CRYSTAL AND MOLECULAR STRUCTURE OF 1,1,4,4-TETRAIODO- AND 1,1,4,4-TETRAPHENYL-1,4-DIGERMANACYCLOHEXADIENE-2,5

N. G. Bokii and Yu. T. Struchkov

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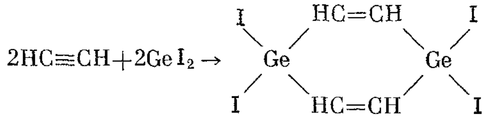
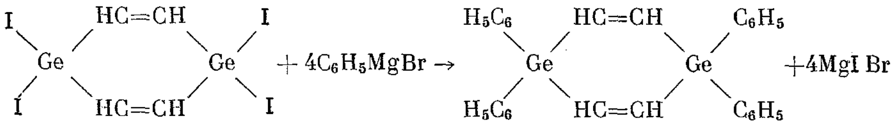
An x-ray structural investigation has been carried out on the product (I) from the addition of germanium (II) iodide to acetylene and on the product (II) of the reaction of (I) with phenylmagnesium bromide. It is shown that the molecules of these compounds contain almost planar six-membered heterocyclic rings analogous to those found previously for other members of this class. The structures were refined by the least squares method in the isotropic approximation with three-dimensional data to R(I) = 15.3% and R(II) = 1.36%. The absence of significant d-π conjugation between the germanium atom and the double bonds of the heterocycle is shown by the equality of the endo- and exocyclic Ge−C bond lengths (1.96 ± 0.02 A) and closeness of the C = C bond length in the heterocycle (1.34 ± 0.02 A) to the standard double bond length.

The present paper is a part of our x-ray structural study of the products of reaction of acetylene and tolane with derivatives of germanium (II) and silicon (II) [1]. It has been shown previously that the compounds $Cl_2Ge(CH)_4GeCl_2$ [2] and $(CH_3)_2Si[C(C_6H_5)]_4Si(CH_3)_2$ [3] contain practically planar six-membered heterocycles. A similar heterocycle is found in two other compounds of this class. The first was obtained directly from the reaction of acetylene with germanium (II) iodide:



I

The second was the product from the treatment of I with phenylmagnesium bromide:



II

EXPERIMENTAL SECTION

An electron diffraction study has been previously carried out on compound I [4] and electron diffraction photographs of two types were obtained which were interpreted in [4] as representing molecules with three- and six-membered rings. Therefore to make sure whether the crystal structure of I depended on the method of growth of the monocrystals, the latter were grown in two ways: by crystallization from carbon tetrachloride solution and from the melt. In both cases, long, cloudy-white platelets were formed which gave identical x-ray photographs. Thus, both materials contained the same crystalline phase, and as further study showed, it contained only molecules with six-membered rings.

Crystals of I belonged to the monoclinic class. The unit cell parameters were obtained from oscillating x-ray photography and by photographing the reciprocal lattice (the same method was used for II):

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$a = 8.56 \pm 0.02\text{Å}$ $V = 679\text{A}^3$
$b = 7.34 \pm 0.02$ $d_{\text{calc}} = 3.45\ \text{g/cm}^3$
$c = 10.81 \pm 0.03$
$\beta = 92.5 \pm 1°$ $N = 2\ [(\text{CH})_4\text{Ge}_2\text{J}_4]$

Systematic absences showed unambiguously that the space group was $P2_1/c$, so that a dimeric molecule with six-membered rings should occupy special positions at the centers of inversion, whereas monomers with three-membered rings would occupy general positions.

To measure the intensities of reflexions layer lines of the types h0*l* to h4*l* and 0k*l* were developed by photographing the reciprocal lattice in unfiltered molybdenum radiation. For films about the b-axis crystals with the dimensions 0.2 x 0.3 x 0.7 mm were used, while for films about the *a*-axis the crystal sizes were 0.2 x 0.3 x 0.3 mm. The crystals were considerably damaged by the radiation and this had a considerable effect on the quality of the x-ray photographs. The intensities of 357 independent reflections were estimated.

Monocrystals of II were grown from benzene solution as colorless platelets. The parameters of the triclinic unit cell are as follows (the density was found by hydrostatic suspension in Thoulet's solution):

$a = 11.54 \pm 0,03\text{Å}$ $V = 1217\text{A}^3$
$b = 10.93 \pm 0,03$ $d_{\text{meas}} = 1.36\ \text{g/cm}^3$
$c = 10.24 \pm 0,03$ $d_{\text{calc}} = 1.38\ \text{g/cm}^3$
$\alpha = 97.5 \pm 1°$
$\beta = 105.0 \pm 1°$ $N = 2\ [(\text{CH})_4\text{Ge}_2(\text{C}_6\text{H}_5)_4]$
$\gamma = 99.5 \pm 1°$

The correctness of the space group P(1) was confirmed by the successful resolution and refinement of the molecular structure.

Layer lines of the types hk0 to hk4 and h0*l*, h1*l* were photographed on an isoclinal Weissenberg camera with unfiltered copper radiation (crystal sizes 0.2 x 0.2 x 0.5 mm and 0.3 x 0.3 x 0.3 mm). In all,1324 independent nonzero reflexions were measured.

Intensities were measured visually against a scale of blackening. In transforming the intensities into structural factors Lorentz and polarization factors were taken into account. Structural factors were related to a single relative scale by comparison of common reflexions on layer lines developed by rotating the crystals about different axes.

Structure of 1,1,4,4-Tetraiodo-1,4-digermanacyclohexadiene-2,5 (I)

The resolutions were begun by examining the 14 highest maxima on the three-dimensional Paterson (left-hand side of Table 1). For space group $P2_1/c$ there should be among these maxima of the first series [5]: 2x2y2z, $2x\frac{1}{2}2z - \frac{1}{2}$, $02y - \frac{1}{2}\frac{1}{2}$. On the linear section $0v\frac{1}{2}$ there is only one maximum (1), so that $2y - \frac{1}{2} = 0.330$, and hence for the heavy atoms (2I + 1Ge) y = ± 0.415 or ± 0.085. The maxima (4) and (11), (5) and (12) permit the determination of the coordinates of atoms I and II, and, as expected, maxima of the type $2x\frac{1}{2}2z - \frac{1}{2}$ are approximately twice as large as those of type 2x2y2z:

	x	*y*	*z*
I	0.106	0.085	0.060
II	0.715	0.085	0.300

However, the coordinates of the maxima of the second series on this basis gave poor agreement with the real interatomic functions:

0.609	0	0.240	(or 0.391	0	0.760)
instead of 0.438	0	0.763	(maximum 7)		
0.821	0.175	0.360	(or 0.179	0.175	0.640)
instead of 0.138	0.165	0.640	(maximum 8)		

We therefore assumed that the crystal possessed only pseudocentric symmetry, and we calculated the three-dimensional electron density distribution in space group Pc starting from the following atomic coordinates:

	x	*y*	*z*
I	0.150	0.085	0.060
II	0.715	0.085	0.300
I'	0.940	0.915	0.940
II'	0.285	0.915	0.700

