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CRYSTAL AND MOLECULAR STRUCTURE OF 13,13-DIMETHYL-8,13-DIHYDRO-5*H*-DIBENZO[*d,g*][1.2.6]DITHIASILONINE

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Summary

The crystal and molecular structure of 13,13-dimethyl-8,13-dihydro-5*H*-dibenzo-[*d,g*][1,2,6]-dithiasilonine has been determined. The intramolecular Si ··· S distances are unequal (4.190 and 3.438(3) Å), the second of these indicating intramolecular transannular Si ··· S interaction which is confirmed also by distorsion of the coordination polyhedron around the Si atom. The 9-membered heterocycle has a distorted *BB* conformation.

Introduction

There are well known examples of Si ··· O and Si ··· N transannular interactions in organosilicon compounds due to the acceptor properties of silicon. As a result, a tetrahedral Si atom attains a trigonal-bipyramidal coordination [1,2]. On the other hand a two-coordinated S atom, because of its donor properties, exhibits a tendency to increase coordination number by interaction with electron acceptors [3]. An additional Si ··· S coordination previously had only one structural confirmation in crystal of $H_3SiSSiH_3$ where this interaction is naturally intermolecular [4].

In the course of our study of tricyclic systems involving silicon and elements of Group VIA in a central cycle we have carried out an X-ray study of 13,13-dimethyl-8,13-dihydro-5*H*-dibenzo[*d,g*][1.2.6]dithiasilonine (I) which, to our knowledge, is the first representative of the intramolecular transannular Si ··· S interaction.

Results and discussion

Two intramolecular Si ··· S distances in the molecule I have different values. However, if the Si ··· S(1) distance of 4.190(3) Å exceeds the sum of the Si and S

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Van der Waals radii of 3.90 Å [5], the Si · · · S(2) distance of 3.438(3) Å corresponds to intramolecular transannular interaction resulting in the (4 + 1)-coordination of the Si atom and (2 + 1)-coordination of the S(2) atom (Fig. 1). Such interaction is displayed by a distinct tendency of the Si atom to attain a trigonal-pyramidal coordination with the S(2) and C(15) atoms in the axial positions (Fig. 1b). The Si

