Journal of Organometallic Chemistry, 212 (1981) 291—300
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF OXO-BIS[TRIBENZYLSILICON(IV)]

CHRISTOPHER GLIDEWELL * and DAVID C. LILES

Chemistry Department, University of St. Andrews, St. Andrews, Fife, KY16 9ST
(Great Britain)

(Received December 22nd, 1980)

Summary

Crystals of oxo-bis[tribenzylsilicon(IV)], $O[(PhCH_2)_3Si]_2$, are triclinic, space group $P\bar{1}$, with a = 9.780(7), b = 9.938(9), c = 10.283(6) Å, α = 93.35(1), β = 115.44(1), γ = 100.73(2)° and Z = 1. The molecule is centrosymmetric with overall symmetry close to $\bar{3}$: the SiOSi skeleton is strictly linear with SiO = 1.613(4) Å. The conformations of molecules and ions isoelectronic with $O[(PhCH_2)_3Si]_2$ are compared and discussed.

Introduction

The germanium and tin μ-oxo compounds $O[(PhCH_2)_3M]_2$ (M = Si, Ge) contain linear MOM chains [1,2] unlike their phenyl analogues which both have bent MOM skeletons [3,4]. The silicon μ-oxo compound $O(Ph_3Si)_2$, by contrast, is linear at oxygen [5] although $O(Ph_3C)_2$ is not [6]. Here we report the crystal and molecular structure of $O[(PhCH_2)_3Si]_2$ which like its germanium and tin congeners contains a linear MOM chain.

Experimental

Oxo-bis[tribenzylsilicon(IV)], $O[(PhCH_2)_3Si]_2$, was prepared from $SiHCl_3$ via $(PhCH_2)_3SiH$ [7,8]. Crystals suitable for X-ray investigation were grown from $CHCl_3$ solution.

Data collection

Data were collected using a Stoe Stadi-2 two circle automatic diffractometer with graphite crystal monochromatised Mo-K_α radiation for a crystal of dimen-

---

* To receive correspondence.

sions 0.2 × 0.3 × 0.25 mm mounted about b. The intensities of 1502 reflections in the hemisphere $\pm h$, $+k$, $\pm l$ with $2° \leqslant \theta \leqslant 30°$, $k = 0$—11 ($0 \leqslant \mu \leqslant 23.160°$) were measured using the ω—2θ scan mode, with a step width of 0.01° in ω, a time of 0.6 s per step and 120 steps per scan. Backgrounds were measured at both ends of the scan for a time of (scantime/2). Standard reflections were measured every 30 reflections and showed only small random deviations from their means. Lorentz and polarisation corrections were applied to the data, but no corrections for absorption were made.

Crystal data

Oxo-bis[tribenzylsilicon(IV)], $C_{42}H_{42}Si_2O$, $M_r = 618.97$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2) $a = 9.780(7)$, $b = 9.938(9)$, $c = 10.283(6)$ Å, $\alpha = 93.35(1)$, $\beta = 115.44(1)$, $\gamma = 100.72(2)°$; $U = 875.90$ Å^3; $Z = 1$; $Dc = 1.173$ Kg dm^{-3}; $F(000) = 330$. Mo-K_α radiation, $\gamma = 0.71069$ Å, μ(Mo-K_α) = 0.97 cm^{-1}.

