

ATRANES

XIII. Crystallographic Parameters of Some Silatranes*

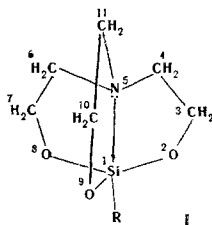
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The X-ray method is used to determine the crystallographic parameters and translation groups of the elementary cells of crystals of 1-substituted methyl-, ethyl-, isopropyl-, vinyl-, phenyl-, and phenoxysilatranes. From the linear and angular parameters calculations are made of elementary cell volumes, the numbers of molecules which they contain, X-ray crystal densities, and the packing coefficients of the molecules in the crystals.

Silatranes (I) [2-10] are of considerable interest on account of their structures [7-9], chemical properties, and biological activity [10].



The relatively high stability of the silatranes, their high dipole moments [7], and resistance to irradiation during X-ray investigation are in all probability due to their molecules containing an intramolecular coordination bond between nitrogen and silicon atoms $\overline{\text{Si}} - \overline{\text{N}}$.

However, a conclusive solution of the structure of silatrane molecules, the relationship between their structures and physicochemical properties, the packing of the molecules in the crystals, and the nature of the bond between nitrogen and silicon atoms, can be secured only by determining crystal structure and establishing the interatomic distance for Si-N by X-ray analysis.

For the purpose of choosing the most suitable subjects for X-ray study, of the structures of the silatranes, we determined linear and angular parameters and the centering of the elementary cells, as well as the calculated number of molecules in the elementary cell of crystals of some 1-aryl-, 1-alkyl-, and 1-oxysilatranes. The monocrystals of silatranes investigated are more or less extended colorless needles, with only one face zone, whose axis coincides with the axis of the needle itself. Such imperfect external faceting of the monocrystals makes it impossible to use optical goniometry to secure preliminary data regarding the symmetry form of a crystal and the relevant parameters, as well as considerably complicating crystal centering and aligning.

*For Part XII see [1].

The mounting of the crystals in the camera, and the subsequent matching of certain crystallographic direction of the elementary cell with the axis of oscillation (or of rotation when taking X-ray pictures for photographing inverse lattices, taking kforograms*) was done with X-ray pictures taken with polychromatic radiation.

X-ray pictures were taken not only with polychromatic radiation, but also by using oscillation and rotation with scanning of the layer lines in the camera for photographing the inverse lattices (CPIL). The exposure time when obtaining oscillation X-ray photos in the angular range up to 20° amounts to 10 hours. Depending on the layer line, the time required to take kforograms varied from 60 to 100 hours. The investigation was carried out using copper radiation, $\lambda_{\text{Cu}} = 1.54 \text{ \AA}$.

The following parameters were found for the monoclinic elementary cell of 1-methylsilatrane crystals, the calculations being based on oscillation X-ray pictures:

$$\begin{aligned} a &= 7.54 \text{ \AA} \\ b &= 9.73 \text{ \AA} \\ c &= 14.16 \text{ \AA} \end{aligned}$$

In no case did the deviation of average values of parameters from those found for the individual layer lines exceed $\pm 0.05 \text{ \AA}$.

$$\text{Monoclinic angle: } \beta = 122.6^\circ$$

$$\text{Elementary cell volume: } V = a \cdot b \cdot c \cdot \sin \beta = 875.22 \text{ \AA}^3$$

Number of molecules in an elementary cell:

$$N = \frac{V \cdot \rho_p}{1.67 \cdot M} = 3.96 \approx 4,$$

where ρ_p is the density of the compound as determined pycnometrically (1.421 g/cm³).

M = molecular weight 189.28.

The volume of the elementary cell entering into the molecule is

$$\frac{V}{N} = \frac{875.22}{4} = 218.8 \text{ \AA}^3.$$

$$\text{The X-ray density is } \rho_R \text{ is } \frac{N \cdot 1.67 \cdot M}{V} = 1.436 \text{ g/cm}^3.$$

*Artificial word derived from the initial letters of Kamera Foto-grafirovaniya Obratnoi Reshetki = Reciprocal lattice camera (De Jong-Bouman method) in X-ray goniometry.

The table gives the crystallographic characters of the 1-substituted methyl-, ethyl-, isopropyl-, vinyl-, phenyl-, and phenoxy-silatrane.

The occurrence of 4 or 8 molecules in the elementary cell necessitated additional proof of the centering of the elementary cells in order to determine the translation group. For this purpose, oscillation X-ray pictures were taken along the faces and 3-dimensional diagonals of elementary cells of crystals of the appropriate silatrane. It was shown that the elementary cells of all the compounds studied are primitive. Regarding the symmetry of the crystals, with the exception of 1-methyl-silatrane whose crystals are monoclinic (monoclinic angle $B = 122.6^\circ$), all the other compounds crystallize in the rhombic system.

