than that in caprylolactam (23·1°), while the χ_C value in the present molecule is nearly the same as in its unsubstituted counterpart (5·8°). The difference in χ_N may be attributed to the indirect effect of the methyl substitution on the hydrocarbon part of the molecule. The correlation between χ_N and the corresponding lengthening of the C—N bond has been discussed by Baker, Hossain & van der Helm (1981). The C—N bond length of 1·344 (4) Å in the present structure is about six standard deviations longer than that normally observed in planar peptides. There is, however, no noticeable shortening of the corresponding C=O bond.

The three molecules of the asymmetric unit are linked together through strong intermolecular N—H···O hydrogen bonds. All hydrogen-bond parameters are listed in Table 6. The molecules are packed so as to form an endless helix around the crystallographic twofold axis. The resulting double helix is shown in a stereodiagram in Fig. 4. The amide units constitute the inner core of the helix while the methyl groups lie on the periphery.

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Hexaphenyl Group IV*a* Ethers*

BY B. MOROSIN AND L. A. HARRAH

Sandia National Laboratories,† *Albuquerque, New Mexico* 87185, *USA*

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Abstract

The crystal structures of hexaphenyl Group IV*a* ethers, Ph_3MONPh_3 (in which $M \neq N$) for Si, Ge and Sn have been solved by the Patterson method using diffractometer data and refined by full-matrix least-squares methods. Crystals of $Ph_3SiOGePh_3$ and $Ph_3GeOSnPh_3$ are triclinic in space group $P\bar{1}$, $Z = 2$, with $a = 11{\cdot}000\,(3)$, $b = 9{\cdot}719\,(2)$, $c = 15{\cdot}449\,(3)$ Å, $\alpha = 92{\cdot}69\,(1)$, $\beta = 103{\cdot}06\,(1)$, $\gamma = 109{\cdot}49\,(1)°$ and $a = 11{\cdot}264\,(3)$, $b = 9{\cdot}744\,(2)$, $c = 15{\cdot}627\,(4)$ Å, $\alpha = 92{\cdot}60\,(2)$, $\beta = 103{\cdot}35\,(2)$ and $\gamma = 109{\cdot}48\,(2)°$, respectively; those for $Ph_3SiOSnPh_3$ are in $P2_1/n$, $Z = 4$ with $a = 19{\cdot}886\,(5)$, $b = 17{\cdot}621\,(4)$, $c = 8{\cdot}830\,(2)$ Å and $\beta = 90{\cdot}07\,(2)°$. The metalloid atoms are disordered in all these structures. For $Ph_3SiOGePh_3$ ($R = 0{\cdot}042$ with a population parameter of 0·503, hence complete disorder), the M—O bond lengths are

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1·704 (4) and 1·718 (3) Å, the *M*—C bond lengths are in the range 1·881–1·906 Å and the *M*—O—*M* angle is 142·5 (2)°; for isomorphic $Ph_3GeOSnPh_3$ ($R = 0{\cdot}063$; population parameter = 0·532) corresponding longer bond lengths [*M*—O of 1·849 (3) and 1·874 (6) Å; *M*—C range 2·01–2·05 Å] are observed with a smaller angle of 134·9 (4)°. In the case of $Ph_3SiOSnPh_3$ ($R = 0{\cdot}053$; population parameter = 0·642), a larger variation of the corresponding values (*M*—O of 1·79 and 1·87 Å; *M*—C range 1·94–2·06 Å; *M*—O—*M* of 144·2°) is observed due to the incomplete disorder found.

Introduction

Hexaphenyldisiloxane, $[(C_6H_5)_3Si]_2O$, $Ph_3SiOSiPh_3$ and its congeners, in which silicon is substituted by other Group IV*a* metalloids (Ge, Sn, Pb), represent sterically crowded molecules in which the differences in the metalloid radii result in configuration changes. These changes strongly influence the rates of formation and stabilities of intramolecular excited-state dimers of the phenyl moieties (excimers). Such excimers are generally formed between properly oriented aromatic chromophores in both solids and fluid solutions [for example, in benzene (Birks, Braga & Lumb 1965), pyrene (Förster & Kasper 1955; Birks, Dyson & Munro, 1963), polystyrene (Vala, Haebig & Rice, 1965), polyvinylcarbazole (Klöpffer, 1969), and polyvinylnaphthalene (Frank & Harrah, 1974)].

The present materials exhibit both excimer and monomer chromophore fluorescence in solution, indicating a significant barrier to excimer formation even though all rotational conformers are equivalent in these molecules. This barrier must arise from necessary configurational changes, in bond angles, and inter-ring separations, which are not required in the carbon-chain analogs (Frank & Harrah, 1974). The influence of these factors on the kinetics of excimer formation and dissociation and on the structure of the excimer state can contribute to the understanding of the formation of the randomly distributed intermolecular excimers found in bulk aromatic polymers (Frank & Harrah, 1974). Previous studies have shown that small misalignment of the principal-axis system of the aromatic chromophores (Chandross & Dempster, 1970) will quench excimer formation but no quantitative data exist relating angular and separation constraints to the excimer-formation process. The diffraction studies reported here are part of a program to define the influence of these parameters on excimer formation.

