Crystal and Molecular Structures of the Tetrakis(diphenylketimine) Derivatives of Silicon, Germanium, and Tin

By **Nathaniel W. Alcock** * and **Melanie Pierce-Butler**, Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL, Warwickshire

The crystal and molecular structures of the title compounds [$M(NCPh_2)_4$; (1) M = Si, (2) M = Ge, (3) M = Sn] have been determined from diffractometer data. Crystal parameters are as follows: (1), triclinic, space group $P\bar{1}$, a = 12.342(6), b = 18.100(8), c = 19.586(15) Å, α = 86.89(5), β = 82.72(5), γ = 84.06(4)°, Z = 4, 2 524 observed reflections, R 0.067; (2), monoclinic, space group $C2/c$, a = 24.050(2), b = 11.971(1), c = 18.839(3) Å, β = 130.44(8)°, Z = 4, 2 189 observed reflections, R 0.058; (3), tetragonal, space group $I4_1/a$, a = 18.142(5), c = 14.461(3) Å, Z = 4, 1 329 observed reflections, R 0.118. All the crystals contain discrete molecules, and the principal differences lie in the M–N=C angles [134.7, 139.5 for (1), 127.0 for (2), 121.3° for (3)]. The deviation of this angle from 120° and its change is attributed to the presence of $p_\pi \rightarrow d_\pi$ bonding, decreasing from Si to Sn. The structures of (2) and (3) were determined by the heavy-atom method, and of (1) by direct methods.

FEW structures of compounds containing the ketimine group (R_2–C=N–M) have been determined, despite its interest as a probe for the nature of the N–M interaction. In three known structures, M is a Group II or III element, Be,[1] B,[2] or Al.[3] In the present work, Group IV elements have been studied systematically, in the determination of the crystal structures of the tetrakis(diphenylketimine) derivatives $M(NCPh_2)_4$ [M = Si (1), Ge (2), and Sn (3)]. The results have revealed significant information about d_π–p_π bonding in these compounds; a preliminary report has been published.[4]

TABLE 1

Crystal data

	Compound	System	a/Å	b/Å	c/Å	α/°	β/°	γ/°	U/Å^3
(1)	$C_{52}H_{40}N_4Si$	Triclinic	12.342(6)	18.100(8)	19.586(15)	86.89(5)	82.72(5)	84.06(4)	4 313
(2)	$C_{52}H_{40}N_4Ge$	Monoclinic	24.050(2)	11.971(1)	18.839(3)	90	130.44(8)	90	4 128
(3)	$C_{52}H_{40}N_4Sn$	Tetragonal	18.142(5)	18.142	14.461(3)	90	90	90	4 758

	D_c	Z	Space group	Molecular symmetry	F(000)	λ/Å	Total refls.	Obs. (3σ) refls.	μ/cm^{-1}
(1)	1.16	4	$P\bar{1}$	1	1 632	0.71069	5 205	2 524	0.89
(2)	1.28	4	$C2/c$	2	1 648	0.71069	2 130	2 189	7.7
						1.5418	1 830		12.9
(3)	1.17	4	$I4_1/a$	$\bar{4}$	1 720	1.5418	1 994	1 329	53.6

EXPERIMENTAL

All three compounds were prepared by the method of ref. 5 from the lithium salt of diphenylketimine and the appropriate Group IV halide:[6]

$$4Ph_2C{=}NLi + MX_4 \longrightarrow 4LiX + (Ph_2CN)_4M$$

The products were obtained as yellow moisture-sensitive crystals, and were recrystallised from hexane. (1) and (2) formed ill defined chunky crystals, whereas crystals of (3) were bipyramidal.

The samples were mounted in Lindemann glass capillaries in a dry box; particular precautions against traces of moisture were required when handling (3), and the capillaries were baked at 360 K for several hours under vacuum.

Crystal Data.—These are listed in Table 1. Data were collected with a Syntex $P2_1$ four-circle diffractometer in the θ—2θ mode with graphite monochromator; accurate cell constants were obtained by a least-squares fit to the reflecting positions of 15 high-angle reflections. No density measurements were made because of the experimental difficulties, but only the values of Z shown give plausible D_c. For (1), because of the large number of possible reflections, the maximum 2θ value was limited to 40° for

---

[1] J. B. Farmer, Ph.D. Thesis, Durham University, 1973.

[2] G. J. Bullen and K. Wade, *Chem. Comm.*, 1971, 1122.

[3] H. M. M. Shearer, R. Snaith, J. D. Sowerby, and K. Wade, *Chem. Comm.*, 1971, 1275, 183.

[4] N. W. Alcock, M. Pierce-Butler, G. R. Willey, and K. Wade, *J.C.S. Chem. Comm.*, 1975, 183.

[5] L.-H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

[6] C. Summerford and K. Wade, *J. Chem. Soc.* (*A*), 1969, 1487.

Table 2

(*a*) Independent atomic co-ordinates ($\times 10^4$) and anisotropic * temperature factors ($\times 10^3$), with standard deviations in parentheses for (1)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	680(4)	9 243(3)	7 515(3)	43(4)	45(4)	55(4)	1(3)	−14(3)	−2(3)
Si(2)	4 613(5)	6 051(3)	2 571(3)	67(5)	53(4)	48(4)	−15(3)	−9(4)	−7(3)
N(11)	−68(10)	9 390(8)	6 837(7)	44(11)	44(11)	58(11)	6(8)	−24(9)	12(8)
N(12)	499(11)	8 376(8)	7 871(6)	39(11)	56(12)	36(9)	−14(9)	1(8)	10(8)
N(13)	1 981(11)	9 358(7)	7 125(6)	29(11)	53(11)	50(10)	−4(9)	−10(9)	8(8)
N(14)	341(10)	9 848(7)	8 180(7)	39(11)	50(10)	34(9)	−7(8)	−9(8)	−10(3)
N(21)	4 628(12)	6 816(8)	2 019(8)	82(14)	60(12)	53(11)	−14(9)	−20(10)	1(10)
N(22)	4 455(10)	5 291(8)	2 142(7)	37(11)	47(11)	80(11)	−21(9)	−19(8)	−20(9)
N(23)	5 809(14)	5 808(8)	2 916(7)	51(14)	62(12)	55(10)	−4(12)	−11(11)	−6(8)
N(24)	3 543(11)	6 291(7)	3 187(7)	90(13)	36(9)	47(9)	0(8)	−3(10)	−9(7)
C(11)	581(15)	51(10)	3 436(8)	62(15)	55(14)	31(12)	−29(12)	11(10)	3(10)
C(12)	292(15)	2 021(10)	2 023(8)	38(13)	56(16)	48(13)	−1(12)	−2(11)	−1(11)
C(13)	2 813(14)	8 969(10)	6 854(8)	30(13)	67(16)	48(13)	−1(8)	−21(11)	11(10)
C(14)	951(13)	10 028(8)	8 616(8)	49(14)	45(11)	31(11)	−1(10)	7(10)	2(9)
C(21)	4 183(16)	7 070(10)	1 498(9)	96(17)	62(15)	34(14)	−31(12)	4(13)	−21(12)
C(22)	4 006(14)	4 690(9)	2 235(8)	55(14)	54(13)	37(12)	6(11)	−5(10)	−34(11)
C(23)	3 165(18)	4 190(9)	7 259(8)	64(18)	35(11)	68(13)	0(13)	−19(13)	4(9)
C(24)	3 363(14)	6 651(9)	3 757(9)	69(15)	33(12)	71(13)	−1(11)	−18(12)	7(10)

