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Benzene radical cations with chlorosilyl substituents: an ESR study

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Abstract

ESR spectroscopy shows that for the radical cations of phenylsilanes, $PhSiR_3{}^{+\cdot}$, the unpaired electron occupies the ψ_A (a_2) orbital when $R_3 = Cl_3$, $PhCl_2$, $MeCl_2$ or Ph_2Cl, but occupies the ψ_s orbital (b_1) when $R_3 = PhHCl$.

Introduction

There has been considerable interest in the electronic influence of silyl substituents on π-electron systems. This has often been concerned with the question of possible participation of *d*-orbitals on silicon, and also with possible hyperconjugative or inductive effects of silyl groups [1–3].

In the benzene radical anion, the evidence is that the Me_3Si group acts as an electron-accepting substituent [4] that stabilises the $\psi_S^\star$ orbital and increases its occupancy by the unpaired electron relative to $\psi_A^\star$. Silyl substituents also appear to be electron-withdrawing in cyclopentadienyl radicals [5], giving an order of electron attracting power: $H < Me_3Si < Me_2HSi < Me_2ClSi < Cl_3Si$. In contrast, in benzene radical cations, the silyl substituents, Me_3Si, MeH_2Si, Me_2HSi and H_3Si, are apparently electron-donating, like alkyl groups, since the ψ_S orbital is destabilised and is therefore occupied by the unpaired electron [6,7]. The conformational preferences adopted by the silyl groups in the $PhSiMeH_2{}^{+\cdot}$ and $PhSiHMe_2{}^{+\cdot}$ cations, in which there is an increased weighting of conformations in which the Si–H bond is normal to the ring plane, demonstrates the importance of hyperconjugation involving Si–H bonds, although the effect is weaker than for C–H bonds, judging by the smaller magnitude of the couplings to Si–H protons than to the C–H protons in the $MeCH_2$ and Me_2CH derivatives. A review of liquid phase ESR work on silicon containing radical cations has been presented by Bock and Kaim [8].

Experimental

All the silanes used were obtained in the highest commercially available grades, and were checked for purity by GLC and ^1H NMR spectroscopy. The procedure for

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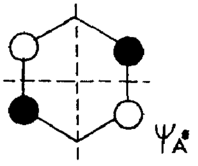
radical cation generation was as outlined previously [9], and the ESR spectra were recorded with a Varian E109 spectrometer.

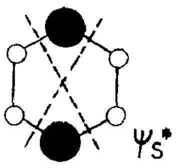
Results and discussion

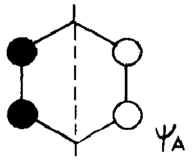
Cl_3Si, Cl_2PhSi, Cl_2MeSi and $ClPh_2Si$ substituents

The ESR results (Table 1) clearly demonstrate that for Cl_3Si, Cl_2PhSi, Cl_2MeSi and $ClPh_2Si$ substituents the unpaired electron occupies the ψ_A (a_2) orbital. The spectrum of the Cl_3Si derivative is shown in Fig. 1, in which anisotropic g and hyperfine components are resolved; the anisotropy was less well resolved in the spectra of the other derivatives, and so average values for the hyperfine couplings are quoted in Table 1.

These results show that, as in cyclopentadienyl radicals, chlorosilyl substituents are electron-withdrawing in benzene radical cations. However, although involvement of the ψ_A orbital was favoured in the cyclopentadienyl radicals, there was







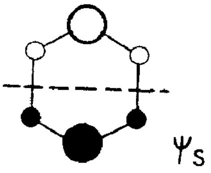


Table 1

ESR coupling constants and SOMO type for silyl substituted benzene radical cations

Substituent	SOMO	Coupling constants (G) [a]
Cl_3Si	ψ_A	(4H) $A_\parallel$ 7.0; $A_\perp$ 6.0; A_{iso} 6.3
$ClPh_2Si$	ψ_A	(4H) 5
Cl_2MeSi	ψ_A	(4H) 6.5
Cl_2PhSi	ψ_A	(4H) 5.5
PhHClSi	ψ_S	(2H) 11.8; (2H) 3.9
Me_3Si	ψ_S	(1H) 11 [b]
		(1H) 8.9 [c]
H_3Si	ψ_S	(1H) 11; (3H) 9; (2H) 3 [b]
		(4H) 9; (2H) 3 [c]
Me_2HSi	ψ_S	(1H) 11; (1H) 18 [b]
		(1H) 10.2; (1H) 16.8 [c]
MeH_2Si	ψ_S	(1H) 10.5; (2H) 17 [c]

[a] 1 G = 10^{-4} T. [b] Ref. 6. [c] Ref. 7.