Because of the varied nomenclature for these ethers, our literature search initially failed to reveal Glidewell & Liles's (1978*a*,*b*,*c*) studies on Ph_3MONPh_3 analogs in which $M = N =$ Si, Ge and Sn and, unfortunately, these structure studies were needlessly repeated. The structure of $Ph_2PbOSiPh_3$ as well as the lattice constants for $Ph_3SnOSiPh_3$ have been reported by Harrison, King, Richards & Phillips (1976). In this paper, we report the structural details for the $M \neq N$ analogs.

Experimental details

The mixed-metalloid hexaphenyl Group IV*a* ethers were synthesized using the Williamson-like reaction of the potassium triphenyl metalloid oxide with the triphenyl metalloid chloride. The potassium salts were prepared by reaction of potassium hydroxide with the corresponding triphenyl metalloid hydroxide in methanol and were crystallized from methanol and added to a solution of the triphenyl metalloid chloride in toluene. The mixture was then refluxed for 4 h, filtered to remove the potassium chloride and evaporated to dryness. The product obtained was recyrstallized from cyclohexane and the expected structure verified by examination and comparison of the infrared spectrum of the product with those of the starting compounds.

Our initial X-ray powder diffraction patterns on materials crystallized from cyclohexane suggested that several different crystal modifications might be present for these analogs. Single crystals were examined by the usual photographic methods and tentative space groups assigned and later verified by the final structure determination. Cell dimensions were obtained with high 2θ values on small prisms not exceeding 0·25 mm in cross section using the θ–2θ scan technique to 50° 2θ for Mo $K\alpha$. An automated Picker diffractometer with an *E* and *A* full-circle orienter was used with a scintillation detector employing pulse-height discrimination. No absorption corrections were applied ($\mu r < 0{\cdot}4$; no significant intensity variation as a function of φ with the crystal at $\chi = 90{\cdot}0$ was noted). Intensities were treated differently if they were measured to be less than 3σ, where $\sigma = 1/(N_{sc} + K^2N_b)^{1/2}$ and N_{sc}, N_b and K are the total scan count, background count and the time ratio of the scan to background, respectively. The Sn-containing analogs proved sensitive to radiation and the intensity data set consists of averages from two crystals on which empirical, non-linear, but isotropic, time-dependent correction factors were employed. The values obtained for the above-mentioned parameters on $M \neq N$ analogs are given in Table 1. Also given in Table 1 are our unit-cell parameters for $(Ph_3Si)_2O$; these differ from previous values (Glidewell & Liles, 1978*a*) which did not represent a reduced cell.*

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* Unit-cell parameters of Glidewell & Liles transformed to the reduced cell are: $a = 8{\cdot}771$, $b = 9{\cdot}539$, $c = 11{\cdot}086$ Å, $\alpha = 95{\cdot}797$, $\beta = 111{\cdot}769$, $\gamma = 113{\cdot}660°$. Another, nonreduced cell (10·041, 11·074, 8·771 Å, 111·68, 119·49, 65·20°) is also present. Our positional parameters on the independently refined structures for the $M = N =$ Si, Ge and Sn are in excellent agreement with those published by Glidewell & Liles, though with slightly larger *R* values.

Table 1. *Data on* Ph_3MONPh_3, *M and N* = Si, Ge *and* Sn, *crystals*

M,*N*	Si,Ge	Ge,Sn	Si,Sn	Si,Si
a (Å)	11·000 (3)	11·264 (3)	19·886 (5)	8·771 (2)
b (Å)	9·719 (2)	9·744 (2)	17·621 (4)	9·542 (3)
c (Å)	15·449 (3)	15·627 (4)	8·830 (2)	11·074 (4)
α (°)	92·69 (1)	92·60 (2)		95·84 (2)
β (°)	103·06 (1)	103·35 (2)	90·07 (2)	111·68 (2)
γ (°)	109·49 (1)	109·48 (2)		113·65 (2)
V (Å^3)	1503·21	1559·23	3094·13	754·08
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	2	2	4	1
D_c (Mg m^{-3})	1·280	1·342	1·427	1·177
μ(Mo *K*α) (mm^{-1})	1·15	0·896	1·85	0·146
Independent *hkl*'s	5296	5535	1968	2767
'less thans'	1642	1550	376	253

Our structure factors were calculated using scattering factors computed from Hartree–Fock wavefunctions (Cromer & Mann, 1968) and for H those of Stewart, Davidson & Simpson (1965). Dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962). In our least-squares requirement, the function $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2$ was minimized. In addition, intensities less than 3σ were considered as 'less thans' and included in the refinement whenever $F_o < F_c$.