(*b*) Co-ordinates ($\times 10^5$) of rigid-group atoms and isotropic temperature factors ($\times 10^3$)

Atom	X	Y	Z	U	Atom	X	Y	Z	U
C(111)	10 850	1 468	40 858	51(4)	C(211)	45 291	77 488	11 252	66(5)
C(112)	12 506	8 631	42 582	52(4)	C(212)	38 047	82 848	8 388	93(6)
C(113)	16 593	9 740	48 754	76(5)	C(213)	42 049	88 880	4 487	110(6)
C(114)	19 023	3 685	53 202	71(5)	C(214)	53 295	89 551	3 450	102(6)
C(115)	17 366	−3 478	51 478	80(5)	C(215)	60 538	84 191	6 315	109(7)
C(116)	13 280	−4 587	45 306	72(5)	C(216)	56 536	78 160	10 216	79(5)
H(112)	10 851	12 755	39 553	111(49)	H(212)	30 389	82 391	9 094	65(4)
H(113)	17 721	14 618	49 928	73(37)	H(213)	37 116	92 530	2 536	227(52)
H(114)	21 806	4 440	57 405	218(61)	H(214)	56 020	93 659	794	380(84)
H(115)	19 021	−7 602	54 507	277(75)	H(215)	68 197	84 648	5 609	112(45)
H(116)	12 151	−9 465	44 132	114(57)	H(216)	61 469	74 509	12 166	61(48)
C(311)	6 894	92 804	31 735	62(4)	C(411)	32 546	67 199	12 263	51(5)
C(312)	17 216	88 976	30 065	105(6)	C(412)	24 685	63 850	16 805	73(5)
C(313)	18 107	81 746	27 719	102(6)	C(413)	16 504	60 412	14 238	90(6)
C(314)	8 678	78 343	27 044	98(6)	C(414)	16 182	60 323	7 128	89(6)
C(315)	−1 644	82 170	28 714	123(6)	C(415)	24 043	63 672	2 586	87(5)
C(316)	−2 535	89 401	31 060	867(6)	C(416)	32 224	67 110	5 153	76(5)
H(312)	23 638	91 294	30 524	−89(31)	H(412)	24 904	63 910	21 646	94(48)
H(313)	25 137	79 139	26 581	197(64)	H(413)	11 151	58 131	17 331	132(45)
H(314)	9 285	73 419	25 446	518(93)	H(414)	10 611	57 982	5 380	218(73)
H(315)	−8 066	79 853	28 255	104(50)	H(415)	23 824	63 612	−2 255	212(69)
H(316)	−9 565	92 007	32 198	97(42)	H(416)	37 577	69 391	2 060	90(39)
C(121)	1 282	27 988	17 275	49(4)	C(221)	34 720	44 386	29 368	55(5)
C(122)	10 135	31 803	14 411	74(5)	C(222)	39 887	45 279	35 184	66(5)
C(123)	8 311	39 019	11 630	88(6)	C(223)	35 143	42 975	41 701	90(6)
C(124)	−2 366	42 420	11 714	86(5)	C(224)	25 231	39 779	42 402	84(6)
C(125)	−11 219	38 605	14 578	87(6)	C(225)	20 064	38 886	36 586	84(5)
C(126)	−9 395	31 389	17 358	62(5)	C(226)	24 808	41 190	30 069	75(6)
H(122)	17 407	29 487	14 354	90(5)	H(222)	46 636	47 455	34 707	65(34)
H(123)	14 340	41 616	9 680	194(5)	H(223)	38 662	43 583	45 662	205(73)
H(124)	−3 609	47 334	9 820	276(5)	H(224)	22 001	38 210	46 841	216(61)
H(125)	−18 491	40 921	14 635	123(44)	H(225)	13 314	36 710	37 063	132(47)
H(126)	−15 424	28 792	19 309	97(36)	H(226)	21 289	40 582	26 108	90(33)
C(321)	14 254	17 554	22 195	55(4)	C(421)	40 261	41 790	16 553	53(5)
C(322)	19 112	21 594	26 679	80(5)	C(422)	41 184	44 966	9 874	69(5)
C(323)	29 127	18 821	28 856	84(5)	C(423)	41 675	40 478	4 212	104(6)
C(324)	34 284	12 008	26 550	86(6)	C(424)	41 242	32 813	5 229	90(6)
C(325)	29 427	7 967	22 067	97(6)	C(425)	40 319	29 637	11 909	95(6)
C(326)	19 412	10 740	19 889	70(5)	C(426)	39 828	34 125	17 570	74(6)
H(322)	15 599	26 235	28 249	35(30)	H(422)	41 479	50 186	9 181	37(33)
H(323)	32 435	21 573	31 910	257(70)	H(423)	42 304	42 641	−337	200(67)
H(324)	41 105	10 120	28 033	312(80)	H(424)	41 576	29 757	1 374	411(107)
H(325)	32 940	3 327	20 496	175(59)	H(425)	40 024	24 417	12 602	164(57)
H(326)	16 104	7 988	16 835	88(43)	H(426)	39 199	31 962	22 119	70(56)
C(131)	28 832	81 423	68 200	67(5)	C(231)	26 691	38 460	79 337	68(5)
C(132)	37 208	76 841	70 873	66(6)	C(232)	28 045	41 610	85 514	84(5)
C(133)	37 516	69 124	70 574	84(6)	C(233)	22 813	38 925	91 756	95(5)
C(134)	29 447	65 988	67 602	89(6)	C(234)	16 228	33 090	91 821	102(6)
C(135)	21 070	70 570	64 928	78(7)	C(235)	14 874	29 940	85 644	111(6)
C(136)	20 762	78 287	65 227	62(6)	C(236)	20 105	32 625	79 403	103(6)
H(132)	42 704	78 976	72 897	105(31)	H(232)	32 529	45 584	85 470	65(41)
H(133)	43 221	66 004	72 395	185(54)	H(233)	23 735	41 071	95 963	236(72)
H(134)	29 657	60 733	67 399	230(69)	H(234)	12 665	31 261	96 072	375(82)
H(135)	15 575	68 435	62 904	189(54)	H(235)	10 389	25 966	85 689	247(68)
H(136)	15 057	81 407	63 406	66(52)	H(236)	19 183	30 480	75 196	77(35)

