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MOLECULAR AND CRYSTAL STRUCTURE OF 13,13-DIMETHYL-8,13-DIHYDRO-5*H*-DIBENZO[*d*,*g*]-1,2-DISELENA-6-SILONINE

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Summary

The molecular and crystal structure of 13,13-dimethyl-8,13-dihydro-5*H*-dibenzo[*d*,*g*]-1,2-diselena-6-silonine was determined. The 9-membered heterocycle has a distorted TBB conformation, long intramolecular distances Si...Se of 4.322 and 4.228(2) Å exclude the possibility of transannular Si ← Se interaction.

Introduction

Our previous paper [1] reports the structure of 13,13-dimethyl-8,13-dihydro-5*H*-dibenzo[*d*,*g*]-1,2-dithia-6-silonine (II) wherein the intramolecular donor–acceptor Si ← S interaction involving one of the S atoms was found for the first time. On account of a similarity of properties and dimensions of S and Se atoms a similar structural feature was proposed for the Se analog I. To verify this proposal an X-ray study of I was carried out.

Results and discussion

Geometrical parameters of the molecule I (Fig. 1) and a series of molecules having Se and Si atoms in a similar surrounding are compared in Table 1. Coincidence or closeness of most of the geometrical parameters in molecules I and II is remarkable. At the same time the torsion angle around the Se–Se bond in I (73.7°) is substantially less than that found in other structures where it is close to the

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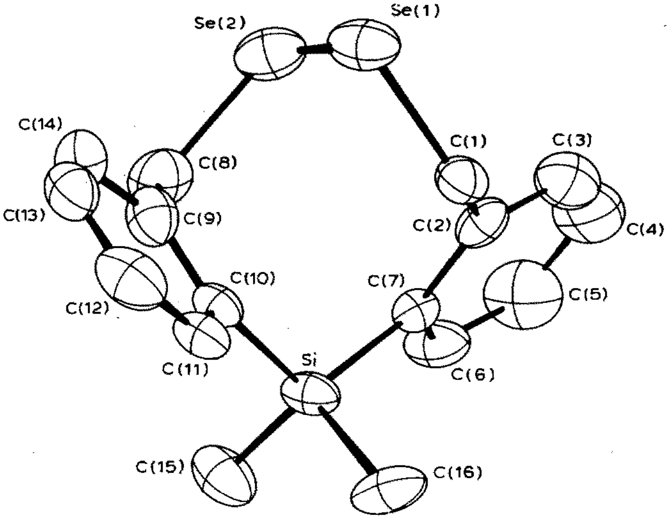

Fig. 1. General view of molecule I. H atoms are omitted.

theoretical value of 90°, and almost coincides with the angle SeSeSeSe (76.4°) in the $Se_4(NPh)_2$ molecule [6].

Intramolecular Si...Se distances in I (4.322 and 4.228(2) Å) are significantly longer than the sum of the Van der Waals radii (4.00 Å according to Bondi [7]). This shows the absence of a transannular donor–acceptor Si ← Se interaction which is clearly evident in the dithia analog II [1]. In this connection it is interesting to compare conformations of 9-membered heterocycles in I and II.

The SiC(7)C(2)C(1)Se(1)Se(2)C(8)C(9)C(10) cycle in I (Fig. 2) is characterized by the following Cremer–Pople parameters [8]: φ_2 273.1°, q_2 2.429 Å, φ_3 90.0°, q_3 0.391 Å, φ_4 274.5°, q_4 0.240 Å, Q 2.472 Å. As in our previous analysis of conformations found in 8-membered siloxane cycles [9], the values q_m and φ_m

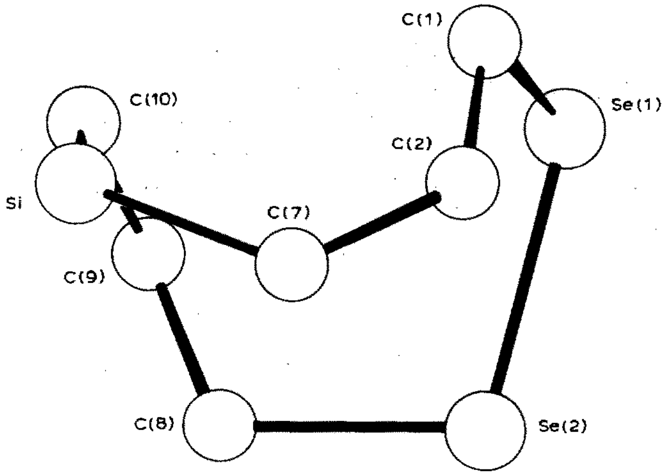

Fig. 2. Conformation of the heterocycle in molecule I.