Calculation of the volume of the elementary cell, due to one molecule, showed that it increases as the molecule gets more complex, starting with 1-methyl-silatrane (218.8 \AA^3) and ending with 1-phenoxy-silatrane (310.58 \AA^3).

From the crystallographic data obtained, and the literature interatomic distances $C-C = 1.54 \text{ \AA}$, $C-H = 1.08 \text{ \AA}$, $C-O = 1.42 \text{ \AA}$, $C-N = 1.41 \text{ \AA}$, $Si-O = 1.64 \text{ \AA}$, $C-Si = 1.88 \text{ \AA}$, the covalent radii of the atoms comprising the molecules of the silatrane $r_{Si} = 1.17 \text{ \AA}$, $r_O = 0.66 \text{ \AA}$, $r_N = 0.70 \text{ \AA}$, $r_C = 0.77 \text{ \AA}$, $r_H = 0.30 \text{ \AA}$, and the intermolecular radii of the corresponding atoms $r_{Si} = 1.34 \text{ \AA}$ (atomic radius), $r_O = 1.40 \text{ \AA}$, $r_N = 1.57 \text{ \AA}$, r_C aliphatic = 1.72 \AA , r_C aromatic = 1.80 \AA , $r_H = 1.17 \text{ \AA}$, the packing coefficients of the molecules (k) in the crystals of the corresponding compounds were calculated. The numerical value of this coefficient enables the packing density of molecules in a crystal to be assessed, and hence to some extent the stabilities of the crystals themselves.

If the volume V_0 of a molecule is made up of increments ΔV for the separate atoms, going to make up the molecule, then

$$k = \frac{N \cdot V_0}{V}$$

where N = number of molecules in an elementary cell and V = elementary cell volume.

The increments ΔV of the individual chemically bonded atoms are equal to the difference between the volume of a sphere radius r , equal to the inter-

molecular radius of the atom under consideration, and the sum of the segments cut off from it by valence-bonded atoms with intermolecular radii r_i , and having interatomic distances d_i . Hence

$$\Delta V = 4/3 \pi r^3 - \sum_0^i 1/3 \pi h_i^2 (3r - h_i)$$

The value of h_i determines the height of a segment, and is equal to

$$h_i = r - \frac{r^2 + d_i^2 - r_i^2}{2d_i}$$

The sum of the increments calculated from the above formula, gives the volume of the silatrane part of the molecule as 134.76 \AA^3 . The volumes of groups R linked to the silatrane part of the molecule, the volumes of the molecules, and the packing coefficients of the molecules are also given in the table.

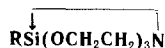
The packing coefficients of the molecules of the silatrane in the crystals show the latter to be made up of quite densely packed molecules, and this is indirectly indicated by the manifest capacity of I for crystallization. The latter is known to drop off as the packing coefficient decreases, and according to existing experimental data, at $k < 0.595$ formation of glasses starts to predominate over crystallization.

As can be seen from the table, crystals of 1-ethyl and 1-isopropyl-silatrane have the lowest packing coefficients (69.12%), and in all probability this is connected with the configurations of the ethyl and isopropyl groups. Possibly the increase in the packing coefficient of the molecules of 1-methylsilatrane to 73.02% is attained on account of lowering of the symmetry of the crystals from rhombic to monoclinic. The increase in the packing coefficients of the molecules in crystals of 1-phenyl (71.95%) and 1-phenoxy-silatrane (71.47%) with preservation of rhombic symmetry, is explained by the compactness of the phenyl rings.

Further X-ray study of the crystal structures of the silatrane is in progress.

It is the author's pleasant duty to express his sincere thanks to M. G. Voronkov and G. I. Zelchan for the particular monocrystals, and for experimental values of ρ_P for the silatrane.

Crystallographic Parameters of Silatrane



R	a, \AA	b, \AA	c, \AA	β	v, \AA ³	N	$\frac{V}{N}$, \AA ³	ρ_P g/cm ³	ρ_R g/cm ³	Volume of group R, \AA ³	Volume of molecule, \AA ³	κ , %
CH ₃ -	7.54	9.73	14.16	126.6°	875.22	4	218.80	1.421	1.436	25.03	159.79	73.02
CH ₃ CH ₂ -	9.33	16.45	6.65		1020.63	4	255.16	1.295	1.323	41.60	176.36	69.12
(CH ₃) ₂ CH-	9.52	17.12	6.85		1116.43	4	279.11	1.25	1.293	58.17	192.93	69.12
CH ₂ =CH-	9.61	30.53	6.62		1942.26	8	242.78	1.378	1.376	37.58	172.34	70.99
C ₆ H ₅ -	13.09	18.37	10.02		2409.43	8	301.18	1.364	1.385	81.93	216.69	71.95
C ₆ H ₅ O-	13.64	8.41	10.83		1242.34	4	310.58	1.43	1.429	87.20	221.96	71.47

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