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ELECTRON DONATION CAPABILITY OF THE TRIMETHYLSILOXY SUBSTITUENT AS STUDIED BY PHOTOELECTRON SPECTROSCOPY AND ELECTRON SPIN RESONANCE OF POLYSUBSTITUTED BENZENE DERIVATIVES

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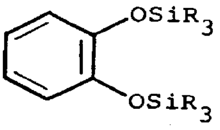
Summary

Poly-trimethylsiloxy substituted benzenes have been studied by UV photoelectron spectroscopy (PES). The observed ionization energies show that the $OSiMe_3$ group is a stronger donor than the methyl group but a weaker donor than OMe or CH_2SiMe_3 groups. Highly substituted derivatives yield radical cations on oxidation with $AlCl_3/CH_2Cl_2/Me_3SiCl$; the electron spin resonance (ESR) as well as the PE results indicate dominating n_O/π interaction, with little or no σ_{O-Si}/π hyperconjugation, for the radical cation ground state.

The trimethylsiloxy substituent $OSi(CH_3)_3$ acts as an electron donor towards π systems such as polyenes or aromatics [1]. Because of its ready formation from carbonyl or alcohol functions and the ease of its hydrolytic cleavage, many useful synthetic procedures employing this substituent have been developed [2]; one representative example involves the Diels–Alder reaction of R_3SiO-substituted "electron rich" dienes [3].

In the present work the benzene π system has been used as a probe for



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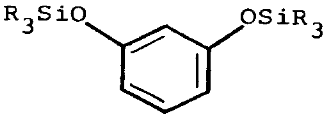

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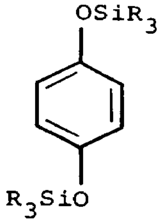

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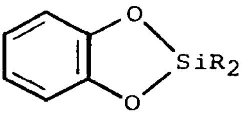

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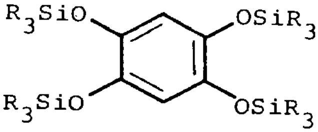

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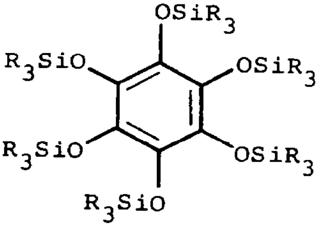

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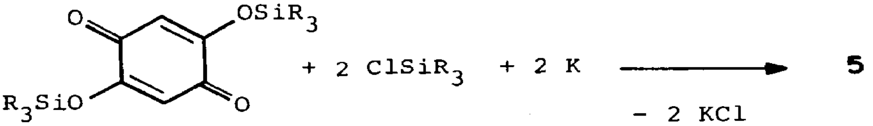
$R = CH_3$

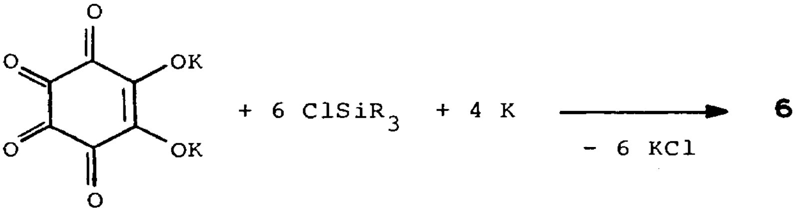
quantitative assessment of substituent effects, the ionization potentials of trimethylsiloxy substituted benzenes **1**–**6** having been measured by UV photoelectron spectroscopy in the gas phase.

Interest in such quantitative information on the substituent effect of $OSiMe_3$ has been stimulated by the fact that accurate data are available for related compounds with OMe [4] and CH_2SiMe_3 substituents [5]. In the latter case conformational features play an important role [4,5], whereas the $OSiR_3$ groups are known to exhibit structural flexibility [6]: C–O–Si bond angles vary between ca. 120 and 170° [7] with typical values around 140° [8] in phenoxytrialkylsilanes; Si–O distances range from 160 to 170 pm [7].

The three disubstituted benzenes **1**–**3** [9] as well as the bicyclic compound **4** [10] have been studied in order to obtain information on geometrical effects, such as *ortho*-interaction or ring size. In addition, the polysubstituted species **5** and **6** [11] have been prepared (by the reactions indicated in eqs. 1 and 2) because they were expected to have very low ionization potentials and to undergo facile one-electron



(1)



(2)

oxidation to the corresponding radical cations in solution [12].

Although it was expected that the ESR spectra of such species would be poorly resolved, the spectra would provide evidence for their formation.