TABLE 1

GEOMETRICAL PARAMETERS OF MOLECULE I AND A SERIES OF MOLECULES HAVING Se AND Si ATOMS IN A SIMILAR SURROUNDING

Compound	Mean bond lengths (Å)				Bond angles (°)			Torsion angle CSeSeC	Ref.
	Se–Se	Se–C(sp^3)	Si–C(Me)	Si–C(Ar) [a]	SeSeC	SeCC	C(Ar)SiC(Ar) [a]		
$Me_2Si(o\text{-}C_6H_4CH_2Se)_2$ (I)	2.288	2.01	1.86	1.89	104.4	113.3	114.9	73.7	This work
$Me_2Si(o\text{-}C_6H_4CH_2S)_2$ (II)	–	–	1.86	1.89	101.1 (SSC)	113.8 (SCC)	114.8	88.6 (CSSC)	1
$(MeSe)_2$	2.326	1.95	–	–	98.9	–	–	87.5	2
$C_{24}H_{20}Se_4$ [b]	2.315	1.99	–	–	101.8	107.7	–	88.1	3
$(Ph_2CHSe)_2$	2.285	1.97	–	–	100.1	109.3	–	82.0	4
$Ph(Me)Si(o\text{-}C_6H_4CH_2)_2$	–	–	1.86	1.88	–	–	111.4	–	5

[a] Ar = phenyl or *o*-phenylene. [b] Dimer of 1*H*,4*H*-naphtho[1,8]diselenepine.

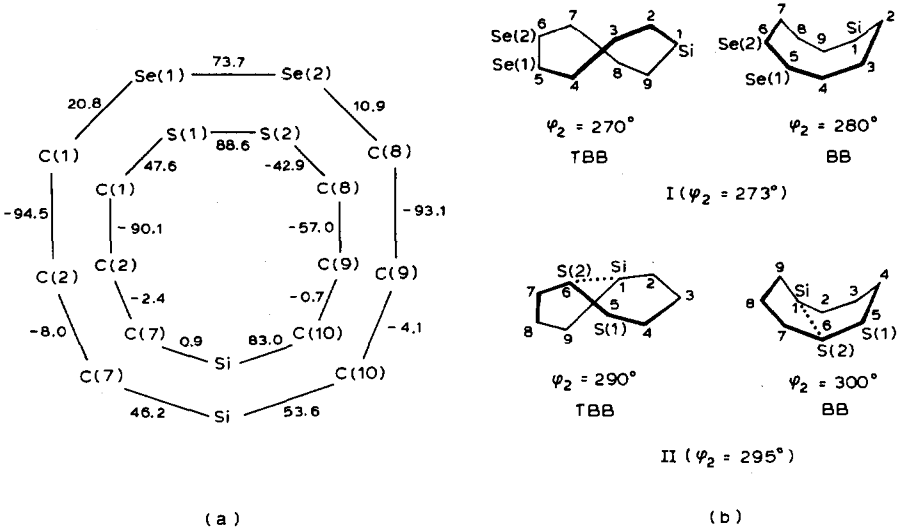

Fig. 3. Comparison of the 9-membered heterocycles in molecules I and II: (a) torsion angles; (b) TBB and BB canonical forms which give the main contributions to the conformations of heterocycles I and II. Canonical and calculated (in parentheses) φ_2 values are listed. For molecule II transannular Si ← S(2) interaction is indicated by dashed lines. It can be seen that in the representations of the cycles in molecules I and II the positions of the corresponding heteroatoms are different.

represent contributions of corresponding canonical forms to conformation of the cycle. Thus, in the case of the 9-membered heterocycle of I the main contributions are represented by TBB and BB forms ($q_2 \gg q_3, q_4$) with the former being predominant (Fig. 3). This heterocycle has an approximate symmetry of a twofold axis passing through the Si atom and the midpoint of the Se–Se bond. The symmetry is clearly seen in Fig. 1 and Fig. 3 where the torsion angles of heterocycles I and II are compared.

