Journal of Organometallic Chemistry, 339 (1988) 41–49
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Contributions to the chemistry of silicon–sulphur compounds

XLV *. σ-Bond conjugation in silicon–sulphur catenates

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(Received March 23rd, 1987)

Abstract

The electronic spectra of some polysilanes and their CT complexes with TCNE have been determined for the series: α,ω-$(RO)_3SiS(SiMe_2)_nSSi(OR)_3$ ($n = 2, 3, 4, 6$) and α-$(RO)_3SiS(SiMe_2)_nMe$ ($n = 2, 4$; R = i-Pr, t-Bu). Additional data for some related compounds are also presented. The results are discussed in terms of σ-silicon–silicon and σ-silicon–sulphur bond conjugation.

Introduction

We previously determined the degree of σ-bond delocalization in alkanes and polysilanes [1]. The results did not show whether for such σ-bond delocalization all the atoms in the chain must be the same or could also operate for polysilane chains interrupted by heteroatoms.

The present work was directed towards determining the degree of σ-bond delocalization when some $SiMe_2$ groups in permethylpolysilanes are replaced by the isoelectronic divalent sulphur atoms. Deviations from normal UV-spectral properties in case of 1- and 2-thio derivatives of heptamethyltrisilane were reported by Pitt [2]. Furthermore, it was previously found that a decamethylpentasilane ring expanded by sulphur insertion [3] shows UV absorption maxima similar to those of cyclo-$(SiMe_2)_6$ but with almost double the extinction coefficient.

Up to now no data on charge-transfer complexes of silicon–sulphur compounds with tetracyanoethylene TCNE have been available.

The recently synthesized trialkoxysilylthio derivatives of permethylpolysilanes [4] provide suitable models for studying the electronic structures of silicon–sulphur catenates in ground and excited states which can be directly related to the simple

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* For part XLIV see ref. 4.

0022-328X/88/$03.50

molecular orbital theory for silicon–sulphur backbone chains at the modified Sandorfy "C" level [1].

Results and discussion

1. The ionization potentials and bond delocalization

Although charge-transfer interactions between permethylpolysilanes and TCNE are weak, well-defined charge-transfer spectra were observed [5,6]. A remarkably good linear relationship between charge-transfer frequencies and ionization potentials of polysilanes was obtained (eq. 1) [6].

$$\nu_{CT}\ (\text{eV}) = 0.771\ IP - 3.716 \qquad (r = 0.999) \tag{1}$$

The CT absorption data obtained for complexes of trialkoxysilylthio derivatives of permethylpolysilanes with TCNE are listed in Table 1. For comparison, data for permethylpolysilanes and some other silicon–sulphur compounds are also given. The spectra mostly show two bands, the first between 16460 and 17360 cm^{-1} and the second between 20620 and 22000 cm^{-1}.

To aid in the interpretation of the data, calculations for the silicon–sulphur backbone chain have been performed at Sandorfy "C" level, as described in ref. 1. For compounds with only one Si–S bond (e.g. compounds **17** and **18**, Tab. 1) the calculations indicate that the HOMO is the non-bonding orbital of the sulphur lone pair (Fig. 1A) and its energy (one β unit) does not depend on the constitution of the compounds.

In considering the origin of this independence we took into consideration the bonding situation in two fragments of the linear silicon–sulphur backbone chain

