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Special features of intermolecular bonding $A\cdots D$ (A = Si, Ge and D = nucleophile) in crystal structures

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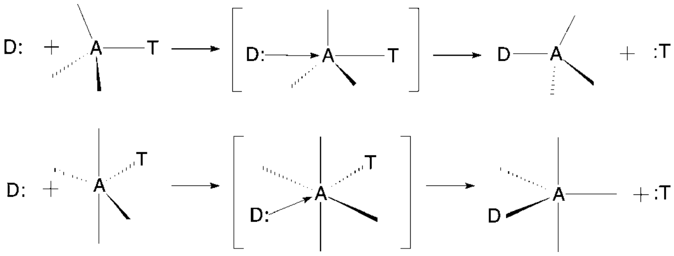
An investigation of the crystal structures of 3346 silicon- and 718 germanium-containing compounds was carried out with a geometrical–topological analysis. The descriptors of inter- and intramolecular contacts $A\cdots D$ are given. Information on the descriptors of $T—A\cdots D$ (where T = leaving group) interactions in terms of a stereoatomic model of crystal structures was described as being helpful in modelling S_N2 reactions. It was established that the formation of multiple intermolecular contacts in crystal structures is unfavorable. The dependence of the descriptors of intermolecular contacts $T—A\cdots$D was studied as a function of the nature of T (leaving group in substitution reactions) and D (nucleophile atom or group of atoms) groups, and the coordination number of an A atom. The constancy of the $T—A$ and $A\cdots D$ bond-order sum in crystal structures was demonstrated.

1. Introduction

The crystal structures of organosilicon and -germanium compounds are widely used (Shaik & Pross, 1982) for the analysis and modeling of reaction paths, as well as the simulation of dynamic processes in the compounds involved by means of the method of structural correlations (MSC). The use of dihedral and basal angles in the reconstruction of the pseudorotation of penta-coordinated P, Si and Ge complexes is a classical approach which is even represented in textbooks. The S_N2 reaction paths for tetrahedral and trigonal-bipyramidal Si, Ge and Sn atoms (Hajdasz *et al.*, 1994) were simulated taking into account the information on typical bond lengths in the coordination polyhedra of these atoms. According to this scheme the bond between a central atom A (A = Si, Ge or Sn) and attacking group D strengthens when the bond of atom A with a *trans*-substituent (leaving group) T weakens (Bassindale *et al.*, 1999).



To model the S_N2-reaction path by means of structural data one should assume that first the sum of the bond orders for $A—T$ and $D—A$ bonds is equal to one, and second that the $D—A—T$ angle must be close to 180°. The first assumption seems to be natural and its validity has been verified in an experimental gas-phase reaction (Hajdasz & Squires, 1986). This assumption was also used in quantum-chemical *ab initio*

Table 1
Some descriptors of Voronoi–Dirichlet (VD) polyhedra faces for Si1 and Ge2 atoms in the structures of $(C_6H_8NO_5)(CH_3)Si$ (DIRSAY; Kemme *et al.*, 1985) and $(C_{44}H_{44}Cl_3Ge_2N_8)[C_7H_6NO_3]\cdot CH_3CN$ (BAHMUT; Shen *et al.*, 2001), respectively.

Central atom A	Atom of surrounding Y	Interatomic distance $r(A-Y)$ (Å)	Solid angle of VD polyhedron face $\Omega(A-Y)$ (%)	p†
Si1	O5	1.66	22.7	0.9
CP = O_3CN	O4	1.70	22.1	0.9
CN = 5	O1	1.70	21.9	0.9
	C7	1.84	14.7	0.6
	#H9	2.11	4.2	0.2
	N1	2.15	11.4	0.4
	#H10	2.47	1.3	< 0.1
	#H11	2.47	1.2	< 0.1
	#C6	2.85	< 0.1	< 0.1
	#H8	3.19	0.1	< 0.1
	#H11	3.24	0.5	< 0.1
Ge2	Cl2	1.69	23.3	0.9
CP = ClN_4	N8	1.94	17.9	0.7
CN = 5	N6	1.94	18.3	0.7
	N5	1.94	17.9	0.7
	N7	1.94	18.2	0.7
	#C39	2.70	0.4	< 0.1
	#C44	2.71	0.3	< 0.1
	#C28	2.71	0.4	< 0.1
	#C33	2.71	0.4	< 0.1
	O1	3.54	2.8	0.1

† p = bond order, calculated using equation (3).

calculations of the molecular dynamics of the free-energy reaction profile in reactions of CH_2Cl_2 with Cl^- or CH_3Cl with Br^- (Pagliai *et al.*, 2001, 2003, respectively). However, the correctness of the second hypothesis raises doubts in many cases. For example, quantum-chemical calculations of the S_N2-reaction of $SiHF_4$ with F^- (Taketsugu *et al.*, 1998) revealed that different variants of nucleophilic attack with various $D-A-T$ angles are possible. The linear arrangement of attacking and leaving groups and the central atom does not mean that a coordinating $D-A$ bond exists in the case where $r(A-D)$ is significantly longer than the sum of the A and D radii. For example, based on the topological analysis of the electron-density distribution in a series of model compounds (Olsson *et al.*, 1995), one may conclude that there is no bonding between Si and D (D = C, N, O, Cl) atoms when $r(\mathrm{Si}-D) > 2.6$ Å. Thus, the MSC is to be applied only in the case of strong $A-T$ and $D-A$ bonds, whilst during the investigation of the initial stage of S_N2 reactions, where only weak interatomic contacts between D and A atoms are present, the MSC theory may give ambiguous results.

