

# ATRANES

## XXXIV.\* MOLECULAR AND CRYSTAL STRUCTURE OF 1-SUBSTITUTED

### SILATRANES AND GERMATRANES

Ya. Ya. Bleidelis, A. A. Kemme,  
G. I. Zelchan, and M. G. Voronkov

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The structures of 1-substituted silatranes and germatranes  $[\overline{XM(OCH_2CH_2)_3N}]$  ( $M = Si, Ge$ ) are discussed on the basis of data from x-ray diffraction analysis and other physicochemical methods. The found values of the interatomic distances and valence angles in molecules of these compounds directly prove the existence of a transannular  $N \rightarrow M$  coordinate bond and confirm the correctness of the previously proposed geometrical model of a molecule with a trigonal-bipyramidal orientation of the valence bonds of the central atom  $M$ . In metalloatranes ( $M = Si, Ge, B$ ), the distance from the nitrogen atom to the plane in which the three oxygen atoms lie is a constant value ( $2.00 \pm 0.05 \text{ \AA}$ ). The effect of substituent  $X$  on the structure of the molecule was established.

The unusual (for alkoxides) chemical stability of silatranes and germatranes  $[\overline{XM(OCH_2CH_2)_3N}]$ ;  $M = Si, Ge$ , their thermal stability, and their monomeric character have made it possible to assume the existence of a transannular donor-acceptor bond ( $N \rightarrow M$ ) in molecules of these compounds [2-7]. This was subsequently confirmed by dipole-moment data [4, 8, 9] and the IR [4, 10, 11], UV [12] and PMR spectra [2, 13-15].

A direct investigation of the molecular and crystalline structure of the atranes by x-ray diffraction analysis seemed of particular interest. It seemed necessary to determine the valence angles and interatomic distances, particularly the  $M-N$  distances, in the atrane molecules and also to establish the coordination of the  $M$  atom; this would make it possible to judge the hybridization of its valence orbitals and ultimately would lead to elucidation of the effect of the nature of substituent  $X$  and central atom  $M$  on the character of the  $N \rightarrow M$  donor-acceptor bond.

The determination and comparison of the crystallographic characteristics of 1-organosilatranes [16] and -germatranes [17] showed that the corresponding compounds of these two series of atranes crystallize isostructurally. In particular, 1-ethylsilatrane and 1-ethylgermatrane proved to be isostructural. The complete structural investigation of atranes was carried out in the case of 1-ethylgermatrane [18] (I, see Table 1) for a number of reasons. An x-ray diffraction investigation of crystals of 1-( $\alpha$ -naphthyl)germatrane [19] (II) was also carried out to elucidate the effect of aromatic substituent  $X$  on the  $N-Ge$  bond length in germatrane molecules.

A determination of the molecular structure of I and II showed that the atrane framework of their molecules is formed by three condensed five-membered heterorings with a common transannular  $N \rightarrow Ge$  donor-acceptor bond. Its length is identical in both structures ( $2.24 \text{ \AA}$ ). This value is  $0.32 \text{ \AA}$  higher than the sum of the covalent radii of the germanium and nitrogen atoms ( $1.92 \text{ \AA}$ ) but is considerably less than the sum of the corresponding van der Waals radii ( $3.8 \text{ \AA}$ ).

\*See [1] for communication XXXIII.

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The coordinated polyhedron about the germanium atom is a distorted trigonal bipyramid caused by the  $sp^3d$  hybridization of the valence orbitals of the central Ge atom, which arises as a result of partial transfer of the unshared pair of electrons of the nitrogen atom to the 4d orbital of the germanium atom. Three oxygen atoms are situated in the equatorial plane of the trigonal bipyramid, while the nitrogen atom and the carbon atom of substituent X ( $C_X$ ) are located at its apexes.

The equal values of the Ge-N distances in the molecules of I and II are apparently determined by the identical intramolecular nonvalence interactions, particularly between the  $C_X$  atom and the oxygen atoms of the equatorial plane of the trigonal bipyramid. This is attested to by the practical identical shifts of the germanium atom from the equatorial plane toward the  $C_X$  atom (0.23 Å in I and 0.25 Å in II). As far as the electronic effect of substituent X is concerned, it apparently has practically no effect on the M-N bond length in the given cases.

The nonvalence interaction between the  $C_X$  atom and the three oxygen atoms determines the direction of shift of the germanium atom and leads to an increase in the O-Ge- $C_X$  valence angles in the I and II molecules of, on the average, 97-98° (they are 90° in the ideal trigonal bipyramid). This fact is also confirmed by the structure of VI [20], in which one of the oxygen atoms is replaced by a more bulky (by a factor of ~2.5) methylene group. In this case, the C-Si- $C_X$  angle increases to 103°, while the two O-Si- $C_X$  angles remain equal to 98°. Considering the small difference in the atomic radii of silicon and germanium (0.05 Å), these angles can be compared in I, II, and VI. The O-Si- $C_X$  angle in V [21] is 100° and is the average value between the corresponding angle in the ideal trigonal bipyramid (90°) and in the tetrahedron (109.5°).

