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CALCULATION OF THE BOND STRUCTURE OF PHENOXYMETHYLSILANES BY THE PARISER–PARR–POPLE METHOD

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SUMMARY

Quantum chemical calculations by the Pariser–Parr–Pople method have been used to study the molecular structure of phenoxytrimethylsilanes, and the results evaluated by comparison with data from the ultraviolet spectra. Account was taken of hyperconjugation calculations from the methyl groups, but this was shown to be a negligible influence. The results show d_π–p_π bonding, with a π-bond order of 0.326–0.331, occurs between the silicon and oxygen atoms.

INTRODUCTION

We previously discussed the ultraviolet and infrared spectra and the dipole moments of phenoxymethylsilanes[1] and reached qualitative conclusions about the bonding, especially about the nature of the silicon–oxygen bonds. The present work reports quantum chemical calculations which confirm our earlier qualitative findings.

QUANTUM CHEMICAL CALCULATIONS

Pariser–Parr–Pople's method has been used for studying the π-bond system of the compounds[2,3]. The ionisation energies of the atoms in a given valency state in the single compounds have been calculated as a function of Burns' effective nuclear charge[4]. Our study showed that shielding factors are determined more correctly by the method of Burns, than by calculations based on the effective nuclear charges according to Slater. In the determination of the shielding parameters, promoted and hybridised states have also been taken into consideration. Ionisation energies have been calculated with the following exponential equations determined by us:

$$U_C = -0.61329\ e^{1.036162}$$
$$U_{O^+} = -0.86598\ e^{0.84590Z}$$
$$U_{Si} = -0.20662\ e^{0.95552Z}$$

where Z is Burns' effective nuclear charge. The following γ_{ii} values, published in the literature[5,6] were used for our calculations: $\gamma_{CC}=11.13$, $\gamma_{OO}=21.53$, $\gamma_{SiSi}=3.762$ eV. The γ_{ij} values were calculated from bond distances by use of Mataga and Nishimoto's relationships[7]. The exchange integrals were calculated with the approximative formula of Wolfsberg and Helmholtz[8]. The proportionality factor k was calculated from the experimental exchange integral of the C–C bond in benzene and from its calculated overlap integral, yielding a value of $k = 0.6426$. The values of the singlet and triplet energy transitions and of the oscillator strengths were calculated using known relationships.

RESULTS

Calculations were carried out for the following compounds: trimethylphenoxysilane(I), *o*-bis(trimethylsiloxy)benzene(II), *m*-bis(trimethylsiloxy)benzene(III), *p*-bis(trimethylsiloxy)benzene(IV). For each compound freedom of rotation of the $(CH_3)_3Si$ group about the aromatic carbon–oxygen axis was assumed. For the calculation of the electron interaction integrals, the spatial arrangement used was that corresponding with the statistical average, *viz.* that in which the plane determined by the $SiOC_{ar}$ atoms is perpendicular to the plane of the benzene ring. (The alternative would have been to use various spatial arrangements occurring with the same probability.) In the case of disubstituted compounds, the silicon atoms were regarded as fixed in trans position. For our calculations, the following published[9,10] bond distances and bond angles were used: $R_{CC} = 1.397$ Å, $R_{CO} = 1.36$ Å, $R_{SiO} = 1.648$ Å, $SiOC_{ar} \measuredangle = 121°$. In the calculation of the overlap integral of the silicon–oxygen bond, account was taken of the fact that the overlap of the p orbital of oxygen and of the d orbital of silicon is not total. The overlap is largest, when the axis of the p orbital makes an angle of 45° with the two perpendicular axes of the d orbital. Owing to the tetrahedral sp^3 hybridisation of the silicon atom, this angle changes, the deviation being 19°28′. If the deviation is 45°, overlap between the orbitals becomes zero.

Thus, the corrected overlap integral is

$$S = S_0 \cos 2\alpha$$

where $2\alpha = 19°28'$. The overlap of the d and p orbitals is shown in Fig. 1. Calculated data for the compounds are listed in Table 1.