The complete calculation of the S_N2 reaction path may be carried out with quantum chemistry methods and augmented with the results of topological analysis in the frameworks of Bader's '*Atoms in Molecules*' (Bader, 1994) theory. Unfortunately, it is impossible to cover the whole set of silicon- and germanium compounds by these investigations. However, the atomic configuration of the initial stage of the S_N2 reaction may be approximated by short interatomic $A\cdots D$ distances in numerous crystal structures. We decided to carry out an investigation of interatomic contacts within the framework of a stereoatomic model of crystal structures suggested by Blatov & Serezhkin (2000). The latter model is based on a mathematically reasonable partition of a crystal space within a unit cell and is free of the MSC assumption, although also based on the experimental X-ray data of the structures of substances.

2. Experimental

2.1. Investigation objects

The goal of our investigation was to analyze special features of intra- and intermolecular contacts $A\cdots D$ (A = Si or Ge, D = N, O, F, Cl, Br, I) and to search for conditions of their existence in the structures of silicon and germanium compounds. The study of intra- and intermolecular contacts has significant importance not only for modeling the initial stage of the S_N2 reaction, but also for providing information about the structure of the solvate shell of Si and Ge atoms in solution. All oxygen-, nitrogen- and halogen-containing compounds of Si and Ge from the Cambridge Structural Database (CSD; November 2006 release; Allen, 2002) were taken into account provided that:

(i) there is no disorder of non-H atoms,

(ii) Si or Ge are the only atoms in the structure that are complexed by ligands,

(iii) the coordination polyhedron of the central atom (Si or Ge) is formed by σ bonds and does not include Si—Si or Ge—Ge bonds.

The CSD contains 3346 silicon- and 718 germanium-containing compounds for which these conditions were met. In the structures of 307 silicon- and 48 germanium-containing compounds, all or some of the H atoms were not located. For these substances the coordinates of the missing H atoms were calculated using the *HSite* (Blatova *et al.*, 2001) program included in the *TOPOS* package (Blatov, 2006; http://www.topos.ssu.samara.ru).

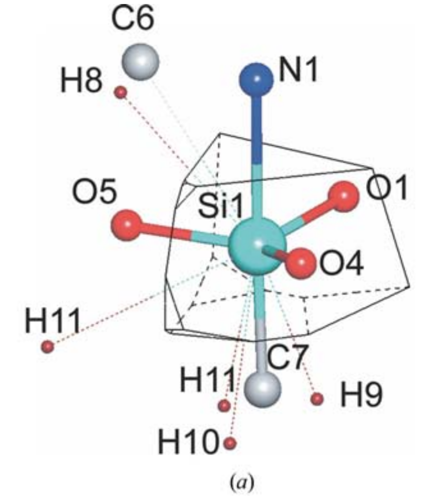
2.2. Stereoatomic model of a crystal structure

Within the framework of the stereoatomic model of the crystal structure (Blatov & Serezhkin, 2000), any atom in the structure may be represented by the corresponding Voronoi–Dirichlet polyhedron (VDP). The Voronoi–Dirichlet polyhedron of an A atom surrounded by $\{Y_i\}$ atoms is a convex polyhedron formed by planes that are drawn perpendicular to $A-Y_i$ contacts at their midpoints. The VDP of an A atom in general has the composition AX_nZ_m, where X are atoms, chemically bound with A, and n is the coordination number (CN) of A. The VDPs of the Z atoms share faces with the VDPs of the A atom, but these $A\cdots Z$ contacts are not chemical bonds. As a result the number of VDP faces (N_f) is equal to $n+m$. In accordance with O'Keeffe (1979), if the midpoint of the $A-Z_i$ bond lies outside the VDP surface, then the Z_i atom is termed an *indirect neighbor* (indirect contacts are marked as $A\cdots\#Z$). The contacts of this type are considered to be caused by steric effects and do not correspond to any chemical interaction. As an example, the results of VDP calculations of Si1 and Ge2 in the structures of

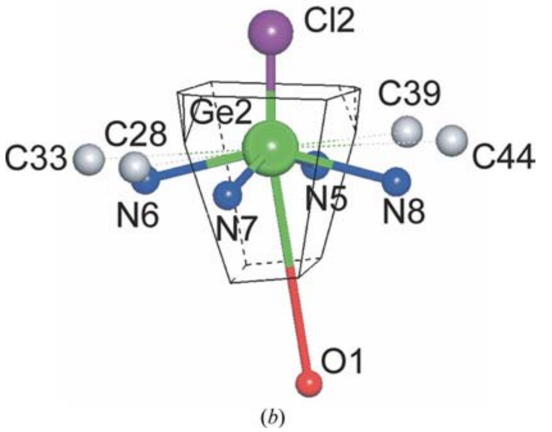
$(C_6H_8NO_5)(CH_3)Si$ (DIRSAY; Kemme *et al.*, 1985) and $(C_{44}H_{44}Cl_3Ge_2N_8)[C_7H_6NO_3]\cdot CH_3CN$ (BAHMUT; Shen *et al.*, 2001), respectively, are given in Table 1. The molecular view of these compounds and the VDPs of the central atoms are depicted in Fig. 1. From hereon, the CSD refcode is given in parenthesis.

