Organothiometallic Compounds. Part I. Infrared and Raman Spectra of some Di(alkylthio)mercury(II) Compounds

By **Paulo Biscarini** * and **Luciano Fusina**, Istituto di Chimica Fisica e Spettroscopia dell'Università, Viale Risorgimento 4, Bologna, Italy
Giandomenico Nivellini, Laboratorio di Spettroscopia Molecolare del C.N.R., Via Castagnoli 1, Bologna, Italy

I.r. and Raman spectra in the range 800—100 cm^{-1} of a series of di(alkylthio)mercury(II) compounds $Hg(SR)_2$ (I; R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, or Bu^t) have been recorded and discussed. The main fundamentals have been identified in the following ranges: ν(C–S), 575—725, ν(S–Hg–S), 200—338 in the solid and 209—371 cm^{-1} in solution. The spectral features agree with a linear S–Hg–S structure and with the characteristic two-co-ordination of mercury. Spectra of the solid (I; R = Bu^t) differ from those of the other compounds and are interpreted on the basis of a polymeric centrosymmetric structure. The spectral pattern of some of the compounds (I) suggest the existence in solution of more than one rotational isomer. The frequency ν(S–Hg–S) in the solid, related to the strength of the mercury–sulphur bond, decreases with increasing electron-releasing ability of the alkylthio-groups. However, a strictly linear correlation between ν(S–Hg–S) and the basicity of the alkyl radicals does not exist.

THE crystal structures of the compounds $Hg(SMe)_2$, $Hg(SEt)_2$, and $Hg(SBu^t)_2$ have been reported.[1,2] So far vibrational spectra of di(alkylthio)mercury(II) compounds have been scarcely studied. Only the Raman spectrum of bis(trifluoromethylthio)mercury(II), $Hg(SCF_3)_2$, has been investigated.[3] The nature of the mercury–sulphur bond is still uncertain. In complexes between organic sulphides and mercury(II) chloride [4,5] or halogenogold(I) [6] a very weak interaction does exist and excludes a synergic σ–π-bond. On the other hand a Hg=S bond has been suggested for mercury(II) thiocyanate, $Hg(SCN)_2$.[7,8] The aim of this work is to correlate the spectral behaviour of di(alkylthio)mercury(II) compounds with their crystal and molecular structure. Moreover, the assignment of ν(S–Hg–S) stretchings should give information on the nature of the metal–sulphur bond and clarify the influence of steric and electronic factors.

EXPERIMENTAL

Preparation.—The di(alkylthio)mercury(II) compounds, (I), were prepared as described [9,10] and crystallized after extraction with ethanol or ethanol–ethyl acetate in a Soxhlet apparatus. All the compounds gave correct analytical figures (see Table 1).

Molecular Weights.—These were determined osmotically in anhydrous pyridine, using a Mechrolab 302b vapour-pressure osmometer at 37 °C; concentrations, in the range 0·01—0·25M, were similar to those used for the i.r. and Raman spectra.† Benzil was used as the standard.

Spectra.—I.r. spectra were recorded on a Perkin-Elmer 180 spectrophotometer flushed with dry air. Spectra were recorded in the range 3 000—180 cm^{-1} in Nujol and hexachlorobuta-1,3-diene mulls, and between 450 and 180 cm^{-1} in pyridine (py) and carbon tetrachloride solution. Raman spectra were recorded with a Cary 81 spectrophotometer by using a 4 880 Å argon-ion laser line. Some samples decomposed under the laser beam and an intensity reduction was often necessary. The samples were observed as powders in capillary tubes in the range 3 000—100 cm^{-1} and in py solution between 450 and 100 cm^{-1}. Carbon tetrachloride could not be used in this region.

