Journal of Organometallic Chemistry, 347 (1988) 33–39
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Transannular donor–acceptor interaction in dibenzochalcogeno-silonines. Crystal and molecular structure of 13,13-diphenyl-8,13-dihydro-5*H*-dibenzo[*d,g*][1,2,6]dithiasilonine

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(Received December 9th, 1987)

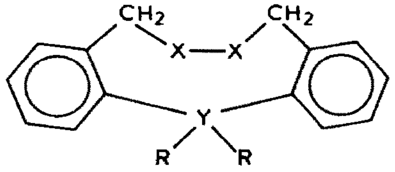
Abstract

An X-ray crystal study of 13,13-diphenyl-8,13-dihydro-5*H*-dibenzo[*d,g*][1,2,6]dithiasilonine was carried out. The compound represents the fifth member in the series of analogous heterocyclic compounds with the transannular donor–acceptor S → Si (Se → Si) interaction which is displayed in a significant shortening of corresponding interatomic distances as compared with the sums of the Van der Waals radii. The donor–acceptor interaction energy is estimated as $\leqslant 3$ kcal/mol. Conformational analysis of the heterocycles studied indicates a consistency between occurrence of the secondary interaction and a jumpwise change in the cycle conformation.

Introduction

The present paper sums up the results of structural studies of tricyclic silicon and germanium compounds with the 9-membered heterocycle which contains, besides Si and Ge, also S or Se atoms [1–4]. In three of five structures (I–V) investigated a noticeable shortening of one of the transannular S...Si(Se...Si) distances relative to the sum of the Van der Waals radii indicates a donor–acceptor X → Y interaction whose strength depends on the nature of participating atoms and their substituents.

0022-328X/88/$03.50



	X	Y	R
I :	Se	Si	Me
II :	Se	Ge	Me
III :	Se	Si	Ph
IV :	S	Si	Me
V :	S	Si	Ph

This interaction is strongest in dithiasilonine (V), whose full X-ray structural data are reported below for the first time.

Results and discussion

A general view of the molecules I–V is shown in Fig. 1. The molecules I and II (Fig. 1a), in which the donor–acceptor X → Y interaction is not observed, have an approximate twofold symmetry axis which is absent in the molecules III–V (Fig. 1b), in which this interaction is manifested in significant shortening of one of the transannular X... Y distances as compared with the sum of the Van der Waals radii of these atoms. Conformational differences between 9-membered heterocycles within each of these two groups of molecules are small, in agreement with such a division.

The X... Y distances in all five molecules and corresponding sums of the Van der Waals radii of X and Y atoms (ΣR_{vdW}) are given in Table 1. Of course, the "sum of radii" criterion is not quite adequate for a characterization of an interatomic interaction. In particular, a value of the Van der Waals radius depends on the orientation of the interaction vector with respect to atomic valence bonds [5,6]. However, in the case discussed the X^2... Y distances in the molecules III–V are noticeably shorter than ΣR_{vdW}, even if the Si atomic radius of 2.1 Å [7] is overestimated by 0.1–0.2 Å (the radii of S and Se atoms used are possibly more reliable). Using a simple model, according to which the Van der Waals repulsion of X and Y atom is equalized by their donor–acceptor interaction, the energy of this