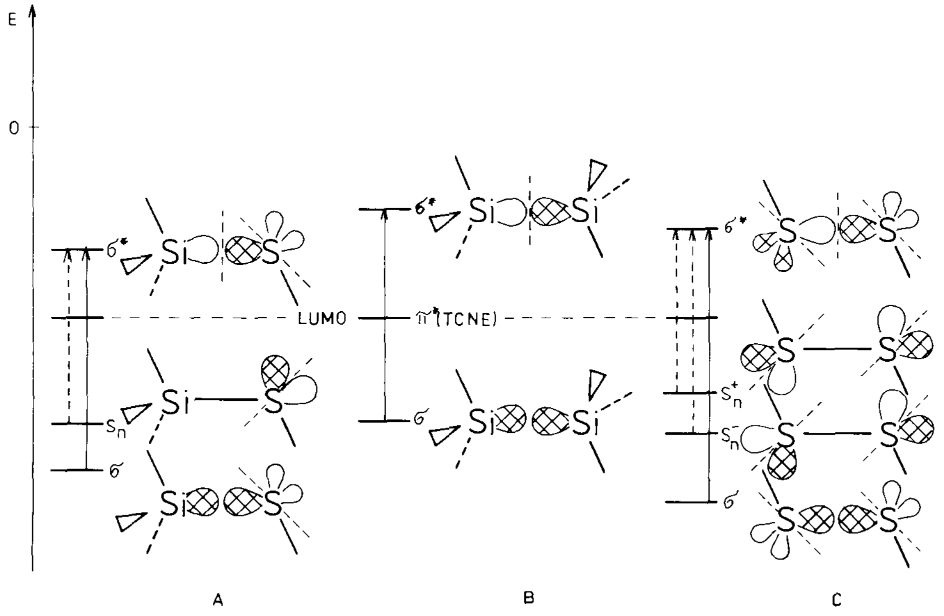

Fig. 1. Transition energy diagrams: A. for Si–S, B. for Si–Si and C. for S–S diatomic backbone chains.

Table 1

VIS absorption data for charge-transfer complexes with TCNE and UV absorption data for trialkoxysilylthio-derivatives of permethylpolysilanes, permethylpolysilanes, and related compounds

No	Compound	CT			UV	
		$\nu_{CT}(cm^{-1})$		IP (eV)	$\nu(cm^{-1})$	ϵ
1	$(t\text{-}BuO)_3SiS(SiMe_2)_2Me$	– [a]		–	49000 [b]	7450
		21240	σ	8.23		
2	$(t\text{-}BuO)_3SiS(SiMe_2)_2SSi(OBu\text{-}t)_3$	17360	S_n	7.82	49000 [b]	10800
		21160	σ	8.22		
3	$(i\text{-}PrO)_3SiS(SiMe_2)_4Me$	– [a]		–	48600	16500
		20620	σ	8.14	41950	16400
4	$(t\text{-}BuO)_3SiS(SiMe_2)_4Me$				49000	18900
					42000	17600
5	$(i-PrO)_3SiS(SiMe_2)_3SSi(OPr\text{-}i)_3$	– [a]		–	49200	9570
		20860	σ	8.18	44000	10400
6	$(t\text{-}BuO)_3SiS(SiMe_2)_3SSi(OBu\text{-}t)_3$	– [a]		–	49530	29800
		20980	σ	8.19	45750	34400
7	$(t\text{-}BuO)_3SiS(SiMe_2)_4SSi(OBu\text{-}t)_3$	16560	S_n	7.6	49120	18700
		– [a]		–	41260	20000
8	$(t\text{-}BuO)_3SiS(SiMe_2)_6SSi(OBu\text{-}t)_3$				49480 [b]	30900
					43840	weak
					37780	28400
9	$Me(SiMe_2)_2Me$	24000 [c]	σ	8.64	50700–	8500–
					50100 [d]	7230
10	$Me(SiMe_2)_3Me$	21000 [c]	σ	8.19	46500 [d]	9020
11	$Me(SiMe_2)_4Me$	19600 [c]	σ	7.98	42500 [d]	14700
12	$Me(SiMe_2)_5Me$ [d]				40000	18400
13	$Me(SiMe_2)_6Me$ [d]				45450	14000
					38500	21100
14	$Me(SiMe_2)_7Me$ [d]				42920	14000
					37520	23000
15	$Me(SiMe_2)_8Me$ [d]				46500	29000
					41580	18000
					36700	38000
16	$Me(SiMe_2)_{10}Me$ [d]				46500	28200
					43480	21000
					39210	24600
					35840	42700
17	$(i\text{-}PrO)_3SiSH$ [e]	16460	S_n	7.57	48700 [b]	611
		21000	σ	8.19		
18	$(t\text{-}BuO)_3SiSH$ [e]	16690	S_n	7.64	48640 [b]	205
		22000	σ	8.35		
19	$[(t\text{-}BuO)_3SiS]_2$ [f]	17460	S_n	7.84		
		– [a]		–		
20	H_3SiSH		S_n	9.97 [g]		
			σ	11.75 [g]		
21	H_3SiSMe		S_n	9.10 [h]		
			σ	10.85 [h]		
22	Me_3SiSMe		S_n	8.69 [i]	48900 [j]	3020
			σ	10.10 [i]	44540 [j]	141
23	$H_3SiSSiH_3$		S_n	9.59 [h], 9.70 [g]		
			σ	10.98 [h], 11.15 [g]		

