The structures of hexaorgano-substituted triatomics $R^1_3M^1XM^2R^2_3$ and related species

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Abstract

Experimental molecular structure data, supported by calculations at the MNDO and EHMO levels of theory, are used to test and refine a structural model for compounds having hexaorgano-substituted molecules of general type $(R^1_3M^1XM^2R^2_3)^{x\pm}$. When X represents one of the first row elements carbon, nitrogen, or oxygen, linearity of the triatomic skeleton MXM′ occurs when $R^1_3M^1$ and/or $R^2_3M^2$ are electron donors: the electron donor capacity of a range of substituents R is assessed. A simple extension of this model to the oxo-bridged antimony(V) compounds of type $YSbR_3OSbR_3Y$ predicts that a linear SbOSb skeleton will be favoured in compounds where the terminal ligand Y is tightly bound, with a short Sb–Y distance.

Introduction

Since we first reported, a decade ago, the structures of hexaorgano-substituted species R_3MOMR_3 containing strictly linear MOM groups [1–6], the structures of a considerable number of analogous systems $(R_3MXMR_3)^{x\pm}$ have been reported, some containing linear, and some non-linear, MXM groups. Once it had become clear that such wide MOM angles could not be accommodated within any structural model based upon limiting $M \cdots M$ non-bonded contact distances [7], we developed a general model [8,9] for the skeletal structures of $(R_3MXMR_3)^{x\pm}$ species based upon the second-order Jahn–Teller effect. This model relates the bending of the linear MXM skeleton to the relative binding energies of the frontier orbitals of the atoms M (in R_3M) and X, and predicts linearity at X when R_3M is of low electronegativity relative to X. An earlier [10] model, based upon p_π–d_π interactions in the MX bonds, which predicted linearity of the MXM fragment when R_3M is an electron acceptor (rather than an electron donor [8,9]) has recently been re-examined and rejected [11], and thus it is timely to survey the results which have been published since our initial reports [1–6] and thus to re-assess the validity of the

various extant models [7–10] for the structures of hexaorgano-substituted triatomics $(R_3MXMR_3)^{x\pm}$.

Results and Discussion

Survey of the structural literature on hexaorgano-substituted triatomics $(R_3MXMR_3)^{x\pm}$ immediately discloses that by far the biggest sub-class containing MOM central fragments is that for which M represents silicon: furthermore the majority of molecular compounds having a linear MXM fragment likewise fall into this category. The species $R^1_3SiOSiR^2_3$ (where R^1 and R^2 may or may not be the same) will be discussed first, together with their group 14 congeners (M = Ge, Sn, Pb), followed by group 15 systems having M = P, As, Sb and X = O, N, C.

Group 14 systems

The known examples of hexaorgano-substituted $R^1_3SiOSiR^2_3$ species which contain linear SiOSi fragments [1,3,6,12–24] are summarised in Table 1, while analogous species containing non-linear SiOSi fragments [25–34] are listed in Table 2: other group 14 species [4,5,35–39] are listed in Table 3. The general model [8,9] for linear $(R_3MXMR_3)^{x\pm}$ predicted that linearity of MXM would result when R_3M was of low electronegativity relative to X; or, an alternative description, MXM is most likely to be linear when the substituent R acts as an electron source, and to be bent when R acts as an electron sink.

Certain substituents (Table 1) clearly have the ability to render SiOSi linear, regardless of environment. Thus when R = Ph, $Ph_3SiOSiPh_3$ contains a linear SiOSi group both in the pure unsolvated compound [1,3] and in solvates with both

Table 1

Hexaorgano-substituted triatomics $R^1_3SiOSiR^2_3$ containing linear SiOSi fragments