TABLE 2 (*Continued*)

Atom	X	Y	Z	U	Atom	X	Y	Z	U
C(331)	37 837	93 449	65 471	58(5)	C(431)	23 734	45 342	68 002	72(6)
C(332)	45 018	90 094	60 171	78(5)	C(432)	12 957	47 654	70 642	84(6)
C(333)	53 962	93 689	57 085	95(6)	C(433)	5 967	51 663	66 408	114(6)
C(334)	55 724	100 640	59 299	90(6)	C(434)	9 754	53 360	59 533	86(7)
C(335)	48 542	103 995	64 600	81(5)	C(435)	20 532	51 048	56 893	81(7)
C(336)	39 599	100 400	67 686	69(5)	C(436)	27 521	47 039	61 127	72(6)
H(332)	43 818	85 361	58 662	26(35)	H(432)	10 377	46 499	75 324	124(43)
H(333)	58 852	91 404	53 475	190(64)	H(433)	−1 372	53 237	68 206	224(83)
H(334)	61 814	103 089	57 198	36(83)	H(434)	4 995	56 090	56 650	300(81)
H(335)	49 742	108 729	66 108	138(52)	H(435)	23 111	52 204	52 211	151(56)
H(336)	34 708	102 685	71 296	250(29)	H(436)	34 861	45 465	59 329	121(80)
C(141)	20 834	96 575	86 857	45(4)	C(241)	22 190	67 438	41 050	59(4)
C(142)	22 724	88 882	87 896	74(5)	C(242)	18 904	73 544	45 178	74(5)
C(143)	33 424	85 532	87 856	85(5)	C(243)	7 971	74 886	48 014	84(6)
C(144)	42 234	89 876	86 776	88(6)	C(244)	323	70 122	46 722	97(6)
C(145)	40 345	97 569	85 736	84(5)	C(245)	3 609	64 016	42 594	101(6)
C(146)	29 645	100 919	85 776	75(5)	C(246)	14 542	62 673	39 758	76(5)
H(142)	16 724	85 924	88 632	34(33)	H(242)	24 112	76 789	46 059	77(56)
H(143)	34 710	80 292	88 564	88(49)	H(243)	5 734	79 045	50 826	124(60)
H(144)	49 521	87 594	86 748	349(78)	H(244)	−7 123	71 037	48 653	165(70)
H(145)	46 345	100 528	85 000	203(60)	H(245)	−1 600	60 771	41 713	238(59)
H(146)	28 358	106 159	85 068	79(39)	H(246)	16 779	58 515	36 946	124(61)
C(341)	5 475	6 346	91 089	48(4)	C(441)	42 589	69 682	40 581	61(5)
C(342)	−2 889	11 556	89 232	57(5)	C(442)	42 904	68 744	47 688	85(6)
C(343)	−6 656	17 534	93 436	78(5)	C(443)	51 206	71 536	50 722	113(7)
C(344)	−2 057	18 303	99 499	85(5)	C(444)	59 192	75 267	46 648	107(7)
C(345)	6 308	13 093	101 356	86(6)	C(445)	58 876	76 206	39 541	112(7)
C(346)	10 074	7 115	97 151	78(5)	C(446)	50 575	73 413	36 508	81(5)
H(342)	−6 021	−11 033	85 103	121(50)	H(442)	37 466	66 203	50 463	8(27)
H(343)	−12 352	−21 082	92 172	159(49)	H(443)	51 421	70 897	55 562	298(82)
H(344)	−4 622	−22 374	102 362	189(60)	H(444)	64 845	77 169	48 714	451(125)
H(345)	9 439	13 617	105 484	303(82)	H(445)	64 315	78 747	36 767	144(74)
H(346)	15 771	3 567	98 416	100(42)	H(446)	50 360	74 053	31 668	50(43)

* In the form: $\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$.

the first 500 reflections, and then reduced to 35°. For (2), the first 2 130 reflections were collected with Mo-K_α ($\lambda = 0.71069$ Å) radiation to 2θ 50°; after a computer malfunction, collection was completed with Cu-K_α ($\lambda = 1.5418$ Å) radiation to $2\theta_{max.}$ 130°. For both these compounds variable scan rates were used, between 1° min^{-1} and 29° min^{-1} in 2θ depending on the intensity of a prescan. Three standard reflections were examined at intervals of 100 reflections; no decomposition was observed during collection for either (1) or (2).

Compound (3) is extremely moisture sensitive, so much so that despite all precautions the mounted crystals had a very limited lifetime. For this reason the diffractometer was used for preliminary investigations instead of standard photographic procedures.

The initial results from the centring procedure pointed to a tetragonal space group; the difference in intensities of possibly equivalent reflections [$F(hkl) = F(\bar{h}kl)$] indicated Laue group $4/m$. Random sampling of the data indicated that the lattice was body-centred as no reflections satisfying the condition $h + k + l = 2n + 1$ were observed. For data collection, a variable scan rate was employed with a minimum speed of 5° min^{-1} in 2θ. Copper radiation was used to $2\theta_{max.}$ 120°. A total of 1 994 unique reflections was measured in 23 h: three standards were remeasured after every hundred reflections. Their fall off in intensity with time showed a slight break after 7 h, and for rescaling this was fitted to the equation: $F = F_0(1.0 + \alpha T)(1.0 + \beta T \sin\theta/\lambda)$ where T is exposure time in hours, and for $T < 7$, $\alpha = 0.023$, $\beta = 0.010$, for $T > 7$, $\alpha = 0.014$, $\beta = 0.031$. The maximum rescale factor for any of the standards was 1.72 (calculated on F). Only for (3) was an absorption correction applied. Transmission factors, calculated by the analytical method with ABSCOR [7] ranged from 0.127 to 0.354. All data were corrected for Lorentz and polarisation factors (monochromator assumed ideally mosaic).