RESULTS AND DISCUSSION

Observed i.r. and Raman lines in the range 800—100 cm^{-1} for compounds (I) are listed in Table 2. The stretching modes ν(C–S) and ν(S–Hg–S) and skeletal bendings δ(C–C–C), δ(C–C–S), δ(C–S–Hg), and δ(S–Hg–S) occur in this range. Strong bands at 313 (i.r.) and 270 cm^{-1} (Raman) in spectra of mercury(II) thiocyanate have been assigned to S–Hg–S asymmetric and symmetric stretching respectively.[11] The Raman line at 243 cm^{-1} was assigned to the latter mode for (I; $R = CF_3$).[3] Raman lines at 297 cm^{-1} for Hg(OH)SCN, 239 cm^{-1} for $[Hg(SCN)_4]^{2-}$, and 238 cm^{-1} for solid Hg(Me)SCN were ascribed to the Hg–S stretching mode.[11] Skeletal bendings δ(S–Hg–S) at 85 cm^{-1} and δ(C–S–Hg) at 148 cm^{-1} were observed in the Raman spectrum of mercury(II) thiocyanate, and δ(C–S–Hg) at 188 cm^{-1} in that of methylmercury(II) thiocyanate.[11] In compounds (I) the bands observed in the region 575—725 cm^{-1} were assigned to C–S stretchings, while those in the region 290—470 cm^{-1} to C–C–C and C–C–S bendings, by direct comparison with spectra and assignments of the corresponding thiolates, sulphides, and disulphides.

The significant feature of the spectra of all compounds (I) (see Figure 1) is the lack of coincidence in the Hg–S stretching region for both solid state and solution. A band, located between 220 and 338 cm^{-1} in the i.r., and between 200 and 322 cm^{-1} in the Raman spectrum, assigned to S–Hg–S asymmetric and symmetric stretching modes respectively, was always observed in the solid. The corresponding bands in py and carbon tetrachloride solutions, were, in some cases, shifted to higher wavenumbers,

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† 1M = 1 mol dm^{-3}.

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TABLE 1

M.p.s, analyses, and molecular weights of compounds $Hg(SR)_2$, (I)

			Found (%)				Calc. (%)			
R	M.p. (θ_c/°C)	*M* *	C	H	S	Hg	C	H	S	Hg
Me	175—178 (decomp.)		8·4	1·95	21·25	67·65	8·15	2·05	21·75	68·05
Et	72—73	327·4 (322·85)	14·95	3·15	19·85	61·35	14·9	3·1	19·85	62·15
Pr^n	67—69	356·5 (350·9)	20·2	3·7	18·2	56·65	20·55	4·0	18·3	57·15
Pr^i	62—63	359·3 (350·9)	20·4	4·7	18·6	56·5	20·55	4·0	18·3	57·15
Bu^n	81—83	378·5 (378·95)	25·2	4·7	16·45	52·05	25·35	4·8	16·9	52·95
Bu^i	90—91	377·8 (378·95)	25·05	4·55	16·85	52·3	25·35	4·8	16·9	52·95
Bu^t	157—159	371·3 (378·95)	25·0	4·5	16·7	52·7	25·35	4·8	16·9	52·95

* Calculated values are given in parentheses.

TABLE 2

I.r. and Raman * bands (cm^{-1}) of the compounds $Hg(SR)_2$, (I)