Table 1

No	Compound	CT		UV	
		$\nu_{CT}(cm^{-1})$	IP (eV)	$\nu(cm^{-1})$	ϵ
24	$Me_3SiSSiMe_3$	S_n	8.74 [i]	49380 [k], 49380 [j]	3360 [k], 2880 [j]
		σ	9.74 [i]	42800 [i] 37000 [k]	weak weak
25	$(t\text{-}BuO)_3SiSSiMe_3$ [l]			49640 [k] 44560 [k] 36570 [k]	1050 weak weak

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[a] Not observable from the spectrum. [b] Asymmetric band. [c] Values from ref. 7. [d] Values from ref. 8. [e] For preparation see ref. 9. [f] For preparation see ref. 10. [g] Values from ref. 11. [h] Values from ref. 12. [i] Values from ref. 13. [j] Values from ref. 14. [k] W. Wojnowski and W. Bocheńska, unpublished results. [l] For preparation see ref. 15.

(Fig. 2), (a) the $SiMe_2$ group with local T_d symmetry (Fig. 2A), and (b) the sulphur atom with local pseudo "T_d" symmetry (Fig. 2B).

Four valence atomic orbitals of each atom (s,p_x,p_y,p_z) can be described as a linear combination of the four degenerate sp^3 hybridized atomic orbitals. Simple transformations by matrix algebra yields the equivalent set of atomic orbitals shown in Fig. 3.

The (t_2) orbitals ϕ_2, ϕ_3, and ϕ_4 are degenerate, and so any linear combination of them can be used as the equivalent wave function. We thus consider two new orbitals which are linear combinations of ϕ_2 and ϕ_3 (Fig. 4). Because only the nearest-neighbour interactions are considered by Sandorfy "C" model, it can be seen from Fig. 4 that the $(1/\sqrt{2})(\phi_2+\phi_3)$ combination cannot be mixed with orbitals of neighbouring silicon atoms (Fig. 2) and has constant energy (1β unit).

In the case of $SiMe_2$ this orbital is strongly lowered in energy by interaction with carbon atoms of methyl groups. For the sulphur atom the appropriate orbital has

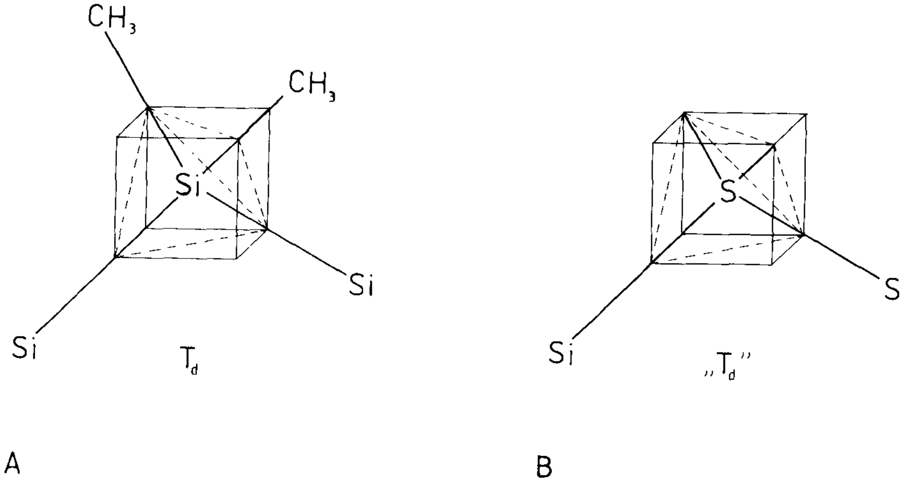

Fig. 2. Local symmetry of bonding orbitals: A. for $SiMe_2$ and B. for S in linear silicon–sulphur chain.

