INVESTIGATION OF COMPOUNDS CONTAINING Si—S AND S—Si—S BONDS BY ULTRAVIOLET SPECTROPHOTOMETRY

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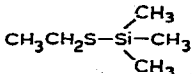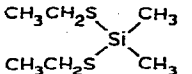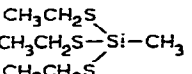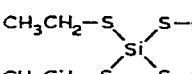
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Summary
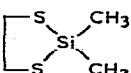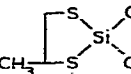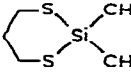
Five- and six-membered ring and open chain compounds containing S—Si and S—Si—S bonds were examined by UV spectroscopy and the $n—\sigma^*$ transition found to show a blue shift compared with that in the analogous carbon compounds. This is a consequence of the $(d—p)\pi$ interaction between the lone electron pair of sulfur and the d orbitals of silicon, at the same time through-conjugation over silicon is not unambiguously proved. The results are in accordance with conclusions based on PES data. Interaction between the sulfur atoms and the aromatic system can be deduced from the spectra and the extent of this effect is similar to that for chlorine in the corresponding derivatives. On the other hand the bathochromic shift of the α and p bands for the silicon compounds indicates that the lone electron pairs of the sulfur atom can form a conjugative connection with the 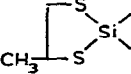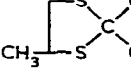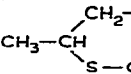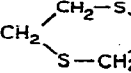aromatic ring. A new transition appearing between the α and p bands can be attributed to charge transfer (CT) interaction; the intensity of the CT band depends on the distance between the sulfur atom and the phenyl group.

There have been many studies designed to elucidate the nature of the silicon—sulfur bond and the methods used include photoelectron spectroscopy [1—4], mass spectroscopy [5], kinetic [6] and ESCA [7] measurements and far ultraviolet spectroscopy [8]. We describe below a study of the UV spectra of some compounds containing Si—S and S—Si—S groups. Our aim was to study the $(d—p)\pi$ interaction between the vacant d orbital of silicon and the lone pair of sulfur and the S—S "through bond" interaction. The results were also analysed in the light of PES data for the same or similar compounds.

Experimental

Compound 1—8 and 10, 11 in Table 1 and 12—20 in Table 3 were prepared by the reaction of the appropriate alkylthiol and chlorosilane derivatives in the
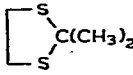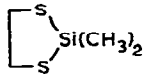
TABLE 1

UV MAXIMA AND INTENSITY FOR NON-AROMATIC COMPOUNDS

	Compound	λ_{max}(nm)	log ϵ	λ_{max}(nm)	log ϵ
1	$CH_3CH_2S-Si(CH_3)(CH_3)-CH_3$	223	2.49		
2	$(CH_3CH_2S)_2Si(CH_3)_2$	224	3.14	190	
3	$(CH_3CH_2S)_3Si-CH_3$	225	3.26	190	3.90
4	$(CH_3CH_2-S)_4Si$	227	3.48	190	
5	cyclic $S_2Si(CH_3)_2$ (1,3-dithia ring)	233	2.38	198	3.58
6	cyclic CH_3-S-Si(CH_3)_2-S ring	233	2.33	198	3.54
7	cyclic $S_2Si(CH_3)_2$ (five-membered)	228	2.82	195	3.58
8	bicyclic CH_3-S-Si-S-CH_3	235	3.03		
9	cyclic CH_3-S-C(CH_3)_2-S	249	2.20	194	3.65
10	$CH_3-CH(CH_2-S)_2Si(CH_3)_2$	240 (sh)	2.42	200	3.56
11	$CH_2(CH_2-S)_2Si(CH_3)_2$	238 (sh)	2.46	200	3.70

presence of triethylamine in benzene [9,10]. Compound 9 was prepared from 1,2-ethanedithiol, acetone and BF_3-etherate [2]. The purity of the compounds was checked by gas chromatography and by determination of the silicon content. The UV spectra were recorded with a Spektromom 202 instrument in n-hexane using quartz cells of 1 and 0.2 cm thickness.