For (3) the systematic extinctions [hkl, $h + k + l \neq 2n$; $hk0$, $h(k) \neq 2n$; $00l$, ($l \neq 4n$)] indicate space group $I4_1/a$ uniquely. For (2) (hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$), and (1) (no extinctions), the alternatives $C2/c$ or Cc and $P\bar{1}$ or $P1$ exist; in each case the first was assumed and shown to be correct by satisfactory refinement. In (2) and (3) the molecule has crystallographic symmetry (Table 1), and for (3) the origin was chosen at the $\bar{1}$ rather than the $\bar{4}$ position.

Structure Solutions.—For (2) and (3) the structures were readily solved by the heavy-atom method, and no difficulty was found in destroying the pseudosymmetry of the initial heavy-atom phased Fourier syntheses. Refinement proceeded normally, with anisotropic temperature factors in the final cycles for all except hydrogen atoms which were included and refined, using statistical weights for (2) and unit weights for (3). Final R values were 0.058 and 0.118 respectively. The latter value is high, but not unexpected in view of the rapid crystal decomposition.

For (1) an initial solution was very much more difficult to obtain. The Patterson synthesis was insufficiently dominated by Si $\cdots$ Si vectors to be interpretable. The first attempt by direct methods used MULTAN;[8] examination of 7 solutions obtained from all sign combinations (except $+++$) for the three most strongly connected reflections did not show two strong peaks for Si atoms, and were therefore rapidly rejected. Application of the PHASE

---

[7] N. W. Alcock, 'The Analytical Method for Absorption Correction,' in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

[8] G. Germain, P. Main, and M. M. Wilson, *Acta Cryst.*, 1971, **A27**, 369.

TABLE 3

Atomic co-ordinates (× 10^4), isotropic and anisotropic * temperature factors (× 10), with standard deviations in parentheses, for (2)

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ge	0	1 310(1)	2 500	21.1(5)	12.0(5)	21.1(4)	0	14.2(4)	0
N(1)	573(3)	2 216(4)	2 377(3)	20(3)	12(2)	32(2)	−2(2)	20(2)	−10(2)
N(2)	583(3)	433(4)	3 568(3)	33(3)	10(2)	26(2)	5(2)	20(2)	3(2)
C(1)	333(4)	3 076(5)	1 854(4)	28(3)	12(3)	22(2)	−2(2)	21(2)	−3(2)
C(2)	904(4)	9 530(5)	3 707(4)	20(3)	7(3)	22(2)	1(2)	11(2)	1(2)
C(21)	984(4)	8 976(6)	3 050(4)	21(3)	23(4)	25(2)	8(2)	15(3)	10(3)
C(22)	861(4)	7 822(6)	2 880(4)	29(4)	18(3)	34(3)	−3(2)	21(3)	2(3)
C(23)	894(5)	7 328(7)	2 246(5)	40(5)	28(4)	50(4)	−12(3)	30(4)	1(4)
C(24)	1 072(5)	7 954(7)	1 805(5)	39(5)	46(5)	40(3)	−3(3)	28(4)	14(4)
C(25)	1 221(5)	9 081(7)	1 998(5)	45(5)	43(5)	49(3)	14(3)	37(4)	21(4)
C(26)	1 166(4)	9 604(7)	2 607(5)	32(4)	30(4)	42(3)	9(3)	27(3)	10(3)
C(27)	1 212(4)	8 910(5)	4 581(4)	29(4)	11(3)	30(3)	−1(2)	18(3)	0(3)
C(28)	864(4)	8 986(6)	4 949(5)	41(4)	22(4)	39(3)	5(3)	28(3)	1(3)
C(29)	1 125(5)	8 401(6)	5 747(5)	61(5)	24(4)	48(5)	−1(3)	41(4)	−9(3)
C(210)	1 741(5)	7 777(7)	6 199(5)	45(5)	28(4)	31(3)	8(3)	20(3)	−3(4)
C(211)	2 119(5)	7 711(7)	5 869(5)	35(5)	28(4)	37(3)	8(3)	17(3)	7(4)
C(212)	1 839(4)	8 268(6)	5 053(5)	32(4)	23(3)	32(3)	3(2)	19(3)	5(3)
C(111)	877(4)	3 783(6)	1 942(4)	33(4)	15(3)	28(2)	0(2)	22(3)	4(3)
C(112)	718(4)	4 349(6)	1 177(4)	34(4)	20(4)	30(3)	1(2)	22(3)	−4(3)
C(113)	1 232(5)	4 989(6)	1 267(5)	49(5)	22(3)	43(3)	3(3)	37(4)	−2(3)
C(114)	1 923(5)	5 110(6)	2 125(6)	45(5)	23(4)	60(4)	−4(3)	44(4)	−7(3)
C(115)	2 091(5)	4 558(7)	2 894(5)	37(4)	35(4)	38(3)	−7(3)	25(3)	−6(3)
C(116)	1 584(4)	3 891(6)	2 803(5)	39(4)	30(4)	36(3)	0(3)	30(3)	−3(3)
C(117)	−440(4)	3 468(6)	1 176(4)	33(4)	23(4)	24(2)	4(2)	21(3)	−8(3)
C(118)	−630(4)	4 561(7)	1 203(5)	31(4)	33(4)	30(3)	5(3)	21(3)	9(3)
C(119)	−1 337(5)	4 941(8)	623(6)	46(5)	46(5)	46(4)	11(3)	34(4)	13(4)
C(120)	−1 889(5)	4 233(9)	−22(6)	42(5)	70(6)	49(4)	24(4)	31(4)	16(5)
C(121)	−1 730(5)	3 168(9)	−113(6)	37(5)	60(6)	40(3)	7(3)	18(4)	−16(4)
C(122)	−1 011(5)	2 772(7)	491(5)	40(5)	27(4)	37(3)	9(3)	20(3)	−4(4)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
H(22)	712(30)	7 386(48)	3 165(32)	−13(9)	H(112)	264(40)	4 244(65)	610(44)	11(15)
H(23)	816(46)	6 574(76)	2 141(53)	29(20)	H(113)	1 118(42)	5 316(69)	723(47)	17(16)
H(24)	1 133(46)	7 554(75)	1 403(52)	30(18)	H(114)	2 292(32)	5 518(53)	2 178(36)	−7(11)
H(25)	1 357(41)	9 568(45)	1 720(65)	12(14)	H(115)	2 552(36)	4 684(59)	3 449(40)	4(13)
H(26)	1 247(35)	10 422(58)	2 701(38)	0(12)	H(116)	1 690(33)	3 482(53)	3 287(37)	−2(11)
H(28)	444(35)	9 282(58)	4 614(40)	5(12)	H(118)	−2 406(50)	5 053(76)	1 670(55)	32(20)
H(29)	843(44)	8 413(70)	5 927(50)	23(16)	H(119)	−1 431(40)	5 859(61)	631(45)	10(15)
H(210)	1 956(44)	7 360(72)	6 797(49)	22(17)	H(120)	−2 357(54)	4 595(93)	−425(63)	50(24)
H(211)	2 560(51)	7 255(80)	6 143(57)	32(20)	H(121)	−2 123(44)	2 728(71)	−541(49)	20(17)
H(212)	2 117(36)	8 224(58)	4 788(40)	6(13)	H(122)	−895(34)	2 004(53)	418(36)	−3(11)

* In the form: $\exp\{-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)\}$.