Ionization potentials

Vertical ionization potentials of the compounds **1**–**6**, derived from their photoelectron spectra (Fig. 1), are compared in Table 1 with data for CH_3-, OCH_3- and $CH_2Si(CH_3)_3$-substituted benzene derivatives.

Assignment of the first two π-ionization energies to the molecular orbitals π_A and π_S of perturbed benzene is straightforward, and corresponds to the literature assignments [4,5]. The other ionizations are poorly resolved, and although broad

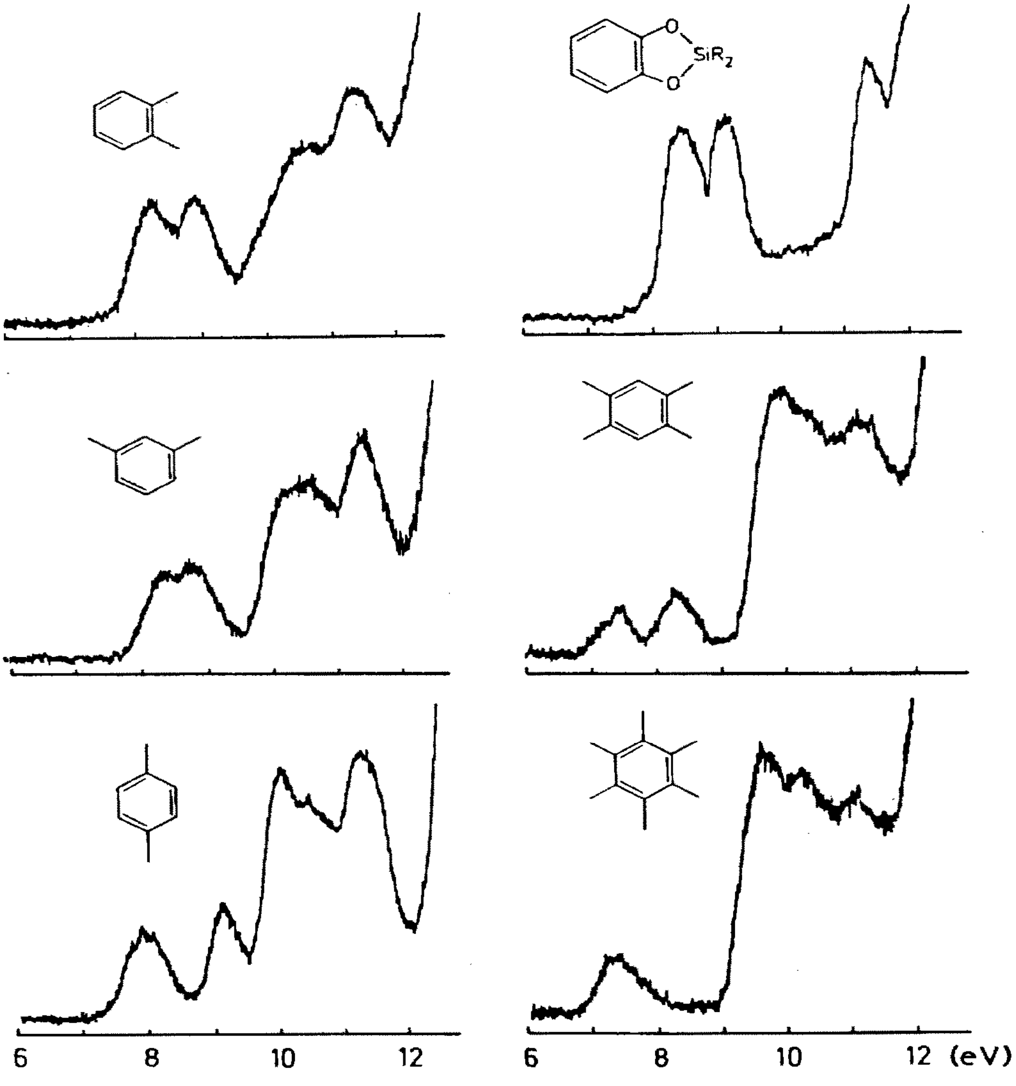
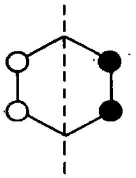
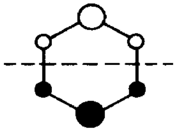


Fig. 1. Low energy photoelectron spectra of the aromatic siloxanes **1**–**6** (——— denotes a trimethylsiloxy substituent).