TABLE 1. Interatomic Vectors of $I_2Ge(CH)_4GeI_2$

Maxima of the interatomic functions					Interatomic vectors							
No.	coordinates			height	coordinates of vector ends			vector type			atoms	weighing
	u	v	w		u	v	w	u	v	w		
1	0	0,330	1/2	56	0	0,324	1/2	0	$2y - {}^1/_2$	${}^1/_2$	$I_{(1)}$	$2Z_I^2$
					0	0,336	1/2	0	$2y - {}^1/_2$	${}^1/_2$	$I_{(2)}$	$2Z_I^2$
					0	0,326	1/2	0	$2y - {}^1/_2$	${}^1/_2$	Ge	$2Z_{Ge}^2$
2	0,138	1/2	0,141	52	0,124	0,492	0,139	$x_1 - x_2$	$y_1 - y_2$	$z_1 - z_2$	$I_{(1)} - I_{(2)}$	$4Z_I^{2*}$
					0,232	1/2	0,146	$2x$	${}^1/_2$	$2z - {}^1/_2$	$I_{(2)}$†	$2Z_I^2$
3	0,355	0	0,288	47	0,356	0,008	0,285	$x_1 + x_2$	$y_1 - y_2 + {}^1/_2$	$z_1 + z_2 + {}^1/_2$	$I_{(1)} - I_{(2)}$	$4Z_I^{2*}$
4	0,213	1/2	0,615	37	0,208	0,495	0,619	$x_1 - x_2$	$y_1 + y_2 - {}^1/_2$	$z_1 - z_2 - {}^1/_2$	$I_{(2)}$ — Ge	$4Z_I Z_{Ge}{}^*$
					0,352	1/2	0,616	$2x$	${}^1/_2$	$2z - {}^1/_2$	Ge †	$2Z^2_{Ge}$
5	0,435	1/2	0,098	37	0,436	0,497	0,096	$x_1 + x_2$	$y_1 + y_2$	$z_1 + z_2$	$I_{(1)}$ — Ge	$4Z_I Z_{Ge}{}^*$
6	0,080	0	0,483	34	0,084	0,003	0,480	$x_1 - x_2$	$y_1 + y_2 - {}^1/_2$	$z_1 - z_2 - {}^1/_2$	$I_{(1)}$ — Ge	$4Z_I Z_{Ge}{}^*$
7	0,438	0	0,763	34	0,440	0,005	0,765	$x_1 + x_2$	$y_1 + y_2$	$z_1 + z_2$	$I_{(2)}$ — Ge	$4Z_I Z_{Ge}{}^*$
8	0,138	0,165	0,640	22	0,124	0,172	0,639	$x_1 - x_2$	$y_1 + y_2 - {}^1/_2$	$z_1 - z_2 - {}^1/_2$	$I_{(1)} - I_{(2)}$	$2Z_I^2$
					0,232	0,164	0,646	$2x$	$2y$	$2z$	$I_{(2)}$†	Z_I^2
9	0,480	1/2	0,420	20	0,480	1/2	0,424	$2x$	${}^1/_2$	$2z - {}^1/_2$	$I_{(1)}$	$2Z_I^2$
10	0,355	0,325	0,788	19	0,356	0,328	0,785	$x_1 + x_2$	$y_1 + y_2$	$z_1 + z_2$	$I_{(1)} - I_{(2)}$	$2Z_I^2$
11	0,213	0,178	0,120	15	0,208	0,169	0,119	$x_1 - x_2$	$y_1 - y_2$	$z_1 - z_2$	$I_{(2)}$ — Ge	$2Z_I Z_{Ge}$
12	0,430	0,175	0,600	14	0,436	0,177	0,596	$x_1 + x_2$	$y_1 - y_2 + {}^1/_2$	$z_1 + z_2 + {}^1/_2$	$I_{(1)}$ — Ge	$2Z_I Z_{Ge}$
13	0,438	0,333	0,265	13	0,440	0,331	0,265	$x_1 + x_2$	$y_1 - y_2 + {}^1/_2$	$z_1 + z_2 + {}^1/_2$	$I_{(2)}$ — Ge	$2Z_I Z_{Ge}$
14	0,088	0,313	0,983	12	0,084	0,323	0,980	$x_1 - x_2$	$y_1 - y_2$	$z_1 - z_2$	$I_{(1)}$ — Ge	$2Z_I Z_{Ge}$
15	0,468	0,163	0,915	5	0,480	0,180	0,924	$2x$	$2y$	$2z$	$I_{(1)}$	Z_I^2
16	0,338	0,188	0,113	4	0,352	0,174	0,116	$2x$	$2y$	$2z$	Ge	Z_{Ge}^2

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*The factor 4 because of the coalescence lying close to the plane of symmetry of the interatomic function.

† This maximum was not resolved in the three-dimensional interatomic function.

TABLE 2. Atomic Coordinates and Individual Temperature Factors for $I_2Ge(CH)_4GeI_2$

Atom	Coordinates			B_j, A²	Atom	Coordinates			B_j,A²
	x	*y*	*z*			*x*	*y*	*z*	
$I_{(1)}$	0,260	—0,410	0,038	5,8	$C_{(1)}$	$0,14_3$	$0,02_2$	$—0,10_6$	$10,_5$
$I_{(2)}$	0,384	0,082	0,177	5,4	$C_{(2)}$	$—0,01_9$	$—0,07_4$	$0,14_4$	$6,_7$
Ge	0,176	—0,087	0,058	3,4					

TABLE 3. Coordinates of the Atoms and Individual Temperature Factors for $(C_6H_5)Ge(CH)_4Ge(C_6H_5)_2$.

Atom	Coordinates			B_j A²	Atom	Coordinates			B_j A²
	x	*y*	*z*			*x*	*y*	*z*	
$Ge_{(1)}$	0,486	0,150	0,064	4,9	$C_{(14)}$	0,808	0,522	0,195	6,6
$Ge_{(2)}$	0,139	0,002	0, 461	4,6	$C_{(15)}$	0, 705	0, 512	0, 080	5, 9
$C_{(1)}$	0, 459	0, 088	—0, 133	6, 3	$C_{(16)}$	0, 610	0, 403	0, 038	5, 5
$C_{(2)}$	0,528	0,028	0,182	5,2	$C_{(17)}$	0,289	0,140	0,524	4,6
$C_{(3)}$	—0, 001	0,056	0,347	4, 7	$C_{(18)}$	0,397	0,121	0,493	6,1
$C_{(4)}$	0,105	—0,060	0,620	4,4	$C_{(19)}$	0,505	0,216	0,541	5,0
$C_{(5)}$	0,335	0,192	0,086	3,5	$C_{(20)}$	0,501	0,338	0,603	7,0
$C_{(6)}$	0,337	0,277	0,201	5,7	$C_{(21)}$	0,389	0,361	0,620	6,0
$C_{(7)}$	0,226	0,309	0,212	6,4	$C_{(22)}$	0,284	0,263	0,581	5,9
$C_{(8)}$	0,117	0,262	0,103	8,5	$C_{(23)}$	0,168	—0,142	0,345	5,6
$C_{(9)}$	0,115	0, 179	—0, 014	6,5	$C_{(24)}$	0, 135	—0, 264	0, 371	6, 2
$C_{(10)}$	0,226	0,145	—0,025	4,1	$C_{(25)}$	0,149	—0,369	0,284	7,7
$C_{(11)}$	0,614	0,308	0,118	4,0	$C_{(26)}$	0,180	—0,352	0,164	8,1
$C_{(12)}$	0,718	0,318	0,232	5,5	$C_{(27)}$	0,210	—0,231	0,136	8,1
$C_{(13)}$	0,816	0, 422	0, 268	7,6	$C_{(28)}$	0, 203	—0, 125	0, 227	6, 0

(atoms I and I', II and II' are linked by the noncoincident pseudocenters, displaced along the x-axis so that the vectors linking atoms I and II correspond to maxima (7) and (8); the atomic factors for iodine were used for all atoms).

In obtaining the electron density distribution (R = 46% with B = 0) the maxima of the atoms mentioned were considerably shifted and a series of additional maxima appeared. Subsequent calculations of the R-factor for several variants of the distribution of the heavy atoms together with analysis of the interatomic distances and of the heights of maxima showed that one of the initially found atoms I and II was germanium, not iodine, but the second iodine atom was also revealed. The structure now appeared centrosymmetric and this was confirmed by successful refinement by least squares in the space group $P2_1/c$. The R-factor was 16.6% at this stage (heavy atoms only). Refinement was carried out by referring the coefficients of the structure amplitudes to an absolute scale K, introduction of the general temperature factor B, correction to K for separate layer lines K_1, and introducing corrected coordinates and individual thermal factors u_j for the iodine and germanium atoms.

A comparison of the vector scheme corresponding to the coordinates obtained with the maxima of the interatomic functions (Table 1) showed that the vectors of the first series 2x2y2z for atoms $I_{(1)}$ and Ge had very small maxima (4-5 relative units), while the vector for $I_{(2)}$ did not appear at all, falling in an area of a higher maximum. The maxima of the vector $2x\frac{1}{2}2z = \frac{1}{2}$ of the atoms $I_{(2)}$ and Ge was not resolved on the three-dimensional Paterson function. These failures of resolution at the first stage complicated further refinement.