For $Ph_3GeOSiPh_3$, the initial models by direct methods as well as by evaluation of the Patterson Fourier synthesis were essentially identical, but incorrect. The correct evaluation of the Patterson synthesis required recognition that the positions of the Ge and Si atoms were disordered. This leads quickly to the model for least-squares refinement. The initial model for $Ph_3GeOSnPh_3$ employed positions found for $Ph_3GeOSiPh_3$. For $Ph_3SiOSnPh_3$, the Patterson map was interpreted correctly assuming disorder in the metalloid positions. Initially, isotropic thermal parameters were employed and these then expanded to anisotropic values. H atom positions were visible on the difference Fourier synthesis; rather than taking such values from these maps, the positions were calculated to bisect the appropriate C—C—C angle with an assumed C—H bond length of 1·0 Å. An isotropic thermal parameter B = 10·0 Å^2 for all H atoms was used. Such positions were redetermined through several cycles of least-squares refinement. The largest shift-to-error ratio did not exceed 0·01 on final cycles. Initially the population parameter to define disorder was set to 0·5 (assuming complete disorder) for these compounds. During refinement of the $Ph_3SiOSnPh_3$ structure, it became apparent that only partial disorder was occurring. The R $(=\sum||F_o| - |F_c||/\sum|F_c|)$ value reduced from 0·071 to the final value of 0·053 with inclusion of a population parameter [p.p. = 0·642 (4) for Sn in $M(2)$ positions]; the values of the thermal parameters also became more realistic and approximately equal to each other. The final R value is not significantly different upon inclusion of a variable population parameter for the other two compounds [for $Ph_3SiOGePh_3$, R = 0·042 with p.p. = 0·503 (2) and hence complete disorder; for $Ph_3GeOSnPh_3$, R = 0·063 with p.p. = 0·532 (3) for Sn in $M(1)$ positions]. Final atomic coordinates and population parameters are given in Table 2,* in which U_{eq} is taken as equal to $\frac{1}{3}$ trace $\tilde{\mathbf{U}}$. Most of the computations were performed with the XRAY system (Stewart, 1976).

Table 2. *Positional parameters* (×10^4; *for M* ×10^5) *and equivalent isotropic thermal parameters* (×10^3 Å^2)

(*a*) $Ph_3SiOGePh_3$

	x	*y*	*z*	U_{eq}
M(1)	41873 (9)	25499 (10)	23472 (6)	44
M(2)	11362 (9)	13015 (10)	25104 (6)	41
O	2676 (3)	1380 (3)	2426 (2)	53
C(1)	1281 (4)	2362 (5)	3609 (3)	42
C(2)	1596 (5)	3871 (5)	3706 (3)	58
C(3)	1643 (6)	4635 (6)	4494 (4)	72
C(4)	1398 (6)	3911 (7)	5204 (4)	77
C(5)	1116 (6)	2432 (7)	5154 (4)	76
C(6)	1053 (5)	1658 (6)	4350 (3)	58
C(7)	335 (4)	2057 (4)	1511 (3)	43
C(8)	−514 (5)	2813 (6)	1570 (3)	60
C(9)	−1083 (6)	3351 (7)	823 (4)	80
C(10)	−820 (7)	3127 (7)	20 (4)	85
C(11)	6 (7)	2369 (7)	56 (4)	81
C(12)	581 (5)	1838 (6)	687 (3)	62
C(13)	208 (4)	−727 (4)	2487 (3)	40
C(14)	853 (6)	−1712 (6)	2675 (4)	64
C(15)	125 (8)	−3205 (6)	2644 (5)	86
C(16)	−1213 (8)	−3703 (6)	2442 (4)	82
C(17)	−1884 (6)	−2751 (6)	2258 (4)	78
C(18)	−1174 (5)	−1270 (5)	2270 (4)	62
C(19)	5475 (4)	2060 (5)	3181 (3)	49
C(20)	6614 (5)	1997 (7)	2977 (4)	70
C(21)	7548 (6)	1639 (8)	3600 (5)	89
C(22)	7379 (6)	1359 (7)	4424 (4)	78
C(23)	6263 (6)	1418 (7)	4641 (4)	74
C(24)	5319 (5)	1765 (6)	4028 (4)	65
C(25)	4292 (4)	2222 (5)	1164 (3)	47
C(26)	3595 (5)	858 (6)	653 (4)	64
C(27)	3666 (6)	594 (7)	−221 (4)	79
C(28)	4450 (7)	1700 (8)	−591 (4)	79
C(29)	5154 (6)	3042 (7)	−107 (4)	76
C(30)	5081 (5)	3319 (6)	771 (4)	64
C(31)	4326 (4)	4556 (5)	2629 (3)	49
C(32)	3588 (5)	5210 (5)	2042 (3)	55
C(33)	3681 (6)	6649 (6)	2254 (4)	69
C(34)	4534 (7)	7471 (6)	3027 (5)	79
C(35)	5269 (7)	6862 (7)	3605 (4)	87
C(36)	5176 (6)	5400 (6)	3415 (4)	69

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* Lists of structure factors and anisotropic thermal parameters for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35679 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