TABLE 4

Atomic co-ordinates (× 10^4), isotropic (× 10^2) and anisotropic * (× 10^3) temperature factors, with standard deviations in parentheses, for (3)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0	2 500	1 250	34(1)	34	34(1)	0	0	0
N	712(9)	3 083(9)	2 093(12)	29(9)	35(9)	54(11)	−12(8)	−15(8)	−13(9)
C(1)	470(11)	3 460(10)	2 822(16)	31(12)	18(10)	72(16)	−10(9)	0(11)	7(11)
C(11)	995(11)	3 759(12)	3 500(13)	37(12)	43(13)	38(14)	−20(10)	−6(9)	2(10)
C(12)	813(15)	4 347(14)	4 053(17)	60(17)	58(16)	58(17)	−23(14)	−4(13)	−7(13)
C(13)	1 341(23)	4 616(18)	4 675(21)	104(27)	66(22)	70(21)	−28(21)	4(21)	−19(18)
C(14)	2 014(25)	4 279(27)	4 740(30)	99(32)	121(37)	82(26)	−67(29)	−40(24)	28(23)
C(15)	2 190(19)	3 697(19)	4 173(24)	78(22)	65(21)	89(23)	−16(19)	−22(19)	9(18)
C(16)	1 694(16)	3 424(17)	3 571(20)	40(18)	73(18)	48(19)	−24(15)	−20(14)	9(16)
C(21)	325(11)	1 402(10)	3 022(15)	43(13)	23(11)	55(13)	5(10)	6(11)	4(10)
C(22)	651(12)	1 640(12)	3 792(16)	56(14)	50(14)	36(11)	17(11)	−12(13)	−4(13)
C(23)	1 374(16)	1 553(15)	3 957(17)	81(19)	58(16)	43(18)	4(15)	−18(14)	−8(13)
C(24)	1 793(20)	1 166(19)	3 312(27)	77(22)	71(20)	102(20)	14(18)	−32(21)	−2(18)
C(25)	1 493(18)	905(22)	2 538(25)	70(21)	112(29)	76(23)	31(20)	2(18)	−24(21)
C(26)	759(14)	1 013(14)	2 365(19)	39(14)	62(16)	76(18)	−2(13)	−12(14)	−2(14)

Atom	X	Y	Z	U	Atom	X	Y	Z	U
H(12)	270(115)	4 473(111)	3 906(155)	7(6)	H(22)	311(68)	2 092(70)	3 920(103)	3(3)
H(13)	1 154(133)	5 004(141)	4 988(178)	5(8)	H(23)	1 565(98)	1 762(96)	4 494(128)	6(5)
H(14)	2 189(144)	4 388(149)	4 975(189)	4(9)	H(24)	2 039(178)	1 211(197)	3 287(250)	9(15)
H(15)	2 669(156)	3 384(152)	4 202(189)	12(10)	H(25)	1 693(153)	735(160)	2 193(195)	7(11)
H(16)	1 695(100)	2 961(89)	3 342(123)	14(6)	H(26)	483(96)	951(94)	1 973(117)	8(5)

* See footnote to Table 2.

program [9] was successful. In the first stage the 87 triple-product relationships needed to specify the sign of 90 'generator' reflections were found (with three signs taken positive for origin definition), with for each relationship a list of those reflections which would change sign if that relationship were false. In order to split the generators into two groups, which are strongly linked internally but have only weak interconnections, a low probability relationship was chosen on which the phases of a large number of generators depended, and it was treated as false; this reversed the signs of 50 reflections. The triple-product relationships were then used to phase a further 525 phases (257 positive) and the corresponding E map did show two major peaks, identified as Si, and 20 peaks, identified as C, which provided a satisfactory starting point for Fourier and least-squares refinement. For the final cycles the phenyl rings were refined as rigid bodies to reduce the number of temperature factors [C–C 1.395, C–H 0.95 Å (ref. 10)] with isotropic parameters for their atoms, anisotropic for the rest. The final R was 0.067. A comparison of the PHASE results with the final phases showed that the initial phasing was not perfect, with 7 incorrect generator phases, but that all the MULTAN results were very poor.

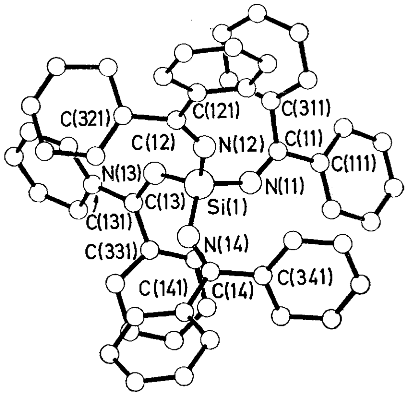

FIGURE 1 Compound (1), molecule (1). Phenyl rings are numbered in sequence C(*mn*1)—(*mn*6), and each hydrogen atom is numbered according to the carbon atom to which it is attached

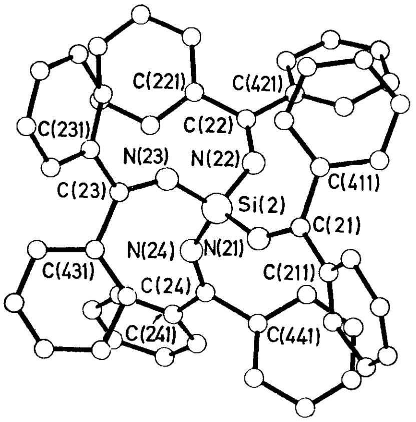

FIGURE 2 Compound (1), molecule (2)

TABLE 5

Bond distances (Å) and angles (°) in (1), with standard deviations in parentheses