Structure solution and refinement

These were carried out using SHELX-76 [9]. As the E statistics were inconclusive as to the presence, or otherwise, of a centre of symmetry in the cell, the solution of the structure was attempted in the space group $P1$. The general direct-methods program in SHELX-76, TANG, failed to give any reasonable solutions. A "boot-strap" method was therefore adopted in which a difference map was calculated, phased by placing one silicon atom in an arbitrary position in the cell. The resulting difference map showed an approximately centrosymmetric distribution of peaks surrounding the Si position. The choice of sub-sets of peaks not related by the pseudo-centring yielded coordinates for the second Si and the atoms bonded to the two Si atoms. Further difference maps gave the positions of the rest of the non-hydrogen atoms in the molecule. Six cycles of least-squares refinement, with the coordinates of one Si fixed to define the origin, and individual isotropic temperature parameters for all non-hydrogen atoms yielded a conventional R index $[= \Sigma\ \Delta/\Sigma F_0(\Delta = [|F_0| - F_c|)]$ of 0.1531 and a generalised index $R_G\ [= (\Sigma w\ \Delta^2/\Sigma w F_0^2)^{1/2}]$ of 0.1757, for 1458 unique observed reflections. At this stage in the refinement, inspection of the geometry of the molecule showed it to be almost centrosymmetric, but with significant variations between chemically equivalent bond length and angles. The refinement was therefore continued in space group $P\bar{1}$, starting with mean coordinates taken from the $P1$ refinement, translated so that the O atom was placed on the centre of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. 6 Cycles of refinement with individual isotropic temperature parameters for all non-hydrogen atoms yielded $R = 0.1616$ and $R_G = 0.1809$. The reduction in R_G by using space group $P1$ instead of $P\bar{1}$ was not significant at the 50% level [10]. The introduction of anisotropic temperature parameters for all non-hydrogen atoms reduced R to 0.1331 and R_G to 0.1510 in 12 cycles of least-squares refinement, blocked such that the Si and O atoms parameters refined in every cycle, but the parameters for each independent benzyl group refined once every 3 cycles. The introduction of hydrogen atoms in calculated positions with separate common isotropic temperature parameters for the H atoms in each phenyl ring, and a fixed isotropic temperature parameter of 0.1 for all the methylene H atoms, in 9 cycles of refinement reduced to R to 0.1173 and R_G to 0.1300, and R to 0.1041 and R_G to 0.1157

TABLE 1

ATOM FRACTIONAL COORDINATES ($\times 10^3$) (FOR Si $\times 10^4$)

	x	y	z
Si	5225(3)	4116(3)	3770(3)
O	500(0)	500(0)	500(0)
C(1)	410(1)	464(1)	196(1)
C(11)	450(1)	612(1)	182(1)
C(12)	368(1)	707(1)	201(1)
C(13)	408(1)	839(2)	188(1)
C(14)	532(2)	894(2)	157(1)
C(15)	618(1)	800(1)	143(1)
C(16)	578(1)	665(1)	154(1)
C(2)	444(1)	222(1)	365(1)
C(21)	276(1)	181(1)	332(1)
C(22)	160(1)	154(1)	190(1)
C(23)	4(2)	124(1)	160(2)
C(24)	—35(2)	114(2)	277(2)
C(25)	82(2)	137(2)	417(2)
C(26)	234(1)	168(1)	445(1)
C(3)	734(1)	441(1)	419(1)
C(31)	837(1)	404(1)	562(1)
C(32)	924(1)	510(1)	683(1)
C(33)	1019(1)	475(1)	815(1)
C(34)	1029(1)	340(1)	832(1)
C(35)	943(1)	237(1)	713(1)
C(36)	848(1)	272(1)	578(1)

TABLE 2

ANISOTROPIC TEMPERATURE PARAMETERS AND THE EQUIVALENT ISOTROPIC TEMPERATURE PARAMETERS (U_{iso}) [a] (Å$^2 \times 10^{-3}$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}
Si	24(2)	44(2)	19(1)	—1(1)	10(1)	6(1)	24
O	30(6)	52(7)	27(5)	—5(5)	13(5)	10(5)	34
C(1)	34(7)	51(8)	27(6)	9(5)	13(5)	1(6)	33
C(11)	27(6)	56(8)	13(5)	—3(5)	4(5)	—6(6)	27
C(12)	26(6)	62(9)	35(7)	20(6)	16(6)	5(6)	32
C(13)	29(8)	96(12)	55(8)	9(8)	15(7)	11(7)	50
C(14)	71(10)	71(10)	37(7)	13(7)	20(7)	—14(8)	51
C(15)	53(9)	66(10)	47(8)	7(7)	31(7)	—1(7)	46
C(16)	37(7)	65(9)	28(6)	9(6)	22(6)	5(6)	33
C(2)	20(6)	83(9)	33(6)	—9(6)	5(5)	4(6)	37
C(21)	13(6)	76(9)	29(6)	—10(6)	4(5)	—6(6)	29
C(22)	37(8)	97(11)	24(6)	—14(7)	—1(6)	—5(7)	43
C(23)	31(8)	76(10)	63(9)	—11(8)	—17(7)	—5(7)	49
C(24)	29(8)	100(13)	133(16)	—30(13)	28(10)	—12(8)	65
C(25)	61(10)	93(11)	85(11)	—4(9)	54(10)	—14(9)	58
C(26)	37(8)	80(9)	33(7)	—4(6)	16(6)	—1(7)	43
C(3)	32(7)	82(9)	28(6)	9(6)	20(5)	10(6)	34
C(31)	21(6)	57(8)	33(6)	6(5)	12(5)	17(5)	29
C(32)	29(7)	54(8)	39(7)	—6(6)	10(5)	1(6)	38
C(33)	38(8)	88(10)	33(7)	13(7)	12(6)	18(7)	45
C(34)	33(7)	89(11)	48(8)	20(8)	11(6)	27(8)	45
C(35)	40(8)	71(10)	78(10)	18(8)	29(8)	31(7)	48
C(36)	38(7)	62(9)	42(7)	2(6)	14(6)	25(6)	39

