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ESR STUDY OF ELECTRONIC EFFECTS AND PREFERRED CONFORMATION OF ALKYL AND SILYL GROUPS ON THE BENZENE CATION RADICAL[1)]

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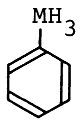
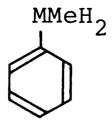
Cation radicals of several alkyl- and silyl-substituted benzenes in frozen trichlorofluoromethane were investigated by ESR. All the substituents were found to act as an electron donor to the benzene cation, preferring the M-H σ bond eclipsing pπ orbitals. The results may afford a good evidence for the conformational consequences of hyperconjugation.

We wish to report herein an ESR investigation of the following alkyl- and silyl-substituted benzene cation radicals.



1a, M = C
1b, M = Si



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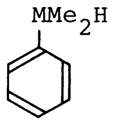

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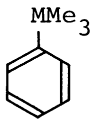

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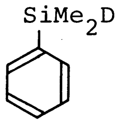
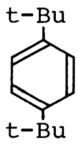


3b'



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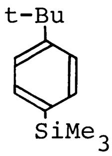

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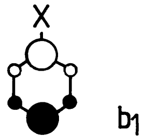
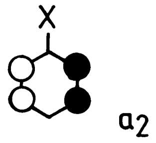
These radicals are particularly interesting, since the donor-acceptor effects of silyl groups on the degenerate singly occupied molecular orbitals (SOMO) of cyclic π radicals depend not only on the substituents on the silicon atom but also on the energy levels of the SOMO as we have demonstrated previously in the study on the substituent effects on cyclopentadienyl radicals.[2)] In addition, large hyperfine splittings (hfs) can be introduced onto the β hydrogens as a good probe for determining the rotational conformation of the substituent, since the SOMO of alkyl- and most silyl- substituted benzene cation radicals are expected to be b_1 rather than a_2.



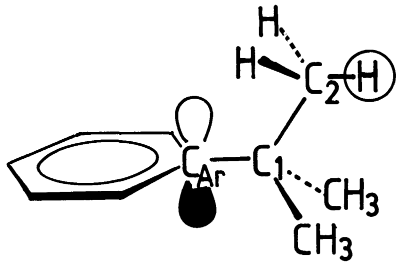


During the course of our studies, Symons and co-workers[3)] *have reported their* very similar results to ours for several alkyl and silyl benzene cation radicals. Nevertheless, our present results will afford new insights into the electronic effects and the preferred conformation of these cation radicals.

All the cation radicals were generated at 77 K by ^{60}Co γ-irradiation of solid solutions containing the parent compounds dissolved in trichlorofluoromethane.[4)]

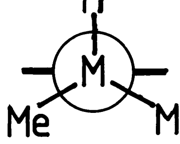
The ESR spectral features were essentially similar to those reported by Symons et al.,$^{3)}$ except for 3a$^{+\cdot}$. The hfs values were confirmed by spectral simulations and listed together with the g values in Table 1. The ESR spectrum of 3a$^{+\cdot}$ showed the presence of two conformers with the concentration ratio of ca 1:1 at 77 K (Fig. 1); one with no splitting and one with a large doublet hfs (2.8 mT) due to the isopropyl methine hydrogen. The spectrum was found to depend reversibly on temperature, affording an apparent triplet pattern at higher temperatures.

We should remark here the unusual feature of the ESR spectra of t-butyl-substituted benzene cation radicals. The ESR spectrum of t-butylbenzene cation radical (4a$^{+\cdot}$) was essentially similar to that reported by Symons et al.;$^{3)}$ an apparent triplet found at 77 K changed reversibly with temperatures, affording a doublet at 153 K. The spectrum was analyzed into a doublet of doublets, where one of the hfs values was strongly temperature dependent. The temperature-independent hfs of ca. 1.0 mT can easily be assigned to the para-hydrogen. Although the origin of the another hfs has not been explained by Symons et al., we assign it to one of the nine hydrogens in the t-butyl group, because similar splittings were observed in other t-butyl derivatives, 5 and 6.$^{5)}$ Freezing of rotation of the methyl groups around the C_1-C_2 bond as well as that of the t-butyl group around the C_{Ar}-C_1 bond may give rise to a unique hydrogen which lies ideally in a W-arrangement. Such a rather unusual freezing of rotations may be attributed partly to the influence of the solid-state morphology, but partly to the intrinsic stabilization of the conformation due to homohyperconjugation.

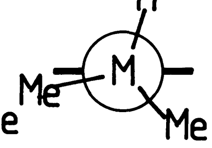


The doublet hfs values of 0.8-1.1 mT of these mono-substituted benzene cation radicals are easily assigned to the para-hydrogens. These values as well as the large hfs values introduced into β hydrogens on the substituents are good indication of the b_1 symmetry of the singly occupied molecular orbital: all the alkyl and silyl groups studied here are thus concluded to be electron donors for the benzene cation radical. Noticeably, even SiH_3 group, which is expected to be the most electron-withdrawing group among those studied here, was found to act as a donor for benzene cation radical. The results confirm the assignment of the two lower ionization bands of 1b at 9.18 and 9.43 eV found by the photoelectron spectroscopy$^{6)}$ as due to the ionization from b_1 and a_2 orbitals, respectively.