(*a*) Distances

Molecule (1)		Molecule (2)	
Si(1)–N(11)	1.703(15)	Si(2)–N(21)	1.710(15)
Si(1)–N(12)	1.707(15)	Si(2)–N(22)	1.684(15)
Si(1)–N(13)	1.718(14)	Si(2)–N(23)	1.707(18)
Si(1)–N(14)	1.723(14)	Si(2)–N(24)	1.708(14)
N(11)–C(11)	1.268(21)	N(21)–C(21)	1.261(24)
N(12)–C(12)	1.260(24)	N(22)–C(22)	1.265(22)
N(13)–C(13)	1.258(21)	N(23)–C(23)	1.271(28)
N(14)–C(14)	1.279(22)	N(24)–C(24)	1.299(21)
C(11)–C(111)	1.506(17) *	C(21)–C(211)	1.468(18) *
C(11)–C(311)	1.496(17) *	C(21)–C(411)	1.528(20) *
C(12)–C(121)	1.497(18) *	C(22)–C(221)	1.513(15) *
C(12)–C(321)	1.522(18) *	C(22)–C(421)	1.493(17) *
C(13)–C(131)	1.492(18) *	C(23)–C(231)	1.514(17) *
C(13)–C(331)	1.484(18) *	C(23)–C(431)	1.479(20) *
C(14)–C(141)	1.506(16) *	C(24)–C(241)	1.486(16) *
C(14)–C(341)	1.499(15) *	C(24)–C(441)	1.493(18) *

(*b*) Angles

Molecule (1)	
N(11)–Si(1)–N(12)	108.49(72)
N(11)–Si(1)–N(13)	101.77(64)
N(11)–Si(1)–N(14)	116.18(66)
N(12)–Si(1)–N(13)	115.26(66)
N(12)–Si(1)–N(14)	105.99(63)
N(13)–Si(1)–N(14)	109.48(68)
Si(1)–N(11)–C(11)	135.6(13)
Si(1)–N(12)–C(12)	135.2(13)
Si(1)–N(13)–C(13)	139.0(13)
Si(1)–N(14)–C(14)	128.2(11)
N(11)–C(11)–C(111)	119.1(14) *
N(11)–C(11)–C(311)	124.3(14) *
C(111)–C(11)–C(311)	116.5(11) *
N(12)–C(12)–C(121)	120.4(14) *
N(12)–C(12)–C(321)	122.4(14) *
C(121)–C(12)–C(321)	117.0(13) *
N(13)–C(13)–C(131)	123.5(15) *
N(13)–C(13)–C(331)	118.9(15) *
C(131)–C(13)–C(331)	117.5(11) *
N(14)–C(14)–C(141)	124.2(12) *
N(14)–C(14)–C(341)	120.3(12) *
C(141)–C(14)–C(341)	115.5(11) *
Molecule (2)	
N(21)–Si(2)–N(22)	110.12(73)
N(21)–Si(2)–N(23)	114.87(79)
N(21)–Si(2)–N(24)	103.32(67)
N(22)–Si(2)–N(23)	103.03(71)
N(22)–Si(2)–N(24)	113.72(70)
N(23)–Si(2)–N(24)	112.23(71)
Si(2)–N(21)–C(21)	138.8(15)
Si(2)–N(22)–C(22)	140.2(12)
Si(2)–N(23)–C(23)	138.9(12)
Si(2)–N(24)–C(24)	138.4(13)
N(21)–C(21)–C(211)	120.4(16) *
N(21)–C(21)–C(411)	123.5(15) *
C(211)–C(21)–C(411)	116.1(12) *
N(22)–C(22)–C(221)	122.1(13) *
N(22)–C(22)–C(421)	120.8(12) *
C(221)–C(22)–C(421)	117.0(11) *
N(23)–C(23)–C(231)	123.5(15) *
N(23)–C(23)–C(431)	120.8(13) *
C(231)–C(23)–C(431)	115.7(14) *
N(24)–C(24)–C(241)	117.7(14) *
N(24)–C(24)–C(441)	122.1(13) *
C(241)–C(24)–C(441)	120.2(11) *

* Standard deviation based solely on contribution from non-phenyl carbon atom.

Views of the molecules with atomic numbering are shown in Figures 1—4. Atomic co-ordinates and temperature factors are in Tables 2—4, and bond lengths and angles in

---

[9] J. M. Stewart, 'Phase Determination as applied in the '*X*-Ray '67' System, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

[10] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

TABLE 6

Bond distances (Å) and angles (°) in (2), with standard deviations in parentheses

(*a*) Distances

Ge–N(1)	1.883(4)	C(119)–C(120)	1.365(14)
Ge–N(2)	1.859(5)	C(120)–C(121)	1.374(15)
N(1)–C(1)	1.275(8)	C(121)–C(122)	1.399(13)
N(2)–C(2)	1.258(8)	C(122)–C(117)	1.393(110)
C(1)–C(111)	1.474(9)	C(21)–C(22)	1.405(10)
C(1)–C(117)	1.492(10)	C(22)–C(23)	1.380(8)
C(2)–C(21)	1.523(7)	C(23)–C(24)	1.379(11)
C(2)–C(27)	1.492(8)	C(24)–C(25)	1.383(12)
C(111)–C(112)	1.403(8)	C(25)–C(26)	1.388(9)
C(112)–C(113)	1.368(10)	C(26)–C(21)	1.389(9)
C(113)–C(114)	1.381(12)	C(27)–C(28)	1.395(8)
C(114)–C(115)	1.393(10)	C(28)–C(29)	1.385(9)
C(115)–C(116)	1.372(10)	C(29)–C(210)	1.358(13)
C(116)–C(111)	1.399(10)	C(210)–C(211)	1.396(11)
C(117)–C(118)	1.397(10)	C(211)–C(212)	1.385(9)
C(118)–C(119)	1.371(12)	C(212)–C(27)	1.385(10)