Calculations were performed with the electronic computer Model Razdan-3 of the Technical University of Budapest. The values of Z_i, U_i, α_i were changed by use of the results obtained in the zeroth approximation, while the values of β_{ij} were kept constant. Approximations were continued to self-consistency. The eigenvalues, linear coefficients, electron densities, partial charges and bond orders were determined for the single compounds. Configuration interactions were also taken into account, and

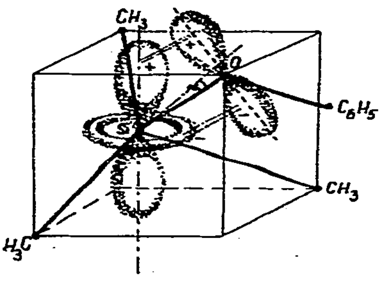

Fig. 1. Overlapping of the p and d orbitals in phenoxysilanes.

TABLE 1

STARTING DATA FOR THE CALCULATION OF THE π-SYSTEM OF PHENOXY METHYL SILANES BY THE PPP METHOD

Z_C	2.80
Z_O	4.30
Z_{Si}	1.75
U_C	−11.16 eV
U_O	−32.90 eV
U_{Si}	− 1.10 eV
β_{CC}	− 2.39 eV
β_{CO}	− 2.1538 eV
β_{SiO}	− 1.2638 eV

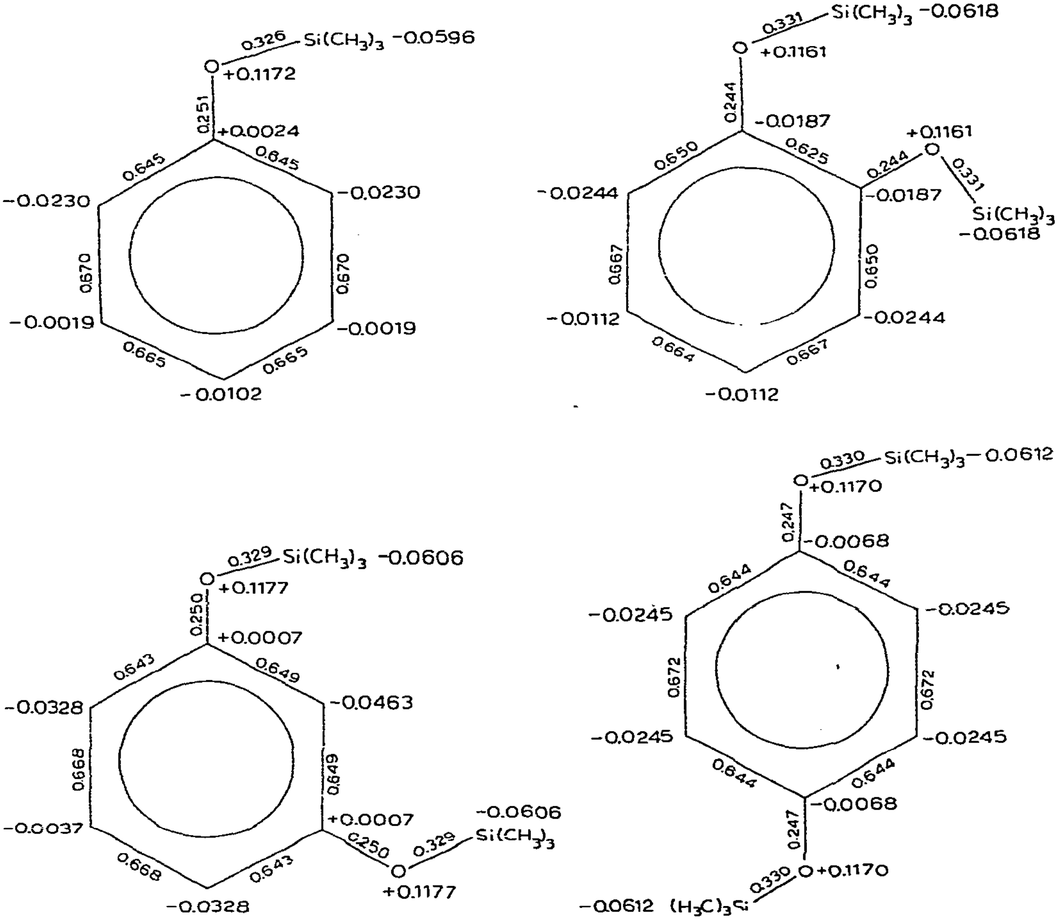

Fig. 2. π-Partial charges and π-bond orders for trimethylphenoxysilane (I), *o*-bis(trimethylsiloxy)benzene(II), *m*-bis(trimethylsiloxy)benzene(III) and *p*-bis(trimethylsiloxy)benzene(IV).

