

THE CRYSTAL AND MOLECULAR STRUCTURES OF SOME GERMATRANE DERIVATIVES

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Summary

The crystal and molecular structures of seven germatrane derivatives have been determined from three-dimensional X-ray data in order to investigate the main geometrical regularities of the germatrane molecules.

Introduction

Atrane compounds of Group IVB elements are attracting particular interest because of their specific biological activity [1]. Moreover, it is very important in terms of modern theoretical chemistry of organo-element compounds to examine the factors responsible for the expansion of the valence shell of the metals in these compounds beyond the limits permitted by the filled octet rule. Among the atrane compounds of Group IVB elements, silatranes have been investigated more thoroughly [1]. Reports about germatrane structures are few in number. Up to now, only the structures of 1-ethylgermatrane (I) and 1-naphthyl germatrane (II) have been investigated [2,3]. The main purpose of this paper is to try to generalize the previously obtained results [2,3] and our results [4–6] about the crystal structures of germatrane derivatives.

Experimental

We determined the crystal structures of seven germatrane compounds, III–IX.

Compounds were synthesized and purified by the method of ref. 7. The intensity data were collected on Enraf–Nonius CAD-4 and Nicolet R3m diffractometers equipped with graphite monochromators. Mo- K_{α} radiation was used and the scan mode was $\theta/2\theta$. All structures were refined by the block-diagonal least-squares method, using anisotropic temperature factors for all the non-hydrogen atoms. In structures III and IV, hydrogen atoms were revealed.

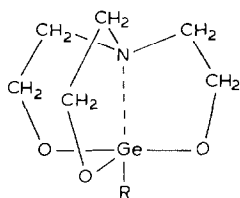
(Continued on p. 122)

TABLE 1
CRYSTAL DATA OF THE GERMATRANE COMPOUNDS EXAMINED

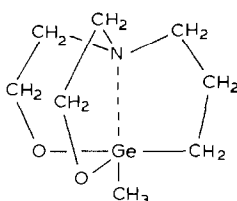
Compound	<i>a</i>	<i>b</i>	<i>c</i>	β	γ	Z	<i>d</i> (calc.)	Space group	Number of reflect- ions	<i>R</i>	Refer- ence
III	9.956	9.956	21.840		120	6	1.47	<i>R</i> 3	826	0.048	This work
IV	7.963	14.689	10.555	110.2		4	1.67	<i>P</i> 2 ₁ / <i>c</i>	1325	0.035	This work
V	14.235	13.554	17.949		93.8	4	1.74	<i>P</i> 2 ₁ / <i>b</i>	2816	0.071	This work
VI	6.927	15.311	12.172		122.6	4	2.20	<i>P</i> 2 ₁ / <i>b</i>	1691	0.143	[4]
VII	11.953	12.893	24.617			16	2.09	<i>Pcab</i>	1263	0.075	This work
VIII	6.875	15.553	9.549		97.2	4	1.53	<i>P</i> 2 ₁ / <i>b</i>	1414	0.066	[5]
IX	10.379	13.597	18.118			8	1.54	<i>Pbca</i>	1626	0.068	[6]

TABLE 2
THE MAIN STRUCTURAL PARAMETERS OF THE GERMATRANE COMPOUNDS (AVERAGE VALUES)

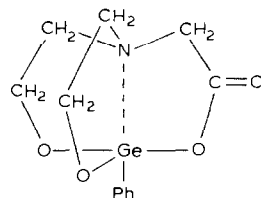
Com- pound	Interatomic distances (Å)					Valence angles (degrees)					Refere- nce		
	Ge...N	Ge-R	Ge-O	C-O	C-C	C-N	C-N	N-Ge-R	O-Ge-R	O-Ge-O		C-N-C	d
I	2.24	1.97	1.74	1.48	1.46	1.47	177	97	118.5	113	2.01	0.23	[2]
II	2.24	1.94	1.77	1.45	1.49	1.41	179	98.3	118.3	114	1.99	0.25	[3]
III	2.24	1.97	1.81	1.41	1.50	1.47	180	98.6	117.8	114.7	1.97	0.27	This work
IV	2.23	1.94	1.81	1.42	1.52	1.47	178	98.1	118.1	114	1.98	0.25	This work
V	2.29	1.95	1.79	1.44	1.52	1.48	176	99	117.4	114	2.00	0.29	This work
VI	2.19	1.98	1.80	1.44	1.53	1.48	175	97	118	114.4	1.98	0.21	[4]
VII	2.09	2.36	1.78	1.44	1.52	1.49	179	94	119.5	112.8	1.98	0.11	This work
VIII	2.44	1.96	1.80	1.42	1.52	1.47	174	99	114	114.5	2.07	0.37	[5]
IX	2.20	1.95	1.79	1.44	1.50	1.51	175	98	118	114	1.95	0.25	[6]
				1.52	1.53	1.45	95						
				1.18			101						



(I-VII)



(VIII)



(IX)

(I, R = C₂H₅, II, R = C₁₀H₇ (naphthyl),

III, R = C(CH₃)₃, IV, R = CH₂CH₂C(O)NH₂ (propionamide),

V, R = CH₂Ge(OCH₂CH₂)₃N (germatranylmethyl),

VI, R = CH₂I, VII, R = Br)

The crystal data of the compounds examined are summarized in Table 1. The R values and the number of measured reflections with $F^2 \geq 3\sigma$ are also given.