---

[a] U_{iso} is defined as the geometric mean of the diagonal components of the diagonalised matrix of U_{ij}. The isotropic temperature parameters for the hydrogens in each phenyl ring refined to 0.06(2), 0.11(2) and 0.08(2) Å^2.

TABLE 3

BOND DISTANCES (Å)

Si—O	1.613(4)				
Si—C(1)	1.875(11)	Si—C(2)	1.875(13)	Si—C(3)	1.885(12)
C(1)—C(11)	1.48(2)	C(2)—C(21)	1.50(2)	C(3)—C(31)	1.49(1)

Within the phenyl rings C(ij)—C(ik)

i = *j*—*k*	1	2	3
1—2	1.41(2)	1.39(1)	1.41(1)
2—3	1.33(2)	1.39(2)	1.38(2)
3—4	1.41(2)	1.41(3)	1.38(2)
4—5	1.41(2)	1.37(2)	1.38(2)
5—6	1.35(2)	1.36(2)	1.40(2)
6—1	1.41(2)	1.38(2)	1.36(2)

in 6 further cycles for 1424 reflections with $F_0 > 6\sigma F_0$. Attempts to introduce weighting schemes of the form $w = 1/(\sigma^2 + n\,F_0^2)$ with n in the range 0.0 to 0.1 led to unstable refinements and higher R factors. Therefore unit weights were used throughout the refinement. In the final cycles of refinement 208 parameters were varied comprising 66 positional parameters, 138 anisotropic temperature components, 3 common isotropic temperature parameters and 1 overall scale factor. A further difference synthesis showed no significant residual features. The reductions in R_G at all stages of the refinement in $P\bar{1}$ were significant at the 99.5% level [10]. A corresponding blocked-matrix refinement in $P1$ (412 parameters) gave $R = 0.1031$ and $R_G = 0.1150$ for 1424 reflections with $F_0 > 6\sigma F_0$, with a Si—O—Si angle of 174(3)°. The reduction in R_G was not signifi-

TABLE 4

BOND ANGLES (°)

Si—O—Si$^{\mathrm{I}}$ [a]	180.0(0)	C(1)—Si—C(3)	109.7(6)
O—Si—C(1)	108.9(5)	C(2)—Si—C(3)	108.7(6)
O—Si—C(2)	110.2(5)	Si—C(1)—C(11)	117.1(6)
O—Si—C(3)	111.3(4)	Si—C(2)—C(21)	115.2(10)
C(1)—Si—C(2)	108.1(4)	Si—C(3)—C(31)	115.0(9)

Within the phenyl rings C(kj)—C(ik)—C(il)/C(i)

i = *j*—*k*—*l*[C(*i*)]	1	2	3
1—2—3	120(1)	120(1)	119(1)
2—3—4	124(2)	119(1)	122(1)
3—4—5	116(1)	120(2)	119(1)
4—5—6	121(1)	121(2)	119(1)
5—6—1	122(1)	121(1)	122(1)
6—1—2	116(1)	119(1)	119(1)
2—1—C(*i*)	122(1)	121(1)	119(1)
6—1—C(*i*)	121(1)	120(1)	122(1)

[a] Superscript I refers to the symmetry position 1 — *x*, 1 — *y*, 1 — *z*.