R	ν(C–S)	δ(C–C–S)	δ(C–C–C)	ν(S–Hg–S) (asym.)	ν(S–Hg–S) (sym.)	δ(C–S–Hg)	CH_2 rock	Other bands
Me *a*	695s			338vs	298w			
	(695s)			(338w)	(298m)	(175w)		(105m)
b				355vs				294w
					(318vs, p)			
Et *a*	656m	406vs		268s			769m	
	(650s)	(395s)			(246s)	(150s)	(770vw)	
b		403s, 370vs		330s, 266m				
		(364m, p)			(304vs, p, 250s, p)			
c		401vs, 372vs		330vs, 264w				
Pr^n *a*	723m	334s	408vs, 392 (sh)	221m			739m	
	(725m)	(332s)	(412w, 395vs)		(200w)			(353vw)
b			435w	359vs, 220w				245w
		(375vw, p)	(434vw, p)		(329vs, p, 209w, p)			[295 (sh), p, 243w, p]
c		400w	438w	359vs				255w
Pr^i *a*	614s	388vs, 349w	438s	256m				
	(627, 617m)	(380m, 355vw)	(432w)		(232vs)	(138s)		
b		396vs, 343 (sh)	433vs	352m, 260m				
		(379m, p, 351vw, p)	(428vw, p)		(323m, p, 237vs, p)			[306 (sh), p]
c		393vs	433vs	345s, br, 263s				
Bu^n *a*	641w	345m, 322m	470w, 436vw, 407w	252vs			744w, 720m	
	(645w)	(351m, 324m)	(473vw, 437vw, 410w)		(218vs)		(745vw, 720m)	
b		377 (sh)		361vs				
		[338 (sh), p]			(325vs, p)			(267vw, p)
c		378 (sh), 345 (sh)	418w	358vs				
Bu^i *a*	724, 718m	345m	429w, 408m	277vs	248 (sh)		809 (sh), 804m	
	(724, 718m)	(348m)	(432w, 408w)	(287m)	(250vs)	(127s)	[810 (sh), 805m]	[210m, 150 (sh)]
b		338 (sh)	430w	366vs, 260vw				224w
		[339 (sh), p]	(428vw, p)		(323vs, p, 244vw, p)			(220vw, p)
c		334w	432w, 416w	371vs, 270w				240w
Bu^t *a*	575vs	322s, 291vw	417, 411w, 378s	337vs				
	(580w)	(321m, 290vw)	(410w, 381m)	(335vw)	(185vs)			
b		358m	435vs, 391m	246s				
		(351m, p)	(429w, p, 382m, p)		(223vs, p)			
c		360m	442vs, 393s	274vs	250m			

* Values in brackets are Raman data. p = Polarized, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, and br = broad.

[a] Solid. [b] In py. [c] In carbon tetrachloride.

260—371 and 209—329 cm^{-1} respectively. Some compounds exhibited a greater number of bands in solution than in the solid. Spectra of the solid compound (I; R = Bu^t) were completely different from those in solution, suggesting a drastic modification of the structure in the two phases.

Spectral behaviour in the range 3 000—800 cm^{-1} for compounds (I) was similar to that of the corresponding thiolates. It appears that vibrations involving the alkyl chains are not substantially influenced by attack of mercury on the sulphur atom.

The crystal structure of compound (I; R = Me) [see Figure 2(*a*)] consists of rows of mercury atoms, at a distance of 3·90 Å, linked by bridging sulphur atoms (Hg–S

2·36 Å), with collinear bonds (S–Hg–S 180 ± 2·5°).[1a] Three other sulphur atoms, at a distance of 3·26 Å from mercury, roughly the sum of the van der Waals radii of mercury and sulphur (3·35 Å), two of which are coplanar with the S–Hg–S group and the third normal to this plane, can be considered to belong to the co-ordination sphere of mercury. The HgS_5 group has an irregular tetragonal-pyramidal structure, and belongs to symmetry point group C_{2v}. Thus all the vibrations should be active in the Raman spectrum. The presence of a strong i.r. absorption at 338 cm^{-1}, with no corresponding Raman line, excludes this. One can conclude that the spectral behaviour of compound (I; R = Me) is not substantially influenced by sulphur atoms not covalently bonded to mercury. By supposing that vibrational coupling between the molecules is small, the planar C–S–Hg–S–C skeleton belongs to symmetry point group C_{2h} and nine fundamentals are expected: 3 A_g(Raman) [sym.: ν(S–Hg–S), ν(C–S), and δ(C–S–Hg)]; 2 A_u (i.r.) [δ′(S–Hg–S) and δ′(C–S–Hg)]; 4 B_u(i.r.) [asym.: ν(S–Hg–S), ν(C–S), δ(C–S–Hg), and δ(S–Hg–S)]. The two intense bands, 298 (Raman) and 338 cm^{-1} (i.r.) were assigned to symmetric and asymmetric stretching of the S–Hg–S group. The presence of two corresponding weak bands, 298 (i.r.) and 338 cm^{-1} (Raman), is probably due to crystal-field effects, as indicated by correlation between the factor, site, and point group together with the selection rules (see Table 3). The spectra in py solution support this interpretation: below 450 cm^{-1} there was in fact only one i.r. band at 355 cm^{-1} and only one Raman line at 318 cm^{-1}. This suggests that in solution also the molecule maintains a centre of symmetry with a linear S–Hg–S group. The wavenumber values, slightly higher in solution than in the solid, could be due to weak intermolecular forces present in the crystal which affect the co-ordination of the mercury atom.