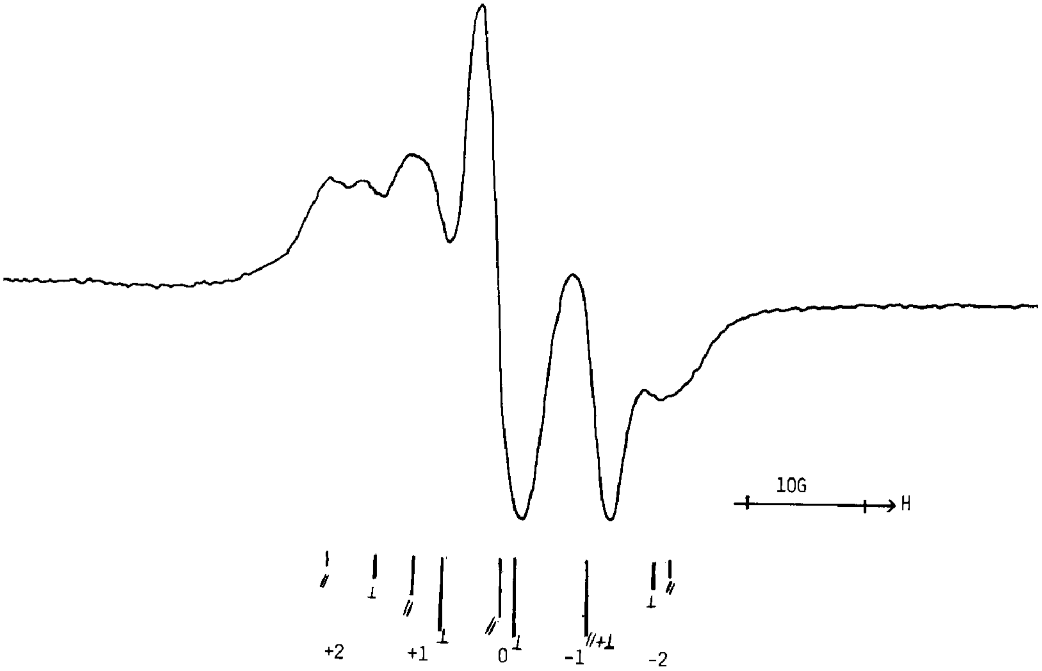


Fig. 1. ESR spectrum of $PhSiCl_3^{+\cdot}$ radical cations in a $CFCl_3$ matrix at 77 K.

apparently still a contribution from the ψ_S orbital [5]. In the present case of benzene radical cations, there seems to be very little contribution from the ψ_S orbital, although the slightly reduced coupling in the $Ph_3SiCl^{+\cdot}$ cation (5 G) may point to a contribution of ca. 17% from ψ_s arising from some thermal mixing of the orbitals.

The PhHClSi substituent

The spectrum of the $Ph_2SiHCl^{+\cdot}$ cation (Fig. 2) shows that, in contrast with the chlorosilyl substituents discussed above, the unpaired electron occupies the ψ_S orbital, as was the case with Me_3Si, MeH_2Si, Me_2HSi, and H_3Si substituents [6,7]. This is difficult to rationalise in terms of a perturbation of the ψ_S and ψ_A orbitals, since PhHClSi must also be an electron-withdrawing substituent, and we feel that a better description is in terms of a fully relaxed cation which has selected the ψ_S state, since this can be stabilised by hyperconjugation involving the Si–H bond. Hyperconjugation is particularly important in cationic species since it provides a highly efficient mechanism for delocalising positive charge density, which results in appreciable stabilisation of the cation. Hyperconjugation by Si–C bonds is evidently less effective than that by Si–H bonds, hence the occupancy of the ψ_A orbital with the other chlorosilyl substituents.

The effect of positive charge delocalisation in radical cations often results in a spin-charge separation effect, which, in certain cases, may be considered to be essentially complete, with the positive charge and the unpaired electron being confined to separate regions of the molecule. Some examples of this kind have been discussed in detail by Roth, who designates them as "non-vertical" radical cations [10].

In benzene radical cations, alkyl and silyl substituents appear to result in a partial spin-charge separation, which places greater spin-density on the *para*-carbon