(*b*) Angles

N(1)–Ge–N(2)	111.15(23)
N(1)–Ge–N(2′)	106.75(25)
N(1)–Ge–N(1′)	109.81(25)
N(2)–Ge–N(2′)	111.25(25)
Ge–N(1)–C(1)	123.78(45)
Ge–N(2)–C(2)	130.08(48)
N(1)–C(1)–C(111)	116.89(58)
N(1)–C(1)–C(117)	127.13(53)
C(111)–C(1)–C(117)	115.96(50)
C(21)–C(2)–C(27)	116.51(51)
C(1)–C(111)–C(112)	122.17(59)
C(1)–C(111)–C(116)	120.35(50)
C(112)–C(111)–C(116)	117.46(61)
C(111)–C(112)–C(113)	121.49(67)
C(112)–C(113)–C(114)	120.50(58)
C(113)–C(114)–C(115)	118.92(65)
C(114)–C(115)–C(116)	120.81(72)
C(115)–C(116)–C(111)	120.78(58)
C(1)–C(117)–C(118)	121.22(60)
C(1)–C(117)–C(122)	122.35(63)
C(118)–C(117)–C(122)	116.43(69)
C(117)–C(118)–C(119)	123.17(76)
C(118)–C(119)–C(120)	119.34(83)
C(119)–C(120)–C(121)	119.88(84)
C(120)–C(121)–C(122)	120.70(85)
C(121)–C(122)–C(117)	120.32(80)
C(2)–C(21)–C(22)	119.68(50)
C(2)–C(21)–C(26)	120.56(60)
C(22)–C(21)–C(26)	119.75(55)
C(21)–C(22)–C(23)	119.83(61)
C(22)–C(23)–C(24)	120.28(72)
C(23)–C(24)–C(25)	120.07(58)
C(24)–C(25)–C(26)	120.62(66)
C(25)–C(26)–C(21)	119.36(73)
C(2)–C(27)–C(28)	119.25(60)
C(2)–C(27)–C(212)	122.52(52)
C(28)–C(27)–C(212)	118.22(56)
C(27)–C(28)–C(29)	120.80(70)
C(28)–C(29)–C(210)	119.94(64)
C(29)–C(210)–C(211)	120.91(61)
C(210)–C(211)–C(212)	118.65(74)
C(211)–C(212)–C(27)	121.40(62)

Tables 5—7. Final structure factors are listed in Supplementary Publication No. SUP 21306 (44 pp., 1 microfiche).* Apart from the local initial data processing program and ABSCOR (a local version), all computation for (1) and (3) was with the ' *X*-Ray ' on a CDC 7600 and IBM 370/195.[11] For (2) the programs of Dr. D. Russell were used on an ICL 4130.

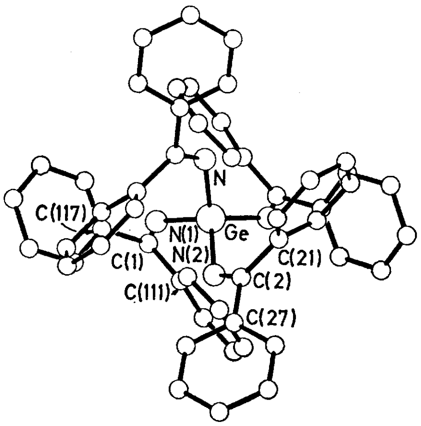

FIGURE 3 Compound (2), viewed along the two-fold axis. Phenyl rings are numbered C(111)—(116), C(117)—(122) and C(21)—(26), and C(27)—(212)

TABLE 7

Bond distances (Å) and angles (°) in (3), with standard deviations in parentheses

(*a*) Distances

Sn–N	2.068(37)	C(15)–C(16)	1.347(49)
N–C(1)	1.330(36)	C(16)–C(11)	1.410(38)
C(1)–C(11)	1.470(36)	C(21)–C(22)	1.332(36)
C(1)–C(21)	1.492(30)	C(22)–C(23)	1.343(37)
C(11)–C(12)	1.374(40)	C(23)–C(24)	1.392(51)
C(12)–C(13)	1.402(49)	C(24)–C(25)	1.332(56)
C(13)–C(14)	1.367(63)	C(25)–C(26)	1.369(43)
C(14)–C(15)	1.374(62)	C(26)–C(21)	1.421(41)

(*b*) Angles

N–Sn–N′	107.71(67)	C(13)–C(14)–C(15)	120.7(38)
N–Sn–N″	110.36(64)	C(14)–C(15)–C(16)	120.8(34)
Sn–N–C(1)	121.5(13)	C(15)–C(16)–C(11)	119.4(28)
N–C(1)–C(11)	120.2(18)	C(1)–C(21)–C(22)	122.4(20)
N–C(1)–C(21)	124.0(18)	C(1)–C(21)–C(26)	119.3(20)
C(11)–C(1)–C(21)	115.7(18)	C(22)–C(21)–C(26)	118.3(20)
C(1)–C(11)–C(12)	121.3(20)	C(21)–C(22)–C(23)	123.0(22)
C(1)–C(11)–C(16)	118.2(20)	C(22)–C(23)–C(24)	118.2(26)
C(12)–C(11)–C(16)	120.5(22)	C(23)–C(24)–C(25)	121.3(33)
C(12)–C(11)–C(13)	118.7(26)	C(24)–C(25)–C(26)	119.9(33)
C(12)–C(13)–C(14)	119.8(32)	C(25)–C(26)–C(21)	119.2(26)

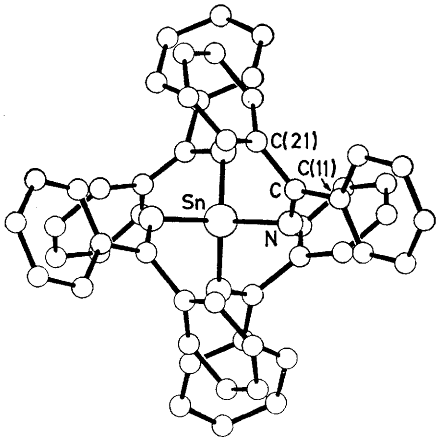

FIGURE 4 Compound (3), viewed along the $\bar{4}$ axis. Phenyl rings are numbered C(11)—(16) and C(21)—(26)

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

DISCUSSION

The general conformation is similar for each of the four molecules [counting the two independent examples of (1)], and they are shown from similar viewpoints in Figures 1—4. Each has an approximately tetrahedral arrangement of four nitrogen atoms about the central atom, with the maximum deviations being those for Si(1) with angles 101.8 to 116.2°. However some major difference must be present to account for the absence of isomorphism, particularly between (1) and (2). This can be identified as the changing M–N–C bond angle, whose average values vary from 139.1 and 134.5 for (1) to 121.3° for (3).