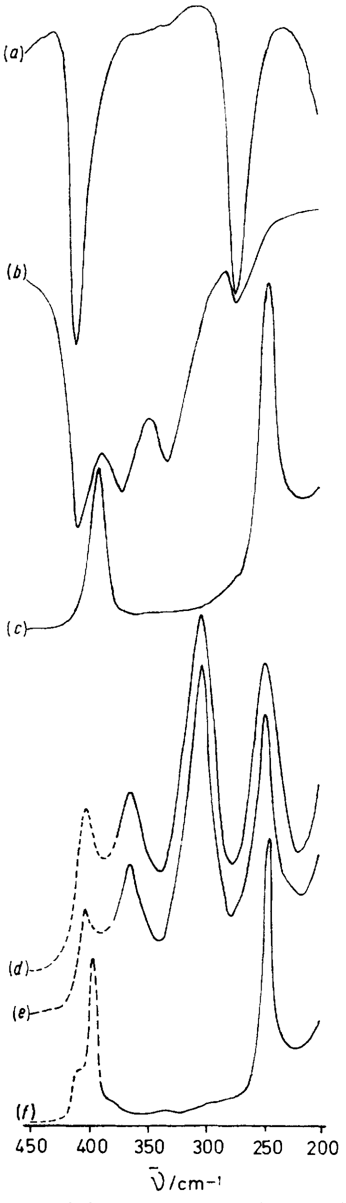
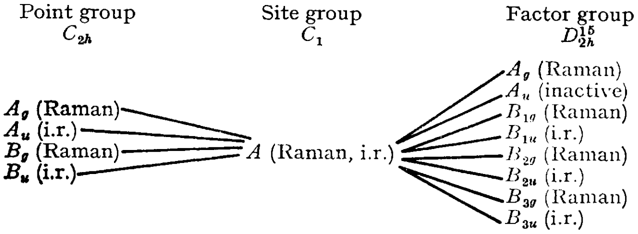


FIGURE 1 Spectra of the compound $Hg(SEt)_2$: i.r. in Nujol (*a*), in py solution (*b*), Raman solid (*c*), in py solution at +20 °C (*d*), at −20 °C (*e*), and frozen at −140 °C (*f*)

TABLE 3

Correlation between the factor, site, and point group and the selection rules for the $Hg(SMe)_2$ crystal



The i.r.- and Raman-active band at 695 cm^{-1}, a wavenumber very similar to that of the corresponding thiolate, was assigned to C–S stretching. As expected, it appears that vibration of the two C–S groups cannot couple because of the presence of the bulk mercury atom interposed and of their relative distance. The Raman line at 175 cm^{-1} was assigned to skeletal bending δ(C–S–Hg), while that at 105 cm^{-1} is probably due to lattice vibration.

The crystal structure of compound (I; R = Et) consists of molecules with two collinear Hg–S bonds (2·54 Å)[1b] [see Figure 2(*b*)]. If we consider four more sulphur atoms, Hg–S 3·54 Å, lying in a plane perpendicular to the molecular axis S–Hg–S, a distorted-octahedral structure is formed around mercury. However, these Hg–S distances, higher than the sum of the van der Waals radii of mercury and sulphur, suggest very weak intermolecular forces and that the molecules vibrate independently. Spectral features in the solid confirmed this situation and are interpreted, as those of (I; R = Me), on the basis of a centrosymmetric structure. The strong i.r. band at 268 cm^{-1} and the Raman one at 246 cm^{-1} were assigned to asymmetric and symmetric S–Hg–S stretching modes.