TABLE 2

EIGENVALUES OF PHENOXY METHYL SILANES

(eV)	Compound			
	(I)	(II)	(III)	(IV)
E_1	−15.0442	−15.4288	−15.2107	−15.1351
E_2	−12.8584	−14.5034	−14.7328	−14.7695
E_3	−10.3206	−12.5877	−12.4197	−12.3525
E_4	− 9.9005	−10.1016	−10.0519	−10.2938
E_5	− 1.2086	− 9.6695	− 9.7161	− 9.5341
E_6	− 0.7906	− 1.3379	− 1.2545	− 1.2778
E_7	− 0.5383	− 1.2223	− 1.1783	− 1.0685
E_8	2.2518	− 0.6291	− 0.6210	− 0.7614
E_9		− 0.4658	− 0.4161	− 0.3369
E_{10}		2.3155	2.3285	2.3238

TABLE 3

ENERGY VALUES AND OSCILLATOR STRENGTHS OF THE $^1E_{CI}$ SINGLET AND $^3E_{CI}$ TRIPLET TRANSITIONS OF PHENOXYSILANES

Compound	$^1E_{CI}$ (eV)	f	$^3E_{CI}$ (eV)
(I)	4.7910	0.007	3.0783
	5.7314	0.187	3.8818
	6.2152	0.022	3.9414
	6.6843	0.423	4.8412
	6.9466	1.097	5.9168
	6.9963	0.695	6.7996
(II)	4.6708	0.014	3.0050
	5.3141	0.132	3.8025
	5.5401	0.187	3.8519
	6.0121	0.008	4.7133
	6.3383	0.204	5.4675
	6.4076	0.099	5.4712
(III)	4.6856	0.008	3.0224
	5.5269	0.098	3.8261
	5.6640	0.312	3.8614
	6.1316	0.016	4.7267
	6.3766	0.090	5.6643
	6.3960	0.154	5.7021
(IV)	4.6549	0.026	2.9719
	5.3818	0.366	3.6650
	5.7383	0.000	3.8823
	6.1352	0.012	4.8704
	6.5171	0.515	5.4152
	6.6650	0.000	5.4673

TABLE 4

DATA USED IN CALCULATIONS INVOLVING HYPERCONJUGATION

$U_{C(\text{methyl})}$	−11.19 eV
$U_{(H_3)}$	−10.26 eV
$\gamma_{CC(\text{methyl})}$	9.71 eV
$\gamma_{(H_3)(H_3)}$	9.33 eV
β_{SiC}	− 1.5521 eV
$\beta_{C(H_3)}$	− 7.4013 eV
$R_{C-(H_3)}$	0.6293 Å

their use allowed the energy values of the singlet and triplet transitions and the oscillator strengths to be calculated. Results are shown in Fig. 2, and summarised in Tables 2 and 3.

In the case of the trimethylphenoxysilane molecule a further calculation was performed, in which the hyperconjugation effect of the methyl groups was taken into account. This hyperconjugation effect arises from the fact that the *s* orbitals of the 3 hydrogens of the methyl group overlap and a hypothetic H_3 pseudo-atom is formed, which is linked to carbon with an element of double-bond character. This electron donor CH_3 group, containing a hypothetic double bond, is conjugated with the other parts of the molecule. The hydrogens of all three methyl groups were assumed to be H_3 pseudoatoms, and the PPP calculation performed for a molecule with 14 centers. Parameters necessary for hyperconjugation calculations were taken in part from the literature[11], and obtained in part from calculations[12] carried out for the methylvinylsilane series. These data are listed in Table 4.

Results of the calculations taking account of the hyperconjugation are shown in Fig. 3 and Table 5.

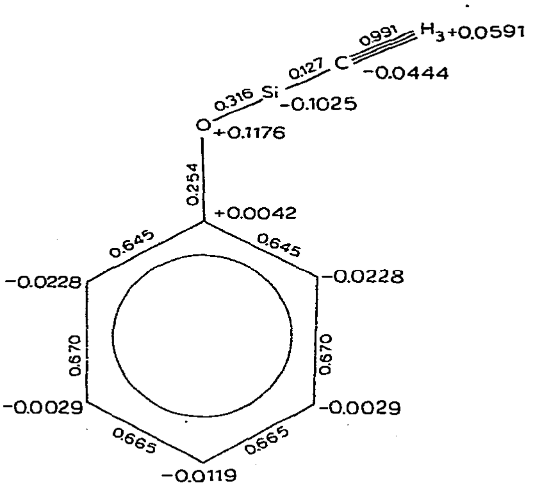

Fig. 3. π-Partial charges and π-bond orders for trimethylphenoxysilane taking account of the hyperconjugation effect.