Unfortunately the poor quality of the x-ray photographs and the presence of the heavy iodine atoms prevented the determination of the coordinates of the carbon atoms. There was a whole range of small maxima in the three-dimensional electron density distribution, the signs of the structural amplitudes of which were determined relative to the coordinates of the iodine and germanium atoms. The highest and sharpest of these may be ascribed to one

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*Program for electronic computer written by V. I. Andrianov (FIKhF AN SSSR).

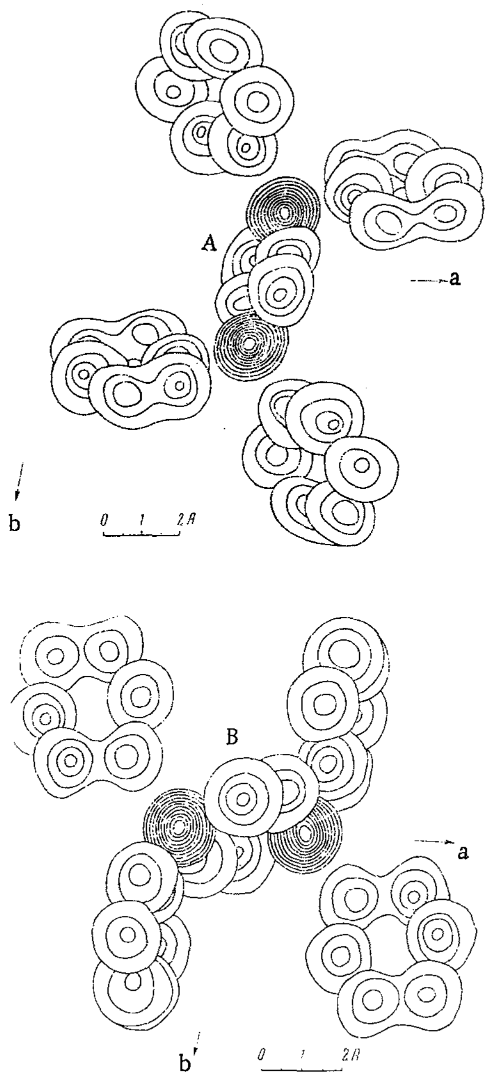

Fig. 1. Sections of the three-dimensional electron density series for $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$ through the centers of the atoms of the two independent molecules A and B.

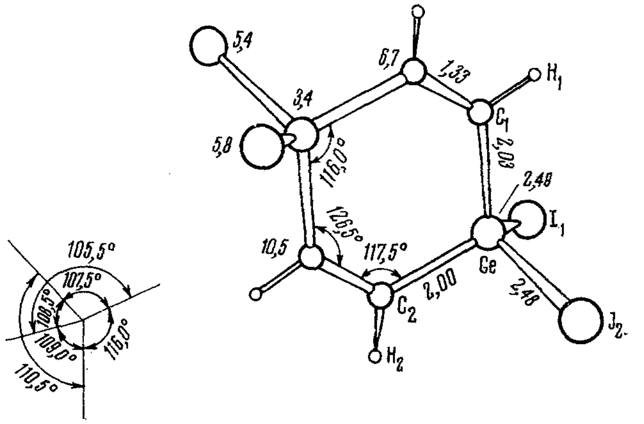

Fig. 2. Numbering of atoms, bond lengths, bond angles, and individual isotropic temperature factors for $I_2Ge(CH)_4GeI_2$.

of the carbon atoms. However, the second carbon atom could not correspond to any of the second order maxima. Its coordinates were therefore calculated geometrically.

Refinement by least squares including the carbon atoms (refining their coordinates and with individual isotropic thermal factors) gave a residual factor of R = 15.3%. However, the R-factor was insensitive to changes in position of the carbon atoms, a shift of about 0.3 A (in the position of the closest maximum of the electron density) increased R by only 0.03%. In the subsequent discussion we shall not put particular emphasis on those concrete values of geometric factors which depend on the positions of the carbon atoms. The final values of the atomic coordinates and their individual isotropic temperature factors are cited in Table 2. The temperature factors for the iodine and germanium atoms have physically reasonable values; those for carbon, especially for $C_{(1)}$, are clearly high which arises from the imprecision in locating these atoms.

Resolution and Refinement of the Structure of 1,1,4,4-Tetraphenyl-1,4-Digermanacyclohexadiene-2,5 (II)

This structure was solved by the heavy atom method. The coordinates of the germanium atoms were found from the three-dimensional Paterson distribution, and the coordinates were then used to assign the signs of the structure amplitudes. In the first approximation to the three-dimensional electron density distribution 11 of the 28 carbon atoms were revealed, and even the remaining 17 showed up approximately. It appeared that the unit cell contained two independent molecules containing six-membered rings and that they occupied centers of inversion (preliminary report [6]). In the account below the molecule with its center at $\frac{1}{2}00$ will be called A and that at $00\frac{1}{2}$ will be called B.

The structure was refined by the least squares method beginning in the same way as for structure I to R = 14.7%. However, the variation in bond lengths was very large (C–C distances in the phenyl rings from 1.24 to 1.67 A). Hence, further refinement was carried out by the method of least squares with additional conditions, as proposed by Waser [7].

In the present case, the minimum of the function

$$\Phi = \Phi_1 + V(\Phi_2 + \Phi_3),$$

was found, where

$$\Phi_1 = \sum_{hkl} w_{hkl} [(K + K_l) \,|F_{\text{exp}}(hkl)| - |F_{\text{theor}}(hkl)|]^2$$

the function which takes into account the convergence of the moduli of the theoretical and experimental structural amplitudes,

$$\Phi_2 = \sum_{pq} w_{pq} \left(r_{pq}^{\text{calc}} - r_{pq}^{\text{given}}\right)^2$$

the function which takes into account the convergence of the distance between the p-th and q-th atoms (r_{pq}) to the given value;

$$\Phi_3 = \sum_{pq,\, lm} w_{pq,\, lm} \left(r_{pq}^{\text{calc}} - r_{lm}^{\text{calc}}\right)^2$$

the function which takes into account the condition of equality of the distances between the pairs of atoms p, q and l, m.

In the refinement, the following conditions were used:

1) convergence of the C–C bond length in the phenyl rings to the tabulated value of 1.40 A;

2) equality of the distances between the carbon atoms in the meta-positions of the phenyl rings (i.e., equality of the C–C–C bond angles);

3) equality of the bonds between germanium and the carbon of the phenyl rings;

4) equality of the germanium–carbon bonds in the heterocycle.

Because our computer program only allows the simultaneous refinement of a maximum of 55 parameters, each of the two independent molecules was refined separately; the stages of atomic coordinate refinement was carried out alternately for molecules A and B. The stages of refinement with additional conditions also alternated with stages of general refinement of the atomic coordinates and calculation of the electron density distribution. At the final stage the distances between the nonbonded germanium and carbon atoms in the heterocycle were taken to be equal in both molecules. The final value of the R-factor was 13.6%. The atomic coordinates and individual isotropic temperature factors corresponding to this R-factor are given in Table 3. The weightings of V, $w(hkl)$, w_{pq}, and $w_{pq,lm}$ were taken as 1 in the final stage of the refinement. The electron density distribution is shown in Fig. 1 as a section through the atomic centers.

Geometry of the Molecule

The individual values of the bond lengths and bond angles are cited in Tables 4 and 5 and Figs. 2 and 3 (the numberings of the atoms and the values of the temperature factors are the same); the values for II, averaged over all the chemically equivalent parameters, are given in Fig. 4. It is noted that the values of the isotropic temperature factors in II increase in general with increasing distance from the center of the molecule, which corresponds to the vibrations of the molecule as a rigid body, although the phenyl rings possibly undergo additional and independent vibration.

Estimation of the probable error of the bond lengths in structure I by Vainshtein's formula [5] gave (Ge–I) = 0.006 and (Ge–C) = 0.036 A which is clearly not a high accuracy (see the variation in individual values in Table 4). As for structure II, the use of this method of refinement does not permit the estimation of error by the usual methods nor generally speaking the error of individual bond lengths and angles. Judging from the variation for the two independent molecules, the precision of the averaged values is probably about 0.1 A for bond lengths and 1° for angles (i.e., approximately the same as for the I–Ge–I angle in structure I).