Cremer–Pople parameters of the heterocycle in the dithia analog II (φ_2 295.0°, q_2 2.220 Å, φ_3 90.8°, q_3 0.326 Å, φ_4 330.9°, q_4 0.268 Å, Q 2.259 Å) also correspond to a conformation which is intermediate between TBB and BB and somewhat distorted, for $q_3 \neq 0$ and $q_4 \neq 0$. However, this conformation is not identical to that found in I as is indicated by different φ_2 values of the cycle in II and its nearest canonical forms (Fig. 3). In II approximate symmetry of a twofold axis is absent and the Si and Se(2) atoms are drawn closer to each other as a result of transannular donor–acceptor interaction. The reason of the difference between I and II is the

TABLE 2

SHORT INTRAMOLECULAR DISTANCES (Å)

Se(1)...C(3)	3.63(1)	Si...C(1)	3.27(1)
Se(2)...C(14)	3.65(1)	Si...C(8)	3.26(1)
Se(1)...C(9)	3.29(1)	C(1)...C(10)	3.35(1)
Se(2)...C(2)	3.33(1)	C(8)...C(7)	3.48(1)
Se(1)...C(10)	3.61(1)	C(6)...C(15)	3.23(1)
Se(2)...C(7)	3.55(1)	C(11)...C(16)	3.21(1)

TABLE 3

ATOMIC COORDINATES ($\times 10^5$ for Se and Si, $\times 10^4$ for C, $\times 10^3$ for H) AND ISOTROPIC TEMPERATURE FACTORS $B_{iso}^{eq} = \frac{1}{3}\Sigma_i \Sigma_j B_{ij} a_i^* a_j^* (a_i a_j)$ (B_{iso} for H atoms)

Atom	x	y	z	B_{iso}^{eq}(Å^2)	Atom	x	y	z	B_{iso}^{eq}(Å^2)
Se(1)	4417(3)	40502(7)	11770(16)	4.27(3)	H(1.1)	48(4)	448(8)	−169(17)	5(3)
Se(2)	11043(4)	37859(6)	30192(16)	4.41(3)	H(1.2)	75(3)	512(6)	−100(13)	4(2)
Si	15655(7)	59394(12)	2111(33)	2.84(6)	H(3)	134(4)	353(6)	−173(13)	5(2)
C(1)	760(3)	4521(5)	−1041(12)	3.4(2)	H(4)	202(3)	278(6)	−239(14)	5(2)
C(2)	1289(3)	4300(5)	−1207(11)	3.1(2)	H(5)	286(7)	379(12)	−105(37)	16(7)
C(3)	1422(5)	3540(7)	−1988(15)	5.1(3)	H(6)	238(3)	486(6)	−34(13)	4(2)
C(4)	1901(4)	3277(6)	−2159(17)	5.5(3)	H(8.1)	164(3)	501(5)	352(11)	3(2)
C(5)	2278(4)	3786(6)	−1543(21)	5.8(4)	H(8.2)	132(3)	489(6)	471(13)	4(2)
C(6)	2158(3)	4561(6)	−751(14)	4.1(3)	H(11)	72(3)	699(5)	50(12)	3(2)
C(7)	1674(3)	4838(5)	−602(11)	2.7(2)	H(12)	6(5)	708(9)	240(22)	10(4)
C(8)	1324(3)	4909(7)	3844(13)	4.2(3)	H(13)	−2(3)	648(5)	500(12)	4(2)
C(9)	971(3)	5587(6)	3394(13)	3.5(2)	H(14)	64(4)	553(7)	539(16)	7(3)
C(10)	1028(3)	6062(5)	1807(11)	2.5(2)	H(15.1)	201(4)	684(7)	146(19)	7(3)
C(11)	672(3)	6675(5)	1479(13)	3.3(2)	H(15.2)	230(4)	597(7)	223(18)	6(3)
C(12)	275(3)	6826(6)	2620(16)	4.6(3)	H(15.3)	229(4)	644(8)	74(20)	7(3)
C(13)	222(3)	6372(6)	4120(14)	4.5(3)	H(16.1)	173(3)	645(6)	−266(13)	4(2)
C(14)	566(4)	5761(7)	4519(14)	4.4(3)	H(16.2)	137(4)	720(6)	−144(15)	5(2)
C(15)	2148(3)	6334(6)	1301(17)	4.8(3)	H(16.3)	114(3)	642(6)	−240(14)	4(2)
C(16)	1444(4)	6588(6)	−1781(15)	4.7(3)					

different positions of the corresponding heteroatoms in the cycles. For an approximate matching of heterocycles I and II it is nessessary to shift atoms of one of them by two positions around the ring, which is clearly seen in Fig. 3. After this transformation the φ_2 values of the corresponding canonical forms will coincide and the difference in the observed φ_2 values of the cycles will be only 2°. Apparently, the slightly larger Van der Waals radius of the Se atom (1.90 Å against 1.80 Å for S [7]) does not allow molecule I to form the cycle conformation identical to that found in II. Abundance of short intramolecular contacts involving Se atoms (Table 2) is in agreement with this assumption.