TABLE 5

RESULTS OF CALCULATIONS FOR TRIMETHYLPHENOXY SILANE TAKING ACCOUNT OF HYPERCONJUGATION

E (eV)	$^1E_{CI}$ (eV)	$^3E_{CI}$ (eV)
−17.1395	4.7856	3.0787
−16.8091	5.5762	3.8754
−16.7859	6.1359	3.9380
−14.9180	6.4649	4.8367
−12.7998	6.9285	5.6781
−10.2818	6.9288	6.5218
− 9.8460		
− 1.3592		
− 0.7538		
− 0.5444		
2.2879		
4.6974		
4.7195		
5.2916		

EVALUATION

It can be seen from the figures and the tables that the silicon–oxygen bond has a partial double-bond character in phenoxymethylsilanes. A d_π–p_π bond is formed between the empty d orbital of the silicon atom and the p electron pair of the oxygen atom, the π-bond order being 0.326–0.331. Simultaneously, a p_π–p_π bond is formed between the oxygen and the carbon atoms, with a bond order of 0.244–0.251. In the four compounds, the p_{SiO}, p_{CO}, δ_{Si} and δ_O values are approximately the same, only the electron distribution of the benzene rings being different. Thus, delocalized

TABLE 6

COMPARISON OF THE EXPERIMENTAL AND CALCULATED SINGLET TRANSITIONS AND OSCILLATOR STRENGTHS OF PHENOXY METHYL SILANES

Compound	^1E[eV] Found	f	$^1E_{CI}$ Calcd.	f	Deviation [eV]
(I)	4.54	0.023	4.79	0.007	−0.25
	5.69	0.102	5.73	0.187	−0.04
			6.22	0.022	
(II)	4.56	0.022	4.67	0.014	−0.11
			5.31	0.132	
	5.74	0.145	5.54	0.187	0.20
(III)	4.56	0.017	4.69	0.008	−0.13
			5.53	0.098	
	5.74	0.152	5.66	0.312	0.08
(IV)	4.23	0.042	4.65	0.026	−0.42
	5.53	0.111	5.38	0.366	0.15
			5.74	0.000	

molecular orbitals with 8 and 10 centers, respectively, are formed from the *p* orbitals of carbon and oxygen atoms and the *d* orbitals of silicon atoms in phenoxysilanes. The values of the singlet energy transitions have been compared with the ultraviolet absorption maxima of the compounds and the calculated oscillator strengths with values established from the ultraviolet spectra, and the relevant data are shown in Table 6. Table 6 reveals a good agreement between the calculated and the experimental values.

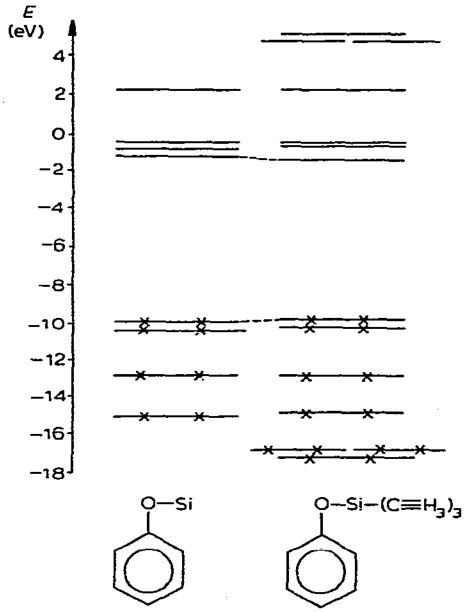

Fig. 4. Energy diagram for trimethylphenoxysilane calculated by two different methods.

The results of calculations taking account of hyperconjugation show that the effect of the methyl groups on the other parts of the molecule can be neglected. Fig. 4 shows the energy diagrams of trimethylphenoxysilane, calculated by the two different methods.

It can be seen from Fig. 4 and from data in the preceding figures and tables that eigenvalues, energy transitions and electron distributions resulting from the two modes of calculation are almost identical, only the p_{SiO} and δ_{Si} values being different. Thus hyperconjugation from the methyl groups can be neglected in the calculation of the π-systems.

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