It has been suggested that there is a correlation between some descriptors of VDPs and the properties of electron density (Blatov, 2004). The central point of a VDP corresponds to a global maximum [point (3,−3)], VDP vertices to (3,+3) critical points, and faces and edges to saddle points (3,−1) and (3,+1), respectively. It should also be noted that according to Blatov (2004), indirect contacts $A\cdots\#Z$ correspond to the faces of atomic domains for which the local concentration of electron density does not take place. That is why only direct intermolecular $A\cdots Z$ interactions should be taken into account to investigate a possible S_N2 reaction path.

The interatomic distance $r(A-Y_i)$ has classically been the main descriptor of an $A-Y_i$ contact. For the model of VD tessellation the additional important parameter of a pair interaction is used, *e.g.* the solid angle of the VDP face, which is common to both interacting atoms. The solid angle (Ω_{ij}, expressed in per cent of 4π steradian) is equal to the segment area of the unit sphere, which is cut by the pyramid formed by the VDP face in the base and a central atom at the vertex (Fig. 2).



(*a*)



(*b*)

Figure 1
The (*a*) Si1 and (*b*) Ge2 Voronoi–Dirichlet polyhedra in the structures of $(C_6H_8NO_5)(CH_3)Si$ (DIRSAY; Kemme *et al.*, 1985) and $(C_{44}H_{44}Cl_3Ge_2N_8)[C_7H_6NO_3]\cdot CH_3CN$ (BAHMUT; Shen *et al.*, 2001), respectively. Atomic labelling coincides with that in Table 1. Indirect $A\cdots\#Z$ contacts are depicted by dashed lines.

In the general case the valence of an A atom with the coordination polyhedron AX_n is distributed among n $A-X$ bonds, in proportion to their shared Ω_i values of respective faces. As

$$\sum_i \Omega_i = 4\pi \text{ (steradian)}, \qquad (1)$$

then $\Omega_i(A-X)$ corresponding to an i face is proportional to the number of electrons E_i that take part in $A-X$ bonding. Therefore, the E_i value for a bond in the structure of a complex with an N electron shell of an A atom may be expressed as

$$E_i = \frac{N\Omega_i}{100}. \qquad (2)$$

Si and Ge atoms are characterized by stable $3s^23p^6$ and $4s^24p^6$ valence shells, respectively (*e.g.* $N = 8$), so (2) makes it possible to also calculate bond order (p_i) for any ith bond as

$$p_i = \frac{E_i}{2} = \frac{4\Omega_i}{100}. \qquad (3)$$

To conclude, it should also be mentioned that in the *TOPOS* package (Blatov, 2006) it is possible to divide all nonvalence $A\cdots Z$ contacts into intra- and intermolecular. This was described by Shevchenko & Serezhkin (2004) and makes it possible to determine bond descriptors in the structure of any number of compounds (Table 2).

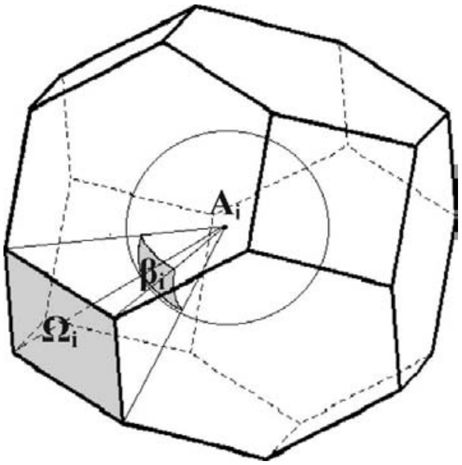


Figure 2
The Voronoi–Dirichlet polyhedron of an A_i atom in the body-centred cubic lattice. The solid angle Ω_i is equal to the shaded β_i segment of the unit sphere cut off by the pyramid with the A_i atom at the vertex and the Voronoi–Dirichlet face in the base.

Table 2
Peculiarities of $A-Y$ contacts (A = Ge, Si; Y = N, O, F, Cl, Br, I).

The following characteristics are given: the number of compounds containing $A-Y$ contacts; μ = the number of these bonds (or contacts); $r(A-X)$ = average interatomic distances $A-X$ for 'classic' coordination polyhedron; $r(A\cdots Z)$ = average interatomic distance between atoms involved in nonvalence contacts of $A\cdots Z$ or $A\cdots\#Z$ type; $\Omega(A-X)$ = range of solid angles, corresponding to $A-X$ chemical bonds; $\Omega_{max}(A-Z)$ = maximal value of a solid angle corresponding to $A\cdots Z$ or $A\cdots\#Z$ contacts; $\sum\mu$ = the total number of $A-Y$ contacts (both chemical and nonvalence ones) realised in the structures of compounds under discussion.