The i.r. spectrum in py showed two bands (403 and 266 cm^{-1}) at wavenumbers near to those in the solid, and two intense bands at 370 and 330 cm^{-1}. In the Raman spectrum an intense line at 250 cm^{-1}, as in the solid, and two other lines at 364 and 304 cm^{-1} were present. It was not possible to scan for lines near 400 cm^{-1} because of the existence in this range of a strong band of the solvent (404 cm^{-1}). The presence of new bands in the spectra in solution cannot be ascribed either to formation of a complex between (I; R = Et) and py, since the i.r. spectral pattern in carbon tetrachloride was very similar, or to dimer formation. In fact the monomeric nature of (I; R = Et) in solution was established by molecular-weight measurements (see Table 1). A plausible explanation can be found by assuming that two different rotational isomers of (I; R = Et) exist. Isomer (A) has the same structure as in the crystal and to its vibrations were assigned the i.r. bands at 403 [δ(C–C–C)] and 266 cm^{-1} [ν(S–Hg–S) (asym.)] and the Raman line at 250 cm^{-1} [ν(S–Hg–S) (sym.)]. The i.r. bands at 370 [δ(C–C–S)] and 330 cm^{-1} [ν(S–Hg–S) (asym.)] and the Raman line at 304 cm^{-1} [ν(S–Hg–S) (sym.)] were assigned to isomer (B). This results from isomer (A) by rotation of the ethyl groups about the S–C bonds, and seems to maintain a centre of symmetry on the mercury atom. The raising of the stretching wavenumbers ν(S–Hg–S) in this isomer could be due to an arrangement of the alkyl groups which causes a field effect on the charge distribution of the S–Hg–S group. The relative intensity of the 250 and 304 cm^{-1} Raman lines of the two isomers was not substantially influenced by a temperature change in the range −20 to +120 °C (see Figure 1). At −140 °C the solidified solution exhibited only the 250 cm^{-1} line, as in the solid, which corresponds to ν(S–Hg–S) of isomer (A).

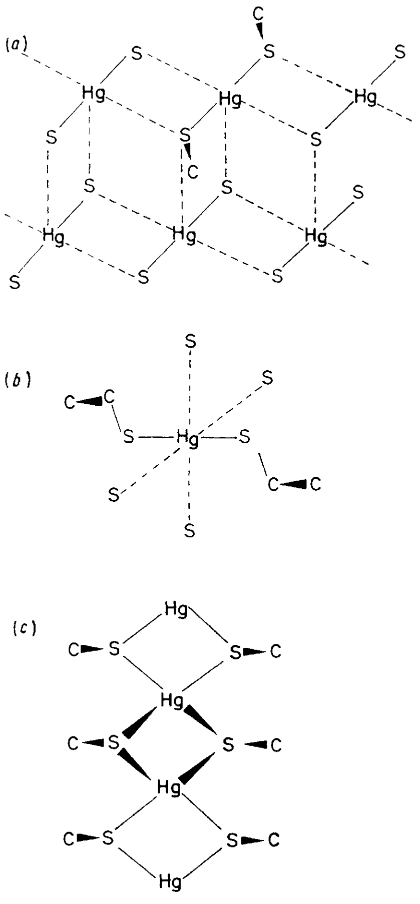


FIGURE 2 Structures of the compound Hg(SMe)$_2$ (*a*), Hg(SEt)$_2$ (*b*), and Hg(SBu^t)$_2$ (*c*)

The spectra in the solid of compounds (I; R = Pr^n, Pr^i, Bu^n, and Bu^i) were similar to those of the methyl and ethyl derivatives and were interpreted on the basis of crystal structures essentially molecular in type with centrosymmetric molecules vibrating independently. The i.r. and Raman activity of S–Hg–S stretching modes for compound (I; R = Bu^i) could be due to a crystal-field effect and/or to a departure from linearity.