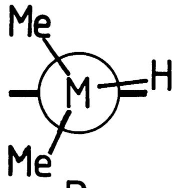
Important results are derived for rotational conformation of the substituents from hfs values of the β-hydrogens by using the Heller-McConnell equation.$^{7)}$ Two conformers with 2.8 and ca. 0 mT splittings due to the β-hydrogen observed for 3a$^{+\cdot}$



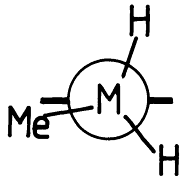
A



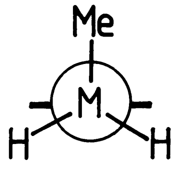
A'



B



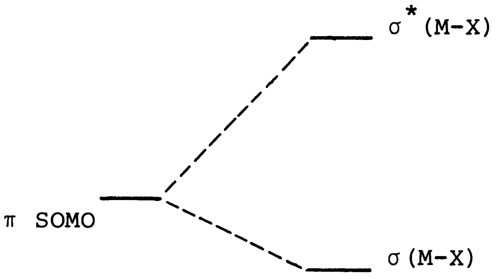
C



D

at 77 K are thus adopted approximately to A (or A') and B (M=C), respectively, whereas only A isomer was found for the silicon analog **3b**$^{+\cdot}$. Similarly, both ethylbenzene (**2a**) and methylsilylbenzene (**2b**) cation radicals are concluded to prefer the conformation C. In contrast, eclipsing of C-C σ bonds appears to stabilize π anion radicals more effectively than that of C-H σ bonds. For instance, the 4,4'-diisopropylbiphenyl radical anion has been reported to exist as a 90:10 mixture of B and A conformers.[8] Several ethyl-substituted aromatic anion radicals[9] have been found to prefer the conformation D rather than C. The intermediate preference of eclipsing to π orbitals between C-H and C-C σ bonds has been observed for alkyl and silyl-substituted cyclopentadienyl radicals.[2c]

Although the preferred rotational conformation should be a consequence of a delicate balance between the steric and electronic factors, the present results may be taken to show that the hyperconjugative stabilization of π radical cations due to the M-H σ bonds is more favorable than that of M-C σ bonds, while the inverse is the case for π radical anions. Such a spectrum of relative importance between σ(M-H) and σ(M-C) hyperconjugation for cyclic π radicals is a good experimental demonstration of the conformational consequences of hyperconjugation as stated by Hoffman et al.[10,2c] Thus, the higher the energy level of the π SOMO becomes on going from cation to neutral to anion radicals, the more important the stabilization by using σ^*(M-X) rather than σ(M-X) orbitals. Whereas the σ(M-H)-π interaction is more effective than the σ(M-C)-π interaction, the σ^*(M-H)-π interaction is ineffctive relative to the σ^*(M-C)-π interaction, since in addition to the less favorable polarity, the former σ^* orbital lies in higher energy than the latter one.



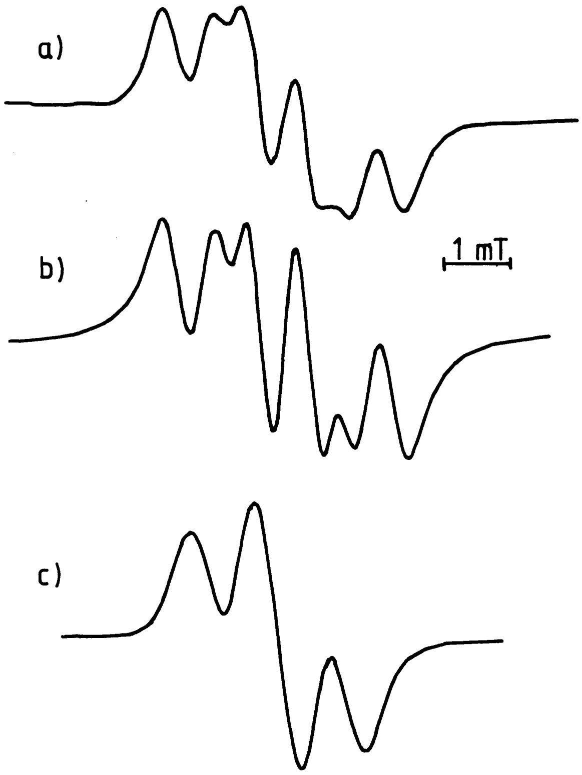


Fig. 1. ESR spectra of isopropylbenzene cation radical in $CFCl_3$ (a) observed at 77 K; (b) its computer simulation assuming overlap of two spectra associated with A (or A') and B conformers using the hfs values and intensity ratios given in Table 1 and employing the Lorentzian lineshapes with the line-width of 0.53 mT for the two components; and (c) observed at 133 K.

Table 1. ESR Parameters of Cation Radicals of Alkyl- and Silyl-Substituted Benzenes

Substituted benzene	T/K	Hfs/mTa)	g
1a	77	1.86 (3H), 1.25 (1H)	
1b	77	0.90 (4H), 0.30 (2H)	2.0035
2a	77	2.83 (2H)b), 1.25 (1H)	2.0031
2b	100	1.70 (2H), 1.05 (1H)	2.0035
3a	77	(A) 2.7 (1H), 0.75 (1H)c)	
		(B) 0.80 (1H)	
	143	1.12 (1H), 1.00 (1H)	
3b	133	1.68 (1H)b), 1.02 (1H)	2.0033
3b	133	0.26 (1D), 0.90 (1H)	2.0033
4a	123	1.05 (1H), 0.81 (1H)	
	153	1.00 (1H)	2.0027
4b	133	0.89 (1H)	2.0035
5	133	0.70 (2H)b)	
6	143	0.73 (1H)b)	2.0033

a) Number of equivalent nuclei is shown in parentheses. b) The hfs value decreased with increasing temperatures. c) A 1:1 mixture of A and B conformers.

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