As already noted, the molecules in the crystals of both compounds contain approximately planar six-membered heterocycles placed at centers of inversion.

The equations of the planes* of the heterocycles and the deviations of the atoms from them are as follows (for the two independent molecules in the case of II):

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*The equations for all the planes in this work were found by the least squares method; all atoms were taken into account with equal weight. For I the calculations were carried out manually, the equations pertaining to the orthogonal system of coordinates:

I) $0.234_9 x_0 + 0.899_2 y_0 + 0.369_6 z_0 = 0$	Ge $+ 0.00_8$ A $C_{(1)} - 0.01_1$ $C_{(2)} - 0.01_0$
II *A*) $10.78_0 x + 1.90_4 y - 1.99_9 z - 5.39_0 = 0$	$Ge_{(1)} + 0.00_7$ A $C_{(1)} - 0.00_9$ $C_{(2)} - 0.00_9$
II *B*) $0.96_1 x + 8.90_8 y + 3.41_2 z - 0.17_1 = 0$	$Ge_{(2)} - 0.01_8$ $C_{(3)} + 0.02_4$ $C_{(4)} + 0.02_4$

The germanium atoms are tetrahedrally bonded. However, the sum of the normal bond angles of 109.5° for the heteroatoms and 120° for the carbon atoms gives 699° for the cycle instead of the 720° required for a planar hexagon, so that the tendency to coplanarity causes distortion of the bond angles C=C–Ge (122° in I, 123° in II) and C–Ge–C (116° in I and 113° in II). It is notable that very similar deformations of the angles were found in the electron diffractometric study of the chloro-analogue of I (v.infra).

There is very little information in the literature on the structures of organogermanium compounds, but our values for bonds at germanium (Ge–C 2.01 (I), 1.95 and 1.96 (II, within and without the ring), and Ge–I 2.48 A) are in agreement with the small number of single bond lengths found in other compounds.

Trimethylcyanogermane is the only structure known to us to have been studied by x-ray methods [8]. The Ge–C bond length in this molecule is 1.98 A for both methyl and cyano groups. Electron diffractometric studies have been made of $Ge(CH_3)_4$ [9] and $(CH_3)GeH_3$ [10] in the gas phase, Ge–C bond lengths were 1.98 and 1.945 A, respectively. Ge–I bond lengths of 2.470 [11], 2.48 [12], and 2.50 A [13] have been found for GeI_4 by electron diffraction.

Our geometric parameters also agree with the electron diffraction data for $I_2Ge(CH)_4GeI_2$ [4] and Cl_2Ge $Cl_2Ge(CH)_4GeCl_2$ [2,4]; as already remarked, two types of electron diffraction pattern were found for the first of these compounds, one pattern corresponding to a dimeric molecule with a six-membered ring, The same type of molecule occurred in the chloro derivative. The germanium-carbon bond lengths were 1.97 for the iodide and 1.93 A for the chloride (a value of 1.98 A was found for the latter by x-ray diffraction [2]), while the germanium-iodine length was 2.51 A. As in the crystalline state, the bond angles were distorted: in the chloro derivative C–Ge–C = 117°20' and Ge–C=C = 121°28' (a model with C–Ge–C = 117° was assumed for the iodo compound). The Ge...Ge distances in the heterocycles were also similar: the electron diffraction figure for the chloro compound is 3.40 A, while the values for the iodo and phenyl compounds are 3.46 and 3.49 A, respectively.

The considerable variation in the Ge–C distance with substituents at Ge in organogermanium compounds should be noted: from 1.94_5 A in CH_3GeH_3 to 2.0_1 A in $I_2Ge(CH)_4GeI_2$. Despite the varying precision of the different studies, this variation seems to us to be real, although the establishment of a reliable correlation of the bond length with the type of substituent requires the accumulation and refinement of the experimental data.

In the phenyl compound II the Ge–C bonds within the heterocycle (1.95 A) and outside it (1.94, 1.97, 1.98, and 1.98 A; mean 1.96 ± 0.02 A) are the same. The carbon-carbon distance within the ring (1.33 A in I and 1.35 A in II) is close to the standard value for C=C. Both these facts indicate the absence of any considerable d-π conjugation between the germanium orbitals and the double bond in the rings, although such conjugation might have been expected from general quantum mechanical considerations.

There remains the conformation of these molecules. In the molecule of the iodo compound I the germanium and iodine atoms lie in a single plane. The equation of the plane and the deviations from it are:

$$x_0 = x + z \cos \beta$$
$$y_0 = y$$
$$z_0 = z \sin \beta$$

For II, the calculations were carried out by computer, using a program compiled at FIKhF, USSR Academy of Science; the equations pertained to obliquely-angled system of coordinates, with x,y, and z expressed in A, but the angles between the coordinates being equal to those of the unit cell of the crystal.

TABLE 4. Bond Lengths and Bond Angles of $I_2Ge(CH)_4GeI_2$

Bond lengths, A		Bond angles,		Bond lengths, A		Bond angles,°	
$\mathrm{Ge}-\mathrm{I}_{(1)}$	$2{,}49$	$\mathrm{I}_{(1)}-\mathrm{Ge}-\mathrm{I}_{(2)}$	$108{,}_5$	$\mathrm{C}_{(1)}-\mathrm{C}_{(2')}$	$1{,}3_3$	$\mathrm{I}_{(2)}-\mathrm{Ge}-\mathrm{C}_{(2)}$	$107{,}_5$
$\mathrm{Ge}-\mathrm{I}_{(2)}$	$2{,}48$	$\mathrm{I}_{(1)}-\mathrm{Ge}-\mathrm{C}_{(1)}$	$109{,}_0$			$\mathrm{C}_{(1)}-\mathrm{Ge}-\mathrm{C}_{(2)}$	$116{,}_0$
$\mathrm{Ge}-\mathrm{C}_{(1)}$	$2{,}0_3$	$\mathrm{I}_{(1)}-\mathrm{Ge}-\mathrm{C}_{(2)}$	$105{,}_5$			$\mathrm{Ge}-\mathrm{C}_{(1)}-\mathrm{C}_{(2')}$	$126{,}_5$
$\mathrm{Ge}-\mathrm{C}_{(2)}$	$2{,}0_0$	$\mathrm{I}_{(2)}-\mathrm{Ge}-\mathrm{C}_{(1)}$	$110{,}_5$			$\mathrm{Ge}-\mathrm{C}_{(2)}-\mathrm{C}_{(1')}$	$117{,}_5$

TABLE 5. Bond Lengths and Bond Angles for Molecules of $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$