The similar spectral patterns in py and carbon tetrachloride solutions exclude solvent co-ordination to the compounds. The existence of an inversion centre on the mercury atom was always suggested by the lack of coincidence in py between the i.r. and Raman S–Hg–S stretching frequencies. I.r. and Raman lines in the ranges 350—370 and 320—330 cm^{-1} for (I; R = Pr^n, Pr^i, Bu^n, or Bu^i) were assigned to asymmetric and symmetric S–Hg–S stretching modes respectively. These values were shifted to higher wavenumbers, *ca.* 100 cm^{-1}, with respect to the same vibrations in the solid. Since the corresponding shift for the compound (I; R = Me) is *ca.* 20 cm^{-1}, one cannot rationalize these shifts on the basis of a solvent effect. Molecular-weight measurements excluded the presence of dimers in solution also for these compounds (see Table 1). It is possible that in solution rotational isomers exist which are different from those in the solid; their structure may be similar to that of isomer (B) of (I; R = Et), since ν(S–Hg–S) falls in the same range. In the case of the compounds (I; R = Pr^n and Pr^i) another rotational isomer was present, similar to that in the solid [type (A)], with i.r. and Raman lines at 220, 260 and 209, 237 cm^{-1} respectively, assigned to S–Hg–S stretching modes.

The crystal structure of the compound (I; R = Bu^t) consists of rows of mercury atoms, at a distance of 3·76 Å, linked by bridging sulphur atoms to form polymeric chains [see Figure 2(*c*)].[2] Each mercury is surrounded by four sulphur atoms, Hg–S 2·59 and 2·66 Å, arranged in a distorted-tetrahedral configuration. Two lines at 337 cm^{-1} in the i.r. and 185 cm^{-1} in the Raman spectrum, assigned to $\mathrm{S}\begin{smallmatrix}\diagup\mathrm{Hg}\diagdown\\ \diagdown\mathrm{Hg}\diagup\end{smallmatrix}\mathrm{S}$ stretching modes, suggest the presence of a centre of symmetry which can be identified in the crystal not on the mercury atom, but on the centre of the (Bu^{t}S)$_2$Hg(Bu^{t}S)$_2$Hg(Bu^{t}S)$_2$ groups of the polymer. These groups belong in fact to symmetry point group C_i and the allowed fundamentals should be i.r.- or Raman-active. The large difference between these frequencies reflects the diversity between the structure of (I; R = Bu^t), where all the S–Hg bonds of the polymeric chain are involved in vibrational modes, and those of the other compounds, where the S–Hg–S groups vibrate independently. No coupling existed between the vibrations of the alkyl chains across the mercury atom: both i.r.- and

Raman-active bands at *ca.* 410, 380, 320, and 290 cm^{-1} were assigned to C–C–C and C–C–S bendings. The spectra of this compound in solution were very different from those in the solid and were similar to those of the other compounds (I). In addition to lines assigned to C–C–C and C–C–S bendings, a strong i.r. band at 246 cm^{-1} and a strong Raman line at 223 cm^{-1} were observed and assigned to asymmetric and symmetric S–Hg–S stretching modes. The phase change causes breaking of the intermolecular links, as evidenced by molecular-weight measurements (see Table 1), and restoration of centrosymmetric molecules with characteristic linear two-co-ordination on mercury.

The spectral behaviour of solid compounds (I) reflects the difference in the crystal structures of the R = Me, Et, and Bu^t derivatives and allows one to predict the structure of those compounds for which a complete *X*-ray analysis has not yet been carried out. A remarkable change in ν(S–Hg–S) was observed when going from a structure that is essentially molecular, and in which the mercury atom has the characteristic linear two-co-ordination, to polymeric structures, where mercury is tetrahedrally co-ordinated.

