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ESR STUDY OF CATION RADICALS OF TRIMETHYLSILYL- AND PENTAMETHYLDISILANYL-SUBSTITUTED BENZENE AND RELATED COMPOUNDS. A SYSTEMATIC EXAMINATION OF THE ELECTRON DONOR-ACCEPTOR EFFECTS ON CYCLIC π RADICALS[1)]

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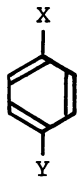
The cation radical of $[PhSiMe_2SiMe_3]^{+\cdot}$ has been found by ESR not to be regarded as a weakly perturbed benzene cation radical like $[PhSiMe_3]^{+\cdot}$ but as an Si-Si σ cation radical similar to $[Me_3SiSiMe_3]^{+\cdot}$.

Group 4B metal substituents such as organosilyl groups may perturb a π electron system as an electron-donor by way of hyperconjugation and/or inductive effects, and as an electron acceptor by using the vacant σ^* orbitals on the metals.[2,3)] The relative importance of these effects depends on the energy levels of the SOMO (singly occupied molecular orbitals) of radicals under consideration (Fig. 1). We have demonstrated previously by ESR that the substituent effects of various organosilyl groups on the hyperfine splitting patterns of the cyclopentadienyl radical[3)] are rather different from those for the benzene anion radical,[4)] reflecting the difference of the relative energy level of the SOMO between the two π radicals.

We wish here to report the first ESR spectra of cation radicals of trimethylsilyl- and pentamethyldisilanyl-substituted benzenes and anisoles (1-6). These radicals were generated by ^{60}Co γ-irradiation of the substrates in frozen $CFCl_3$ solution.[5)] The results are important to get insight into the electronic nature of the group 4B metal substituents, especially of the unusual behavior of a polysilanyl group, since the SOMO level of the benzene cation radical is even lower than that of the cyclopentadienyl radical.



1; X = $SiMe_3$, Y = H
2; X = $SiMe_3$, Y = D
3; X = $SiMe_3$, Y = $SiMe_3$
4; X = $SiMe_3$, Y = OMe
5; X = $SiMe_2SiMe_3$, Y = H
6; X = $SiMe_2SiMe_3$, Y = OMe

The cation radical of phenyltrimethylsilane (1) afforded a doublet ESR spectrum whose hyperfine splitting constant (hfs) was 8.9 G (g = 2.0035). Since the ESR spectra of the cation radicals of 4-deuteriophenyltrimethylsilane (2), and 1,4-bis(trimethylsilyl)benzene (3) were found to be a broad singlet, the hfs of $1^{+\cdot}$ can easily be assigned to that of the para proton. Combining the McConnell equation[6)]

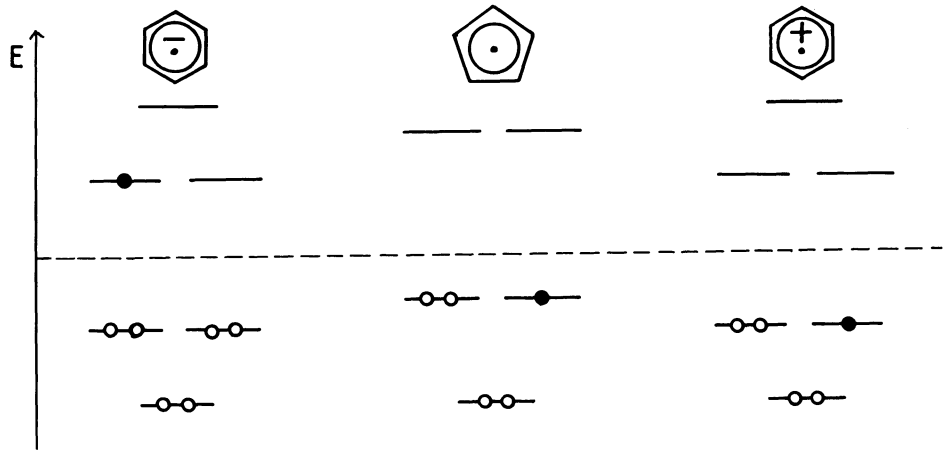


Fig. 1. Schematic representation of energy levels of SOMO for benzene anion, cyclopentadienyl, and benzene cation radicals.

with the ^{1}H hfs of the parent benzene cation radical (a_H = 4.4 G),[7] the π spin density on the para-position of $\underset{\sim}{1}^{+\cdot}$ can be estimated to be 0.34. The SOMO of $\underset{\sim}{1}^{+\cdot}$ is determined to be b_1 rather than a_2. The results confirm the conclusion from the photoelectron spectroscopy[8] that the HOMO of $\underset{\sim}{1}$ is b_1. The trimethylsilyl group is concluded to perturb the degenerated SOMO of the benzene cation radical as a donor in contrast to the case for cyclopentadienyl and benzene anion radicals (Fig. 2).