Molecule A at $^1/_{200}$		Molecule B at $^{001}/_2$	
Bond lengths, A			
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(1)}$	1,95	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(3)}$	1,95
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(2)}$	1,95	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(4)}$	1,95
$\mathrm{C}_{(1)}-\mathrm{C}_{(2')}$	1,35	$\mathrm{C}_{(3)}-\mathrm{C}_{(4')}$	1,34
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(5)}$	1,94	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(17)}$	1,98
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}$	1,97	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}$	1,98
$\mathrm{C}_{(5)}-\mathrm{C}_{(6)}$	1,39	$\mathrm{C}_{(17)}-\mathrm{C}_{(18)}$	1,41
$\mathrm{C}_{(6)}-\mathrm{C}_{(7)}$	1,41	$\mathrm{C}_{(18)}-\mathrm{C}_{(19)}$	1,40
$\mathrm{C}_{(7)}-\mathrm{C}_{(8)}$	1,40	$\mathrm{C}_{(19)}-\mathrm{C}_{(20)}$	1,41
$\mathrm{C}_{(8)}-\mathrm{C}_{(9)}$	1,39	$\mathrm{C}_{(20)}-\mathrm{C}_{(21)}$	1,40
$\mathrm{C}_{(9)}-\mathrm{C}_{(10)}$	1,41	$\mathrm{C}_{(21)}-\mathrm{C}_{(22)}$	1,40
$\mathrm{C}_{(10)}-\mathrm{C}_{(5)}$	1,40	$\mathrm{C}_{(22)}-\mathrm{C}_{(17)}$	1,41
$\mathrm{C}_{(11)}-\mathrm{C}_{(12)}$	1,40	$\mathrm{C}_{(23)}-\mathrm{C}_{(24)}$	1,40
$\mathrm{C}_{(12)}-\mathrm{C}_{(13)}$	1,40	$\mathrm{C}_{(24)}-\mathrm{C}_{(25)}$	1,41
$\mathrm{C}_{(13)}-\mathrm{C}_{(14)}$	1,40	$\mathrm{C}_{(25)}-\mathrm{C}_{(26)}$	1,41
$\mathrm{C}_{(14)}-\mathrm{C}_{(15)}$	1,40	$\mathrm{C}_{(26)}-\mathrm{C}_{(27)}$	1,40
$\mathrm{C}_{(15)}-\mathrm{C}_{(16)}$	1,40	$\mathrm{C}_{(27)}-\mathrm{C}_{(28)}$	1,41
$\mathrm{C}_{(16)}-\mathrm{C}_{(11)}$	1,41	$\mathrm{C}_{(28)}-\mathrm{C}_{(23)}$	1,40
Bond angles, °			
$\mathrm{C}_{(1)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(2)}$	114,0	$\mathrm{C}_{(3)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(4)}$	112,0
$\mathrm{C}_{(1)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(5)}$	108,5	$\mathrm{C}_{(3)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(17)}$	111,0
$\mathrm{C}_{(1)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}$	106,5	$\mathrm{C}_{(3)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}$	107,0
$\mathrm{C}_{(2)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(5)}$	107,0	$\mathrm{C}_{(4)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(17)}$	110,0
$\mathrm{C}_{(2)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}$	112,5	$\mathrm{C}_{(4)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}$	106,5
$\mathrm{C}_{(5)}-\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}$	108,0	$\mathrm{C}_{(17)}-\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}$	109,5
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(1)}-\mathrm{C}_{(2')}$	123,0	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(3)}-\mathrm{C}_{(4')}$	123,5
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(2)}-\mathrm{C}_{(1')}$	122,5	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(4)}-\mathrm{C}_{(3')}$	124,0
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(5)}-\mathrm{C}_{(6)}$	121,0	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(17)}-\mathrm{C}_{(18)}$	119,5
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(5)}-\mathrm{C}_{(10)}$	117,5	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(17)}-\mathrm{C}_{(22)}$	120,5
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}-\mathrm{C}_{(12)}$	118,0	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}-\mathrm{C}_{(24)}$	119,0
$\mathrm{Ge}_{(1)}-\mathrm{C}_{(11)}-\mathrm{C}_{(16)}$	122,0	$\mathrm{Ge}_{(2)}-\mathrm{C}_{(23)}-\mathrm{C}_{(28)}$	120,0
$\mathrm{C}_{(5)}-\mathrm{C}_{(6)}-\mathrm{C}_{(7)}$	119,5	$\mathrm{C}_{(17)}-\mathrm{C}_{(18)}-\mathrm{C}_{(19)}$	119,5
$\mathrm{C}_{(6)}-\mathrm{C}_{(7)}-\mathrm{C}_{(8)}$	119,0	$\mathrm{C}_{(18)}-\mathrm{C}_{(19)}-\mathrm{C}_{(20)}$	120,5
$\mathrm{C}_{(7)}-\mathrm{C}_{(8)}-\mathrm{C}_{(9)}$	120,0	$\mathrm{C}_{(19)}-\mathrm{C}_{(20)}-\mathrm{C}_{(21)}$	119,5
$\mathrm{C}_{(8)}-\mathrm{C}_{(9)}-\mathrm{C}_{(10)}$	120,0	$\mathrm{C}_{(20)}-\mathrm{C}_{(21)}-\mathrm{C}_{(22)}$	120,5
$\mathrm{C}_{(9)}-\mathrm{C}_{(10)}-\mathrm{C}_{(5)}$	119,0	$\mathrm{C}_{(21)}-\mathrm{C}_{(22)}-\mathrm{C}_{(17)}$	120,0
$\mathrm{C}_{(10)}-\mathrm{C}_{(5)}-\mathrm{C}_{(6)}$	121,0	$\mathrm{C}_{(22)}-\mathrm{C}_{(17)}-\mathrm{C}_{(18)}$	119,0
$\mathrm{C}_{(11)}-\mathrm{C}_{(12)}-\mathrm{C}_{(13)}$	120,0	$\mathrm{C}_{(23)}-\mathrm{C}_{(24)}-\mathrm{C}_{(25)}$	119,5
$\mathrm{C}_{(12)}-\mathrm{C}_{(13)}-\mathrm{C}_{(14)}$	120,5	$\mathrm{C}_{(24)}-\mathrm{C}_{(25)}-\mathrm{C}_{(26)}$	119,5
$\mathrm{C}_{(13)}-\mathrm{C}_{(14)}-\mathrm{C}_{(15)}$	119,5	$\mathrm{C}_{(25)}-\mathrm{C}_{(26)}-\mathrm{C}_{(27)}$	121,0
$\mathrm{C}_{(14)}-\mathrm{C}_{(15)}-\mathrm{C}_{(16)}$	120,0	$\mathrm{C}_{(26)}-\mathrm{C}_{(27)}-\mathrm{C}_{(28)}$	120,0
$\mathrm{C}_{(15)}-\mathrm{C}_{(16)}-\mathrm{C}_{(11)}$	120,0	$\mathrm{C}_{(27)}-\mathrm{C}_{(28)}-\mathrm{C}_{(23)}$	119,5
$\mathrm{C}_{(16)}-\mathrm{C}_{(11)}-\mathrm{C}_{(12)}$	119,5	$\mathrm{C}_{(28)}-\mathrm{C}_{(23)}-\mathrm{C}_{(24)}$	119,5

TABLE 6. Intermolecular Distances (A) in the $I_2Ge(CH)_4GeI_2$ Crystal*

$I_{(1)} \cdots I_{(1')x}$	4,44	$I_{(2)} \cdots I_{(2')cx}$	4,43	$I_{(1)} \cdots H_{(1)c\bar{y}}$	3,25
$I_{(1)} \cdots I_{(1')\bar{y}}$	4,67	$I_{(1)} \cdots C_{(1)\bar{c}}$	4,01	$I_{(1)} \cdots H_{(1')c\bar{y}}$	3,67
$I_{(1)} \cdots I_{(2')x}$	4,60	$I_{(1)} \cdots C_{(1)\bar{y}}$	4,58	$I_{(1)} \cdots H_{(2)c\bar{y}\bar{z}}$	3,78
$I_{(1)} \cdots I_{(2')cx}$	4,24	$I_{(1)} \cdots C_{(2')\bar{c}}$	4,18	$I_{(2)} \cdots H_{(1)c}$	3,58
$I_{(1)} \cdots I_{(2')\bar{y}}$	4,14	$I_{(1)} \cdots C_{(2)c\overline{yz}}$	4,59	$I_{(2)} \cdots H_{(1')x}$	3,30
$I_{(1)} \cdots I_{(2)c\overline{yz}}$	4,28	$I_{(2)} \cdots C_{(1')x}$	4,20	$C_{(1)} \cdots H_{(2')c}$	3,37
$I_{(2)} \cdots I_{(2')x}$	4,54	$I_{(2)} \cdots C_{(1)c}$	4,27	$C_{(1)} \cdots H_{(2)c\overline{yz}}$	3,30

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*The figures in parentheses give the numbering of the initial molecule (without dashes, atoms whose coordinates are cited in Table 2; with dashes, atoms linked with them via the center of symmetry at (000)); the indices x,y,z indicate the molecules connected by the corresponding translation; the index c indicates the molecule related to the initial molecule by the glide plane c.

$$-0.46_6\,x_0 - 0.22_5\,y_0 + 0.85_5\,z_0 = 0 \qquad \begin{array}{l} Ge - 0.01_2 \text{ A} \\ I_{(1)} + 0.00_4 \\ I_{(2)} + 0.00_4 \end{array}$$

As was to be expected, this plane is perpendicular to the plane of the heterocycle (interfacial angle 89.7°) and the molecule belongs to point group D_{2h} within the limits of precision of the study. The bond angles at the germanium atom (apart from the C–Ge–C angle, the reason for the widening of which has already been noted) are nearly tetrahedral (mean 108°; Table 4).