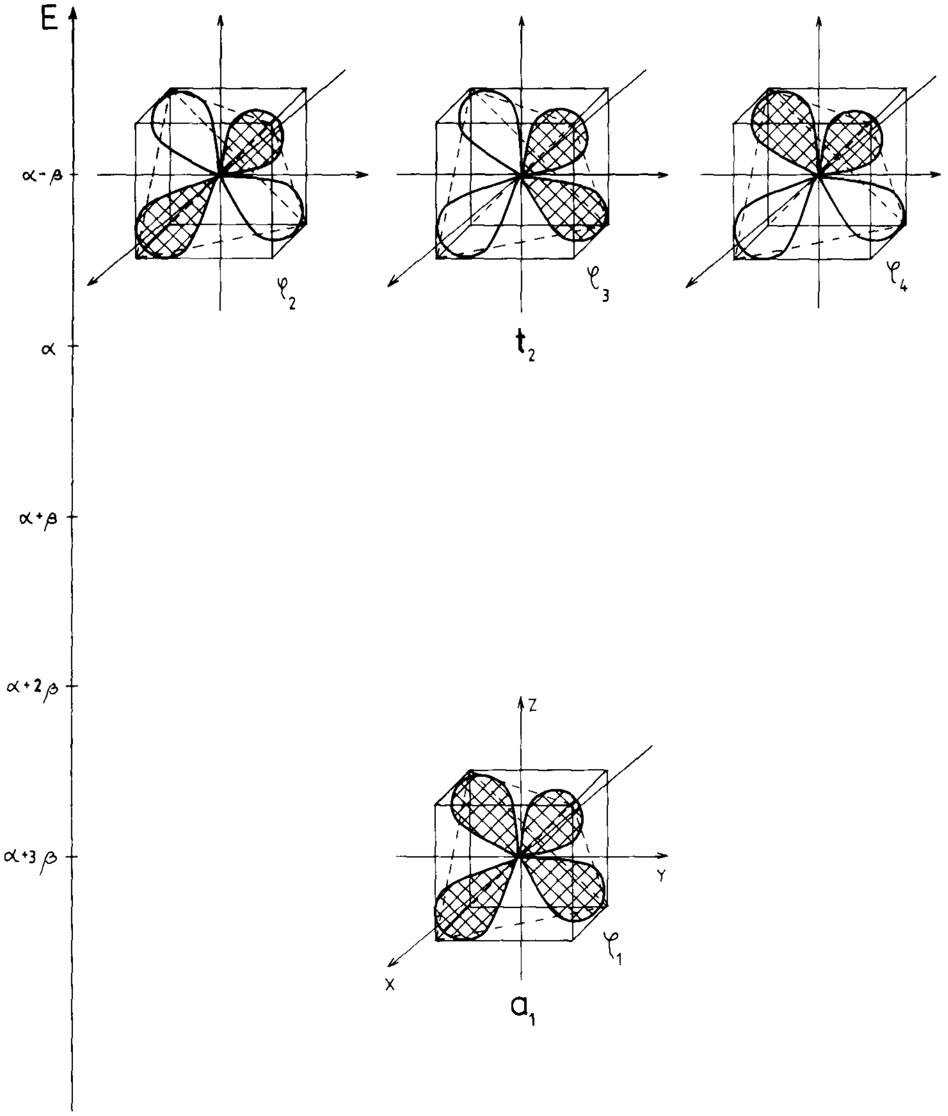

Fig. 3. Valence set of Sandorfy "C" atomic orbitals of Si or S which are equivalent to standard s, p_x, p_y, and p_z atomic orbitals.

constant energy, and since other sulphur orbitals are lowered by bonding interactions with other silicon atoms, the $(1/\sqrt{2})(\phi_2 + \phi_3)$ orbital is predicted to be the HOMO of the sulphur lone pair. Thus the first band observed in charge-transfer spectra is assigned to the $S_n \rightarrow$ TCNE transition, and the second to the $\sigma \rightarrow$ TCNE transition. This interpretation is in agreement with assignments from PES data; see data for compounds **20**, **21**, and **22**, Tab. 1.