Molecule	$d(Si \cdots Si)$ (Å)	Reference
$Ph_3SiOSiPh_3$	3.232	1,3
$Ph_3SiOPh_3 \cdot 2(C_6H_6)$	3.238	12
	3.235 [a]	13
$Ph_3SiOSiPh_3 \cdot 2(HNC_5H_{10})$	3.232 [a]	13
$(PhCH_2)_3SiOSi(CH_2Ph)_3$	3.226	6
$(Me_3CO)_3SiOSi(OCMe_3)_3$	3.112	14
$(Me_3COO)_3SiOSi(OOCMe_3)_3$	3.180	15
$(CH_2=CH)_3SiOSi(CH=CH_2)_3$	3.228	16
$Ph_3SiOSi(CH=CH_2)_3$	3.198	17
$Ph_2(C_5H_{10}NCH_2CH_2)SiOSi(CH_2CH_2NC_5H_{10})Ph_2$	b	18
$N(CH_2CH_2CH_2)_3SiOSi(CH_2CH_2CH_2)_3N$	3.262	19
$(1\text{-}C_{10}H_7)(CH_2)_3SiOSi(CH_2)_3(1\text{-}C_{10}H_7)$	3.201	20
$[(Me_3Si)_3C]F_2SiOSiF_2[C(SiMe_3)_3]$	3.234	21
$(C_2B_{10}H_{11}CH_2)(Me_3SiO)_2SiOSi(OSiMe_3)_2(CH_2C_2B_{10}H_{11})$	3.192 [c]	22
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe]F(CH_3)SiOSi(CH_3)F[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$	3.206 [d]	23
$[Me_2(Me_3C)SiO](Pc)SiOSi(Pc)[OSi(CMe_3)Me_2]$	3.222 [e]	24

[a] At 150 K. [b] Datum not quoted [18]. [c] Central Si $\cdots$ Si distance: peripheral Si $\cdots$ Si distances are 3.152 Å and 3.154 Å with < (SiOSi) of 159.7° and 157.8° respectively [22]. [d] 3.223 Å at 120 K [23]. [e] Pc = phthalocyanine dianion: central Si $\cdots$ Si distance, peripheral Si are disordered.

Table 2

Hexaorgano-substituted triatomics $R_3^1SiOSiR_3^2$ containing non-linear SiOSi fragments

Molecule	Angle SiOSi (°)	d(Si $\cdots$ Si) (Å)	Reference
$Me_3SiOSiMe_3$	148.8	3.132	25
$(Me_3SiO)_3SiOSiMe_3$ [a]	143.9	3.078	26
	147.9	3.109	
$Ph_3SiOSi(CH_3)Ph_2$	158.9	3.190	27
$Ph_2(Me_3C)SiOSi(CMe_3)Ph_2$	152.6	3.178	28
$(PhCOC_6H_4)Me_2SiOSiMe_2(C_6H_4COPh)$	145.2	3.139	29
$Ph_2(HO)SiOSi(OH)Ph_2$ [b]	147.6	3.104	30
	156.8	3.168	
	161.9	3.180	
$(Me_2CH)_2(HO)SiOSi(OH)(CHMe_2)_2$ [c]	163.9	3.202	31
	164.4	3.212	
$[Me_2(O)SiOSi(O)Me_2]^{2-}$ [c,d]	144.2	3.149	32
	146.7	3.186	
$(Me_3C)_2(HO)SiOSi(Me)_2OSi(OH)(CMe_3)_2$	161.3	3.183	33
	162.6	3.194	
$Me_3SiOSi(Pc)OSiMe_3$ [e]	156.6	3.214	34
	157.9	3.225	

[a] Si(OSiMe$_3$)$_4$ of exact C_2 (2) symmetry, and approximate S_4 ($\overline{4}$) molecular symmetry [26]. [b] Three independent molecules in asymmetric unit. [c] Two independent molecules in asymmetric unit. [d] As disodium salt tetrahydrate [32]. [e] Pc = phthalocyanine dianion.

benzene [12,13] and piperidine [13]: the vinyl substituent is another such, as linear SiOSi fragments are found both in the homosubstituted $(CH_2=CH)_3Si-OSi(CH=CH_2)_3$ [16] and in the mixed derivative $(CH_2=CH)_3SiOSiPh_3$ [17]. On the other hand methyl substituents clearly render negative the SiOSi bending force constant at linearity [8,9], to yield a bent SiOSi equilibrium structure in $Me_3SiOSi-$

Table 3

Other group 14 hexaorgano-substituted species $R_3^1M^1OM^2R_3^2$

Molecule	Angle M^1OM^2 (°)	$d(M^1 \cdots M^2)$ (Å)	Reference
(a) Linear M^1OM^2			
$(PhCH_2)_3GeOGe(CH_2Ph)_3$		3.460	5
$(PhCH_2)_3SnOSn(CH_2Ph)_3$		3.483	4
(b) Non-linear M^1OM^2			
$Ph_3SiOGePh_3$ [a]	142.5	3.240	35
$Ph_3SiOSnPh_3$ [a]	144.2	3.483	35
$Ph_3SiOPbPh_3$	142	3.669	36
$Ph_3GeOGePh_3$	135.2	3.267	37
$[\eta^5-C_5H_5(CO)_2Fe]Me_2GeOGeMe_2-$			
$[Fe(CO)_2(\eta^5-C_5H_5)]$	133.9	3.286	38
	142.2	3.25	
$Ph_3GeOSnPh_3$ [a]	134.9	3.438	35
$Ph_3SnOSnPh_3$	137.3	3.642	39

[a] M^1, M^2 disordered [35].