In the crystal of the phenyl derivative II the equation of the plane, which passes through the germanium atoms and the carbon atoms of the phenyl groups directly bonded to germanium, and the deviations from it are:

$$A)\ 0.51_5\,x - 3.87_6\,y + 9.56_0\,z - 0.24_7 = 0 \qquad \begin{array}{l} Ge_{(1)} - 0.02_3 \text{ A} \\ C_{(5)} + 0.00_7 \\ C_{(11)} + 0.00_7 \end{array}$$

$$B)\ 2.35_6\,x - 6.26_4\,y + 8.27_7\,z - 4.13_8 = 0 \qquad \begin{array}{l} Ge_{(2)} + 0.00_8 \text{ A} \\ C_{(17)} - 0.00_2 \\ C_{(23)} - 0.00_2 \end{array}$$

The interfacial angles between these planes and those of the heterocycles are 87.6° for A and 89.6° for B, i.e., as in I the exocyclic bonds of the germanium atoms are in planes perpendicular to the heterocycles. However, the symmetry of both independent molecules of II seem to be lower than that of I; because of the different inclination of the two phenyl groups at a germanium atom to the plane of the heterocycle, only the center of inversion is retained and this is reflected in the crystal. The relative orientation of the phenyl groups and the heterocyclic ring is different in the two independent molecules A and B, as can be seen from projections of the molecules onto the plane of the heterocyclic ring (Fig. 5). The equations of the planes of the phenyl rings and the deviations from them are as follows:

$$A \quad 1)\ 2.26_8x + 9.10_4y - 6.39_1z - 1.98_1 = 0$$

$$\begin{array}{ll} C_{(5)} + 0.02_0\text{A} & C_{(8)} - 0.00_8\text{A} \\ C_{(6)} - 0.02_2 & C_{(9)} + 0.00_5 \\ C_{(7)} - 0.01_6 & C_{(10)} - 0.01_1 \end{array}$$

$$Ge_{(1)} - 0.08_0\text{A}$$

$$A \quad 2)\ 8.40_8x - 5.10_5y - 7.09_9z - 2.77_2 = 0$$

$$\begin{array}{ll} C_{(11)} + 0.02_4\text{A} & C_{(14)} + 0.02_8\text{A} \\ C_{(12)} + 0.01_0 & C_{(15)} + 0.00_5 \\ C_{(13)} - 0.03_6 & C_{(16)} - 0.03_1 \end{array}$$

$$Ge_{(1)} - 0.09_3\text{Å}$$

TABLE 7. Intermolecular Distances (A) in $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$ Crystals*

$C_{(1)} \cdots C_{(17)\bar{z}}$	3,69	$C_{(12)} \cdots H_{(21')xy}$	3,11	$C_{(19)} \cdots H_{(6)}$	2,95
$C_{(2)} \cdots C_{(18)\bar{z}}$	3,78	$C_{(12)} \cdots H_{(27')x\bar{z}}$	3,12	$C_{(19)} \cdots H_{(18')x}$	3,06
$C_{(3)} \cdots C_{(9')\bar{x}}$	3,74	$C_{(13)} \cdots H_{(21')xy}$	3,06	$C_{(20)} \cdots C_{(26')x}$	3,75
$C_{(3)} \cdots C_{(10')\bar{x}}$	3,72	$C_{(14)} \cdots C_{(25)xy}$	3,72	$C_{(20)} \cdots H_{(1)z}$	3,19
$C_{(3)} \cdots H_{(9')\bar{x}}$	3,02	$C_{(14)} \cdots C_{(21')xy}$	3,62	$C_{(20)} \cdots H_{(6)}$	3,11
$C_{(3)} \cdots H_{(10')\bar{x}}$	2,98	$C_{(14)} \cdots C_{(22')xy}$	3,56	$C_{(21)} \cdots H_{(1)z}$	3,14
$C_{(4)} \cdots C_{(10)z}$	3,77	$C_{(14)} \cdots H_{(21')xy}$	2,97	$C_{(22)} \cdots H_{(1)z}$	2,94
$C_{(4)} \cdots H_{(10)z}$	2,78	$C_{(14)} \cdots H_{(22')xy}$	2,85	$C_{(22)} \cdots H_{(7)}$	3,17
$C_{(4)} \cdots H_{(12')z}$	3,10	$C_{(14)} \cdots H_{(26')x\bar{z}}$	3,02	$C_{(23)} \cdots H_{(9')\bar{x}}$	2,91
$C_{(5)} \cdots H_{(28)}$	3,11	$C_{(15)} \cdots C_{(21')xy}$	3,71	$C_{(23)} \cdots H_{(19')z}$	2,95
$C_{(5)} \cdots H_{(15')y}$	2,82	$C_{(15)} \cdots C_{(26')x\bar{z}}$	3,54	$C_{(24)} \cdots H_{(14)\bar{x}\bar{y}}$	2,89
$C_{(6)} \cdots C_{(18)}$	3,60	$C_{(15)} \cdots H_{(16')y}$	3,01	$C_{(24)} \cdots H_{(19')x}$	2,98
$C_{(6)} \cdots C_{(19)}$	3,69	$C_{(15)} \cdots H_{(21')xy}$	3,03	$C_{(25)} \cdots H_{(7)\bar{y}}$	3,13
$C_{(6)} \cdots H_{(15')y}$	2,85	$C_{(15)} \cdots H_{(26')x\bar{z}}$	2,60	$C_{(25)} \cdots H_{(14)\bar{x}\bar{y}}$	2,91
$C_{(7)} \cdots C_{(22)}$	3,76	$C_{(16)} \cdots C_{(16')y}$	3,57	$C_{(25)} \cdots H_{(20')x}$	3,12
$C_{(7)} \cdots H_{(25)y}$	3,06	$C_{(16)} \cdots C_{(26')x\bar{z}}$	3,66	$C_{(26)} \cdots H_{(20')x}$	3,17
$C_{(7)} \cdots H_{(15')y}$	3,07	$C_{(16)} \cdots C_{(27')x\bar{z}}$	3,68	$C_{(27)} \cdots H_{(8')\bar{x}}$	3,11
$C_{(8)} \cdots H_{(3)}$	2,98	$C_{(16)} \cdots H_{(16')y}$	2,96	$C_{(27)} \cdots H_{(9')\bar{x}}$	3,03
$C_{(8)} \cdots H_{(15')y}$	3,11	$C_{(16)} \cdots H_{(21')xy}$	3,17	$C_{(28)} \cdots H_{(9')\bar{x}}$	2,61
$C_{(9)} \cdots C_{(27')\bar{z}}$	3,77	$C_{(16)} \cdots H_{(26')x\bar{z}}$	3,03	$H_{(2)} \cdots H_{(18)}$	2,55
$C_{(9)} \cdots C_{(28')\bar{z}}$	3,62	$C_{(16)} \cdots H_{(27')x\bar{z}}$	3,08	$H_{(2)} \cdots H_{(19)}$	2,55
$C_{(9)} \cdots H_{(15')y}$	3,07	$C_{(17)} \cdots H_{(1)z}$	2,79	$H_{(4)} \cdots H_{(10)z}$	2,52
$C_{(10)} \cdots H_{(15')y}$	2,90	$C_{(18)} \cdots H_{(1)z}$	2,98	$H_{(4)} \cdots H_{(12')z}$	2,13
$C_{(11)} \cdots H_{(21')xy}$	3,16	$C_{(18)} \cdots H_{(2)}$	3,07	$H_{(7)} \cdots H_{(25)y}$	2,29
$C_{(11)} \cdots H_{(27')x\bar{z}}$	2,91	$C_{(18)} \cdots H_{(2')z}$	3,12	$H_{(14)} \cdots H_{(22')xy}$	2,56
$C_{(12)} \cdots H_{(4')x}$	2,99	$C_{(18)} \cdots H_{(18')x}$	3,04	$H_{(18)} \cdots H_{(18')x}$	2,49
		$C_{(19)} \cdots H_{(1)z}$	3,09	$H_{(18)}$ $H_{(19')x}$	2,55
		$C_{(19)} \cdots H_{(2)}$	3,08		

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*The numbers in brackets indicate the numbering of the atoms of the initial molecule (without dashes, atoms whose coordinates are cited in Table 3; with dashes, atoms linked with them via the center of symmetry ½ 00 for molecule A and 00½ for molecule B); the indices x,y,z indicate molecules related to the initial one by the corresponding translation: The following are cited: C...C < 3.8, C...H < 3.2, and H...H < 2.6 A.