		Chemical bonds in a coordination polyhedron AX_n			Nonvalence contacts									
					Direct $A\cdots Z$						Indirect $A\cdots\#Z$			
					Intramolecular contacts			Intermolecular contacts						
Atom Y	No. of compounds	Average $r(A-X)$ (Å)	Range $\Omega(A-X)$ (%)	μ	Average $r(A\cdots Z)$ (Å)	$\Omega_{max}(A-Z)$ (%)	μ	Average $r(A\cdots Z)$ (Å)	Ω_{max} $(A-Z)$, (%)	μ	Average $r(A\cdots Z)$ (Å)	Ω_{max} $(A-Z)$ (%)	μ	$\sum\mu$
Contacts Si$-Y$														
N	1307	1.8 (1)	6.1–26.8	2683	2.9 (3)	< 12.9	237	2.7 (9)	< 3.7	22	3.1 (5)	< 4.9	745	3687
O	2255	1.7 (1)	4.1–28.5	5888	3.1 (2)	< 8.5	356	3.6 (5)	< 5.7	20	3.4 (5)	< 5.4	1288	7552
F	284	1.6 (1)	11.1–26.2	654	3.0 (2)	< 6.2	91	2.8 (7)	< 4.4	17	3.4 (4)	< 2.5	176	938
Cl	278	2.1 (1)	8.4–24.6	539	3.5 (2)	< 3.7	123	4.2 (2)	< 2.2	48	4.0 (6)	< 3.3	271	981
Br	66	2.4 (1)	9.1–20.1	43	3.6 (2)	< 4.0	9	3.8 (7)	< 5.6	5	3.6 (4)	< 1.8	97	154
I	22	2.5 (1)	13.1–17.7	5	3.8 (1)	< 1.9	2	4.3 (6)	< 1.3	5	4.2 (5)	< 1.0	25	37
Contacts Ge$-Y$														
N	357	2.0 (1)	10.1–27.7	774	2.9 (3)	< 12.6	56	3.7 (6)	< 5.3	26	3.2 (6)	< 4.9	132	988
O	365	1.8 (1)	6.0–26.4	1205	3.0 (2)	< 8.2	122	3.4 (4)	< 5.8	23	3.5 (4)	< 6.2	255	1605
F	60	1.8 (2)	10.3–24.9	90	3.0 (3)	< 10.7	19	3.8 (5)	< 10.4	12	3.3 (6)	< 5.6	78	199
Cl	179	2.2 (1)	9.1–23.3	399	3.7 (3)	< 4.7	13	3.9 (4)	< 10.2	50	4.1 (4)	< 4.0	65	527
Br	25	2.4 (1)	10.8–23.2	48	3.9 (1)	< 3.0	2	3.7 (3)	< 11.9	6	3.8 (8)	< 2.7	5	61
I	23	2.7 (2)	10.8–21.4	31	–	–	–	3.8 (1)	< 7.8	2	4.4 (6)	< 0.4	6	39

Table 3
Distribution (%) of 10 747 and 2875 direct Si$-Y$ and Ge$-Y$ contacts, respectively (Y = N, O, F, Cl, Br, I), depending on the contact type.

The percentage of $A-X$ bonds and $A\cdots Z$ contacts (inter- and intramolecular ones) among all $A-Y$ contacts. The corresponding number of contacts is given in Table 2.

	Si						Ge					
Contact type	N	O	F	Cl	Br	I	N	O	F	Cl	Br	I
Intermolecular	0.7	0.5	2.0	3.8	8.8	41.7	3.0	1.7	9.9	10.8	10.7	6.1
Valence	91.1	93.7	86.5	78.7	75.4	41.7	90.4	89.3	74.4	86.4	85.7	93.9
Intramolecular	8.2	5.8	11.5	17.5	15.8	16.6	6.6	9.0	15.7	2.8	3.6	0

3. Results and discussion

3.1. Coordination number and number of faces for Si and Ge atoms

Some characteristics of $A-Y$ contacts (A = Si, Ge; Y = O, N, F, Cl, Br or I) are presented in Table 2. In the structures of compounds under discussion $2 \leq \mathrm{CN}(A) \leq 6$, whilst the number of VDPs faces varies from 4 to 34, and from 6 to 37 for Si and Ge, respectively. The fact that $N_f(A) \geq \mathrm{CN}(A)$ is conditioned by the presence of a large amount of non-valence $A\cdots Z$ contacts. As can be seen from Tables 2 and 3, for a fixed nature of surrounding atoms, the majority of VDP faces belong to valence bonds $A-X$, characterized by the shortest interatomic distances $r(A-X)$ and the largest solid angles $\Omega(A-X)$. Moreover, the smaller the electronegativity of the X atom, the larger the corresponding average $r(A-X)$. Non-valence contacts have longer interatomic distances and, at the same time, larger s.u.s that mean a more diffuse distribution of $A\cdots Z$ interatomic distances. All non-valence interactions are divided into two sets which are intra- and intermolecular interactions. The former have shorter average distances $r(A-Z)$ and significantly larger solid angles (Table 2). The analysis of the dependence of the contacts on the nature of Z atoms for all direct $A\cdots Z$ contacts shows that Si$\cdots$I and Ge$\cdots$Hal (Hal = F–I) contacts are mainly intermolecular, whilst contacts of the $A\cdots$O, $A\cdots$N (A = Ge, Si) and Si$\cdots$Hal (Hal = F–Br) type appear to be intramolecular (Table 3).

3.2. Intermolecular contacts $A\cdots Z$ (Z = N, O, F, Cl, Br or I)

In our opinion, the peculiarities of the initial stage of an S_N2 reaction can be identified by means of an investigation into direct non-valence intermolecular contacts. All $A\cdots Z$ (Z = N, O, F, Cl, Br or I) contacts of this type are given in Table 4 (given as an example of compounds with CN of Si or Ge equal to 2 and 3), and Tables 5 and 6 (given as supplementary

Table 4
Characteristics of direct intermolecular contacts $T—A\cdots D$ (A = Si, Ge) in the structure of one silicon- and 24 germanium-containing compounds with CN(A) < 4.