A shift of atom M from the equatorial plane of the trigonal bipyramid toward substituent X is also observed in molecules of the other compounds presented in Table 1. An exception to this is boratrane (VII) [22, 23], the absence of substituent X in which excludes the nonvalence interactions peculiar to the structures of I-VI and VIII and creates the prerequisite for the formation of "double concave" structure with a B-N interatomic distance of 1.65 Å, which only slightly exceeds the sum of the single covalent radii of boron and nitrogen (1.58 Å).

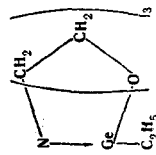
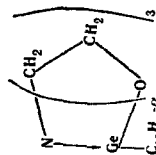
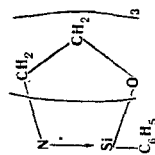
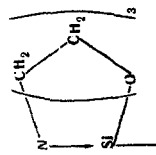
The magnitude of the shift of atom M from the equatorial plane of the trigonal bipyramid in silatranes and germatranes (I-VI) toward substituent X ( $\Delta$ ) and in boratrane (VII) toward the nitrogen atom are associated with the M-N interatomic distance by the simple dependence  $r_{M-N} - \Delta = d$ , where d is the distance from the nitrogen atom to the equatorial plane of the trigonal bipyramid. It is interesting that in I-VI this distance is approximately the same:  $d = 2.00 \pm 0.05$  Å (see Table 1). This indicates that the O-M- $C_X$  angles and M-N distances in I-VI are equivalent and are due to competition of the intramolecular nonvalence interactions between the  $C_X$  and oxygen atoms, on the one hand, and the strain forces in the heterorings, on the other.

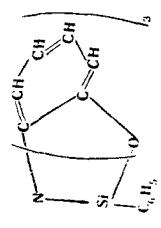
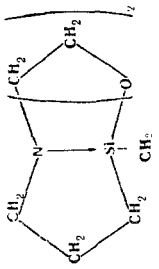
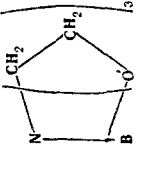
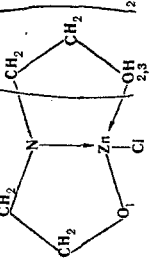
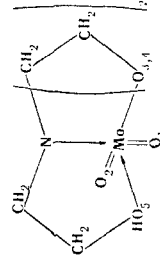
The interatomic Ge-N distance in germatranes I and II is 2.24 Å. In full accordance with this, the Si-N distance in 1-organosilatrane III [24] is 2.19 Å. This shortening of the M-N bond by 0.05 Å corresponds to the difference in the covalent radii of the germanium (1.22 Å) and silicon (1.17 Å) atoms [25]. The Si-N interatomic distance in 1-m-nitrophenylsilatrane (IV) [26] is 2.12 Å, i.e., 0.07 Å shorter than in III. This shortening is the result of the powerful electron-attracting effect of the nitro group, which increases the electron-acceptor properties of the silicon atom. The greatest Si-N distance in the silatranes (2.34 Å) is observed in V and VI. In VI, substitution of one of the three equatorial oxygen atoms by the more electropositive methylene group weakens the electron-acceptor properties of the silicon atom; this also leads to an increase in the Si-N interatomic distance.

On comparison, the change in the M-N interatomic distance in I and II and III and IV with VI shows that replacement of the oxygen atom of the atrane portion of the molecule by the more bulky and more electropositive methylene group has a considerably greater effect on the M-N bond length than different variations of the X substituents. The further lengthening of the M-N bond in the case of successive replacement of the remaining two oxygen atoms by a  $CH_2$  group seems inevitable; this is particularly attested to by the decrease in the stability of such derivatives. In the V molecule,  $p, \pi$  conjugation of the unshared pair of electrons of the nitrogen atom with the three aromatic rings lowers its electron-donor properties, as a result of which the Si-N interatomic distance increases.