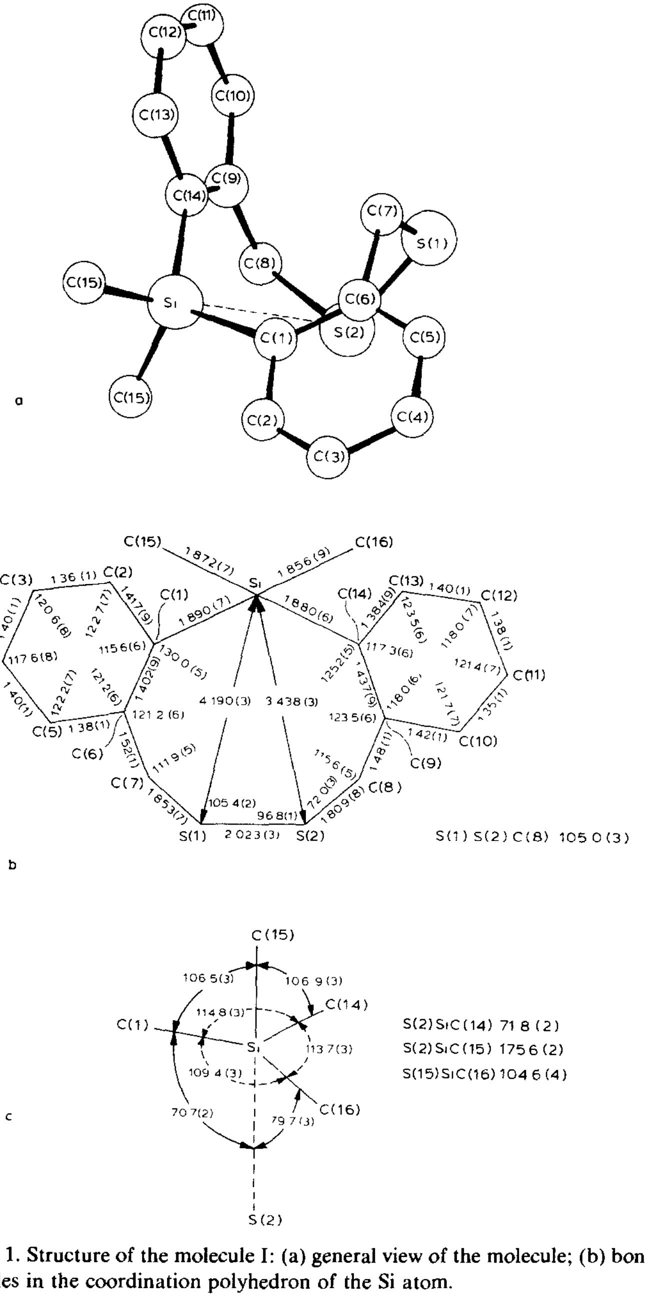

Fig. 1. Structure of the molecule I: (a) general view of the molecule; (b) bond lengths and angles; (c) bond angles in the coordination polyhedron of the Si atom.

and C(15) atoms are situated on one side of the equatorial plane passing through the C(1), C(14) and C(16) atoms at a distance of 0.518 and 2.389 Å from it. The S(2) atom is situated on the other side at a distance of 2.901 Å.

In the structure of $H_3SiSSiH_3$ [4], where the S atom coordinates two Si atoms of neighboring molecules at the distances of 3.55 and 3.56(1) Å, which are somewhat larger than in the structure of I, both Si atoms have a distorted trigonal-bipyramidal (4 + 1)-coordination and the S atom has a (2 + 2)-coordination as in the structure of I. In both structures the S–Si ··· S angle between the axial substituents of the Si atom is close to 180°.

The Si–C bond lengths in the molecule I of 1.856–1.890(7) Å are within the range of 1.84–1.90 Å typical of the Si–C distances in derivatives of tetrahedral silicon [6]. Thus, there is no lengthening of the axial Si–C(15) bond which is usually found in molecules with a strong transannular interaction with participation of the Si atom, e.g. in silatranes [1,2]. The greatest lengthening of the covalent axial Si–N bond was found in pentameric dimethylsilylamine, where its value is equal to the length of transannular coordinative Si ··· N bond of 1.98 Å and the Si atom has a nearly undistorted trigonal-bipyramidal coordination [7].

The S–S distance of 2.023(3) Å in the molecule I is typical of organic disulphides, e.g. 2.030 Å in bis(1,3-benzothiazolyl)-2,2′-disulphide [8]. The bond distances S(1)–C(7) of 1.853(7) Å and S(2)–C(8) of 1.809(8) Å differ significantly, being respectively longer and shorter than the standard S–C(sp^3) distance of 1.817(5) Å [9], although in general S–C bond lengths in organosulphur compounds vary in a rather wide range. The CSS bond angles at the S(1) atom with the (2)-coordination and the S(2) atom with the (2 + 1)-coordination are almost equal (105.4(2) and 105.0(3)°). The S(1)S(2)Si and C(8)S(2)Si angles of 96.8(1) and 72.0(3)° indicate a favourable orientation of one of the lone electron pairs of the S(2) atom for additional transannular S(2) ··· Si interaction.

The 9-membered heterocycle in the molecule I is folded along the S(2) ··· C(1) line by 96.2°, though the C(1)SiC(14)C(9)C(8)S(2) and C(1)C(6)C(7)S(1)S(2) moieties are only approximately planar. This cycle has a distorted *BB* conformation [10] with an approximately. symmetry plane passing through the C(7) atom and the middle point of the C(9)–C(14) bond. The dihedral angle formed by the Ph cycles is 97.1°.

Intermolecular distances in crystal have usual Van der Waals values. The shortest intermolecular distance S(2) ··· C(12) $(x, y, z + 1)$ with participation of the S atom is 3.702(8) Å.