(*b*) $Ph_3GeOSnPh_3$

	x	y	z	U_{eq}
M(2)	10697 (11)	11263 (13)	25004 (8)	57
M(1)	42240 (12)	24676 (14)	23181 (9)	63
O	2658 (6)	1068 (8)	2409 (5)	81
C(1)	1277 (8)	2329 (10)	3642 (6)	62
C(2)	1597 (12)	3832 (12)	3722 (8)	92
C(3)	1683 (14)	4635 (14)	4479 (10)	106
C(4)	1488 (15)	4003 (19)	5211 (9)	113
C(5)	1198 (15)	2508 (18)	5187 (8)	111
C(6)	1101 (11)	1685 (12)	4410 (8)	83
C(7)	328 (9)	1988 (10)	1441 (6)	69
C(8)	−521 (12)	2740 (13)	1476 (7)	85
C(9)	−1024 (16)	3276 (16)	742 (12)	119
C(10)	−713 (18)	3087 (18)	−41 (11)	126
C(11)	130 (17)	2370 (17)	−77 (9)	113
C(12)	636 (13)	1794 (13)	648 (8)	92
C(13)	35 (9)	−995 (9)	2491 (6)	64
C(14)	608 (11)	−2046 (12)	2674 (9)	89
C(15)	−144 (18)	−3503 (15)	2618 (11)	112
C(16)	−1465 (18)	−3954 (14)	2434 (9)	111
C(17)	−2066 (12)	−2967 (14)	2255 (9)	106
C(18)	−1338 (12)	−1513 (12)	2281 (8)	96
C(19)	5627 (9)	1997 (10)	3214 (7)	69
C(20)	6710 (11)	1901 (14)	2968 (9)	99
C(21)	7656 (14)	1609 (19)	3625 (13)	131
C(22)	7489 (15)	1315 (17)	4466 (12)	115
C(23)	6408 (15)	1345 (15)	4670 (9)	102
C(24)	5492 (12)	1686 (15)	4052 (9)	96
C(25)	4317 (10)	2112 (11)	1043 (7)	64
C(26)	3620 (11)	794 (12)	516 (9)	89
C(27)	3722 (14)	585 (16)	−339 (10)	108
C(28)	4461 (16)	1666 (20)	−672 (9)	112
C(29)	5193 (15)	2997 (18)	−172 (11)	117
C(30)	5119 (12)	3232 (13)	704 (9)	91
C(31)	4282 (10)	4555 (12)	2645 (7)	76
C(32)	3504 (12)	5175 (14)	2040 (8)	86
C(33)	3540 (14)	6609 (15)	2265 (10)	112
C(34)	4338 (19)	7401 (17)	3032 (14)	127
C(35)	5107 (16)	6831 (19)	3608 (12)	131
C(36)	5077 (13)	5383 (16)	3426 (9)	115

(*c*) $Ph_3SiOSnPh_3$

	x	y	z	U_{eq}
M(1)	33677 (14)	14502 (16)	3798 (30)	35
M(2)	16811 (8)	14128 (9)	−6910 (18)	39
O	2468 (5)	1479 (6)	463 (10)	64
C(1)	1708 (8)	496 (12)	−2040 (23)	59
C(2)	1469 (11)	548 (11)	−3507 (28)	81
C(3)	1470 (14)	−53 (18)	−4457 (24)	103
C(4)	1732 (12)	−740 (15)	−3928 (39)	97
C(5)	1966 (12)	−790 (17)	−2519 (42)	115
C(6)	1952 (11)	−181 (16)	−1552 (26)	83
C(7)	1550 (10)	2383 (10)	−1968 (26)	71
C(8)	1905 (11)	2477 (14)	−3271 (30)	92
C(9)	1765 (17)	3086 (22)	−4158 (28)	118
C(10)	1285 (15)	3625 (16)	−3673 (40)	103
C(11)	951 (13)	3530 (16)	−2364 (38)	110
C(12)	1075 (11)	2897 (14)	−1431 (22)	85
C(13)	1001 (8)	1333 (10)	1052 (18)	42
C(14)	477 (10)	825 (11)	981 (21)	67
C(15)	−1 (9)	767 (12)	2134 (27)	78
C(16)	106 (10)	1224 (13)	3406 (24)	70
C(17)	606 (11)	1742 (12)	3484 (23)	73
C(18)	1085 (9)	1775 (12)	2342 (25)	71
C(19)	3636 (8)	2356 (9)	1504 (16)	40
C(20)	3158 (10)	2799 (13)	2241 (20)	73
C(21)	3361 (13)	3454 (13)	2988 (22)	89
C(22)	4061 (14)	3644 (14)	3099 (24)	89
C(23)	4505 (10)	3199 (16)	2399 (25)	81
C(24)	4315 (10)	2554 (12)	1588 (20)	68
C(25)	3592 (11)	515 (9)	1427 (17)	52
C(26)	4272 (11)	306 (13)	1382 (20)	71
C(27)	4504 (12)	−353 (18)	2113 (29)	92
C(28)	4060 (18)	−806 (15)	2839 (29)	93
C(29)	3425 (18)	−626 (13)	2898 (22)	95
C(30)	3153 (10)	50 (14)	2188 (21)	76
C(31)	3686 (8)	1461 (14)	−1734 (17)	52
C(32)	3559 (10)	826 (12)	−2620 (30)	89
C(33)	3855 (17)	897 (19)	−4164 (37)	120
C(34)	4119 (16)	1500 (22)	−4685 (27)	108
C(35)	4209 (14)	2113 (16)	−3811 (33)	122
C(36)	3976 (10)	2086 (12)	−2341 (27)	75