The first ionization potentials IP(S_n) given in Tab. 1 were calculated for CT complexes (see Fig. 5A) by use of eq. 2 [16].

$$\nu_{CT} = 3690\, IP - 11941 \qquad (SE\ 42\ \mathrm{cm}^{-1}) \qquad (2)$$

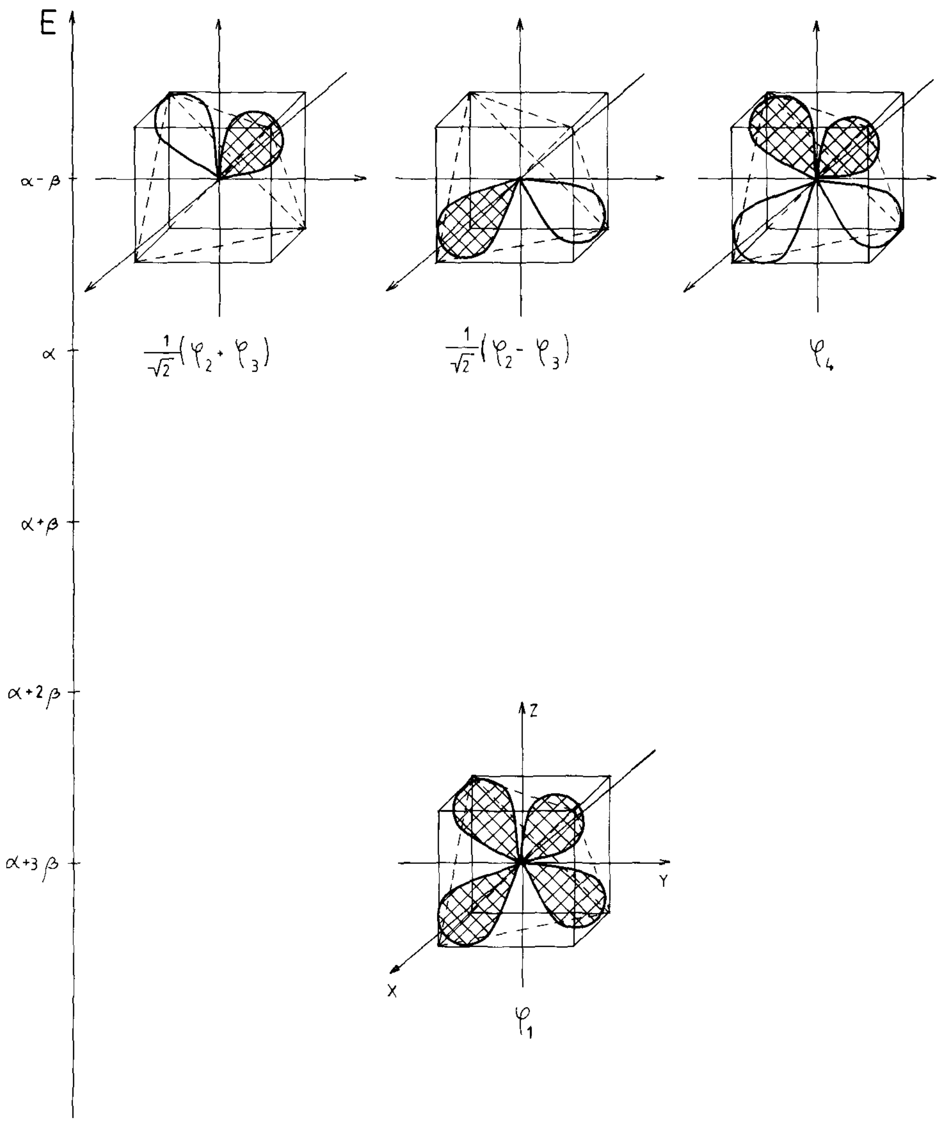

Fig. 4. Diagrammatic illustration showing that the $1/\sqrt{2}(\phi_2 + \phi_3)$ combination cannot be used as bonding orbital in a linear silicon–sulphur chain.

The IP's for σ electrons were calculated from eq. 1 for the CT complexes (see Fig. 5B).

The substitution of hydrogen (compounds **20**, **21**, and **23**) for more electronegative methyl group (compounds **22** and **24**) or alkoxy groups (compounds **17** and **18**) lowers the *IP*'s of the sulphur lone pair and of the σ electrons. The very low *IP* value ($\approx$ 7.6 eV) for the non-bonding lone pair of sulphur is noteworthy.