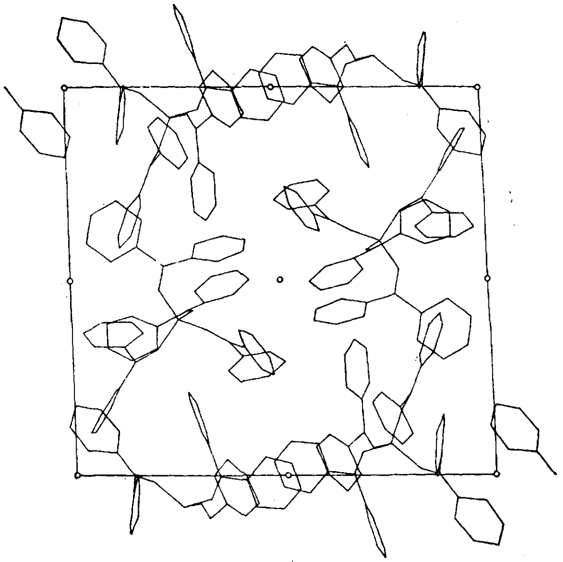

FIGURE 5 Packing diagram for compound (1), viewed down *a*, with *c* across, *b* down from the origin at top left

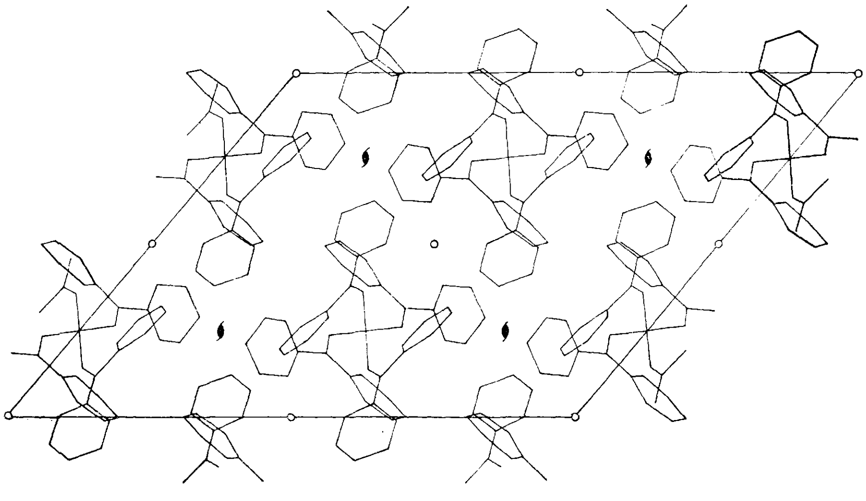

FIGURE 6 Packing diagram for compound (2), viewed down *b*

One possible explanation for this is in terms of the packing of bulky groups, as M changes size. This is, however, insufficient, as Si and Ge are very similar in radius. The alternative is that the hybridization at N is changing from sp^2 in (3) towards sp, moving its lone pair into a p orbital which can more effectively form a p_π–d_π dative bond. In the light of this explanation it is not unexpected both that the Si–N–C angles are not 180° and also that they are not all equal. The maximum possible p_π–d_π donation would be of four electron pairs, but it seems clear that Si only accepts substantially less than this in compound (1), and therefore the Si–N–C angles need not be 180°. It is also reasonable that a suitable total donation can be achieved with differing donation from each nitrogen. This then allows the bond angles to vary as a result of external influences, in particular packing interactions between the bulky phenyl groups.

The M–N–C angles show a steady decrease from (1) to (3) (means 137.1, 127.0, and 121.3°) indicating substantially reduced π bonding to Ge, with none detectable to Sn. Similar conclusions can be reached by considering the M–N bond lengths, although this is less straightforward because of the difficulty of providing standard single-bond lengths. The most reliable estimates (Table 8) can probably be derived by combining M–C, C–C (1.544), and C–N= (1.475°).[12] The differences between Si and Ge are clear, and there is an indication that the shortening with Sn is smaller (but subject to a relatively large error).

TABLE 8

M–N and N–C distances (Å)

			M–N			
	M	M–C	Calc.	Obs. (mean)	Δ *	C=N †
(1)	Si	2.352	1.879	1.717(10)	0.162	1.270(7)
(2)	Ge	2.450	1.928	1.872(5)	0.056	1.266(6)
(3)	Sn	2.810	2.108	2.06(4)	0.048	1.33(4)

* Δ = Calc.—Obs. † Mean obs.

[11] Technical Report TR 192, Computer Science Center, University of Maryland, 1972.

[12] *Chem. Soc. Special Publ.*, No. 18, 1965.

It has been suggested that π interactions in similar Si compounds can occur, not from the lone pair but from the C=N π orbitals. However this is not identifiable in the present structure, where the observed distances (Table 8) show no significant lengthening compared to a normal C=N estimated from atomic radii[12] (1.265 Å).

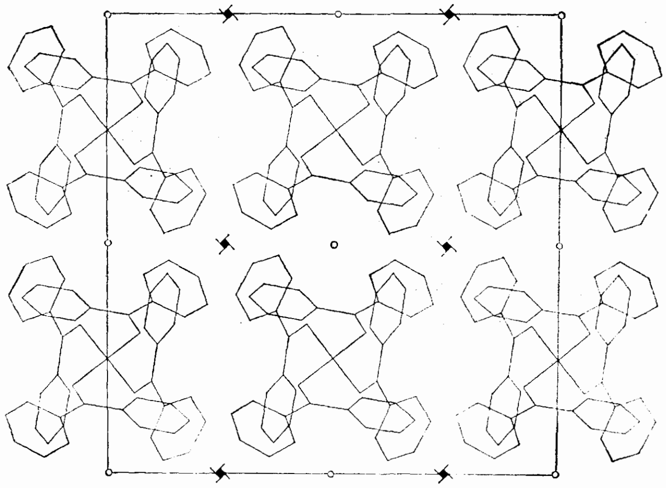

FIGURE 7 Packing diagram for compound (3), viewed down *c*

In conjunction with these compounds, the other ketimino-compounds whose structures are known illustrate the effectiveness of the group as a π donor, and the sensitivity of the M–N–C angle to the amount of π-donation. In both the Be and B diphenylketimines[1,2] the angle is close to 180° while in $LiAl(NCBu^t{}_2)_4$ the terminal ketimino-groups bound to Al have angles of 167° (ref. 13). The π donation is presumably into empty *p* orbitals for Be and B, and into *d* orbitals for Al.

Molecular Packing.—Packing diagrams are shown in Figures 5—7. There are no unusually short intermolecular distances, and it seems that all the molecules behave approximately as spheres. It is very noticeable how the reduction in the M–N–C bond angle leads to more regular arrangement of the phenyl rings, and a more compact packing. This is shown particularly by the molecular volumes, 1 078 Å^3 for (1) and 1 032 Å^3 for (2). All the molecules have C(Ph)–C–C(Ph) angles of *ca.* 115°, and the slight reduction from the expected 120° is presumably due to packing constraints.

We thank Dr. G. R. Willey, Dr. K. Wade for preparing the crystals and for drawing the problem to our attention, and the S.R.C. for a studentship (to M. P.-B.) and a grant for the diffractometer (to N. W. A.).

[5/802 *Received*, 29*th April*, 1975]

[13] R. West, *J. Organometallic Chem.*, 1965, **3**, 314.