TABLE 5

LEAST-SQUARES PLANES THROUGH THE PHENYL CARBON ATOMS C(*ij*), DISTANCES OF ATOMS FROM THE PLANES AND DIHEDRAL ANGLES BETWEEN THE PLANES FOR $O[(PhCH_2)_3M]_2$, M = Si [a], Ge [b] AND Sn [b]

(the planes are defined in orthogonal Ångstrom coordinates by the equation $Ax + By + Cz + D = 0$)

M	*i*	*A*	*B*	*C*	*D*
Si	1	−0.185(1)	−0.0547(6)	−0.981(3)	2.42(1)
	2	0.217(4)	−0.974(2)	−0.061(3)	1.23(2)
	3	0.9558(3)	0.1714(3)	−0.2388(2)	−4.045(6)
Ge	1	−0.0009(4)	−0.997(1)	−0.0746(3)	2.656(4)
Sn	1	0.091(1)	0.992(5)	−0.086(2)	−2.28(1)

Distances of atoms from the planes ($Å \times 10^{-3}$)

M	*i*	C(*i*1)	C(*i*2)	C(*i*3)	C(*i*4)	C(*i*5)	C(*i*6)	C(*i*)
Si	1	9(15)	−10(16)	0(18)	13(17)	−10(17)	12(16)	1(16)
	2	−14(21)	18(22)	−10(23)	−3(25)	2(23)	9(22)	−68(21)
	3	3(13)	−6(14)	5(16)	0(16)	−4(16)	0(15)	−14(14)
Ge	1	4(6)	−4(7)	0(7)	3(7)	−3(7)	−2(7)	3(7)
Sn	1	−10(10)	5(10)	4(10)	−10(10)	1(10)	7(10)	−27(10)

Dihedral angles between the planes (°)

M	i_1	i_2 [c]	Angle
Si	1	2	85.8(3)
	1	3	87.3(5)
	2	3	86.9(2)
Ge	1	1^{I} [c]	86.4(1)
Sn	1	1^{I}	89.6(1)

[a] Molecule has a centre of inversion. [b] Molecule has $\overline{3}$ (S_6) symmetry [1,2]. [c] I refers to the plane through the phenyl ring in symmetry position *y*, *z*, *x* or *z*, *x*, *y*.

cant at the 50% level [10]. Complex neutral-atom scattering factors [11] were employed for all atoms throughout the structure solution and refinement. The results from the final least-squares cycle are given in Tables 1 and 2. These, together with the full-covariance matrix were used to calculate the bond lengths and angles which are given with e.s.d's in Tables 3 and 4 *. Least-squares planes were calculated for each phenyl ring: these are given, together with the equivalent planes for $[(Ph_3CH_2)M]_2O$, M = Ge and Sn (for comparison), in Table 5. Figure 1 is a perspective view of the molecule showing the atom numbering scheme.

Results and discussion

The structure comprises isolated molecules which lie across a centre of inversion, so that the SiOSi chain is strictly linear, as found also in $O(Ph_3Si)_2$ and $O[(PhCH_2)_3M]_2$ (M = Ge, Sn) [5,1,2]. The SiO distance of 1.613(4) Å is identi-

---

* A table of observed of calculated structure factors may be obtained from the authors on request.