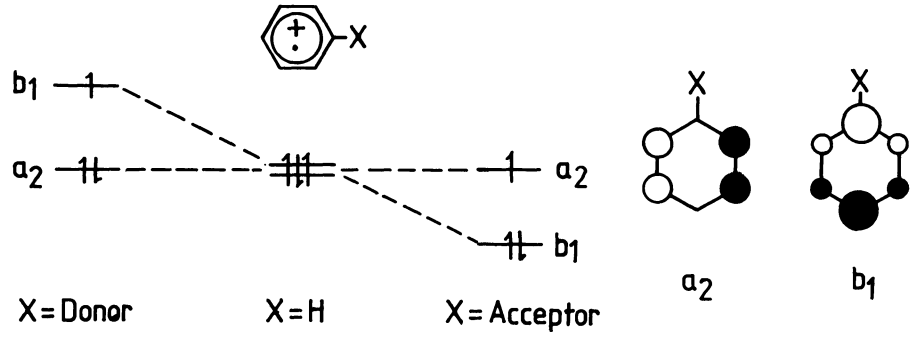


Fig. 2. Splitting of degeneracy of the highest occupied molecular orbitals in the mono-substituted benzene cation radical.

On the other hand, the cation radical from phenylpentamethyldisilane ($\underset{\sim}{5}$) showed a very different feature from $\underset{\sim}{1}^{+\cdot}$ in the ESR spectrum. The spectrum of $\underset{\sim}{5}^{+\cdot}$, which consisted of more than 10 lines with a spacing of ca. 4.7 G, showed a very similar pattern to that of the cation radical of hexamethyldisilane ($\underset{\sim}{7}^{+\cdot}$).[9] The g value of $\underset{\sim}{5}^{+\cdot}$ was determined to be 2.0067 which is slightly smaller than that of $\underset{\sim}{7}^{+\cdot}$ (g = 2.0077)[9b] but definitely larger than the cation radical of benzene. Therefore, $\underset{\sim}{5}^{+\cdot}$ can be regarded no longer as a perturbed benzene cation radical but as an

Si-Si σ cation radical. The results agree quite well with the conclusion from the photoelectron[10] and charge-transfer spectra of phenylpentamethyldisilane with tetracyanoethylene,[11] where we have demonstrated that the HOMO of $\underset{\sim}{5}$ can be described as a mixture of the Si-Si σ bonding orbital (70%) and the benzene b_1 orbital (30%).

The contribution of the Si-Si σ orbital to the HOMO of $\underset{\sim}{5}$ may be diminished by introducing an electron-donating para substituent such as the methoxy group to the benzene ring. γ-Irradiation of p-methoxyphenylpentamethyldisilane ($\underset{\sim}{6}$) afforded, however, a cation radical with similar spectral features with $\underset{\sim}{5}^{+\cdot}$, the species being assignable to the Si-Si σ cation radical. In contrast, the cation radical of p-trimethylsilylanisole ($\underset{\sim}{4}$) was found expectedly to be a π radical cation (Fig. 3), where the SOMO of the anisole cation radical[12] was slightly modified by a trimethylsilyl group: the hfs's of $\underset{\sim}{4}^{+\cdot}$ are 4.8 G (3H) and 3.5 G (2H), and g = 2.0029. Both the smaller hfs (3.8 G) and g value (2.0049) of $\underset{\sim}{6}^{+\cdot}$ than those of $\underset{\sim}{5}^{+\cdot}$ and $\underset{\sim}{7}^{+\cdot}$ are suggestive of the significant electron delocalization from the anisole ring π system.