The following characteristics are given: chemical composition and shape of the coordination polyhedron (CP); the contact types are the atom names which are involved in the direct interatomic contact; $r(A—D)$ = the interatomic distance between a central atom A (Si or Ge) and the nearest atom of a nucleophile group D; $(T—A—D)$ = angle between atoms given in the column 'the contact type'; $\Omega(A—D)$ = the solid angle of the face corresponding to the intermolecular contact; T = a living atom (or group of atoms); D = a nucleophile atom (or group of atoms).

Refcode	CP composition	CP	Contact type $T—A\cdots D$†	$r(A—D)$ (Å)†	$(T—A—D)$ (°)†	$\Omega(A—D)$ (%)†	Atom T ‡	Atom D ‡
Central atom – Si								
CINWAX	C_3	Pyramid	C—Si2···Cl	4.75	155.8	2.2	Ar	Cl—Ar
Central atom – Ge								
ABENEA	N_3	Pyramid	N—Ge···N	3.93	143.6	1.7	N_3^-	Het
FASSUO	Cl_3	Pyramid	Cl—Ge···Cl	3.72, 4.16	164.3, 149.7	5.4, 1.9	Cl	Cl
			Cl—Ge···N	3.57	173.6	2.9	Cl	$R—N(R')_2$
PICGEH	Cl_3	Pyramid	Cl—Ge···N	3.97, 4.08	157.2, 156.6	0.8, 0.6	Cl	Het
RUNMOC	N_2Cl	Pyramid	Cl—Ge···N	3.56, 3.82	161.6, 151.0	4.1, 2.3	Cl	Het
TAVZOF	N_3	Pyramid	N—Ge4···N	3.94, 4.23	143.8, 169.3	1.8, 0.6	Het	Het
UFUHEI	N_2Cl	Pyramid	Cl—Ge···N	3.89	148.4	2.8	Cl	Het
RUNMES	N_2O	Pyramid	O—Ge···O	3.87	152.2	3.0	CF_3SO_3	CF_3SO_3
ZEQNUE	N_3	Pyramid	N—Ge2···O	3.38,	152.4,	3.4,	Het	$C_4H_8O_2$
			N—Ge2···Cl	3.79	143.2	2.0	Het	Ge—Cl
MERDOC	N_2	V-shaped	N—Ge···F	3.10, 4.60	157.9, 171.3	10.4, 1.0	Het	F—Ar
			T—Ge···F	4.20, 4.30	–	1.2, 0.1	–	F—Ar
RURKEU	C_2	V-shaped	T—Ge···F	3.38, 4.38	–	5.3, 2.3	–	F—R
			C—Ge···F	3.61	157.7	6.0	Ar	F—R
TOXNUP	O_2N	Pyramid	O—Ge···F	3.78	151.8	6.9	R—O	F—R
CGEBTZ	NCl_2	Pyramid	Cl—Ge···Cl	3.50	173.9	6.42	Cl-Het	Cl-Het
ESOFUN	Cl_3	Pyramid	Cl—Ge···Cl	3.37, 3.86, 4.24	171.8, 168.9, 162.2	10.2, 5.1, 1.4	Cl	Ge—Cl
EZOVIY	OCl_2	Pyramid	O—Ge···Cl	4.17	130.7	2.8	$(R_2H)P{=}O$	Ge—Cl
GODKIT	Cl_3	Pyramid	Cl—Ge···Cl	3.97, 3.98, 4.46	171.5, 174.0, 156.6	3.9, 3.5, 0.7	Cl	Ge—Cl
IKOFOD	Cl_3	Pyramid	Cl—Ge···Cl	3.43, 3.85	174.4, 167.9	7.1, 5.3	Cl	Ge—Cl
IRATUQ	ONCl	Pyramid	N—Ge···Cl	4.11	152.9	2.1	R_3N	Ge—Cl
LAHQOA	Cl_3	Pyramid	Cl—Ge···Cl	3.90 (×3)	165.5 (×3)	8.8 (×3)	Cl	Ge—Cl
NAPVAB	Cl_3	Pyramid	Cl—Ge···Cl	3.72, 3.87, 4.10	173.8, 169.6, 143.1	4.9, 4.9, 1.4	Cl	Ge—Cl
SIPFAY	Cl_3	Pyramid	Cl—Ge1···Cl	4.02	155.7	3.1	Cl	Ge—Cl
	Cl_3	Pyramid	Cl—Ge2···Cl	4.00, 4.76	156.6, 173.6	3.4, 1.2	Cl	Ge—Cl
WUKWUU	Cl_3	Pyramid	Cl—Ge···Cl	3.28, 3.29, 3.29	174.2, 167.4, 167.4	7.8, 7.1, 7.1	Cl	Ge—Cl
WUKWUU01	Cl_3	Pyramid	Cl—Ge···Cl	3.19, 3.20, 3.29	171.4, 172.6, 159.0	8.2, 7.4, 7.6	Cl	Ge—Cl
NIWTIW	Br_3	Pyramid	Br—Ge···Br	3.40, 3.81, 3.86	172.4, 168.8, 154.7	10.9, 5.6, 5.7	Br	Ge—Br
IACGER	O_2I	Pyramid	O—Ge···I	3.75,	171.1,	7.8,	$RR'—C{=}O$	Ge—I
			I—Ge···I	3.82	160.5	3.2	I	Ge—I

