Journal of Organometallic Chemistry, 303 (1986) 83–86
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CRYSTAL AND MOLECULAR STRUCTURE OF 2,2,6-TRIMETHYL-6-SELENONO-1,3-DIOXA-2-SILA-6-PHOSPHACYCLOOCTANE

V.E. SHKLOVER*, Yu.T. STRUCHKOV, N.M. KUDYAKOV and M.G. VORONKOV

Nesmeyanov Institute of Organoelement Compounds of the Academy of Sciences of the U.S.S.R., 28 Vavilov Str., Moscow B-312 (U.S.S.R.)

(Received September 25th, 1985)

Summary

An X-ray structural study of 2,2,6-trimethyl-6-selenono-1,3-dioxa-2-sila-6-phosphacyclooctane ($R = 0.029$ for 1340 reflections) was carried out. The molecule has C_s symmetry and its eight-membered heterocycle has a crown conformation. The intramolecular Si...Se distance of 4.437(1) Å precludes the possibility of the corresponding transannular attractive interaction.

Introduction

A number of X-ray investigations have been devoted to exploring the possibility of transannular interaction in eight-membered heterocycles. For example, the transannular P...N interaction was observed in the molecular of 2-oxo-2-methyl-6-aza-6-phenyl-1,3,2-dioxaphosphacynane (I) [1] and a distinct Si...S interaction was found in the molecule of 13,13-dimethyl-8,13-dihydro-5*H*-dibenzo[*d*,*g*][1.2.6]dithiasilonine (II) [2]. However, in the molecule of *trans*-2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclooctane-2,6-disulphide (III) the transannular interaction is absent [3].

In the present paper we report the results of an X-ray study of 2,2,6-trimethyl-6-selenono-1,3-dioxa-2-sila-6-phosphacyclooctane (IV) (m.p. 98.5–99.5°C; the synthesis will be described in a separate paper).

Results and discussion

The eight-membered heterocycle of molecule IV, which has the crystallographic C_s symmetry (Fig. 1), is characterized by an essentially undistorted crown conformation (puckering parameters: $q_2 = 0.012$, $q_3 = 0.018$, $q_4 = 1.915$, $Q = 1.916$ Å, φ_2 225.03, φ_3 292.51° [4]).

The intramolecular distance Si...Se of 4.437(1) Å as well as the intermolecular

0022-328X/86/$03.50

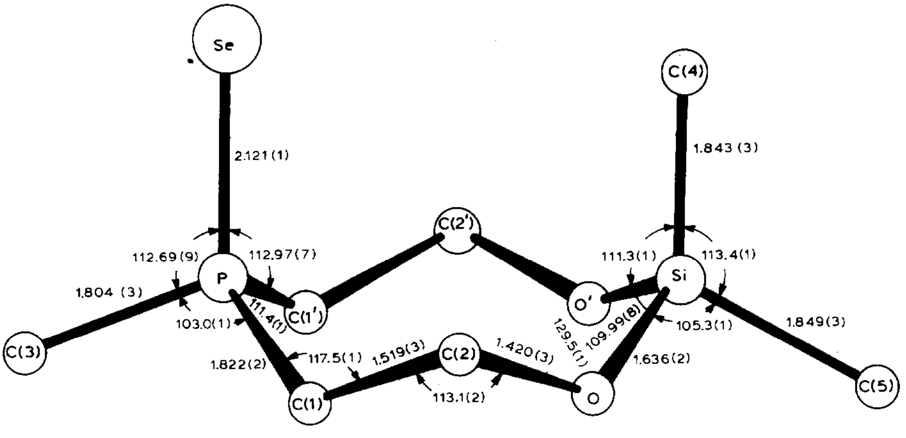

Fig. 1. Structure of molecule IV, having C_s symmetry.

distances (the shortest being 5.451(1) Å) between these atoms exceed the sum of Van der Waals radii of 4.00 Å [5], thus excluding attractive intramolecular and intermolecular interactions involving the silicon atom in structure IV.

The silicon atoms has slightly distorted tetrahedral geometry: the OSiC bond angles involving the pseudo-axial Me substituent C(4) are somewhat increased (111.3(1)°), while those associated with the pseudo-equatorial Me substituent C(5) are decreased (105.3(1)°). Equal values of the bond angles at the Si atom would possibly result in shortened intramolecular contacts of the Me group C(4) with the C(2) and C(2′) atoms, because the intramolecular distances C(4)... C(2) of 3.398(3) Å and C(4)... H(2.2) of 2.94(2) Å, observed in the crystal of IV, in fact coincide with the sum of the Van der Waals radii (3.40 and 2.90 Å, respectively [5]).

The Si–O and Si–C bond lengths, which are equal to 1.636(2) Å and 1.843, 1.849(3) Å, respectively, are in agreement with those found in the molecule of 2,2,5-trimethyl-5-thiono-1,3-dioxa-2-sila-5-phosphorinane (1.66 and 1.84 Å) [6] and with those in other molecules containing carbosiloxane moieties, e.g. in the molecule of 1,3-disila-2-oxa-5-carboxy-1,1,3,3-tetramethylcyclohexane (1.630 and 1.837 Å) [7].

The phosphorus atom has distorted tetrahedral geometry. The S=P–C bond angles (112.69(9) and 112.97(7)°) are somewhat larger than the C–P–C angles (103.0(1) and 111.4(1)°). This inequality is unexceptional for R_3PX (X = O, S or Se) type compounds. For instance, in the molecule of methylpropylphosphineselenide (V) the Se=P–C angles are equal to 112.6(1), 112.9(1) and 113.8(1)° and the C–P–C angles are equal to 105.0(2), 105.4(2) and 106.5(2)° [8]. Noteworthy is the fact that the endocyclic CPC bond angle in IV is significantly larger than the two other CPC angles. This effect was also observed in other P-heterocycles, e.g. in III (endocyclic CPC 109.0(1)°, exocyclic 101.6(1) and 103.8(1)°).