Structural details

The Ph_3MONPh_3 compounds prove to be rather interesting. There are five known structure types represented by the C,C ($P2_1/c$; Glidewell & Liles, 1978*d*), Si,Si ($P\bar{1}$, $Z = 1$), Si,Ge ($P\bar{1}$, $Z = 2$), Si,Sn ($P2_1/n$) and Si,Pb ($P2_1/a$; Harrison, King, Richards & Phillips, 1976) analogs.* Since the *M*—O and *M*—C bond lengths increase as the atomic number increases, the molar volume should serve as a measure of the packing efficiencies for this series. Excluding the C,C structure type, one can show that the Si,Pb structure type appears to represent the best packing and the Si,Si the poorest; one also might deduce that Si,Ge may be slightly better than Si,Sn as a structure type by considering differences in volumes as one progresses along the available members; further, we originally crystallized the Ge,Sn analog in the Si,Sn structure type, but to date have been unable to reproduce those crystals. Examination of the packing of these molecules (Fig. 1) shows that the Si,Ge and Si,Pb structure types have phenyl groups so oriented that they appear to stack upon each other while this appears to be much less so for the Si,Sn and does not occur at all for the Si,Si structure types. Within a structure type, as the metalloid radius increases, the *M*—O—*N* angle decreases. Unfortunately, the trend does not hold between structure types. The case of the Si,Si analog is anomalous in that the Si—O—Si bond angle is 180° with the molecules situated on a center of inversion. The subject of the variation of bridging bond angle *M*—O—*M* as a function of *M*—O distance, particularly in silicates, has been ascribed alternately to the effect of Si(3*d*)–O(2*p*) π bonding (Cruickshank, 1961) or to the effect of repulsion between positively charged Si atoms (Mitchell, 1969). More recently Tossell & Gibbs (1978)

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* A thio-analog, Ph_3CSCPh_3, belongs to an additional triclinic structure type ($P\bar{1}$, $Z = 2$) which differs from the Si,Ge analog (Jeffrey & Robbins, 1980).

have used molecular-orbital calculations to explain the observed angular trends without invoking *d*-*p* π bonding or nonbonded repulsion forces. Their study also showed that the Si—O—Si angle should decrease as the Si—O length increases. Their calculated energy *versus* angle for particular lengths appears sufficiently flat near Si—O lengths of 1·6 Å that packing forces might be sufficient to dictate the geometry, contrary to the recent observation of Barrow, Ebsworth & Harding (1979) that the packing in crystals appears to adapt itself to the geometry of the free molecule rather than *vice versa*. Indeed, we noted above that the trend in the