In conclusion, substituent effects of silyl groups on a series of cyclic π radicals vary succesively among benzene anion, cyclopentadienyl, and benzene cation radicals in the order of the level of SOMO. It is also noticed that $\underset{\sim}{5}$ affords a π type anion radical when an extra-electron is added to the system,[4b] but an Si-Si σ cation radical when an electron is removed from the system.

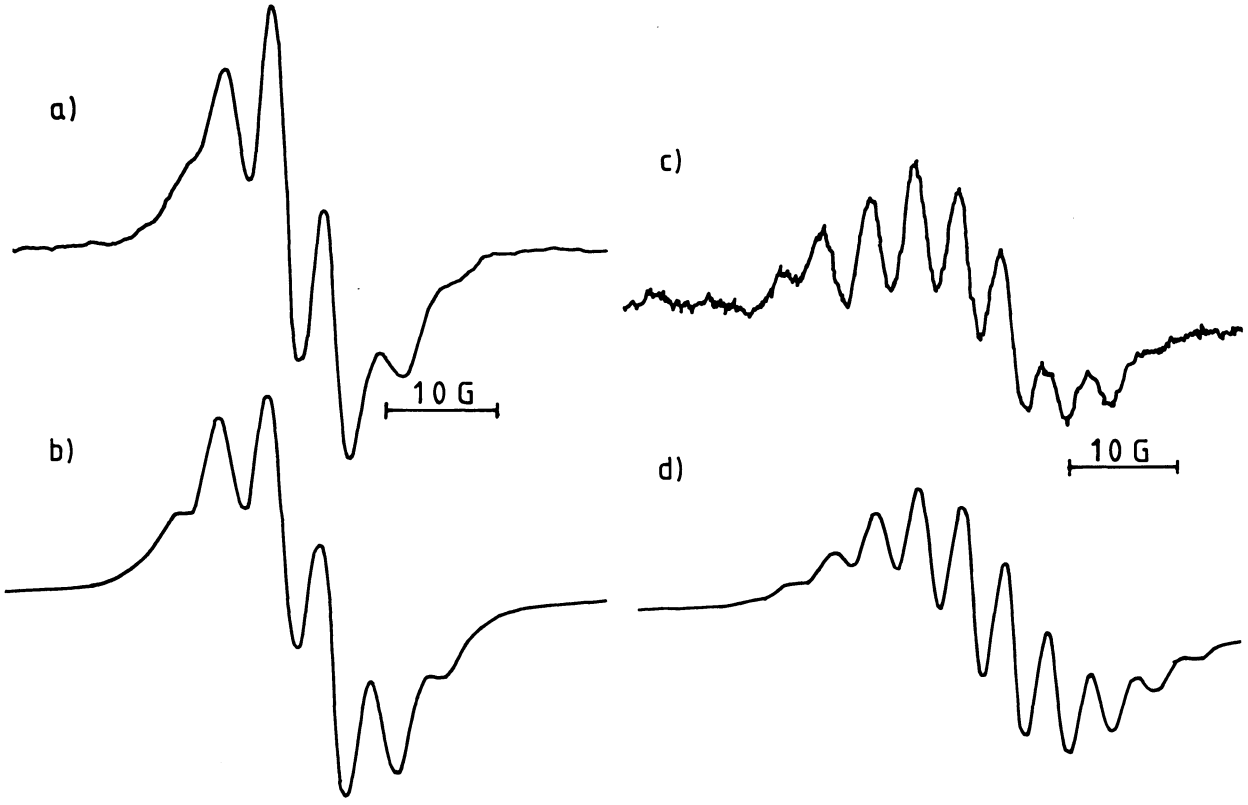


Fig. 3. The observed and simulated ESR spectra of the cation radicals of silyl-substituted anisoles. (a) ESR spectrum of $[p\text{-}MeOC_6H_4SiMe_3]^{+\cdot}$ ($\underset{\sim}{4}^{+\cdot}$) in $CFCl_3$ at -130 °C; (b) simulated spectrum for $\underset{\sim}{4}^{+\cdot}$. (c) ESR spectrum of $[p\text{-}MeOC_6H_4SiMe_2SiMe_3]^{+}$ ($\underset{\sim}{6}^{+\cdot}$) in $CFCl_3$ at -130 °C; (d) simulated spectrum for $\underset{\sim}{6}^{+\cdot}$.

Extension of the present study to the various alkyl- and silyl-substituted benzenes will be described in a forthcoming paper.

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