† In the case where the compound contains more than one crystallographically independent type of A atom, the number of atoms involved in intermolecular bonding is given. The columns '$(T—A—D)$' and 'T' contain information for the T atom (or group of atoms) in the case where $T—A\cdots D < 130°$, otherwise the T atom cannot be localized. If there is more than one intermolecular contact in a compound, characteristics of the former are separated with a comma. ‡ The following abbreviations were used: R, R' = aliphatic hydrocarbon, Ar = aromatic hydrocarbon, Het = heterocycle, —O and —S = alcoholate or thioalcoholate, C=O, S=O = ketone and thioketone, —COO = carboxyl, —CN = cyanide, —NC = isocyanide, —SN = thiocyanide, C_xB_y = carborane, R≡C = alkyne, R=C = alkene, μ = bridge atom between 2 or more Ge or Si atoms.

material because of their size). According to the results obtained, there is a correlation between intermolecular contact descriptors (interatomic distances, $T—A—Z$ angle, solid angle of a corresponding face) on one hand, and CN(A), the nature of the nucleophile (D) and leaving groups (T) on the other. These correlations are discussed in more detail below.

3.2.1. Compounds with low coordination numbers (CN = 2, 3) of Si and Ge. Coordination numbers 2 and 3 were found in the structures of 53 silicon- and 113 germanium-containing compounds. A special feature of these complexes is the formation of 'opened' coordination polyhedra, such as V-shaped (CN = 2) or trigonal pyramidal with an A atom as its vertex (CN 3). As a result only 37.8–72.3% of the A atom total solid angle corresponds to $A—X$ chemical bonds and the rest to non-valence $A\cdots Z$ contacts. For example, in the structures of germanium compounds 405 Ge—X bonds and 2188 non-valence Ge···Z contacts were found. More than half of the latter (1525 contacts) are Ge···H interactions. Nevertheless, as can be seen from Table 4, direct intermolecular contacts $A\cdots Z$ (Z = N, O, Hal) were found in the structures of only one Si complex ($SiC_{18}H_{13}ClS$, CINWAX; Bel'skii *et al.*, 1984) and 24 Ge complexes. The vast majority of Ge compounds involved with CN(Ge) = 3 contain trichloro- or tribromo-germanium molecules forming infinite chains by means of Hal—Ge···Hal contacts.

In the structures of compounds with low CN(A), $A\cdots Z$ contacts with high (exceeding 10.9 %) solid angles were found. Nevertheless, in many cases our attempts to describe these contacts in the frameworks of the MSC theory, *e.g.* to distinguish both nucleophile group (or Z atom that belongs to this group) and the atom, bound with A and belonging to the

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SO5014). Services for accessing these data are described at the back of the journal.

leaving T group, were unsuccessful. There are many cases with angles $T—A\cdots Z < 160°$ (Table 4); moreover, we were not able to locate the T group in the cases of $(C_6H_2(CF_3)_3)_2Ge$ (RURKEU; Bender *et al.*, 1997) and $(C_{29}H_{41}GeN_2)[C_{36}HB_2F_{30}O]$ (MERDOC; Stender *et al.*, 2001). This fact is not surprising because the presence of intermolecular contacts for Si and Ge complexes with low CNs is conditioned by the 'opened' shape of a coordination polyhedron and results in the tendency of these compounds to react by addition rather than substitution of a ligand.

It is also worth noting that, in many cases, pronounced dipole–dipole interactions exist between Si- or Ge-containing species. Silicon and germanium trichlorides, tribromides and cyanides which form infinite chains $T—A\cdots D$ ($T = D$ = Hal or CN, Fig. 3) are examples of these interactions (Tables 4–6). Taking these examples into account one may claim that distortion of a coordination polyhedron is not evidence of chemical bond formation (see also supplementary material). So, although the Ge atom in $(CH_3)_3PH(GeCl_3)$ (GODKIT; Bender *et al.*, 1997) has an 'opened' trigonal pyramidal coordination polyhedron (Fig. 3) and high solid angles corresponding to intermolecular contacts (exceeding 3.9%, Table 4), the respective Ge$\cdots$Cl contacts do not become valence ones.

3.2.2. Coordination numbers 4 and 5. Among all compounds containing intermolecular $A\cdots Z$ contacts the most representative subset of 66 silicon and 36 germanium complexes (or 93 and 78%, respectively, structures with direct intermolecular contacts) is characterized by CN(A) = 4. The coordination polyhedron is most often a tetrahedron; in the structure of $C_{32}H_{16}N_8Si$ (PHPRSI; Aldoshin *et al.*, 1980), however, the CP is a square. Besides, the Ge atoms have the bisphenoid coordination polyhedra in the structures of five compounds (Table 5 of the supplementary material), namely $C_{14}H_{18}GeN_4O_2$ (MELNUM; Hubler & Hubler, 2000), $C_{13}H_{19}GeN_2{\cdot}CF_3SO_3$ (UFUHOS; Ayers & Dias, 2002), $C_4H_8O_2{\cdot}Cl_2Ge$ (DIOXGC01; Marsh, 1997; or DIOXGC02; Denk *et al.*, 1998) and $C_4H_8O_2{\cdot}Br_2Ge$ (FITLUP; Gar *et al.*, 1987). There are also five Si and ten Ge compounds with CN = 5, where the CP is a square pyramid (A atom is situated in the base) or a trigonal bipyramid. It was established that solid angles of intermolecular contacts in the structure of complexes with CN = 4, 5 are less than those in the structure of complexes with low CN and do not exceed 9.1%. Nevertheless, for this group of compounds T leaving groups (or atoms) can easily be determined (see Tables 5 and 6 of the supplementary material), because the corresponding angles $T—A\cdots Z$ vary from 140.1 to 179.8°. The following analysis of Tables 5 and 6 (of the supplementary material) has shown that Si(Ge) atoms with CN = 4, 5 in crystal structures with nucleophiles form only one intermolecular contact. This means that the formation of multiple weak interactions between nucleophiles and Si(Ge) atoms with CN = 4, 5 is unfavorable and indicates that Si or Ge complexes form in solution only one bond with a polar solvent.