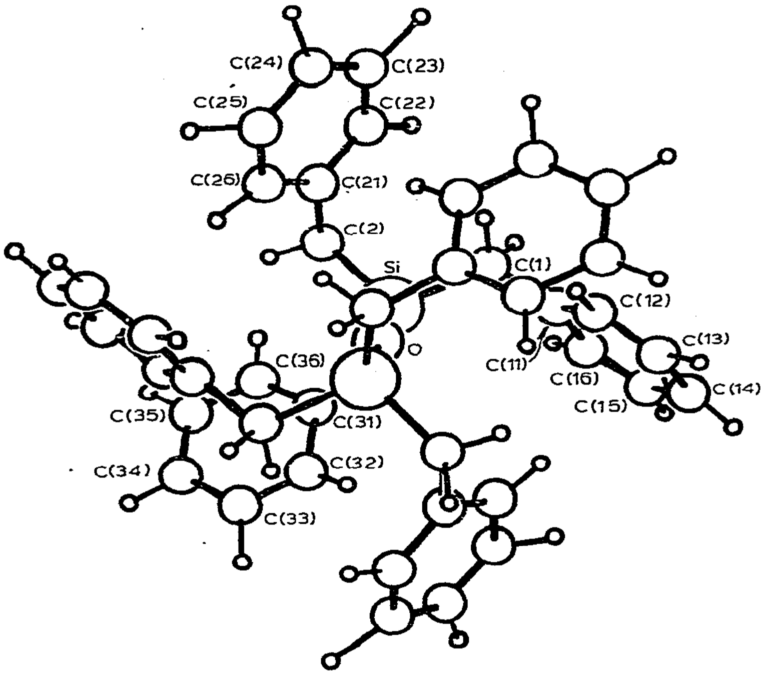

Fig. 1. A perspective view of the molecule showing the atom numbering scheme.

cal within experimental uncertainty with that in the phenyl analogue, 1.616(1) Å. The SiC distances, (Table 3), mean value 1.88(1) Å, are typical of such distances in alkylsilanes [12,13]. The bond angles about the silicon atoms (Table 4) are all close to tetrahedral, whereas the angles Si—C(*i*)—C(*i*1) (*i* = 1, 2, 3) are all much larger than the tetrahedral angle with mean value 116(1)°: the corresponding values for the germanium and tin analogues are 115.4(3)° and 113.9(1)° [1,2]. In $O[(PhCH_2)_3Ti]_2$ this angle is 113.4(4)° [14].

The dihedral angles between the planes of the three phenyl rings are all close to 90° (Table 5): similarly in the germanium and tin analogues the planes are again almost perpendicular, as they are also in $O[(Ph_3CH_2)_3Ti]_2$, where the interplane angle is 87.3°. Consequently, because of the centre of inversion, in each of $O[(PhCH_2)_3M]_2$ (M = Si, Ge, Sn, Ti) the six phenyl planes describe an almost cubic enclosure, with the MOM chain lying along its body diagonal. Although for M = Ge, Sn, Ti, the crystals are rhombohedral, space group $R\bar{3}$, in contrast to the triclinic $P\bar{1}$ found when M = Si, the molecules in all four cases are virtually identical, save only for the magnitudes of the M—O and M—C distances: in particular the skeletons have the same overall symmetry, $\bar{3}$ (S_6) for M = Ge, Sn, Ti, and very close to $\bar{3}$ for M = Si.

The essential properties of the $O(Ph_3M)_2$ and $O[(PhCH_2)_3M]_2$ structures are recorded in Table 6 for M = C, Si, Ge, Sn. Within the phenyl series, the largest MOM angle occurs in the silicon compound and the smallest in the carbon compound: in all the phenyl derivatives the MOM angle is significantly larger than the approximately tetrahedral value expected for two-coordinate oxygen. The

TABLE 6

GEOMETRICAL DATA FOR $O(R_3M)_2$

M	R = Ph					R = $PhCH_2$				
	Space-group and *z*	<MOM (°)	*r*(M—O) (Å)	*r*(M···M) (Å)	Ref.	Space group and *z*	<MOM (°)	*r*(M—O) (Å)	*r*(M···M) (Å)	Ref.
C	$P2_1/c$, 4	127.9(1)	1.454(2) 1.465(2)	2.622(2)	[6]					
Si	$P\bar{1}$, 1	180.0(0) [a]	1.616(1)	3.232(2)	[5]	$P\bar{1}$, 1	180.0(0) [a]	1.613(4)	3.226(8)	This work
Ge	$P\bar{1}$, 2	135.2(2)	1.765(3) 1.769(3)	3.268(1)	[3]	$R\bar{3}$, 1	180.0(0) [a]	1.730(1)	3.460(2)	[1]
Sn	$P2_1/c$, 4	137.3(1)	1.957(2) 1.953(2)	3.641(1)	[4]	$R\bar{3}$, 1	180.0(0) [a]	1.919(0)	3.838(0)	[2]

[a] Molecule lies across a centre of inversion.