TABLE 2

FIRST IONISATION ENERGIES OF SOME COMPOUNDS CONTAINING SULFUR BASED ON PES
MEASUREMENTS

Compound	IE (eV)
CH_3SH	9.44
SiH_3SH	9.97
GeH_3SH	9.69
CH_3SSiH_3	9.10
$CH_3SSi(CH_3)_3$	8.69
CH_3SCH_3	8.71
SiH_3SSiH_3	9.70
GeH_3SGeH_3	9.25
$Si(CH_3)_3SSi(CH_3)_3$	8.74
$SHCH_2SH$	9.42
	10.49
$CH_3SCH_2SCH_3$	8.67
	8.92
$CH_3SC(CH_3)_2SCH_3$	8.39
	8.71
	8.62
	8.84
$CH_3SSi(CH_3)_2SCH_3$	8.72
	8.98
	8.95
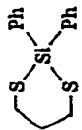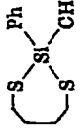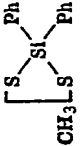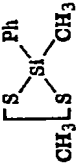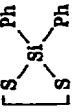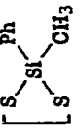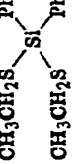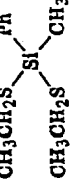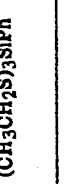
Results and discussion

(a) Aliphatic and saturated cyclic compounds

The positions and intensities of the UV absorption maxima are summarized in Table 1.

In interpreting the spectra the following factors have to be taken into account: (i) hyperconjugative effects of methyl and $SiMe_n$ groups, (ii) $(d\!-\!p)\pi$ interaction between the lone electron pair of sulfur and the d orbital of silicon, (iii) inductive effects, and (iv) long range (though bond) interaction between sulfur atoms. Analyses of the facts played by these effects can be assisted by consideration of the photoelectron spectra of compounds of similar type. In Table 2 are listed the first ionization potentials of some compounds containing S—C, S—Si and S—Ge bonds [1—4,11]. It is well established from the PES data and theoretical calculations that this ionization energy relates to the lone electron pair of the sulfur atom. It can than be concluded that the absorption bands of medium intensity in the ultraviolet spectra between 220 and 240 nm arise from $n\!-\!\sigma^*$ or $n\!-\!3d$ (sulfur) transitions. In view of the large difference in the transition energy between the silicon and carbon compounds the first possibility seems the more likely. This opinion is supported by Cumper et al. [12].

TABLE 3

UV MAXIMA AND INTENSITIES OF AROMATIC COMPOUNDS

Compound	α band λ_{max} (nm)	log ε	CT band λ_{max} (nm)	log ε	p band λ_{max} (nm)	log ε	β band λ_{max} (nm)	log ε
12 (ring S–Si(Ph)(Ph)–S)	273 276 260(sh)	2.79 2.91 2.94			220	4.15	194	4.73
13 (ring S–Si(Ph)(Ph)(CH₃)–S)	272	2.55	236(sh)	3.43	218	4.14	198	4.51
14 (ring CH₃S–Si(Ph)(CH₃)–S)	273	2.86	245	3.63	223	4.27		
15 (ring CH₃S–Si(Ph)(Ph)–S)	276 266	2.44 2.58	245(sh)	3.05	217	3.88	192	4.44
16 (S–Si(Ph)(Ph)–S)	274	2.88	245(sh)	3.55	221	4.20	197	4.83
17 (S–Si(Ph)(CH₃)–S, CH₃)	274 266	2.45 2.61	245(sh)	3.13	220(sh)	3.86	194	4.52
18 (CH₃CH₂S–Si(Ph)(Ph)–SCH₂CH₃)	273 266 261	2.85 2.99 3.01	245(sh)	3.50	222(sh)	4.28	195	4.85
19 (CH₃CH₂S–Si(Ph)(CH₃)–SCH₂CH₃)	272 265	2.44 2.59	238(sh)	3.24	216(sh)	3.91		
20 (CH₃CH₂S)₃SiPh	273 266	2.70 2.48	240(sh)	3.43	218(sh)			

It can be seen from Fig. 3 of ref. 1 that the first ionization energy of silicon compounds is relatively large, indicating some kind of anomaly for these compounds. Since the overlap between the lone electron pair of sulfur and the d orbital of atom X is largest for X = Si, this can reasonably be attributed to $(d-p)\pi$ interaction. This interaction is also responsible for the considerable hypsochromic shift of the $n-\sigma^*$ band of silicon derivatives compared with that of carbon analogous.