Me$_3$ [25]: even a single methyl substituent instead of phenyl, as in Ph$_3$SiOSiMePh$_2$ [27] is sufficient to provide a non-linear SiOSi fragment: the t-butyl substituent as in Ph$_2$(Me$_3$C)SiO(CMe$_3$)Ph$_2$ is similar in its effect [28], although the benzyl substituent, in contrast, is capable of rendering MOM fragments linear as in (PhCH$_2$)$_3$SiOSi(CH$_2$Ph)$_3$ [6] and even in (PhCH$_2$)$_3$GeOGe(CH$_2$Ph)$_3$ and (PhCH$_2$)$_3$SnOSn(CH$_2$Ph)$_3$ [4,5] (see below, and Table 3).

Excellent support for the model [8,9] is provided by the observation of linear SiOSi fragments in the presence of the unambiguously electron donating substituents Me$_3$CO [14] and Me$_3$COO [15], although in view of the skeletal non-linearity in Ph$_2$(Me$_3$C)SiOSi(CMe$_3$)Ph$_2$ [28], it is perhaps a little surprising to find a linear SiOSi fragment in Ph$_2$(C$_5$H$_{10}$NCH$_2$CH$_2$)SiOSi(CH$_2$CH$_2$NC$_5$H$_{10}$)Ph$_2$ [18]. Another closely related pair of structures, one containing a linear, and the other a non-linear skeleton, are (1-C$_{10}$H$_7$)(CH$_2$)$_3$SiOSi(CH$_2$)$_3$(1-C$_{10}$H$_7$) [20] and (PhCOC$_6$H$_4$)Me$_2$SiOSiMe$_2$(C$_6$H$_4$COPh) [29].

For several of the compounds of Table 1, having linear SiOSi fragments, it is possible that steric factors may play some role: this is undoubtedly so in the bis-phthalocyanine derivative [Me$_2$(Me$_3$C)SiO](Pc)SiOSi(Pc)[OSi(CMe$_3$)Me$_2$] [24]. In the two diols Ph$_2$(HO)SiOSi(OH)Ph$_2$ [30] and (Me$_2$CH)$_2$(HO)SiOSi(OH)(CHMe$_2$)$_2$ [31], containing respectively three and two independent molecules in the asymmetric unit, the values of the angles SiOSi (Table 2) in the several independent molecules are likely to be influenced by hydrogen bonding, since the SiOSi bending force constant is generally low: the same is true for both the anion [Me$_2$(O)SiOSi-(O)Me$_2$]$^{2-}$ characterised [32] as the tetrahydrate of the disodium salt, and for the neutral [(Me$_3$C)$_2$(HO)SiO]$_2$SiMe$_2$ [33].

Both linear and non-linear SiOSi fragments span a comparatively narrow range of Si $\cdots$ Si distances between pairs of four-coordinate silicon, 3.078–3.238 Å, not significantly inconsistent with a limiting non-bonded contact radius [7] for silicon of 1.55 Å: however application of the same model [7] to the non-linear group 14 hexaorgano-substituted species R$^1_3$M^{1}OM^{2}R$^2_3$ listed in Table 3 shows serious non-additivity of the corresponding non-bonded radii. On the other hand, comparison of the linearity of MOM in (PhCH$_2$)$_3$MOM(CH$_2$Ph)$_3$ for Me = Ge [5] and Sn [4] with its non-linearity in Ph$_3$MOMPh$_3$ for M = Ge [37] and Sn [39] indicates that the linearity of the SiOSi fragment in for example (PhCH$_2$)$_3$SiOSi(CH$_2$Ph)$_3$ [6] cannot be ascribed to steric factors, but rather to the electron donor capacity of the (PhCH$_2$)$_3$Si group.

The foregoing deductions on the electron donor capacity of substituents at silicon, (and other group 14 atoms) were substantiated by MNDO [40–42] calculations on model systems (CH$_3$)$_2$Si(R)OH, containing a range of substituents R including OCH$_3$ (as a simple model for OC(CH$_3$)$_3$), and CH$_2$CH$_2$NH$_2$ (as simple model for CH$_2$CH$_2$NC$_5$H$_{10}$). In Table 4 are presented the calculated values of the net total charge on the OH fragments in (CH$_3$)$_2$Si(R)OH as a function of R. These results show that the electron-donor capacity of these substituents R increases in the following order: H < CH$_3$ < C$_6$H$_5$ < C(SiH$_3$)$_3$ $\simeq$ CH$_2$CH$_2$NH$_2$ < CH$_2$C$_6$H$_5$ < CH$_2$NH$_2$ < 1-C$_{10}$H$_7$(naphthyl) < OCH$_3$ < NH$_2$.