The change in the hybridization of the valence orbitals of the carbon atom in five-membered heterocycles from  $sp^3$  to  $sp^2$  leads to planarity of the heterocycles and also to a decrease in the Si-N-C valence angles to 101-102°. The strain of the molecule, which is caused by the planarity of the heterocycles and the decrease in the three valence angles at the tetrahedral nitrogen atom of this silatrane, may also be com-

TABLE 1. Structural Characteristics of Atranes and Their Analogs

Com- pound	Formula	Crystallo- graphic char- acteristics	Axial characteristics			Equatorial characteristics			<M-N-C, deg	Shift of atom M from the equatorial plane, Δ, Å	d, Å	Liter- ature
			M <sub>4</sub> -N, Å	M-X, Å	<N-M-X, deg	<O-M-X, deg	<O-M-O, deg	M-O, Å				
1	2	3	4	5	6	7	8	9	10	11	12	13
I		<i>P2<sub>1</sub>2<sub>1</sub></i> <i>a</i> = 9.34 <i>b</i> = 16.75 <i>c</i> = 6.72	2.24	1.97	177	100 96 95	117 119 120	1.69 1.74 1.78	105 105 109	0.23	2.01	18
II		<i>Pna2<sub>1</sub></i> <i>a</i> = 9.57 <i>b</i> = 14.54 <i>c</i> = 10.64	2.24	1.94	179	98 99 98	118 121 116	1.78 1.77 1.77	104 106 104	0.25	1.99	19
III		<i>Pbca</i> <i>a</i> = 13.22 <i>b</i> = 18.52 <i>c</i> = 10.05	2.19	1.88	178	99 96 96	118 119 119	1.64 1.66 1.67		0.20	1.99	24
IV		<i>P2<sub>1</sub>/c</i> <i>a</i> = 10.10 <i>b</i> = 11.01 <i>c</i> = 12.96 <i>β</i> = 110°	2.12	1.90	180	95 96 97	119 120 119	1.66 1.66 1.65	106 105 106	0.17	1.95	26

V		$Cmc2_1$ $a = 11.23$ $b = 14.77$ $c = 11.94$	2,34	1,85	180	100 100 100	118 118 116	1,65 1,65 1,64	101 101 103	0,30	2,04	21
VI		$Pna2_1$ $a = 15.07$ $b = 6.79$ $c = 9.74$	2,34	1,88	177	98 98 103 C-Si-C	117 O-Si-C 116 118	1,66 1,66 Si-C 1,90	107 102 103	0,29	2,05	20
VII		$Pca2_1$ $a = 11.37$ $b = 6.57$ $c = 9.68$	1,65				115 113 115	1,43 1,43 1,43	103,5 104 104	-0,33*	1,98	22, 23
VIII		$P1$ $a = 8.09$ $b = 8.39$ $c = 7.53$ $\alpha = 101.8^\circ$ $\beta = 105.6^\circ$ $\gamma = 90^\circ$	2,15	2,26	170	95 103 96	115 124 114	2,01 Zn-O2 2,12 Zn-O3 2,14	106 110 110	0,32	1,83	31
IX		$P2$ $a = 11.88$ $b = 7.86$ $c = 11.52$ $\beta = 92^\circ$	2,44	Mo-O1 1,80				Mo-O2 1,75 Mo-O3 1,91 Mo-O4 1,94 Mo-O5 2,34				32

\*The minus sign indicates a shift toward the N atom.

pensated by a certain withdrawal of the nitrogen and silicon atoms that are linked by an N  $\rightarrow$  Si donor-acceptor bond.

The five-membered heterorings in germatranes I and II have an envelope conformation that arises due to deviation of the carbon atoms in the  $\alpha$  position (relative to the nitrogen atom) from the N-Ge-O-C planes which are situated, on the average, at an angle of 120° relative to one another. This same phenomenon is also observed in silatranes III and IV.

In contrast to silatranes III-V, in which the plane of the phenyl and m-nitrophenyl groups is perpendicular to one of the three planes of the heterorings, the  $\alpha$ -naphthyl group in germatrane II is coplanar with one of the five-membered heterorings. This is due to the specifics of the packing of the molecules in the elementary cell of the crystal.

The Ge-C<sub>X</sub> bond lengths in germatranes I (1.97 Å) and II (1.94 Å) coincide, within the limits of error, with those in the few investigated structures of other organogermanium compounds [27-30]. The average values of the Ge-O interatomic distances in I and II are 1.74 and 1.77 Å respectively. This is 0.1 Å less than the sum of the single covalent radii of the germanium (1.22 Å) and oxygen (0.66 Å) atoms; this indicates the increased multiplicity of these bonds.

A comparison of the M-N interatomic distances in VIII [31] and IX [32] and other atranes (I-VI) is not valid, since they do not have the structure of true metalloatranes.

Thus the molecular structure (particularly the M-N bond length) of metalloatranes depends on both the three-dimensional interaction of the valence-nonbonded intramolecular atoms and on the electronic effects of the X substituents. According to the available data, replacement of the oxygen atoms in the five-membered heterorings by a CH<sub>2</sub> group leads to a sharper change in the structure of the atranes than variation of the X substituents.

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