TABLE 7

M—X—M ANGLES AND MEAN TORSION ANGLES [a] FOR SOME μ-OXO COMPOUNDS AND OTHER ISOELECTRONIC COMPOUNDS OR IONS OF THE GENERAL FORM $[(R_3M)_2X]^{n+}$ (see also Fig. 2)

Index Number	Compound	M—X—M (°)	Torsion angle (°)	Ref.
1	$[(Ph_3P)_2N]^+[V(CO)_6]^-$	180.0(0) [b]	60.0(0)	18
2	$[(Ph_3P)_2N]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$	154.6(3)	4.6(4)	19
3	$[(Ph_3P)_2N]^+[TcOCl_4]^-$	147.4(3)	5.7(3)	20
4	$[(Ph_3P)_2N]^+[Fe(CO)_4C_3H_7]^-$	145.9(8)	53.5(7)	21
5	$[(Ph_3P)_2N]^+[Os_3(CO)_9HS]^-$	144.7(13)	58.4(8)	22
6	$[(Ph_3P)_2N]^+[IOs_5(CO)_{15}]^-$	142.3(13)	54.2(10)	23
7	$[(Ph_3P)_2N]^+[Cr_2(CO)_{10}I]^-$	142(1)	22.5(7)	24
8	$[(Ph_3P)_2N]^+[Mo(CO)_4BH_4]^-$	141.8(6)	46.4(4)	25
9	$[Ph_3P)_2N]^+[HFe_2(CO)_8]^-$	140.9(5)	38.4(5)	26
10	$[(Ph_3P)_2N]^+[Ru_3H(CO)_{11}]^-$	139.7(6)	52.2(4)	27
11	$[(Ph_3P)_2N]_2^+[W_2Ni_3(CO)_{16}]^{2-}$	139.0(7)	38.5(4)	28
12	$[(Ph_3P)_2N]_2^+[Mo_2Ni_3(CO)_{16}]^{2-}$	137.5(5)	39.0(4)	28
13	$[(Ph_3P)_2N]_2^+[Cr_2(CO)_{10}]^{2-}\cdot CH_2Cl_2$	137(1)	38.7(7)	29
14	$[(Ph_3P)_2N]_2^+[MO_2(CO)_{10}]^{2-}\cdot CH_2Cl_2$	137(2)	39.9(8)	29
15	$[(Ph_3P)_2N]^+[HOs_3(CO)_{10}\cdot O_2C\cdot Os_6(CO)_{17}]^-$	137(4)	32.7(23)	30
16	$[(Ph_3P)_2N]_2^+[H_2Os_4(CO)_{12}]^{2-}$	135.6(6)	42.8(3)	31
17	$[(Ph_3P)_2N]^+[Fe(CO)_4CN]^-$	134.6(3)	40.8(2)	32
18	$(Ph_3Si)_2NH$	138.5(6)	27.1(6)	33
19	$(H_3Si)_2O$ (at 108 K)	142.2(3)	2(7)	34
20	$(Me_3Si)_2O$ (at 148 K)	148.8(2)	57.4(2)	34
21	$(Ph_3Si)_2O$	180.0(0) [b]	60.0(0)	5
22	$[(PhCH_2)_3Si]_2O$	180.0(0) [b]	60.0(0)	This work
23	$(Ph_3Ge)_2O$	135.2(2)	49.3(10)	3
24	$[(PhCH_2)_3Ge]_2O$	180.0(0) [c]	60.0(0)	1
25	$(Ph_3Sn)_2O$	137.3(1)	52.5(10)	4
26	$[(PhCH_2)_3Sn]_2O$	180.0(0) [c]	60.0(0)	2
27	$Ph_3PbOSiPh_3$	142(1)	52.5(16)	35
28	$(ClO_4Ph_3Bi)_2O$	142.2(7)	51.6(10)	36

[a] The mean torsion angle is defined as the absolute value of the mean angle between the projection of each R—M bond and the projection of the nearest R′—M′ bond, onto a plane perpendicular to the line through M—M′. [b] The molecule has a centre of inversion. [c] The molecule has $\bar{3}$ (S_6) symmetry.