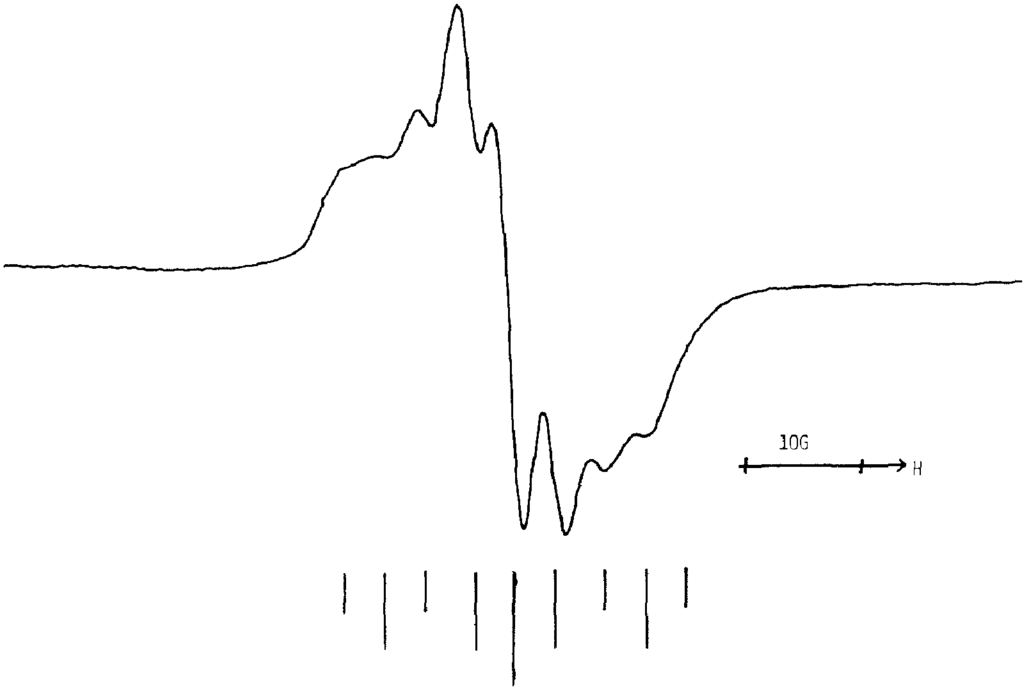


Fig. 2. ESR spectrum of $Ph_2SiHCl^{+\cdot}$ radical cations in a $CFCl_3$ matrix at 77 K.

than is observed in the Jahn/Teller distorted form of the $C_6H_6^{+\cdot}$ cation in a freon matrix at 4 K [11], in which the unpaired electron occupies the ψ_S orbital. This effect also seems to operate in the $Ph_2SiHCl^{+\cdot}$ cation, since the *para*-proton coupling (11.8 G) is greater than that in the distorted $C_6H_6^{+\cdot}$ cation (8.4 G). This suggests that the PhHClSi substituent is effective in stabilising regions of enhanced positive charge, in accord with our suggestion that the selection of the ψ_S state, in contrast to the behaviour of the other chlorosilyl groups, is due to hyperconjugation.

The coupling to the Si–H proton in the PhHClSi group is significantly reduced from that in either the Me_2HSi or MeH_2Si group (Table 1), and we interpret this in terms of a steric effect in which the bulky substituent phenyl group avoids the ring plane, with a decrease in the weighting of conformations in which the Si–H proton is strongly coupled; it was proposed previously that the conformations adopted by substituent silyl groups in benzene radical cations depend on a compromise between steric and electronic effects [6].

In the $Ph_2SiHCl^{+\cdot}$ cation, a small triplet coupling of 3.9 G was observed in addition to coupling to the *para*- and Si–H-protons; a small coupling of this type was noted previously in the case of the $PhSiH_3^{+\cdot}$ cation [6,7]. This is obviously due to either the *ortho*- or the *meta*-protons, which are equivalent in pairs, and it is of interest to decide which pair is the more strongly coupled.

Hückel MO calculations indicate that overlap between the fragment orbitals of the benzene ring and those of a silyl group results in a highest occupied orbital which is perturbed from the ψ_S symmetry, and which has a higher coefficient on the *ortho*- than the *meta*-carbon atoms [12]. If the unpaired electron in the silylbenzene cations occupies an orbital which is essentially of this type, then we can assign the

3.9 G coupling to the *ortho*-protons, with the *meta*-proton couplings too small to be resolved.

In a photoelectron (PES) study of fluorosilyl and chlorosilyl benzene derivatives CNDO/S calculations were used to assign observed ionisation potentials to particular orbitals [13]. In trifluorosilylbenzene, the first ionisation potential was assigned to the ψ_A orbital, since the ψ_S orbital is stabilised by the electron-withdrawing SiF_3 substituent. For $PhSiMeF_2$ the choice is less clear, and for all the chlorosilyl derivatives considered, the calculations predict that the ψ_S orbital is highest occupied. However, for these assignments to be correct, the ψ_A orbital would need to be stabilised to a greater extent by the chlorosilyl substituents than is the ψ_S orbital. This appears unlikely because of the node which passes through the unsubstituted carbon atom in ψ_A. We therefore suggest that the CNDO/S order is incorrect, and propose a reverse assignment of the first two PES bands.

Acknowledgement

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