Experimental

Crystals of I are orthorhombic, $a = 16.5274(8)$, $b = 22.272(2)$, $c = 8.5940(7)$ Å, $V = 3163.4(7)$ Å^3, $d_{calc} = 1.25$ g cm^{-3}, $Z = 8$, $C_{16}H_{14}SiS_2$, space group *Pbca*.

Cell parameters and intensities of 3052 independent reflections were measured with a four-circle automated Hilger & Watts diffractometer at 20°C (λ (Cu-K_α), $\theta/2\theta$ scan, $\theta_{max} = 66°$). The structure was solved by direct methods using the MULTAN program and refined by full-matrix least squares with anisotropic thermal parameters for nonhydrogen atoms and isotropic for H atoms located in the difference Fourier map. The final R value is 0.089 ($R = 0.098$) for 1802 reflections with $I \geqslant 3\sigma(I)$. All calculations were performed with an Eclipse S/200 computer

TABLE 1

ATOMIC POSITIONAL ($\times 10^4$, for H atoms $\times 10^3$) AND THERMAL PARAMETERS (B_{iso}^{eq} for nonhydrogen, B_{iso} for H atoms)[a]

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B(Å^2)
S(1)	5336(1)	4155(1)	2733(3)	4.42(6)	H(2)	213(3)	351(2)	319(6)	2(1)
S(2)	4943(1)	3308(1)	3119(2)	4.14(6)	H(3)	195(6)	410(5)	571(10)	9(3)
Si	3196(1)	3412(1)	966(2)	2.74(4)	H(4)	275(4)	506(3)	585(9)	3(2)
C(1)	3165(4)	3981(3)	2596(7)	2.8(2)	H(5)	390(4)	513(3)	431(8)	2(1)
C(2)	2484(4)	3928(4)	3590(8)	3.9(2)	H(7.1)	437(6)	424(4)	86(10)	8(3)
C(3)	2356(5)	4301(4)	4820(10)	5.0(2)	H(7.2)	460(3)	498(2)	201(6)	2(1)
C(4)	2893(5)	4772(4)	5135(10)	4.7(2)	H(8.1)	492(8)	248(7)	179(10)	13(4)
C(5)	3552(4)	4838(3)	4167(9)	3.7(2)	H(8.2)	559(6)	272(5)	135(10)	12(3)
C(6)	3693(4)	4456(3)	2934(8)	2.7(2)	H(10)	602(8)	290(6)	116(10)	6(3)
C(7)	4448(4)	4566(3)	1693(9)	3.5(3)	H(11)	569(4)	371(3)	−361(8)	4(2)
C(8)	5104(4)	2917(4)	1300(9)	4.3(2)	H(12)	433(6)	402(4)	−439(10)	11(3)
C(9)	4876(4)	3254(3)	−125(8)	3.0(2)	H(13)	337(4)	403(3)	−198(7)	3(1)
C(10)	5480(4)	3359(4)	−1275(9)	4.2(2)	H(15.1)	221(4)	388(3)	−53(9)	4(2)
C(11)	5314(4)	3657(4)	−2610(10)	4.2(2)	H(15.2)	177(7)	347(5)	32(10)	10(3)
C(12)	4554(5)	3882(4)	−2907(9)	4.1(2)	H(15.3)	214(5)	317(4)	−102(9)	5(2)
C(13)	3949(4)	3787(3)	−1790(8)	3.2(2)	H(16.1)	342(6)	263(5)	260(10)	13(3)
C(14)	4080(3)	3491(3)	−396(8)	2.4(2)	H(16.2)	266(7)	237(6)	138(10)	18(4)
C(15)	2259(4)	3533(4)	−218(10)	4 3(2)	H(16.3)	298(9)	308(7)	240(10)	18(5)
C(16)	3079(5)	2646(4)	1785(11)	5.1(2)					

[a] $B_{iso}^{eq} = 1/3 \Sigma B_{ij} (\vec{a}_i \vec{a}_j) a_i a_j$.

using INEXTL programs [11]. Atomic coordinates are given in Table 1, a general view of the molecule is shown in Fig. 1a, bond distances and angles are listed in Fig. 1b.

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