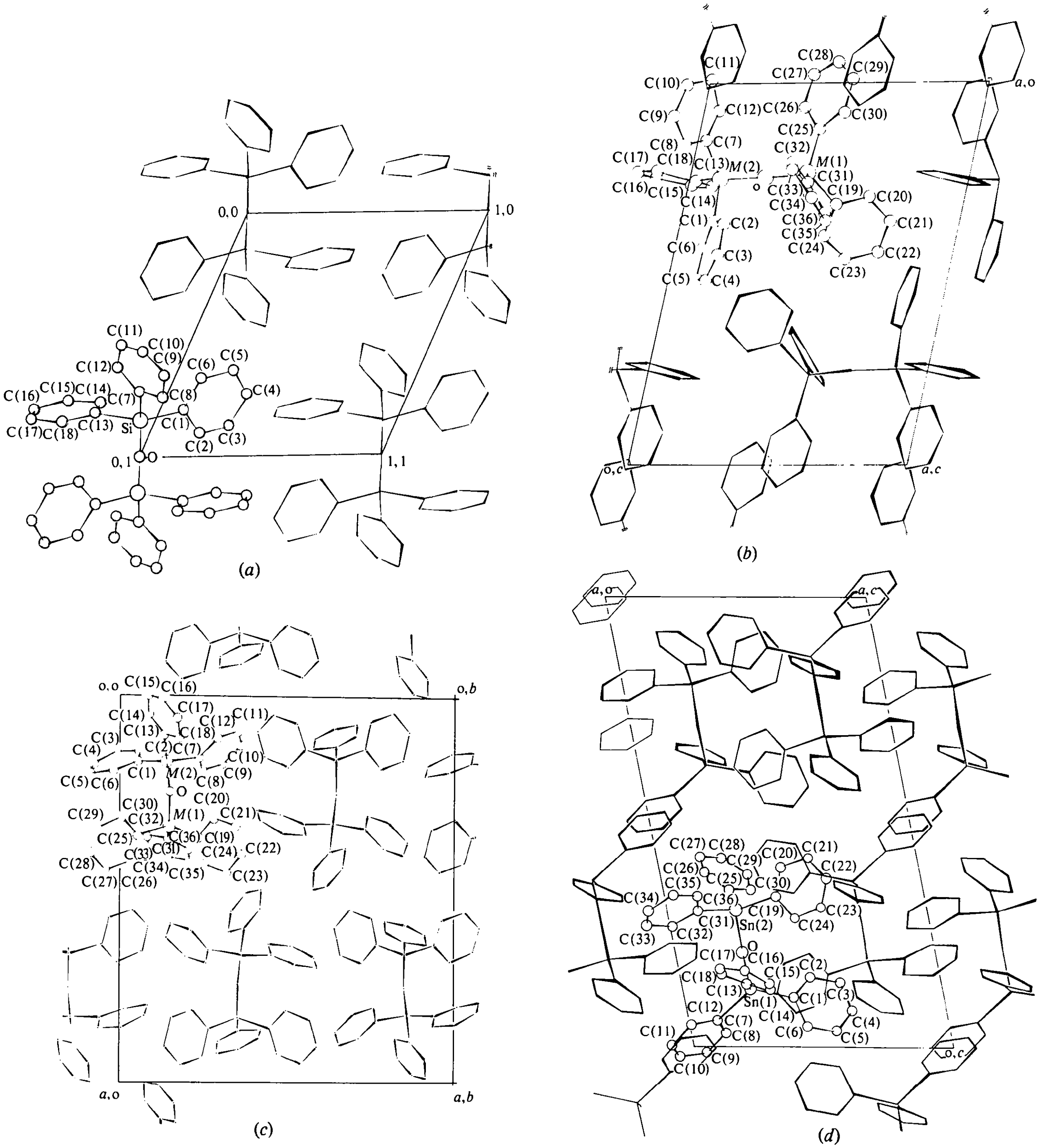
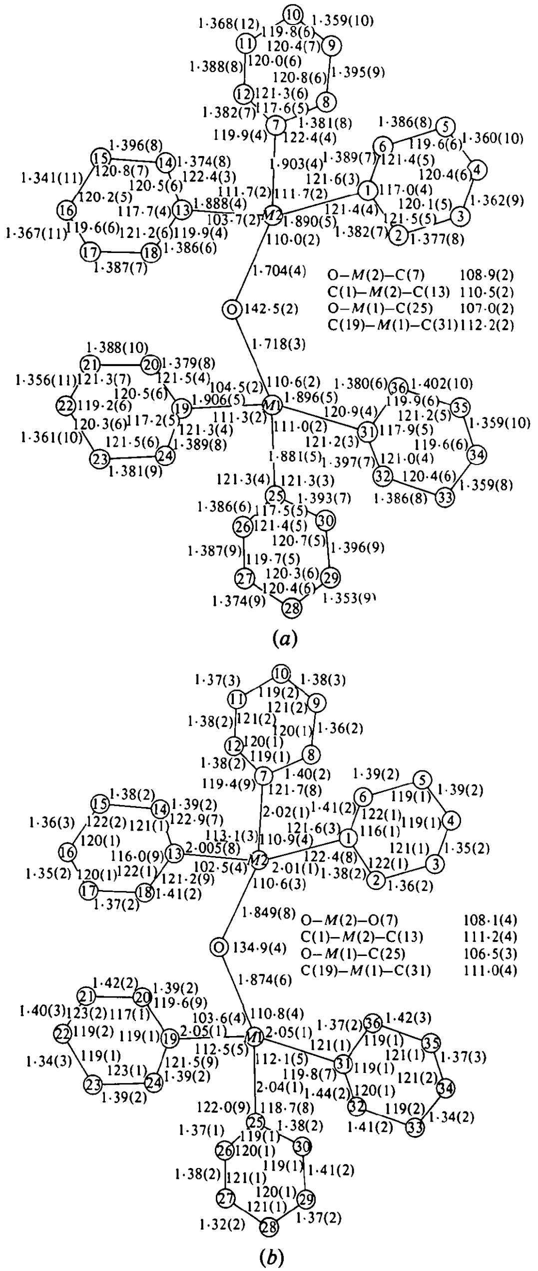


Fig. 1. (*a*) A view of $Ph_3SiOSiPh_3$ along *a*. Molecules are at inversion centers in this packing arrangement. (*b*) A view of $Ph_3SiOGePh_3$ along *b* projected on the *ac* plane. The Ge,Ge and Ge,Sn analogs also have this structure type. Note the orientation of the phenyl groups across the top of this illustration. (*c*) A view of $Ph_3SiOSnPh_3$ along *c* projected on the *ab* plane. The initial form of the Ge,Sn analog which crystallized is also in space group $P2_1/n$. (*d*) A view of $Ph_3SnOSnPh_3$ along *b*. The Si,Pb analog also crystallizes in $P2_1/a$. This structure packing appears to be the most efficient of this group of compounds.