As shown by the data in Table 2, the ionization energies of open-chain compounds are smaller than those of the corresponding cyclic compounds. It is therefore surprising that the opposite effect is observed in the UV spectra, the energy of the $n-\sigma^*$ transitions increasing in the following order: five-membered cyclic < six-membered cyclic < open-chain compounds. It is noteworthy that Oae and his co-workers [13] observed a similar sequence in the rates of the base-catalysed tritium—hydrogen exchange reaction of analogous carbon compounds, the relative rates for compounds I, II, III and IV being 1/1.55/5.37/19.1.
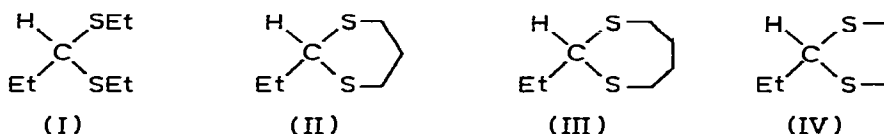
The corresponding UV spectra show a different sequence for the maximum wavelength transition: six-membered > five-membered > seven-membered ring > acyclic compounds. The dependence of the UV spectra on the ring size was also observed for the cyclic monosulfides [14]. In this case the absorption maxima concerned are of very low intensities and the order of the position of the λ_{max} is 4 > 3 > 5 > 6. For the cyclic monosulfides the explanation was based on the change of the electron density at the sulfur atom. The spectra of the compounds containing the S—C—S entity can be interpreted in terms of the nonbonding interaction between two sulfur atoms, involving their $3d$ orbitals, where a singlet radical structure has been suggested for the photo-excited state [13]. The smaller bond angles of sulfides as compared with ethers, the longer bond length of the C—S linkages, the much greater Van der Waals radius of sulfur as compared with the oxygen atom, the large neighbouring group effect of sulfur atom in solvolysis reactions and the larger polarizability of the sulfur atom, all argue strongly in favour of a contribution to the photoexcited state of a three-membered ring structure (a).

In the silicon derivatives the $3d$ orbitals of the sulfur atoms are less involved in such bonds because of the lower electronegativity of silicon. At the same time the empty d orbitals of silicon can easily participate in the bonding, so it is reasonable to suggest structure (b). Nevertheless the PE spectra of the compounds containing S—X—S group indicate a combination of the lone pairs of the two sulfurs; the splitting is much smaller for X = Si than for X = C due to

TABLE 4

UV MAXIMA AND INTENSITY OF SOME METHYLPHENYLSILANES

Band	PhC(CH3)3	PhSI	PhSI		PhSi(CH3)F2		PhSi(CH3)Cl2		PhSi(CH3)Br2		PhSi(CH3)(SCH2CH3)2	
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
α	266	2.07	270	2.10	270	2.66	272	2.58	273	2.52	272	2.44
	263	2.13	265	2.24	264	2.74	265	2.68	266	2.64	265	2.59
	257	2.20	258	2.26	258	2.60	259	2.56	260	2.55		
	251	2.14	252	2.23	253(sh)	2.39	254(sh)	2.37	255(sh)	2.39		
CT	—	—	—	—	—	—	—	—	—	—	238(sh)	3.24
p	208	3.98	211	4.00	211	3.83	216	3.88	218	3.73	216	3.91
β			185		191		192					

the larger distance, and for compound 5 the splitting can no longer be observed [2,11]. The ultraviolet maxima in the series $(Me)_{4-n}Si(SEt)_n$ are shifted only very slightly with increasing n, and at the same time the intensity increases considerably. Thus it can be concluded that the interaction between the sulfur atoms is small and that in the $n{-}\sigma^*$ transition the sulfur atoms participate independently. The same conclusion can be reached by comparing the spectra of compounds 6 and 8.

At the same time, the fact that for compound 1 the minimum at 217 nm can hardly be detected and that the monosulfides (with silicon or carbon) have markedly different spectra indicates the existence of some interaction between the sulfur atoms.