B 1) $0.81_5x - 4.78_3y + 9.28_7z - 4.37_8 = 0$

$C_{(17)} - 0.01_9A$ $C_{(20)} - 0.01_8A$
$C_{(18)} + 0.02_7$ $C_{(21)} + 0.02_7$
$C_{(19)} - 0.02_4$ $C_{(22)} + 0.00_7$
$Ge_{(2)} - 0.00_8A$

B 2) $9.78_8x - 1.64_8y + 2.75_0z - 2.81_1 = 0$

$C_{(23)} - 0.01_4A$ $C_{(26)} + 0.01_4A$
$C_{(24)} + 0.03_4$ $C_{(27)} + 0.00_5$
$C_{(25)} - 0.03_4$ $C_{(28)} - 0.00_5$
$Ge_{(2)} - 0.18_5A$

The relative orientations of the various parts of the molecules are characterized by the following interfacial angles:

	A	B
heterocycle–phenyl (1)	65.5°	84.4°
heterocycle–phenyl (2)	61.3°	70.7°
phenyl (1)–phenyl (2)	84.7°	57.8°

The following angles correspond to the deviation of the germanium atoms from the planes of the phenyl rings: A1) 2.3°, A2) 2.7°, B1) 0.2°, B2) 5.6°. In three cases these angles are large and are undoubtedly caused by steric strain (v.infra).

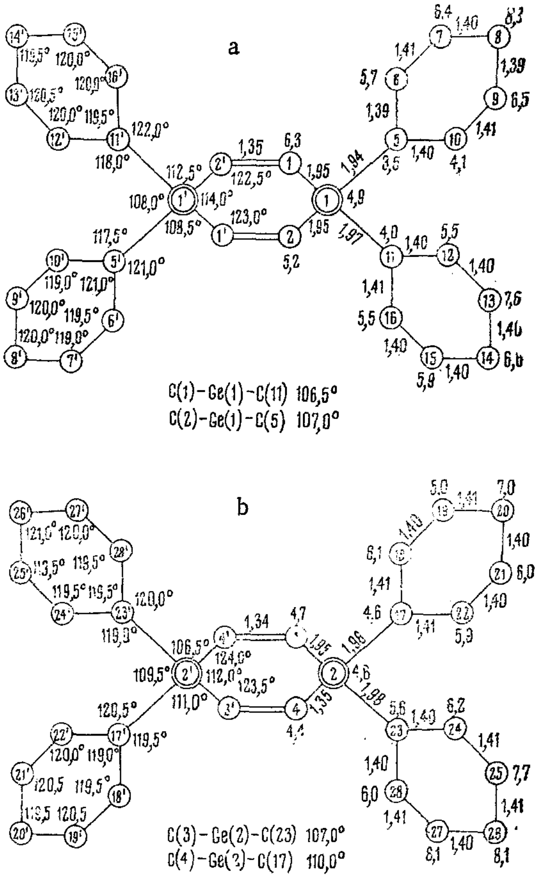

Fig. 3. Numbering of atoms, bond lengths, bond angles, and the individual isotropic temperature factors for $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$: a) molecule A; b) molecule B.

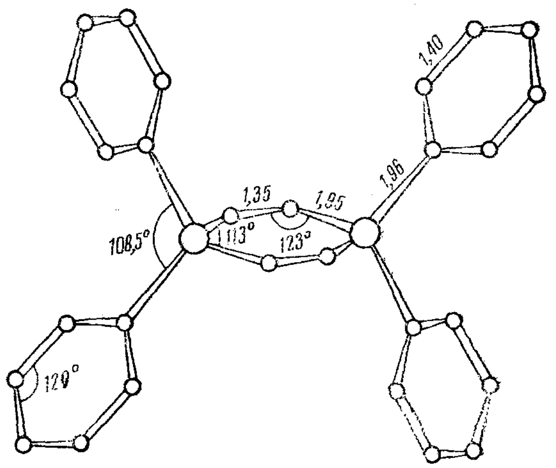

Fig. 4. Averaged geometrical parameters of the molecule.

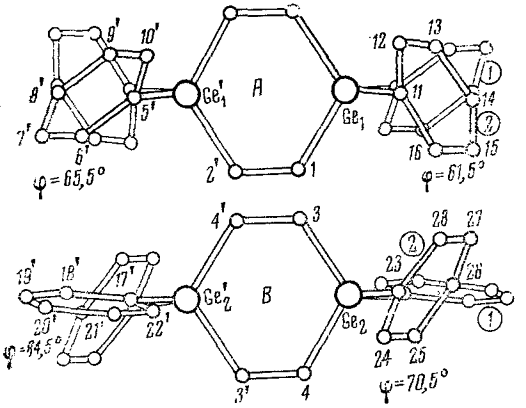

Fig. 5. Projections of the independent molecules of $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$ on the plane of the heterocycle.

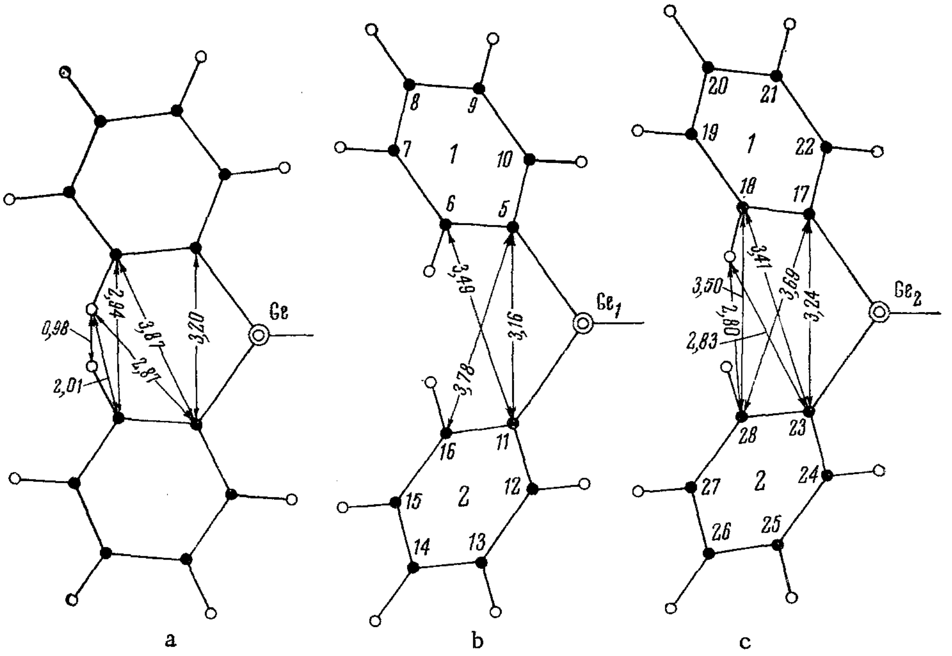

Fig. 6. Short nonbonded distances: a) hypothetical molecule with symmetry D_{2h}; b) molecule A; c) molecule B.