Thus the most powerful donors are those having a lone pair of electrons α to the silicon centre, followed by 1-naphthyl as the most powerful donor of the hydrocarbyl groups studied (cf. (1-C$_{10}$H$_7$)(CH$_2$)$_3$SiOSi(CH$_2$)$_3$(1-C$_{10}$H$_7$) which contains [20] a linear SiOSi fragment). Each of CH$_2$NH$_2$, CH$_2$CH$_2$NH$_2$ (cf.

Table 4

Calculated net charges, $q(\text{OH})$, for hydroxyl fragment in $(CH_3)_2Si(R)OH$

R	$q(\text{OH})$
H	-0.3609
CH_3	-0.3652
NH_2	-0.3873
CH_2NH_2	-0.3736
$CH_2CH_2NH_2$	-0.3673
OCH_3	-0.3748
$C(SiH_3)_3$	-0.3672
C_6H_5	-0.3666
$C_6H_5CH_2$	-0.3718
$1\text{-}C_{10}H_7$	-0.3740

$CH_2CH_2NC_5H_{10}$ [18]) and $CH_2C_6H_5$ was found to be a more powerful donor than C_6H_5, itself more powerful than CH_3 or H. The comparatively low position of the phenyl substituent in this series, compared with benzyl, accounts for the differences observed in R_3MOMR_3 (M = Ge, Sn; R = Ph, CH_2Ph [4,5,37,39]; Table 3).

Phosphorus compounds

Molecules of type R_3PCPR_3, where R is alkyl or aryl, in general have non-linear P–C–P skeletons: the known examples include Me_3PCPMe_3 [43], $Ph_2(CH_3)PCP$-$(CH_3)Ph_2$ [44], and Ph_3PCPPh_3 [45,46]. However, when the substituent R is an electron donor, such as Me_2N, then linearity at carbon is observed in $(Me_2N)_3PCP$-$(NMe_2)_3$ [47]. While in the great majority of salts of $(Ph_3PNPPh_3)^+$ the PNP fragment is non-linear, a linear PNP fragment is observed when the counter-ion is $[V(CO)_6]^-$ [48] or $[Au\{Co(CO)_4\}_2]^-$ [49]. Just as the electron donor substituent Me_2N can confer linearity on a PCP skeleton, so also it confers linearity on the POP skeleton of $[(Me_2N)_3POP(NMe_2)_3]^{2+}$ [50]: similarly, a linear POP fragment is observed in the N-morpholino derivative $[\{O(CH_2)_4N\}_3POP\{N(CH_2)_4O\}_3]^{2+}$ [51]. The structures of these phosphorus species $(R_3PXPR_3)^{x\pm}$ are summarised in Table 5: linearity of the PXP skeleton in the presence of electron-donor substituents is fully consistent with the postulated electronic model [8,9].

Oxo-bridged antimony compounds

Closely related to the hexaorgano-substituted triatomics $R_3MXM'R_3$ discussed above are the oxo-bridged antimony species $YR_3SbOSbR_3Y$ in which R is usually

Table 5

Hexaorganosubstituted triatomics R_3PXPR_3 containing linear PXP fragments

Molecule or ion	$d(\text{P} \cdots \text{P})$ (Å)	Reference
$(Me_2N)_3PCP(NMe_2)_3$	3.168	47
$[Ph_3PNPPh_3]^+ [V(CO)_6]^-$	3.078	48
$[Ph_3PNPPh_3]^+ [Au\{Co(CO)_4\}_2]^-$	3.094	49
$[(Me_2N)_3POP(NMe_2)_3]^{2+} (CF_3SO_3^-)_2$	3.146	50
$[\{O(CH_2)_4N\}_3POP\{N(CH_2)_4O\}_3]^{2+} (CF_3SO_3^-)_2$	3.176	51