The significant difference between the lengths of the endocyclic (1.822(2) Å) and exocyclic (1.804(3) Å) P–C bonds in IV is similar to that observed in numerous cyclic organophosphorus compounds (e.g. 1.821, 1.828(2) and 1.800(3) Å in III). The steric origin of this effect (as well as of the widening to 117.5(1)° of the endocyclic PC(1)C(2) and PC(1′)C(2′) bond angles) seems to be quite real: the Se... C(2) distance of 3.612(2) Å and the Se... H(2.2) distance of 3.02(2) Å are close to the corresponding sums of Van der Waals radii (3.60 and 3.10 Å [5]).

TABLE 1

ATOMIC COORDINATES ($\times 10^5$ for Se; $\times 10^4$ for P, Si, O and C; $\times 10^3$ for H) AND THERMAL PARAMETERS ($B_{\text{iso}}^{\text{eq}}$ for non-H, B_{iso} for H)

Atom	x	y	z	B
Se	19755(4)	$\frac{1}{4}$	4041(3)	1.10(1)
P	−277(1)	$\frac{1}{4}$	1513(1)	0.75(2)
Si	3225(1)	$\frac{1}{4}$	5034(1)	0.76(2)
O	1953(2)	4094(2)	4680(2)	1.36(3)
C(1)	−376(3)	4290(2)	2555(2)	1.08(4)
C(2)	1428(3)	4899(2)	3389(2)	1.21(4)
C(3)	−2490(4)	$\frac{1}{4}$	372(4)	1.79(8)
C(4)	5197(4)	$\frac{1}{4}$	4086(3)	1.37(7)
C(5)	3927(4)	$\frac{1}{4}$	6953(3)	1.48(7)
H(1.1)	−138(3)	419(3)	311(2)	1.2(5)
H(1.2)	−84(3)	509(3)	180(3)	2.5(6)
H(2.1)	126(3)	605(3)	353(3)	2.3(6)
H(2.2)	236(3)	479(3)	283(2)	1.0(5)
H(3.1)	−264(4)	168(3)	−26(3)	2.3(6)
H(3.2)	−348(5)	$\frac{1}{4}$	85(4)	2.2(8)
H(4.1)	501(6)	$\frac{1}{4}$	309(5)	5.0(10)
H(4.2)	594(4)	164(3)	437(3)	3.0(5)
H(5.1)	280(6)	$\frac{1}{4}$	719(5)	4.0(10)
H(5.2)	465(3)	160(3)	723(3)	2.6(6)

The length, 2.121(1) Å, of the P=S double bond agrees well with the values observed earlier, e.g. 2.119(2) Å in molecule V.

Experimental

The colourless crystals of IV are monoclinic, a 7.339(2), b 8.407(3), c 9.719(4) Å, β 99.78(3)°, V 590.9(5) A^3, $M_r = 271.0$, d_{calc} 1.542 g cm^{-3}, $Z = 2$, $C_7H_{17}O_2PSeSi$, space group $P2_1/m$, μ 36.1 cm^{-1}, $F(000) = 276$.

The cell parameters and intensities of 1531 independent reflections were measured with a four-circle Syntex P2$_1$ diffractometer at 150 K (λMo-K_α, $\theta/2\theta$ scan, $\theta_{\max}$ 28°). The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for H atoms located in the difference Fourier map. Final values of $R = 0.029$ and $R_w = 0.038$ were obtained for 1340 reflections with $I \geqslant 3\sigma$. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [9]. Absorption correction was applied using the DIFABS program [10]. The atomic coordinates are listed in Table 1; bond lengths and angles with participation of non-hydrogen atoms are given in Fig. 1.

References

1 A.E. Kalinin, V.G. Andrianov and Yu.T. Struchkov, J. Strukt. Khim., 16 (1975) 1041.

2 V.E. Shklover, Yu.T. Struchkov, O.G. Rodin, V.F. Traven' and B.I. Stepanov, J. Organomet. Chem., 266 (1984) 117.

3 C. Piccini-Leopardi, G. Germain, J.P. Declercq, M. Van. Meersche, J.B. Robert and K. Jurkschat, Acta Crystallogr., B, 38 (1982) 2197.
4 V.A. Palyulin, N.S. Zefirov, V.E. Shklover and Yu.T. Struchkov, J. Mol. Struct., 70 (1981) 65.
5 A. Bondi, J. Phys. Chem., 68 (1964) 441; 70 (1966) 3006.
6 A.I. Gusev, M.G. Los', N.V. Alexeev, N.M. Kudyakov and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 270 (1983) 1398.
7 I.L. Dubchak, T.V. Timofeeva, V.E. Shklover, Yu.T. Struchkov, A.A. Zhdanov, E.A. Kashutina and O.I. Schegolichina, J. Strukt. Khim., 1, 22 (1981) 74.
8 Z. Galdecki, M.L. Glowka, J. Michalski, A. Okruszek and W.J. Stec, Acta Crystallogr., B, 33 (1977) 2322.
9 R.G. Gerr, A.I. Yanovsky and Yu.T. Struchkov, Kristallographiya, 28 (1983) 1029.
10 N. Walker and D. Stuart, Acta Crystallogr., A, 39 (1983) 158.