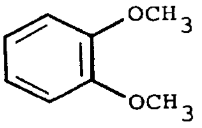
π_A



π_S

features such as the hump between 10 and 11 eV are recognized as σ_{C-Si} ionizations [13], their detailed assignment is not attempted here.

The results from Table 1 show that $OSiMe_3$ substitution leads to π-ionization energies lower than those for methyl-substituted compounds but higher than those bearing methoxy or trimethylsilylmethyl substituents. Unusual conformational effects, e.g. of steric crowding, are not detectable by PES, but the bicyclic compound **4** exhibits a slightly higher ionization potential than the related 1,2-bis(trimethylsiloxy)benzene (**1**). Such a difference is not observed in the alkoxy series [4], and may be attributed to the small C–O–Si angle enforced by the five-membered ring, which apparently disfavours n_O/π overlap. The even larger difference between the open-chain and cyclic system in the silylmethyl series has been satisfactorily explained [13] in terms of the geometric requirements for effective σ_{C-Si}/π hypercon-



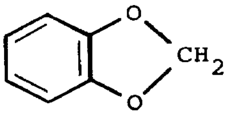


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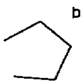
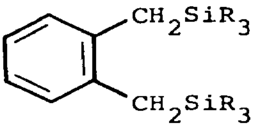
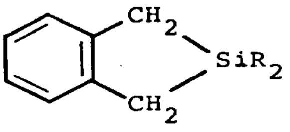
TABLE 1

FIRST IONIZATION POTENTIALS[a] OF DONOR-SUBSTITUTED BENZENES

Benzene substitution pattern	Substituents			
	$OSi(CH_3)_3$	OCH_3 [4]	$CH_2Si(CH_3)_3$ [5]	CH_3 [5]
1.2	8.30 (**1**)	8.17	8.05	8.56
	8.95	8.94	8.55	9.00
1,3	8.33 (**2**)	8.14	8.05	8.55
	8.80	8.72	8.40	9.00
1,4	8.00 (**3**)	7.96	7.75	8.44
	9.15	9.16	8.75	9.05
 [b]	8.47 (**4**)	8.21 (**7**)	8.41 (**8**)	8.46
	9.15[c]	9.15	d	9.04[e]
1,2,4,5	7.45 (**5**)		7.10	8.05
	8.40		7.75	8.55
1,2,3,4,5,6[f]	7.40 (**6**)		7.4	7.85

[a] Vertical ionization potentials (eV) from photoelectron spectroscopy. [b] Five-membered ring systems **4**, **7**, **8** and indane. [c] Values of the monomeric species. [d] Value calculated from charge transfer spectra. [e] Indane; F. Brogli, E. Giovannini, E. Heilbronner and R. Schurter, Chem. Ber., 106 (1973) 961. [f] Degenerate radical cation ground state.





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jugation. Such an interaction is apparently less significant in the siloxy series because the energies of σ_{C-Si} orbitals are distinctly higher than those of the σ_{O-Si} orbitals [13,14]. The small but detectable increase of the π-ionization energies upon replacement of methoxy by trimethylsiloxy substituents may be attributed to back-bonding from silicon to oxygen which, incidentally, is also responsible for the change in geometry. Such interactions, involving hyperconjugative mechanisms [15] rather than *d*-orbital participation [16], reduce the electron density in the oxygen lone pair orbitals and lower the donor capacity of the entire substituent.

Nevertheless, polysubstituted species such as **5** and **6** are still fairly electron-rich (Table 1), as is also evident from studies of charge transfer complexes [17]: compound **5** but not the most sterically crowded **6**, forms a charge transfer complex with the acceptor tetracyanoethylene (TCNE). A comparison of absorption maxima for **5** · TCNE (700 nm, 460 nm) with that of the methoxy analogue (1,2,4,5-tetramethoxybenzene · TCNE: 800 nm [18]) again illustrates the slightly smaller donor strength of the $OSiMe_3$ group.