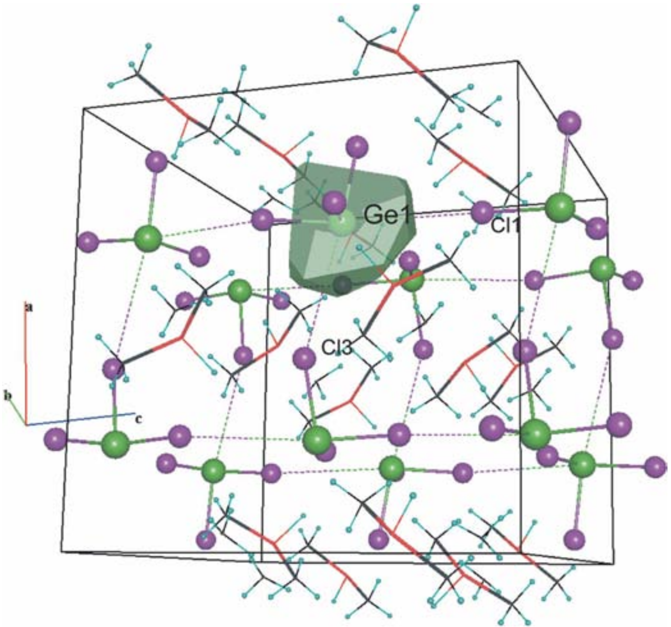

Figure 3
Fragment of crystal packing and VDP of Ge1 in the structure of $(CH_3)_3PH(GeCl_3)$ (GODKIT; Bender *et al.*, 1997). Intermolecular contacts Ge$\cdots$Cl are given with dashed lines, the solid angle values Ω(Ge1—Cl1) and Ω(Ge1—Cl3) are equal to 3.5 and 3.9%, respectively.

3.2.3. Coordination number 6 of silicon and germanium. In the structures of all 3346 silicon- and 718 germanium-containing compounds only 158 and 83 complexes, respectively, contain central atoms with CN(A) = 6. Some of them {such as $(CH_3NH_3)[C_6H_{15}N_3Br_3Ge]_2Br_3{\cdot}C_2H_3N$ (GIQXOT; Willey *et al.*, 1998), $C_{32}H_{46}F_2N_2O_2Si{\cdot}0.25C_4H_8O_2$ (XAGGIV; Haberecht *et al.*, 2000) or $C_{19}H_{24}Cl_2N_4O_2Si{\cdot}2\,CHCl_3$ (WEFHAQ; Kalikhman *et al.*, 2000)} contain solvate molecules of acetonitrile, 1,4-dioxane or chloroform in their structures. However, the only compound with CN = 6 that contains intermolecular contacts is $({}^nBu_2N)_2(GeI_4)$ (TECDOU; Mitzi, 1996), where two I—Ge$\cdots$N contacts were found with solid angles of only 0.4 and 0.5%. Because of this it may be suggested that Si or Ge atoms with CN > 5 rarely form intermolecular contacts because of the shielded central atom. This also means that a compound with a high CN of Si or Ge can hardly take part in an S_N2 reaction because of the steric barriers to the formation of the starting complex with intermolecular bonding between the central atom and the electron-pair donor.

3.3. Some VDP descriptors and S_N2 reaction paths

3.3.1. Order of Si—*X* and Ge—*X* bonds. As previously mentioned, the sum of the bond orders for $A—T$ and $D—A$ bonds being equal to one is a base hypothesis for the method of structural correlations. Silatranes and germatranes are the classical models to verify this statement. Let us take $(C_6H_8NO_5)(CH_3)Si$ (DIRSAY; Kemme *et al.*, 1985) as an example. According to our calculations by (3), both equatorial Si—O bonds are ordinary and the bond-order sum of axial bonds is also equal to one [p(Si—N) and p(Si—C) are 0.4 and 0.6, respectively]. In the stereoatomic model the Si—C bond with the methyl group is supposed to be stronger than the Si—

N bond because it has a larger solid angle (Table 1). The same observations and conclusions are valid for other atranes of silicon and germanium. There are 58 sila- and 58 germatranes in the CSD without disordered atoms. The average sum of the bond orders for axial bonds is equal to 1.2 (1), and the order of the $A-D$ bond is somewhat larger than that of the $A-T$ interaction.