M—O—*N* angle did not appear to hold as the structure type changed.

The bond lengths and angles are summarized in Fig. 2. The errors on the values involving C atoms are large for the Sn-containing analogs. This may partly result from the radiation sensitiveness of these crystals such that the data are of lower quality than normal. Examination of the metalloid–oxygen or metalloid–carbon bond lengths in these disordered compounds suggests that the Si–O lengths (1·616 Å) observed in $Ph_3SiOSiPh_3$ might be slightly shorter than expected for a system with an angle not equal to 180°. This is also consistent with Tossell & Gibbs's (1978) length *vs* angle calculations. Rather than employing that length, a better one might be the average of 1·628 Å found in SiH_3OSiH_3 and $(CH_3)_3SiOSi(CH_3)_3$ by Barrow, Ebsworth & Harding (1979). Even so, the present observed average values (Table 3) for the analogs involving Si are slightly longer than expected for the *M*—O and slightly shorter for the *M*—C bond lengths (given in parentheses in Table 3); however, they are still within the pooled standard deviation. In the case of the Si,Sn analog, the unequal, significantly different values shown for *M*(1) and *M*(2) (Fig. 2*c*) are consistent with the expected values, allowing for the determined population parameter. With p.p. = 0·642


(*a*)

(*b*)

Fig. 2. Bond lengths (Å) and angles (°) for (*a*) $Ph_3SiOGePh_3$, (*b*) $Ph_3GeOSnPh_3$.

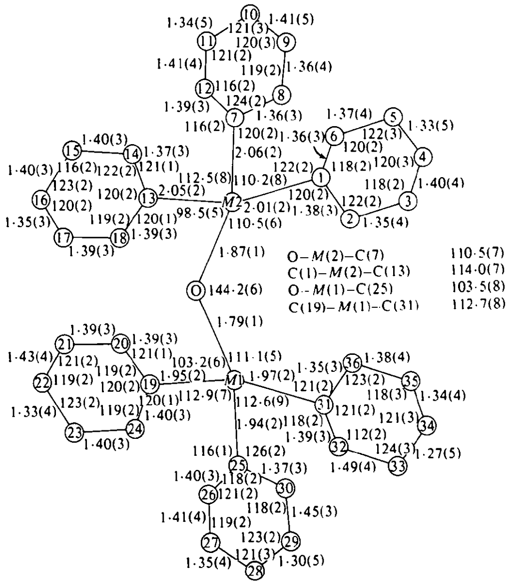

(*c*)

Fig. 2 (*cont.*) (*c*) $Ph_3SiOSnPh_3$.

Table 3. *Average values for* Ph_3MONPh_3 *analogs*

	MOM (°)	*MO* (Å)	*MC* (Å)	References
C,C	127·9	1·454	1·465	*a*
Si,Si	180	1·616	1·864	*b*
Si,Ge	142·5	1·711 (1·699)	1·894 (1·903)	*c*
Si,Sn	144·2	1·83 (1·79)	2·00 (2·00)	*c*
Ge,Ge	135·2	1·767	1·942	*d*
Ge,Sn	134·9	1·862 (1·861)	2·03 (2·04)	*c*
Sn,Sn	137·3	1·955	2·135	*e*
Si,Pb	142	1·87 (Si) 2·01 (Pb)	1·86 2·15	*f*

References: (*a*) Glidewell & Liles (1978*d*); (*b*) Glidewell & Liles (1978*a*); (*c*) present work; (*d*) Glidewell & Liles (1978*b*); (*e*) Glidewell & Liles (1978*c*); (*f*) Harrison, King, Richards & Phillips (1976).

Table 4. *Angles (°) between least-squares planes through phenyl groups*

The top entry of each three is for the Si,Ge, the middle for the Ge,Sn, and the bottom for the Si,Sn analog.

	C(1)–C(6)	C(7)–C(12)	C(13)–C(18)	C(19)–C(24)	C(25)–C(30)	C(31)–C(36)
M(1),O,*M*(2)	66·9 (4) 68·1 (5) 70·9 (3)	73·3 (2) 70·3 (4) 63·3 (7)	18·6 (3) 18·3 (7) 41·5 (13)	67·9 (1) 68·0 (10) 48·7 (8)	66·8 (2) 67·8 (6) 67·0 (3)	66·8 (4) 67·8 (5) 68·2 (15)
C(1)–C(6)		50·9 (4) 51·5 (6) 50·9 (7)	85·4 (5) 86·3 (7) 79·2 (13)	72·7 (4) 73·8 (12) 71·3 (8)	25·9 (4) 23·4 (6) 89·1 (4)	49·7 (5) 49·0 (6) 51·6 (15)
C(7)–C(12)			82·6 (3) 79·8 (12) 75·6 (15)	24·9 (2) 23·8 (8) 79·0 (9)	76·6 (2) 78·3 (8) 38·4 (7)	52·8 (4) 53·1 (8) 53·4 (17)
C(13)–C(18)				69·8 (13) 70·3 (12) 36·9 (14)	84·4 (3) 84·7 (9) 84·8 (13)	50·5 (4) 52·0 (8) 29·0 (21)
C(19)–C(24)					83·4 (2) 81·0 (12) 64·3 (8)	74·8 (4) 72·3 (12) 58·3 (17)
C(25)–C(30)						65·0 (4) 67·0 (7) 77·7 (15)