The energy of the highest bonding σ orbitals in trialkoxysilylthio derivatives of permethylpolysilanes increases with the Si–S chain length (see compounds **17** and **3** for i-propoxy derivatives and compound **18**, **1**, **2**, and **6** for t-butoxy derivatives);

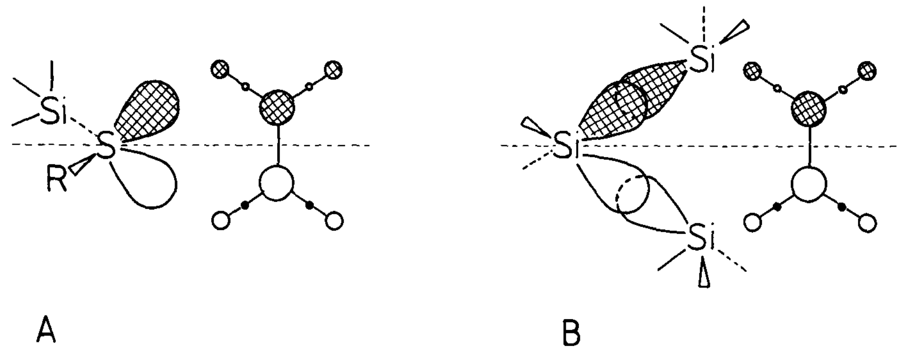

Fig. 5. The postulated geometry of the CT complexes with TCNE: (A) for the $S_n \rightarrow \pi^\star$TCNE transition; (B) for the $\sigma \rightarrow \pi^\star$TCNE transition.

this trend is in qualitative agreement with the results of our Sandorfy "C" calculations and confirms the importance of bond conjugation in ground states of silicon–sulphur chains.

2. *The ultraviolet spectra and bond delocalization*

The ultraviolet absorption data for the trialkoxysilylthio derivatives of permethylpolysilanes are listed in Tab. 1, and compared with those for permethylpolysilanes and other silicon–sulphur compounds.

The results of the Sandorfy "C" calculations suggest that $S_n \rightarrow \sigma^\star$ transitions are forbidden (zero transition moment by symmetry) and should not be observable. Only one or two bands are observed (Fig. 1) for compounds with only one Si–S bond (compounds **17**, **18**, and **22**, Tab. 1). The high intensity $\sigma \rightarrow \sigma^\star$ transition lies in the higher energy range, and the $S_n \rightarrow \sigma^\star$ transition is of very low intensity and lies in the lower energy range of the spectrum; e.g. for $(i\text{-PrO})_3SiSH$ and $(t\text{-BuO})_3SiSH$ (compounds **17** and **18**, Tab. 1) there is a single intense asymmetric band at 48700 cm^{-1}; for Me_3SiSMe there is one intense band at 48900 and a weak one at 44540 cm^{-1} [14].

For compounds with an Si–Si–Si chain (compounds **24** and **25**) our calculations are in accord with the experimental data (Tab. 1) suggesting the occurrence of three absorption bands, two in the lower energy range for the $S_n \rightarrow \sigma^\star$ transition and an intense band in the higher energy range for the two $\sigma \rightarrow \sigma^\star$ transitions (Fig. 6). The increase in the energy of the highest bonding σ orbitals (see section 1 above) with increasing chain length is accompanied by a decrease in the $\sigma^\star$ LUMO's. Furthermore the number of σ and $\sigma^\star$ orbitals of comparable energy increases with the increasing length of the silicon–sulphur chain. These features explain the observed red shift of the first electronic transitions with increasing silicon–sulphur chain length (compounds **1** and **4** for $(t\text{-BuO})_3SiS(SiMe_2)_nMe$ derivatives; compounds **2**, **6**, **7** and **8** for $\alpha,\omega\text{-}(t\text{-BuO})_3SiS(SiMe_2)_nSSi(OBu\text{-}t)_3$ series. Similar trends were observed for linear permethylpolysilanes [17] (see compounds 9–16 for comparison) *.

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* Quantitative evaluation of UV spectra requires the use of an SCF-Cl quantum chemical model.