values in the germanium and tin phenyl compounds are unlikely to be a consequence of repulsion between the phenyl groups on different metal atoms, since in the corresponding benzyl compounds in which the aromatic fragments attached to different metal atoms are even further apart, because of the CH_2 groups, the angles MOM are not merely larger than tetrahedral, but exactly 180°. Similarly if the linearity at oxygen in the phenyl silicon compound were to be ascribed primarily to phenyl interactions [15], then it is hard to understand why the phenyl carbon compound, in which the phenyls are closest together, has the smallest observed value of the angle MOM. In $O(Ph_3C)_2$ there is in fact strong evidence for many non-bonded contacts, between phenyl groups in different Ph_3C fragments, which are shorter than twice the Van der Waals radius for carbon in a phenyl ring: nevertheless the COC angle only attains a value of 127.9°. We believe that the rationalisation previously suggested [16,17] affords a much more convincing explanation of the observed geometries.

For the molecules of Table 6 which contain a centre of inversion, the torsion

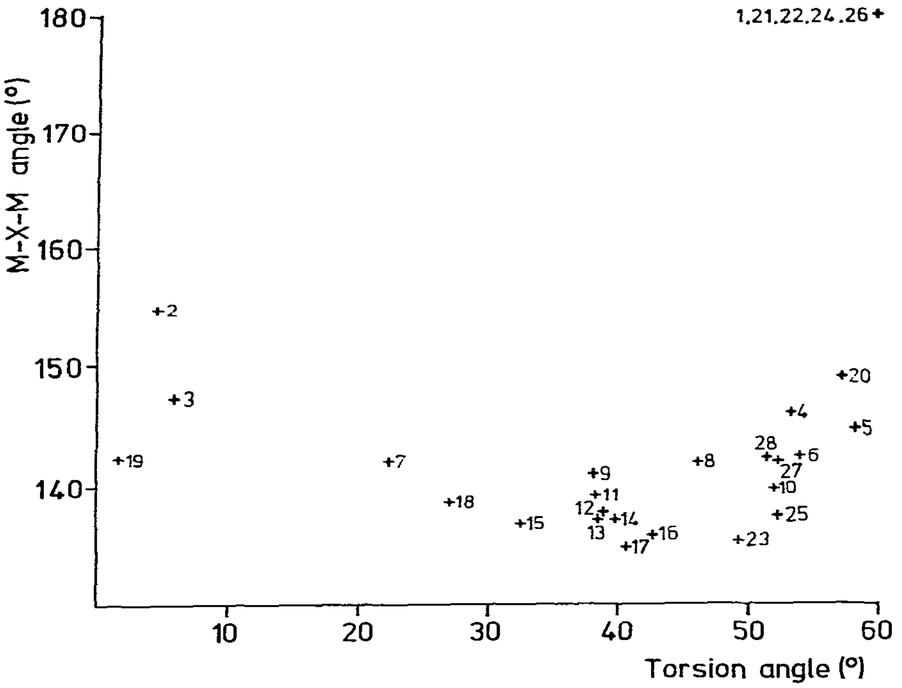

Fig. 2. M—X—M angle vs. mean torsion angle for some μ-oxo compounds and other compounds or ions of the general formula $[(R_3M)_2X]^{n+}$. See Table 7 for the key to the numbering.

angle between the substituents on M, as defined in Table 7, must be 60° : for molecules without a centre of inversion, no such constraint applies, and a range of torsional angles is observed for similar isoelectronic species $R_3MXM'R_3$. Table 7 records values of the torsional angles for species in which the triatomic skeleton MXM' has formally eight valence electrons. These angles are plotted against angle MXM in Fig. 2, which shows a reasonably smooth variation of the one angle with the other: there are many data available for the cation $[(Ph_3P)_2N]^+$ which is widely used as a counter ion for polynuclear carbonylate anions, and for this ion, <PNP ranges from 180°, compound 1, [18] to 134.6°, compound 17 [32] while the torsional angle ranges from 60.0°, compound 1 to 4.6°, compound 2 [19], with a significant clustering of the values around <PNP of ca. 140° and a torsion angle of ca. 40°. For such an ion, there is clearly only a modest potential barrier to rotation about PN bonds, as confirmed by a PCILO study of the related ion $[(Me_3P)_2N]^+$ [37], and only a *modest force constant for deformation of the skeleton from linearity.*

Rather similar conformations are found for $O(Me_3Si)_2$, compound 20, [34]; $O(Ph_3Ge)_2$, compound 23 [3]; $O(Ph_3Sn)_2$, compound 25 [4], and $Ph_3SiOPbPh_3$, compound 27 [35], although $O(H_3Si)_2$, compound 19, [34] has a markedly different conformation, possibly connected with the intermolecular association found for this compound in the solid state.