Similar calculations were carried out for structures with intermolecular contacts $A\cdots D$. One may find in Table 4, and Tables 5 and 6 of the supplementary material, that $A\cdots D$ interactions mainly have small solid angles which do not exceed 1% (and the largest Ω = 10%, Table 4), *e.g.* the contribution of the $A\cdots D$ bond to the sum of bond orders is insignificant. Hence, $A-T$ bonds in the structure of complexes modeling the initial stage of S_N2 reactions should have the sum of $T-A$ and $A\cdots D$ bond orders close to one. Indeed, the Ge—Cl bond (the leaving group in terms of the MSC) in the structure of $(C_{44}H_{44}Cl_3Ge_2N_8)[C_7H_6NO_3]\cdot CH_3CN$ (BAHMUT; Shen *et al.*, 2001; Table 1) has the nearest bond order to one among all the chemical bonds, including the Ge atom in this compound. Moreover, the average sum of the bond orders for $A-T$ and $A\cdots D$ bonds is 0.9 (1) for all compounds represented in Tables 5 and 6 of the supplementary material. Thus, the sum $A-T$ and $A\cdots D$ bond orders are equal to one for the model compounds of the initial and final stages of the S_N2 reaction, supporting the constant bond-order sum during a reaction path.

3.3.2. Nature of a leaving group. The constancy of the bond-order sums during the S_N2 reaction path leads to a few conclusions. First, atoms and groups of atoms for which $p(A-T) > 1$ [*e.g.* $\Omega(A-T) > 25\%$] are poor leaving groups, because they make the formation of the initial molecular associate $T-A\cdots D$ for an S_N2 reaction impossible. Among all 1085 bonds with Ω(Si—T) > 25%, 669, 251, 101, 57 and 7 correspond to T = O, H, C, N and F, respectively. Chemical bonds with such high solid angles for Ge atoms are rare. Only 46 bonds have been found and 32 of them are Ge—H bonds. Thus, all functional groups that form strong covalent bonds with Si or Ge (such as siloxanes, methyl, phenyl, silazanes, silaneimines and phosphozanes) are poor leaving groups. Secondly, as can be seen from Table 2, the increase in atomic weight of T (T = halogenide, chalcogenide or pnictogenide) for silicon and germanium halogenides is accompanied by a decrease in $\Omega(A-T)$. Hence, the larger the polarizability of a leaving group coordinated by Si or Ge, the weaker the $A-T$ bond, and the smaller its energy of dissociation. Therefore, it is not surprising that an iodine anion in silicon and germanium compounds is usually a counterion and not coordinated to the central atom. This conclusion is in accordance with the results obtained by reaction-activity investigations for Si(Ge) compounds. Where the reaction activity of a group connected with Si or Ge has yet to be studied, this information can be evaluated by calculating the corresponding bond order obtained by analysis of crystallographic data. In our opinion, information about solid angles corresponding to $T-A$ and $A-D$ bonds may be helpful in the synthesis of new silicon and germanium complexes.

Let us consider as an example the synthesis method of tris(pentafluorophenyl)silyl derivatives [with the general formula $R(Si(C_6F_5)_3)$] by means of $RSiCl_3$ reacting with pentafluorophenylmagnesium bromide (Dilman *et al.*, 2005). The reaction was investigated with the help of 11 silicon allyl-, benzyl-, phenyl-, vinyl- or alkyltrichlorides. Unfortunately, the crystal structures of the initial substances have not yet been investigated, but the CSD includes six trichlorosilanes, similar to that described by Dilman *et al.*, 2005 (their refcodes are JIRMAY, NAYPAE, NAYPEI, PEDMOA, RIGCAL and RIWQOD). In these compounds all Si—Cl bonds have Ω = 22.6 (3)%, whilst for Si—C bonds Ω depends on the nature of the R ligand and varies from 14.3 to 18.4%. There also exist 2, 3, 11 and 71 benzyl-, allyl-, vinyl- and phenyl-containing silicon derivatives, for which Ω(Si—C) = 18.0 (5), 18.0 (12), 20.8 (5) and 21.1 (7)%, respectively. In addition, in the structures of three pentafluorophenylsilanes, eight C_6F_5—Si bonds are characterized by Ω(Si—C) = 21.6 (5)%. Taking all these data into account it is obvious that, firstly, solid angles of Si—Cl bonds in initial complexes are optimal for initializing intermolecular bonding and reaction; indeed, half of these silicon derivatives form intermolecular contacts in their structures (Table 5 of the supplementary material). Secondly, solid angles of Si—Cl bonds are larger than those for any initial, secondary or final ligand, which explains the substitution of all three chlorides.

4. Conclusions

Analysis of 3346 silicon- and 718 germanium-containing compounds within the framework of the stereoatomic model was carried out. It was established that the tendency to form the interatomic contacts Si$\cdots D$ and Ge$\cdots D$ in crystal structures decreases with an increase in the coordination number of the central atom. Molecular associates were detected with a large diversity of interatomic distances $T-A$, $A\cdots D$ and $T-A-D$ angles, whilst the sum of the $T-A$ and $A\cdots D$ bond orders was found to be constant and approximately equal to one. It was stated that in the frameworks of the stereoatomic model the increase of polarizability of an atom or group of atoms facilitates the elimination of the atom or group of atoms. It was concluded that the formation of multiple weak interactions between nucleophiles and Si(Ge) atoms with CN = 4, 5 is unfavorable and indicates that in solution Si or Ge complexes form only one bond with the polar solvent. Information on the descriptors of the $T-A\cdots D$ interaction in terms of the stereoatomic model of crystal structures was proved to be helpful in modeling S_N2 reactions.

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