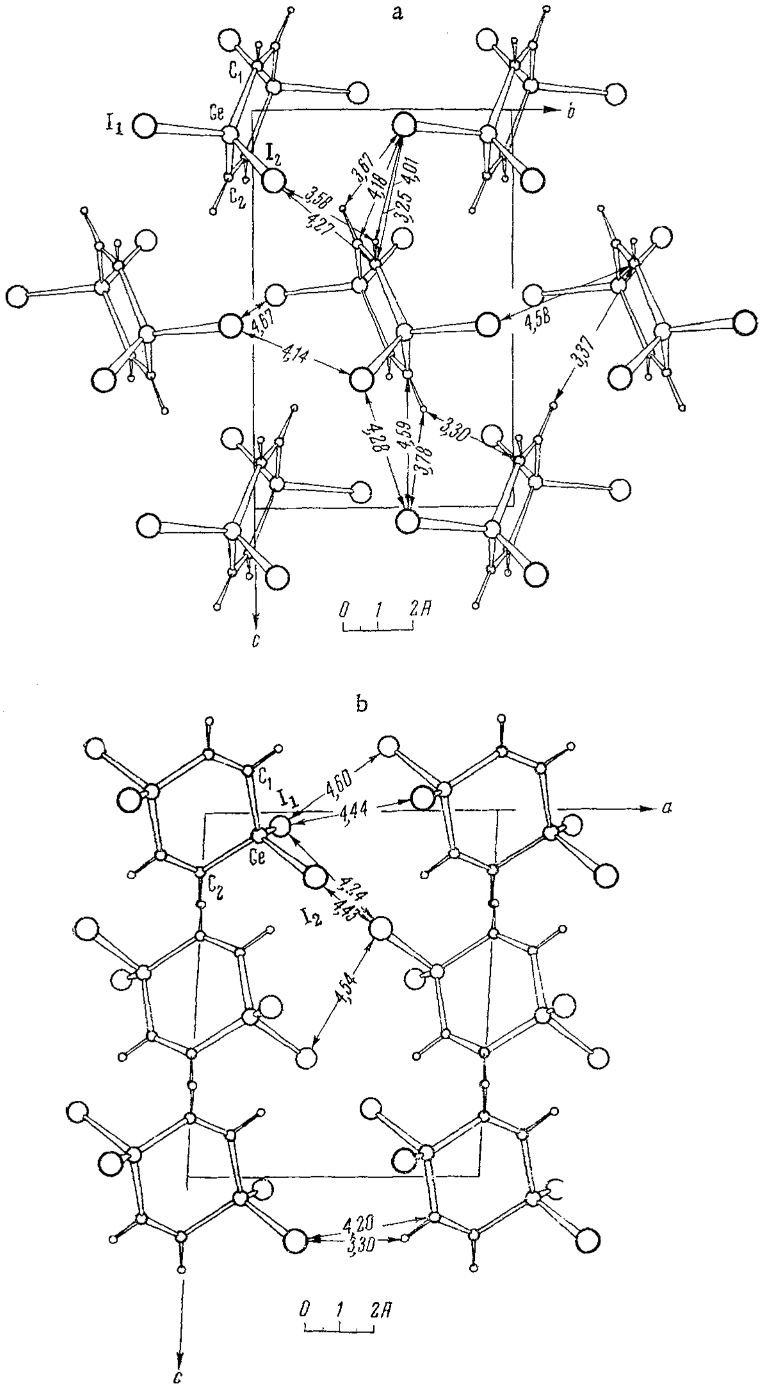

Fig. 7. Position of $I_2Ge(CH)_4GeI_2$ molecules in the crystal, and their intermolecular distances: a) in the 0yz layer; b) between layers.

Since there is no conjugation between the heterocycle and the phenyl nuclei, rotation of the latter about the Ge–C bond in the free molecule is determined only by interactions between nonbonded atoms. We have not carried out a complete conformational analysis, but even an examination of the distances between nonbonded atoms permits some conclusions to be drawn. As Fig. 6 shows, if the phenyl nuclei were normal to the plane of the heterocycle, the molecule would be considerably strained because of the considerable number of nonbonded contacts in this conformation which are small in comparison with the equilibrium distances (C...C 3.8, C...H 3.1, H...H 2.4 A [14]). Rotation of both rings from this position by 90° in the same direction completely removes steric hindrance, but there is a short distance between the carbon atoms linked to germanium which does not depend on the rotation. This conformation of the molecule would be less compact so that insufficiently dense packing would arise. The actual conformations of molecules A and B occupy intermediate positions between the two extreme cases. In this way there are few short contacts while the compactness is not reduced much (Fig. 6), and what short contacts there

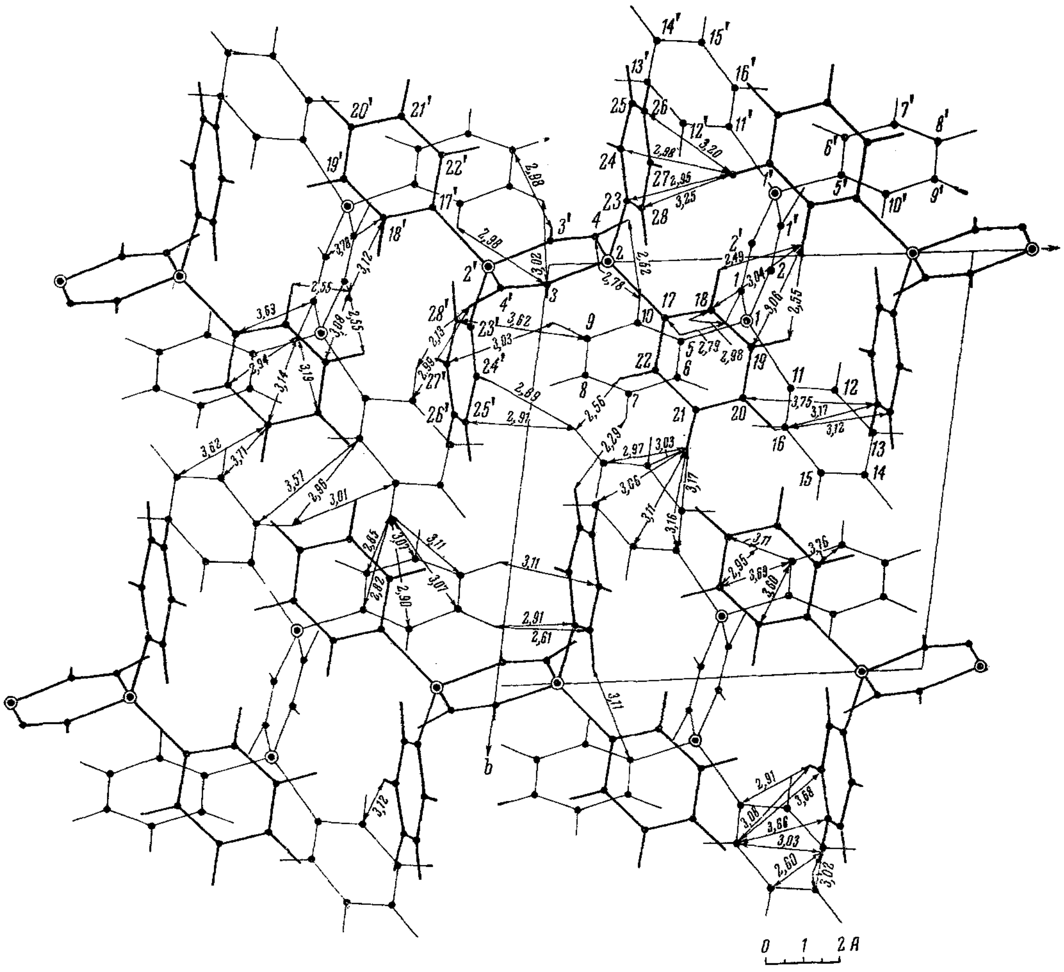

Fig. 8. Intermolecular distances in the crystal of $(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$.

are are reasonable. As for the different conformations of the independent molecules (molecule B has the smaller steric strain), this is evidently due to their different environments in the crystal, i.e., to different intermolecular interactions.

Molecular Packing

The intermolecular distances, taking into account the hydrogen atoms whose coordinates were calculated by normal structural chemical concepts, are shown in Tables 6 and 7 and Figs. 7 and 8. Unfortunately the germanium atoms do not take part in the intermolecular contacts so that their van der Waals radius cannot be determined from the structural data.

In the structure of I all the intermolecular distances are equal to or greater than the sums of the van der Waals radii; most of the contacts involve the iodine atoms. The values taken for the interatomic radii were R_I 2.1, R_C 1.8, R_H 1.2 A [5].

In the structure of II most of the distances equal or exceed the sums of the van der Waals radii. There are few somewhat shorter distances which involve hydrogen atoms, but since the real positions of the latter in the crystal are imprecisely known, these shortenings cannot be considered to be real.

The coordination numbers of the molecules (10 for compound I, 12 for both molecules of II) are normal for crystals of organic compounds.

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