Intermolecular distances in the crystal are of the usual values. The shortest distance Se(1)...C(12) ($-x$, $1-y$, $-z$) with participation of the Se atom is 3.72(1) Å.

Experimental

Crystal data of I: Yellow crystals, orthorhombic, a 26.6978(10), b 16.0101(7), c 7.5329(2) Å, V 3219.8(2) Å^3, d_{calc} 1.519 g cm^{-3}, $\mu(\mathrm{Cu}\text{-}K_\alpha)$ 70.3 cm^{-1}, $Z = 8$, $C_{16}H_{18}Se_2Si$, space group *Pccn*.

TABLE 4

BOND LENGTHS (Å) FOR THE NON-HYDROGEN ATOMS

Se(1)–Se(2)	2.288(1)	C(3)–C(4)	1.35(2)
Se(1)–C(1)	2.02(1)	C(4)–C(5)	1.38(2)
Se(2)–C(8)	1.99(1)	C(5)–C(6)	1.41(2)
Si–C(7)	1.89(1)	C(6)–C(7)	1.37(1)
Si–C(10)	1.88(1)	C(7)–C(2)	1.41(1)
Si–C(15)	1.87(1)	C(9)–C(10)	1.42(1)
Si–C(16)	1.85(1)	C(10)–C(11)	1.39(1)
C(1)–C(2)	1.46(1)	C(11)–C(12)	1.39(1)
C(8)–C(9)	1.48(1)	C(12)–C(13)	1.35(2)
C(2)–C(3)	1.40(1)	C(13)–C(14)	1.38(1)
		C(14)–C(9)	1.40(1)

TABLE 5

BOND ANGLES (°) BETWEEN NON-HYDROGEN ATOMS

Se(1)Se(2)C(8)	104.5(3)	C(1)C(2)C(7)	121.8(7)
Se(2)Se(1)C(1)	104.2(3)	C(8)C(9)C(10)	121.1(8)
C(7)SiC(10)	114.9(4)	C(8)C(9)C(14)	119.9(8)
C(7)SiC(15)	109.3(4)	C(2)C(3)C(4)	123.3(10)
C(7)SiC(16)	107.6(4)	C(3)C(4)C(5)	118.4(11)
C(10)SiC(15)	108.6(4)	C(4)C(5)C(6)	119.8(11)
C(10)SiC(16)	109.0(4)	C(5)C(6)C(7)	122.1(9)
C(15)SiC(16)	108.2(5)	C(6)C(7)C(2)	117.5(8)
Se(1)C(1)C(2)	112.7(6)	C(7)C(2)C(3)	118.9(8)
Se(2)C(8)C(9)	113.8(7)	C(9)C(10)C(11)	117.0(7)
SiC(7)C(2)	124.2(6)	C(10)C(11)C(12)	122.5(8)
SiC(7)C(6)	118.2(6)	C(11)C(12)C(13)	120.3(9)
SiC(10)C(9)	124.1(6)	C(12)C(13)C(14)	119.7(9)
SiC(10)C(11)	118.8(6)	C(13)C(14)C(9)	121.6(9)
C(1)C(2)C(3)	119.3(8)	C(14)C(9)C(10)	118.9(8)

Unit cell parameters and intensities of 2482 independent reflections were measured with a four-circle automated Hilger & Watts diffractometer at 20°C (λ(Cu-K_α), $\theta/2\theta$ scan, θ_{max} 66°). The structure was solved by direct methods using the MULTAN program and refined by block-diagonal least-squares method in anisotropic approximation for non-hydrogen atoms and isotropic for H atoms located in the difference Fourier map. The final R value is 0.097 ($R_w = 0.12$) for 1899 reflections with $I > 3\sigma(I)$. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [10]. Atomic coordinates and thermal parameters are given in Table 3, bond lengths and bond angles are listed in Tables 4 and 5.

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