reviewed by G. Vincow in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 151.

(2) A. Reymond and G. K. Fraenkel, *J. Phys. Chem.*, **71**, 4570 (1967); D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965); I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

(3) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 6830 (1969).

(4) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

(5) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 302 (1967).

(6) Estimated errors of splitting constants are ± 0.05 G.

(3) G. V. D. Tiers, *Proc. Chem. Soc. London*, 389 (1960).

(4) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

(5) J. S. Waugh, L. M. Huber, and U. Haeberlen, *Phys. Rev. Lett.*, **20**, 180 (1968).

Table I. Comparison of Observed and Predicted Hyperfine Splitting Constants

Position	Observed hfsc	Calcd hfsc ^a	Calcd hfsc ^b	Calcd hfsc ^c
Hexamethylbenzene				
CH ₃	6.45	6.45	6.45	6.45
Pentamethylbenzene				
1,2,4,5-CH ₃	10.05	9.7	9.87	9.34, 9.42
3-CH ₃	<0.3	0	0.34	0.71
6-H	<0.3	0	0.24	0.32
Durene				
1,2,4,5-CH ₃	10.70	9.7	9.87	10.85
3,6-H	0.80	0	0.24	1.61
1,2,3,4-Tetramethylbenzene				
1,4-CH ₃	15.13	12.9	12.85	12.12
2,3-CH ₃	2.78	3.2	2.95	3.79
5,6-H	2.21	2.2	2.45	2.35
1,2,3,5-Tetramethylbenzene				
2-CH ₃	16.82	12.9	13.70	13.27
5-CH ₃	14.36	12.9	12.09	11.76
1,3-CH ₃	2.96	3.2	3.46	3.32
4,6-H	1.76	2.2	2.04	2.39
1,3,5-Tri- <i>t</i> -butylbenzene				
2,4,6-H	5.18	4.4	4.4	5.17
<i>t</i> -Bu-CH ₃	0.63			
1,4-Di- <i>t</i> -butylbenzene				
2,3,5,6-H	2.1	2.2	2.28	1.41
<i>t</i> -Bu-CH ₃	0.95			

^a Simple unmodified HMO calculation using $Q_H = 26.4$ and $Q_{CH_3} = 38.7$ G, which are derived from the benzene and hexamethylbenzene radical cations. ^b Inductive MO model with $h = -0.13$ and McLachlan $\lambda = -1.2$, using the above Q values. ^c Valence-bond model¹¹ with the above Q values.

mum slope) was 0.3 G. Under the conditions used, no other radical derived from hexamethylbenzene was observed.⁷

The pentamethylbenzene radical cation spectrum contained at least nine evenly spaced lines with a line width of 0.8 G, separated by 10.05 G. Despite the relatively poor resolution, these results confirm the suggestion that the esr signal obtained by Hulme and Symons⁸ from hexamethylbenzene in oleum was indeed not the pentamethylbenzene radical cation.

The esr spectrum of the durene (1,2,4,5-tetramethylbenzene) radical cation consisted of at least seven equally spaced triplets separated by 10.70 G. The small hyperfine splitting constant was 0.80 G and is no doubt due to the two hydrogen atoms in the 3 and 6 positions. This splitting had not previously been observed in concentrated oleum.⁴

The 1,2,3,4-tetramethylbenzene radical cation gave an esr spectrum from which the following hyperfine splitting constants (G) were extracted: $a_{2CH_3} = 15.13$, $a_{2CH_3} = 2.78$, and $a_{2H} = 2.21$. The 1,2,3,5-tetramethylbenzene radical cation gave a more complex spectrum, which could be computer simulated using the following hyperfine splitting constants (G): $a_{1CH_3} = 16.82$, $a_{1CH_3} = 14.36$, $a_{2CH_3} = 2.96$, and $a_{2H} = 1.76$. The line width in both systems was 0.33 G.

The esr spectra of the radical cations derived from 1,3,5-tri-*t*-butylbenzene and *p*-di-*t*-butylbenzene are shown in Figure 1. The hyperfine splitting constants (G) obtained from these spectra were $a_{3CH_3} = 0.63$ and $a_{3H} = 5.18$ (line width = 0.25 G), and $a_{2CH_3} = 0.95$ and $a_{4H} = 2.1$ (line width 0.35 G), respectively.

(7) L. S. Singer and I. C. Lewis, *J. Amer. Chem. Soc.*, **87**, 4695 (1965); R. Hulme and M. C. R. Symons, *J. Chem. Soc., A*, 466 (1966).

(8) R. Hulme and M. C. R. Symons, *Nature*, **206**, 293 (1965).

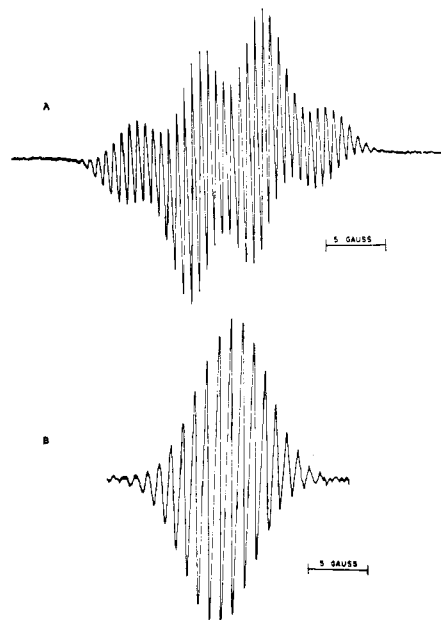


Figure 1. ESR spectra of the radical cations of 1,3,5-tri-*t*-butylbenzene (A) and 1,4-di-*t*-butylbenzene (B).

In general, our data (Table I) are qualitatively consistent with simple HMO predictions taking into account the inductive interactions of the alkyl substituents. As expected on the basis of symmetry considerations, the tetramethylbenzene cations showed the same spin density distributions as the xylene anions, while the pentamethylbenzene cation was similar to the toluene anion. Most significant is the finding that the degeneracy of the two highest filled π orbitals of the unsubstituted benzene cation is not lifted by 1,3,5 trisubstitution, as evidenced by the 1,3,5-tri-*t*-butylbenzene radical cation. The large methyl splittings in 1,2,3,4- and 1,2,3,5-tetramethylbenzene cations indicate the importance of hyperconjugation, and are in accord with the prediction that the effective $Q^{H}_{CH_3}$ for the cation is larger than that for the anion.^{9,10} The observed results also agree fairly well with valence-bond calculations,¹¹ which do not differ greatly from those obtained from a molecular orbital approach.

Extension of this work to other radical cations as well as temperature dependence studies and theoretical investigations are in progress.

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(9) D. Purins and M. Karplus, *J. Amer. Chem. Soc.*, **90**, 6275 (1968).

(10) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(11) T. H. Brown and M. Karplus, *J. Chem. Phys.*, **39**, 115 (1963).

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Flash Photosensitizations by Cadmium and Zinc Atoms

Sir:

We wish to report a novel flash photolysis-kinetic spectroscopic technique for the study of metal atom