C–S *Frequencies.*—The stretching frequency of the C–S bond is sensitive to the type of alkyl group bonded to the sulphur atom. A plot of $\tilde{\nu}$(C–S) against Taft's σ^* parameters, which are a measure of the basicity of the alkyl groups,[12] shows [see Figure 3(*a*)] an approximately linear correlation [$R = 0{\cdot}75$ and rose to 0·99 if the values for (I; R = Pr^n and Bu^i), which show similar deviations in an analogous plot for thiolates, were excluded]. As expected, with increasing electron-donor power of the aliphatic groups, polarization of the C–S bond is favoured; thus the ν(C–S) frequencies decrease.

S–Hg–S *Frequencies.*—A plot of $\tilde{\nu}$(S–Hg–S) (asym.) in py solution against Taft's σ^* parameters of compounds with the type (A) conformation [see Figure 3(*b*)] showed a poor linear correlation ($R = 0{\cdot}76$, 85% level of significance). This suggests that in addition to the basicity of the ligands, other effects influence significantly the force constant of the Hg–S bond. The positive gradient is unexpected, since increasing the donor power of the alkylthio-group is expected to strengthen the mercury–sulphur bond. The observed trend could be due to a prevalent mass effect and/or to repulsion between the non-bonding electrons of sulphur and those of filled 5*d* orbitals of the mercury atom. This effect increases with the electronic charge on sulphur, which in turn depends on the electron-releasing ability of the alkyl group. If the Hg–S bond has partial double-bond character, due to back donation from filled 5*d* orbitals of mercury to empty 3*d* orbitals of sulphur, which adds to the σ-donor–π-acceptor bond between sulphur and the metal atom, the suggested electron repulsion reduces the synergic σ–π-bonding. This hypothesis is consistent with the fact that ν(S–Hg–S) frequencies are higher in type (B) than in (A) isomers. This difference could be due to interaction between the hydrogen atoms of the alkyl group and the electronic cloud of the sulphur and mercury atoms in the type (B) isomers. A rough calculation on the crystallographic data showed that Hg–H_β and S–H_β distances for isomer (B) of (I; R = Et) are below the sum of the van der Waals radii. The field effect $H_3C \cdots S$–Hg may be relevant and could determine lowering of the electron density on the sulphur and mercury atoms, which reduces repulsion and allows formation of a stronger metal–sulphur bond.

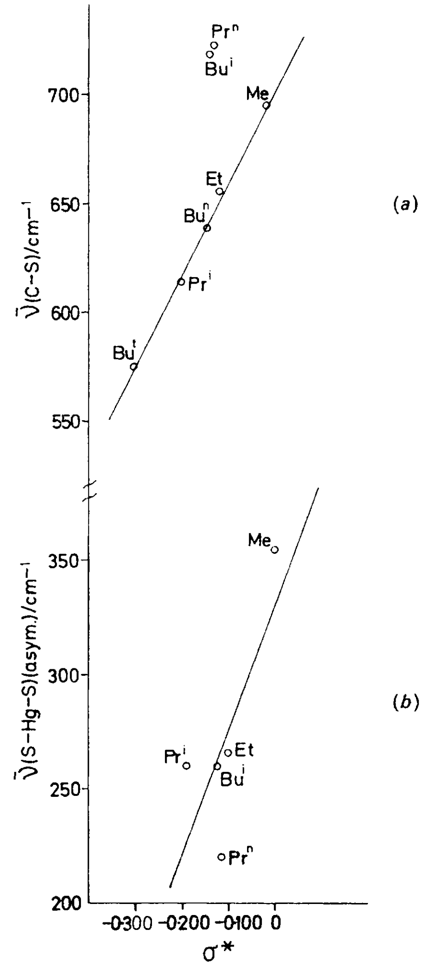


FIGURE 3 Plots of $\tilde{\nu}$(C–S) (*a*) and $\tilde{\nu}$(S–Hg–S) (asym.) in py solution (*b*), against Taft's σ^* for compounds (I)

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