Table 5. *Displacements* (Å) *of atoms from least-squares planes through phenyl groups*

	Ge,Si	Ge,Sn	Si,Sn	Si,Si
Metalloid				
maximum	0·079 (8)	0·079 (9)	0·158 (11)	0·063 (4)
average	0·022 (6)	0·034 (11)	0·038 (14)	0·040 (3)
Carbon				
maximum	0·011 (7)	0·026 (18)	0·038 (26)	0·008 (6)
average	0·004 (4)	0·008 (11)	0·011 (14)	0·002 (3)

for Sn in *M*(2) sites expected values are 1·84 and 2·04 Å for *M*(2)–O and *M*(2)–C, and 1·75 and 1·96 Å for *M*(1)–O and *M*(1)–C, respectively. A similar argument is not made for the Ge,Sn analog since there is no statistical significance in the differences from the average observed values for those bond lengths.

An examination was made of the relative orientation of the phenyl groups within the molecule and with respect to the *M*(1),O,*M*(2) plane (Table 4). The Ge,Si structure type has one phenyl plane closer to the metalloid–oxygen plane than in the Si,Sn structure type; in addition, two sets of phenyl groups also are in closer alignment for that structure type. We have not yet correlated these orientations with the spectral results. The displacements of the metal atoms from the least-squares planes of the phenyl group are shown in Table 5. The Si,Sn structure type, which was deduced to have the best packing efficiency, shows the largest maximum metalloid displacement, and interestingly, the largest average metalloid displacement is shown by the poorest-packing-efficiency (Si,Si) structure type. In general, the average metalloid displacements exceed the maximum carbon displacements from the least-squares planes through the phenyl groups.

Fluorescence of crystals

All hexaphenyl Group IV*a* ethers studied exhibit spectra characteristic of excimer formation in the crystal. With the exception of hexaphenyldisiloxane, these spectra show a single broad band with maximum-intensity wavelengths given below:

	$\lambda_{\max}$	Half width
Si,Si	3233,3375 Å	–
Si,Ge	3243	584 Å
Ge,Ge	3230	450
Ge,Sn	3230	450
Si,Sn	3190	530.

The hexaphenyldisiloxane emission spectrum consists of two maxima, one at 3233 Å, nearly the same wavelength as the maximum in the mixed compounds, and the other at a longer wavelength, with some indication of structure in the band tail beyond 3500 Å. From the observed crystal structure (Glidewell & Liles, 1978*a*) for this compound, it is likely that this structured emission occurs from an intramolecular excimer state which involves considerable distortion of the linear molecular framework.

The remaining compounds exhibit spectra with fluorescence maxima between 3190 and 3243 Å and half widths of from 450 to 584 Å. The crystal structures observed indicate that for these materials a site is available for intermolecular excimer formation without appreciable strain during formation and the spectra are similar to that found in bulk polystyrene (Frank & Harrah, 1974).

Solution spectra of these compounds exhibit both monomer and intramolecular excimer fluorescence. The ratio of these two emissions is temperature dependent, indicating that all compounds show a conformational barrier to excimer formation. Barrier-height determinations are now under way.

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The Structures of 1,2,3,4,5,6-*cis*-Cyclohexanehexacarboxylic Acid and Its Hexamethyl Ester

BY SERGIO BRÜCKNER AND LUCIANA MALPEZZI GIUNCHI

Istituto di Chimica, Politecnico di Milano, via Golgi 39, 20133 *Milano, Italy*

AND GIUSEPPE DI SILVESTRO AND MARIA GRASSI

Istituto di Chimica Industriale, Cattedra di Chimica Macromolecolare, Università di Milano, via Saldini 50, 20133 *Milano, Italy*

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Abstract

$C_{12}H_{12}O_{12}.3H_2O$ is orthorhombic, $P2_12_12_1$, with a = 13·44 (1), b = 11·18 (1), c = 10·37 (1) Å, M_r = 402·3, Z = 4, final R = 0·055; $C_{18}H_{24}O_{12}$, is orthorhombic, *Pbca*, with a = 34·79 (3), b = 20·63 (2), c = 11·58 (1) Å, M_r = 432·4, Z = 16 (two independent molecules per asymmetric unit), final R = 0·059. A comparison is drawn between observed geometries and data calculated for a model molecule by use of the molecular-mechanics method.

Introduction

1,2,3,4,5,6-*cis*-Cyclohexanehexacarboxylic acid (I) and its hexamethyl ester (II) were prepared as part of a study concerning gyrochiral molecules (high-symmetry

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