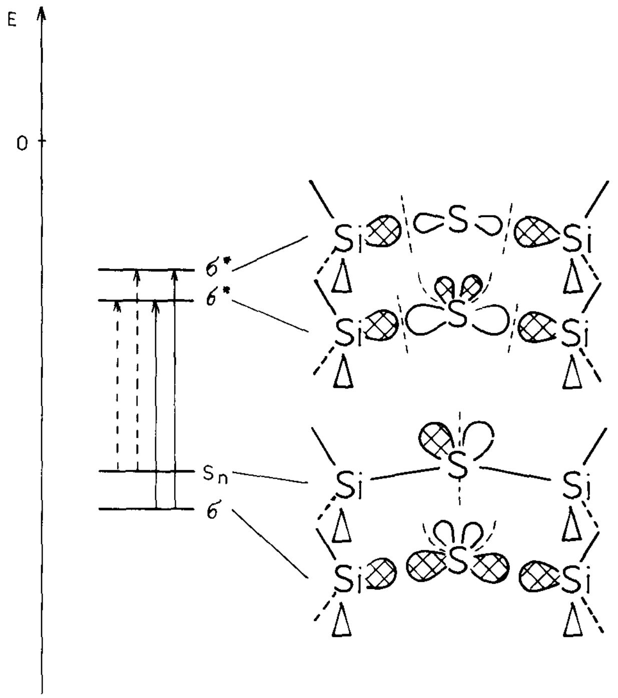

Fig. 6. Transition energy diagram for a Si–S–Si triatomic linkage.

The transition diagrams for Si–S, Si–Si and S–S chains shows considerable similarity (Fig. 1). In the case of disilanes the calculated transition energy ($\Delta E = 2.28\beta$) is a little higher than that for Si–S chains ($\Delta E = 2.23\beta$), in agreement with the experimental data (Tab. 1); e.g. the energy of the $\sigma \rightarrow \sigma^{\star}$ transition for $Me_3SiSiMe_3$ is a little higher than that for Me_3SiSMe. This similarity also applies to the UV spectra of Si–S–Si and Si–Si–Si backbone chains (compounds **24** and **10** for example) and the longer Si–S catenates Si–Si–Si–Si, Si–S–Si–Si (compounds **11** and **1**), etc. (Tab. 1).

Also noteworthy is the similarity between the UV spectra of longer heteroatomic silicon–sulphur chains and those of homoatomic polysilane chains (Tab. 1). Two absorption bands, not always well resolved, are seen beginning with six membered chains of silicon atoms (compound **13**) or of silicon–sulphur atoms (compounds **2**, **3**, and **4**). Three bands appear beginning with eight-membered chains, and four bands with ten. In all cases the first and the last bands are the most intense, and this seems to be a general phenomenon.

Overall the results show that in silicon–sulphur catenates there is considerable σ-bond conjugation in both the ground and excited states.

Experimental

The syntheses of the trialkoxysilylthio derivatives of permethylpolysilanes [4] and the crystal structures of compounds **2**, **6** and **8** (Tab. 1) have been described previously [18].

CT spectra were measured at room temperature on a Specord UV/VIS (Carl Zeiss Jena) spectrometer, 1 cm quartz cells containing 0.15–0.44 *M* solutions in $CHCl_3$ saturated with TCNE 0.015 *M* were used, as previously described [5]. The $CHCl_3$ solutions of all the compounds examined (Tab. 1) are colourless, and absorb only below 31250 cm^{-1}. The UV spectra of 10^{-5} *M* solutions in cyclohexane in 1 cm quartz cells were determined at room temperature with the same spectrometer.

Sandorfy "C" calculations were performed as described previously [1], with $k^{\mathrm{vic}} = 1.14$ for Si and 1.4 for S; $k^{\mathrm{gem}} = 1.00$ and 0.8; $h = 0.00$ and 1.8, respectively, and $k^{\mathrm{vic}}_{\mathrm{Si-S}} = 1.2$.

Acknowledgment

The authors are grateful to the Polish Academy of Sciences (CPBP 01.13.3.6) for financial support and to Professor H. Bock (University of Frankfurt, Germany) for suggesting determination of the CT spectra.

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