Acknowledgement

We thank the S.R.C. for support.

References

1 C. Glidewell and D.C. Liles, J. Organometal. Chem., 174 (1979) 275.
2 C. Glidewell and D.C. Liles, Acta Cryst., B, 35 (1979) 1689.
3 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 119.
4 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 1693.
5 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 124.
6 C. Glidewell and D.C. Liles, Acta Cryst., B, 34 (1978) 696.
7 J.W. Jenkins, N.L. Lavery, P.R. Guenther and P.W. Post, J. Org. Chem., 13 (1948) 862.
8 J.W. Jenkins and H.W. Post, J. Org. Chem., 15 (1950) 552.
9 G.M. Sheldrick, SHELX-76 program system, University of Cambridge, (1976).
10 W.C. Hamilton, Acta Cryst., 18 (1965) 502.
11 D.T. Cromer and J.B. Mann, Acta Cryst., A, 24 (1968) 321.
12 A. Almenningen, H.M. Seip and R. Seip, Acta Chem. Scand., 24 (1970) 1697.
13 B. Beagley, J.J. Monaghan and T.G. Hewitt, J. Mol. Struct., 8 (1971) 401.
14 H. Stoeckli-Evans, Helv. Chim. Acta, 57 (1974) 684.
15 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th Edition, Wiley, New York, 1980, p. 379.
16 C. Glidewell, Inorg. Chim. Acta, 29 (1978) L283.
17 C. Glidewell, J. Organometal. Chem., 159 (1978) 23.
18 R.D. Wilson and R. Bau, J. Amer. Chem. Soc., 96 (1976) 7601.
19 J.L. Pederson, P.L. Johnson, J. O'Connor, L.F. Dahl and J.M. Williams, Inorg. Chem., 17 (1978) 3460.
20 F.A. Cotton, A. Davison, V.W. Day, L.D. Gage and H.S. Trop, Inorg. Chem., 18 (1979) 3024.
21 G. Huttner and W. Gartzke, Chem. Ber., 108 (1975) 1373.
22 B.F.G. Johnson, J. Lewis, D. Pippard and P.R. Raithby, Acta Cryst., B, 34 (1978) 3767.
23 A.V. Rivera, G.M. Sheldrick and M.B. Hursthouse, Acta Cryst., B, 34 (1978) 3376.
24 L.B. Handy, J.K. Ruff and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 7327.
25 S.W. Kirtly, M.A. Andrews, R. Bau, G.W. Grynkewich, T.J. Marks, D.L. Tipton and B.R. Whittlesey, J. Amer. Chem. Soc., 99 (1977) 7154.
26 H.B. Chin and R. Bau, Inorg. Chem., 17 (1978) 2314.
27 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Süss, J. Chem. Soc. Dalton, (1979) 1356.
28 J.K. Ruff, R.P. White, Jr., and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 2159.
29 L.B. Handy, J.K. Ruff and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 7312.
30 J.J. Guy and G.M. Sheldrick, Acta Cryst., B, 34 (1978) 1718.
31 B.F.G. Johnson, J. Lewis, P.R. Raithby, G.M. Sheldrick and G. Süss, J. Organometal. Chem., 162 (1978) 179.
32 S.A. Goldfield and K.N. Raymond, Inorg. Chem., 13 (1974) 770.
33 C. Glidewell and H.D. Holden, Acta Cryst., B, in press.
34 M.J. Barrow, E.A.V. Ebsworth and M.M. Harding, Acta Cryst., B, 35 (1979) 2093.
35 P.G. Harrison, T.J. King, J.A. Richards and R.C. Phillips, J. Organometal. Chem., 116 (1976) 307.
36 F.C. March and G. Ferguson, J. Chem. Soc. Dalton, (1975) 1291.
37 C. Glidewell, Inorg. Chim. Acta, in press.