However the variation of the nature of the ring atoms and the UV maxima cannot be explained only in terms of the interaction between the sulfur atoms. In our opinion the differences among the spectra of compounds containing the different ring atoms are caused primarily by conformational factors. A full explanation can be given only when the exact geometry is known.

Aromatic compounds

The UV maxima of the compounds and the intensities of the absorption bands are summarized in Table 3.

The spectra reflect the aromatic structure. The α band with vibrational fine structure (between 260 and 270 nm) and the p band (between 216 and 223 nm) can readily be distinguished. For some compounds, the position of the β band can also be observed, and in other cases the position of the relevant maximum can be deduced from the shape of the spectrum.

The spectra of the linear, five- and six-membered ring compounds do not show characteristic differences. The spectra of mono- and di-phenyl compounds differ from each other, as expected, mainly in intensity, which is larger for the diphenyl derivatives. In addition a slight bathochromic shift is observed for the diphenyl derivatives compared with the monosubstituted compounds; the shift is 1 to 7 nm in the p band and somewhat smaller in the α band. This indicates a little conjugation between the phenyl groups through the silicon atom.

The spectra of compounds 19 and 20 indicates that an increase of the number of sulfur atoms causes an increase in the intensity of the bands.

Table 4 gives a comparison of the ultraviolet maxima of some compounds with the general formula $C_6H_5Si(CH_3)X_2$ (X = CH_3, F, Cl, SC_2H_5) [15,16]. There is a bathochromic displacement for the silicon as compared with the analogous carbon compounds. This is caused by the inductive effect of the silicon and by $(d{-}p)\pi$ bonding between the silicon atom and the phenyl group. The change of the spectra on variation of substituent X can be explained by the change in the inductive effect of X; in addition the lone electron pair of X can enter in a conjugative interaction of variable importance with the silicon [16]. On the basis of the data in Table 4 it is evident that the effect of SC_2H_5 groups is nearly the same as that of chlorine.

The spectra differ from those of benzene derivatives bearing weakly interacting substituents in that the minimum between the α and p band disappears, thus a monotonic increase of the extinction coefficient is observed towards the

TABLE 5

UV MAXIMA AND INTENSITIES OF SOME SULFUR-CONTAINING AROMATIC COMPOUNDS

Band	PhSCH$_2$CH$_3$		PhCH$_2$SCH$_2$CH$_3$		Ph(CH$_2$)$_2$SCH$_2$CH$_3$		PhSi(CH$_3$)(SCH$_2$CH$_3$)$_2$	
	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
α	270(sh)	3.40	265	2.40	268	2.15	272	2.44
			260(sh)	2.58	265	2.25	265	2.59
					259	2.35		
					253	2.28		
					248	2.22		
CT	256	3.90	240	3.90	—	—	238(sh)	3.24
p	210				212	3.95	216(sh)	3.91

shorter wavelengths. Since the intensity of n—σ^* transitions expected in this region is much smaller, these cannot be responsible for the disappearance of the minimum. Thus the formation of a new band in the range of 230 to 250 nm seems to be a reasonable assumption, and this is supported by the appearance of a shoulder in the spectra. Table 5 gives an explanation for the formation of this band. The data for the carbon derivatives in Table 5 were taken from the paper by Fehnel and Carmack [17].

For C$_6$H$_5$SC$_2$H$_5$ a very intense band is observed at 256 nm, which can be attributed to charge transfer (CT) interaction of the lone electron pair of sulfur with the phenyl group. The α band appears in the spectrum only as an inflexion at 270 nm. If the aromatic ring is isolated from the sulfur atom, the intensity of the CT bands will gradually decrease and the usual aromatic spectrum will develop. It can be seen that one carbon atom is not enough to isolate the aromatic ring, but the intensity of the CT band diminishes and the α band begins to appear. With two carbon atoms the CT band is no longer observed, and the fine structure of the α band can be distinguished. The isolating effect of a silicon atom is roughly equivalent to that of carbon. While the distance between the aromatic ring and the sulfur atom is larger in the presence of a silicon atom at the same time the size of the lone pair of the sulfur is increased [18] because of the smaller electronegativity of silicon and so the extent of CT interaction remains unchanged.

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