The structural parameters of the germatrane derivatives (including the data for I and II from refs. 2 and 3) are summarized in Table 2.

Results and discussion

The Ge...N intramolecular distances in all the compounds investigated equal 2.1–2.4 Å; these distances are significantly shorter than the sum of the Van der Waals radii of these elements (3.5 Å). The shortest Ge...N distance, 2.09 Å, is found for 1-bromogermatrane (VII), and the largest, 2.44 Å, for 1-methyl-2-carba-germatrane (VIII).

The coordination around Ge is trigonal-bipyramidal in which the nitrogen atom and the substituent R are placed at the axial positions, and the three oxygen atoms are in the equatorial plane.

The intramolecular distance Ge...N can be represented [1] by the sum of two values: from the nitrogen atom to the equatorial plane (d), and from the equatorial plane to the germanium atom (Δ). As can be seen from Table 2, d is approximately constant for all the molecules studied and equals 2.0 Å. (It is interesting to note that in silatranes d is also 2.00 ± 0.05 Å [1].) Thus the variation of the Ge...N interatomic distances is determined by the value of Δ . However, the closer the germanium atom approaches the equatorial plane, the more distinctive is its coordination from tetrahedral. So the value of Δ characterizes the hybridization state of germanium.

The nature of the M ← :N interaction in atrane compounds of Group IVB elements has often been discussed in the literature [1,8]. This interaction was initially considered in terms of the partial transfer of a lone nitrogen pair to vacant $3d_{z^2}$ -AO dsp^3 -hybridized metal [1], but some investigators criticized this point of view strongly. Instead, a hypothesis of the existence of so-called "hypervalence R–M ← :N bonding" in atrane compounds of Group IVB elements was proposed [9,10]. The obvious consequence of this hypothesis is the possibility of transferring the influence of the σ -bonding substituent R via the $3p_z$ -AO of the metal ("trans-influence").

Indeed, the addition of an R substituent with a strong electron-acceptor effect (CH₂, I, Br) is accompanied with shortening of the Ge...N distance up to 2.09–2.19 Å (Table 2), whereas in compounds I–V this distance equals 2.23–2.32 Å. The

stronger the R-Ge \leftarrow :N interaction, the closer the germanium atom is to the equatorial plane, and the angles R-Ge-O should tend to 90° and vice versa. As seen from Table 2, the smallest value of Δ among the molecules investigated is that found for VII (0.11 Å), and the largest, for III and V (0.27 and 0.29 Å, respectively). The R-Ge-O angles in VII equal 94°, but in III and V they equal 98–99°.

The substitution of the less electronegative methylene group for oxygen leads to a very strong variation in the R-Ge \leftarrow :N interaction (e.g. 1-methyl-2-carba-germatrane, VIII). The Ge...N distance in this molecule increases to 2.436 Å, and the R-Ge-O and R-Ge-CH₂ angles to 98–99° and 107°, respectively.

There are two independent molecules in the structure of V; every molecule has two germatrane fragments bonding to the methylene group. The addition to the methylene carbon of two germatrane substituents with large volumes increases the Ge-CH₂-Ge angles to 119.0 and 122.3° (the ideal tetrahedral value being 109.5°). As a rule, such an increase in the angles is accompanied with an appropriate change in the bond lengths, but we did not observe one in our case. The Ge-C bond lengths in V equal 1.95 Å and agree with the lengths of the Ge-C bonds in methylgermane molecules [11].

The mutual orientation of the atrane fragments in V is staggered when the semi-cycle of one fragment projects into the cavity between semi-cycles of the other.

The Ge-O bonds are the most stable parts of the germanium polyhedron in the investigated molecules. Their lengths remain essentially constant (1.78–1.80 Å) and are independent of the enhancing or weakening of the R-Ge \leftarrow :N bonding.

The lengths of the C-O and C-C bonds hardly change from one molecule to another. The C-O bond lengths are similar to those observed in alcohols and dioxane-type saturated heterocycles.

The nitrogen bonds of the atrane framework in all the molecules investigated have a trigonal-pyramidal configuration. The C-N bond lengths are in the small range 1.45 to 1.50 Å. The C-N-C angles are equal to 113–114°, and only in IX are they smaller (104–108°).

The five-membered heterocycles $\overline{\text{Ge-O-CH}_2\text{-CH}_2\text{N}}$ forming the atrane framework have an "α-envelope" conformation. The carbon atoms forming the envelope angles deviate from the average plane of the rest of the atoms by approximately 0.5 Å.

As known [9,10], the hypervalent bonding increases as the metal ionization potential decreases. Therefore this effect should be manifested more distinctly in germatranes than in silatranes. However, a comparison of the structural parameters for silatrane- and germatrane-related molecules shows that parameters such as the M...N distance and the R-M-O angles agree well with each other (allowing for the difference between the Ge and Si covalent radii).

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