Table 6

Hexaorgano-substituted species $(YSbR_3)_2O$

Molecule	Angle SbOSb (°)	$d(Sb \cdots Sb)$ (Å)	$d(Sb-Y)$ (Å)	Reference
(a) Linear SbOSb				
$[CF_3CO(CHCOCH_3)Sb(C_6H_4Cl)_3]_2O$		3.885	2.180 [a,b]	52
$(Me_3COOOSbPh_3)_2O$		3.949	2.088 [b]	53
$(HOCH_2CH_2SO_2OSbPh_3)_2O$		3.872	2.276 [b]	54
(b) Non-linear SbOSb				
$(N_3SbPh_3)_2O$	139.6	3.726	2.236 [c]	55
$[C_2(CN)_3OSbPh_3]_2O$	140.0	3.684	2.326 [b]	56
$(PhSO_2OSbPh_3)_2O$	139.8	3.686	(2.247 [b] (2.280	57
$(CF_3SO_2OSbPh_3)_2O$	136.5	3.639	(2.347 [b] (2.37	57
$(ClSbPh_3)_2O.2(C_6H_6)$	139.0	3.715	(2.553 [d] (2.583	58

[a] Geometry at antimony intermediate between five- and six-coordination. [b] Sb–O distance. [c] Sb–N distance. [d] Sb–Cl distance.

aryl, and Y can represent a wide range of nucleophilic anions. The structures of several such compounds have recently been reported [52–58] and the important structural data are summarised in Table 6. The electronic effects of Y can readily be accommodated by a simple extension of the model [8,9] originally developed for R_3MXMR_3 species. In the absence of the terminal ligands Y, the electronic configuration of the MXM′ bridge, here SbOSb, can be written [9] as: $(1\sigma_g^+)^2(1\sigma_u^+)^2(1\pi_u)^4(2\sigma_g^+)^0(2\sigma_u^+)^0$: the addition of two ligands Y, which act primarily as σ donors (cf. Table 6) should leave the binding energy of $1\pi_u$ largely unchanged but should cause the binding energies of both $2\sigma_g^+$ and $2\sigma_u^+$ to be reduced. The stronger the bonding between Y and Sb, the greater the energy shift of $2\sigma_g^+$ and $2\sigma_u^+$. This conjecture was fully confirmed by calculations, at the EHMO level [59,60] and using published atomic parameters [61–63], on the simple model compounds $(H_3SbOSbH_3)^{2+}$ and $(H_4SbOSbH_4)$: upon introduction of the terminal hydride ligands to complete the trigonal bipyramidal coordination of antimony, then with the model parameters $d(Sb-O)$ 2.0 Å and $d(Sb-H)$ 1.8 Å, the calculated separation of $1\pi_u$ and $2\sigma_g^+$ increased from 11.1 to 15.0 eV.

With a larger gap, the likelihood that the force constant for skeletal bending will be negative is decreased [9]: the EHMO calculations showed furthermore that as the bond distance to the terminal ligand became shorter, so the $1\pi_u-3\sigma_g^+$ energy gap became steadily larger. Thus it follows on the basis of the earlier model [9] as modified here that species $YSbR_3OSbR_3Y$, for given organic substituent R and variable terminal ligand Y, are more likely to exhibit linearity of the SbOSb skeleton when Y is a tightly bound ligand giving a short Sb–Y distance. There are not really sufficient examples in Table 6 to provide an adequate test of this: in particular, only a single example is yet recorded having (for R = phenyl) a halide or nitrogen ligand respectively in the terminal site. Of the five compounds in Table 6 having R = phenyl together with an oxygen donor ligand at the terminal site, the two examples [53,54]

having linear SbOSb fragments are those with the shortest terminal SbO distances: however, the small number of examples available makes these results merely suggestive rather than definitive.

That this conclusion is entirely consistent with the earlier model can be demonstrated by a consideration of the case of very weak terminal ligand binding in $YSbPh_3OSbPh_3Y$, leading in the limit to a formulation $(Ph_3SbOSbPh_3)^{2+}$ $(Y^-)_2$ (eg for $Y^- = BPh_4^-$); clearly in the cation, the substituent Ph_3Sb^+ is strongly electron attracting, and any such free cation is expected therefore to be markedly non-linear at oxygen.

Where the structures are known for pairs of compound $YSbPh_3OSbPh_3Y$ and Ph_4SbY having identical Y, the Sb–Y distance appears always to be much larger for a given ligand Y in Ph_4SbY than in $YSbPh_3OSbPh_3Y$: thus when Y is $PhSO_3$, the corresponding Sb–O distances are 2.506 Å [64] and 2.26 Å [57], and when Y is Cl, the corresponding Sb–Cl distances are 2.74 Å [65] and 2.57 Å [58]. The influence of the substituents Y on the structure of Ph_4SbY has recently been discussed [66].

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