Chemical oxidation

The oxidation of some trialkylsiloxy substituted aromatics has recently been studied by electrochemistry [19]. Although the potentials reported are rather low, in accord with the electron-rich nature of these species, the oxidation was irreversible; oxidative desilylation gave the corresponding quinones in good yields [19]. Since it has been found [20] that solutions of $AlCl_3$ in dichloromethane and related solvents are mild one-electron oxidants for compounds with first ionization potentials below ca. 7.75 eV [5,12], this procedure was applied to compounds **5** and **6** in the presence of some Me_3SiCl in order to prevent desilylation [21]. Radicals were formed slowly by this procedure, but unfortunately, the ESR spectra were not resolved (line width ca. 4 G, $g = 2.0039$). The lack of resolution may be traced to the hyperfine splitting pattern expected for the radical cations $\mathbf{5}^{+}$ and $\mathbf{6}^{+}$: the very small coupling expected with numerous silylmethyl protons in δ-position to the spin-bearing π system, the low-intensity ^{29}Si satellite lines (^{29}Si: 4.7% natural abundance, $I = 1/2$) [5,22], and a small ring proton splitting in the radical cation $\mathbf{5}^{+}$ [23] should all lead to considerable overlap and to very low resolution. Nevertheless, this result is in agreement with the dominant n_O/π interaction invoked to account for the PE spectra. Neither the oxygen nor the carbon nuclei have a nuclear spin in sufficient natural abundance to cause detectable features in the ESR spectra of these radical cations.

A much more favourable situation for resolution of ESR spectra has been shown to exist for the silylmethyl-substituted π radical cations [5,22]. Here extensive σ_{C-Si}/π hyperconjugation leads to considerable delocalization of spin density on to the substituents, so that methyl, silylmethyl and ^{29}Si hyperfine splittings become fairly large and hence well resolved. In agreement with the results presented here for benzene radical cations, the observation has been made [24] that radical anions containing the trimethylsiloxy substituent have the unpaired electron pushed away from the $OSiMe_3$ substituted centres, thereby indirectly indicating the electron releasing capacity of this substituent.

Experimental

^1H NMR: Varian T 60, TMS as internal standard. PE spectroscopy: Perkin–Elmer PS 16 and Leybold-Heraeus UPG 200, calibration with $Xe(^2P_{3/2}) = 12.13$ eV and $Ar(^2P_{3/2}) = 15.76$ eV peaks. Study of the charge transfer complex was carried out in CH_2Cl_2, using sublimed TCNE [1]; spectra were measured on a Pye Unicam SP 1800 spectrometer. Radical cation formation was performed by the $AlCl_3/CH_2Cl_2$ oxidation procedure described previously [12]; Me_3SiCl was added to prevent oxidative desilylation [21]. ESR spectra were recorded on a Varian E 9 apparatus; g values were determined by the double-cavity technique relative to the perylene radical anion [25].

Compounds **1–3** [9] and **4** [10] were prepared by published procedures.

*1,2-Bis(trimethylsiloxy)benzene (**1**).* ^1H NMR ($CDCl_3$) δ 0.23 (s, 18H), 6.80 (ps, 4H).

*1,3-Bis(trimethylsiloxy) benzene (**2**).* ^1H NMR ($CDCl_3$) δ 0.27 (s, 18H), 6.3–6.6 (m, 3H), 6.9–7.2 (m, 1H).

*1,4-Bis(trimethylsiloxy)benzene (**3**).* ^1H NMR ($CDCl_3$) δ 0.28 (s, 18H), 6.67 (s, 4H).

*1,2-Phenylenedioxydimethylsilane (**4**).* ^1H NMR as reported in ref. 10; the vapour pressure during PES measurement indicated the presence of the monomer.

*1,2,4,5-Tetrakis(trimethylsiloxy)benzene (**5**).* 2,5-Bis(trimethylsiloxy)-1,4-benzoquinone [26] (2.2 g, 7.7 mmol) was treated with 2.6 g (23.3 mmol) of trimethylchlorosilane and 0.92 g (23.3 mmol) of potassium in refluxing THF. After 1 h the mixture was allowed to cool down to room temperature, then filtration, evaporation of the solvent and careful sublimation at 90°C (10^{-3} Torr) gave 0.5 g (1.2 mmol, 16%) of the product (m.p. 116°C). ^1H NMR ($CDCl_3$) δ 0.23 (s, 36H), 6.33 (s, 2H).

Found: C, 49.99; H, 8.82. $C_{18}H_{38}Si_4O_4$ calcd.: C, 50.18; H, 8.89%.

*Hexakis(trimethylsiloxy)benzene (**6**) [11].* The dipotassium salt of rhodizonic acid (2.0 g, 8.2 mmol) was treated with 6.5 g (60 mmol) of trimethylchlorosilane and 1.6 g (40 mmol) of potassium in refluxing THF. After 20 h the mixture was allowed to cool and then filtered. Evaporation of the solvent and careful sublimation of the residue yielded 0.6 g (1 mmol, 12%) of the desired product (m.p. 220°C). ^1H NMR ($CDCl_3$) δ 0.16 (s, 54H).Found: C, 47.75, H, 9.02. $C_{24}H_{54}Si_6O_6$ calcd.: C, 47.47; H, 8.96%.

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