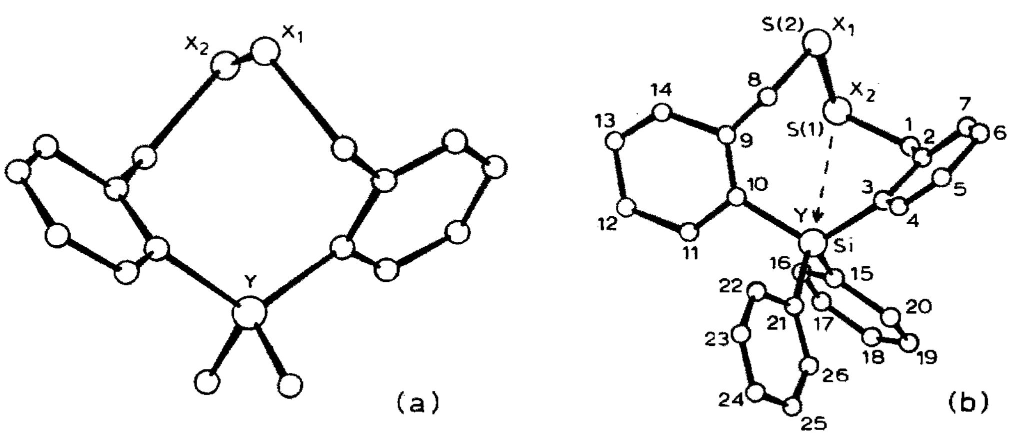


Fig. 1. General view of the molecules I, II (a) and III–V (b). Atom numbering in (b) is given for structure V.

Table 1

Geometrical parameters (Å) of the donor–acceptor S → Si or Se → Si interaction in structures I–V

	X	Y	R	$X^1...Y$	$X^2...Y$	R_{VdW} [a]	Interaction X → Y
I	Se	Si	Me	4.322(2)	4.228(2)	4.0	–
II	Se	Ge	Me	4.327(1)	4.216(1)	4.1	–
III	Se	Si	Ph	4.382(5)	3.608(5)	4.0	+
IV	S	Si	Me	4.190(3)	3.438(3)	3.9	+
V	S	Si	Ph	4.193(3)	3.372(3)	3.9	+

[a] Sums of the Van der Waals radii of X and Y atoms according to [7].

interaction can be evaluated. Atom–atom potentials, employed as a rule in conformational calculations, are less reliable in the repulsion region. Therefore it is better to perform the evaluation mentioned on the basis of more accurate interaction potentials for atoms of noble gases with approximately the same Van der Waals radii. Thus for the Ar–Kr pair a distance shortening from $\Sigma R_{\mathrm{VdW}} = 3.8$ to 3.3 Å, i.e. by 0.5 Å, results in increasing the repulsion energy by ca. 3 kcal/mol (calculated from data of ref. 8). This value may be considered as the upper energy limit of the donor–acceptor interaction in the structures III–V, naturally bearing in mind the approximations mentioned above.

A secondary (donor–acceptor) interaction of such energy certainly can not essentially change bond lengths and bond angles of the X and Y atoms (Table 2). Though the endocyclic CYC bond angles in the molecules III–V are on average somewhat larger than the angles in the molecules I and II and the two X–C bond lengths are unequal, the corresponding differences in these values are not correlated with the strength of the $X^2 \rightarrow Y$ interaction. Nevertheless, the interaction energy is quite sufficient to change torsion angles in the heterocycle considerably, i.e. its conformation.

Conformational analysis of the heterocycles I–V carried out according to the scheme (see ref. 9) has shown their general form is, in fact, the same, being intermediate between the canonical forms TBB ("twist–boat–boat") and BB ("boat–boat"). However, positions of heteroatoms in the asymmetric cycle depend on the presence or absence of the $X^2 \rightarrow Y$ interaction (Fig. 2). The stability of a given form of the heterocycle seems to be caused by the much lower number of its degrees of freedom in comparison with the case of the "normal" (without transan-

Table 2

Bond lengths (Å) and bond angles (°) in heterocycles of molecules I–V [a]

I	X^1–X^2	X^1–C [b]	X^2–C	Y–C	Y–C′	CX^1X^2	X^1X^2	CYC′
I	2.288(1)	2.02(1)	1.99(1)	1.89(1)	1.88(1)	104.2(3)	104.5(3)	114.9(4)
II	2.285(1)	2.003(9)	1.97(1)	1.918(8)	1.953(7)	104.3(2)	104.1(3)	113.6(3)
III	2.285(3)	2.03(2)	1.93(1)	1.91(1)	1.92(2)	100.4(5)	102.7(4)	115.6(6)
IV	2.023(3)	1.853(7)	1.809(8)	1.890(7)	1.880(6)	105.4(2)	105.0(3)	114.8(3)
V	2.020(1)	1.844(3)	1.822(3)	1.891(2)	1.888(2)	103.70(8)	104.50(9)	115.9(1)

[a] Designations of heteroatoms as in Fig. 1. [b] C(8) in molecule V.

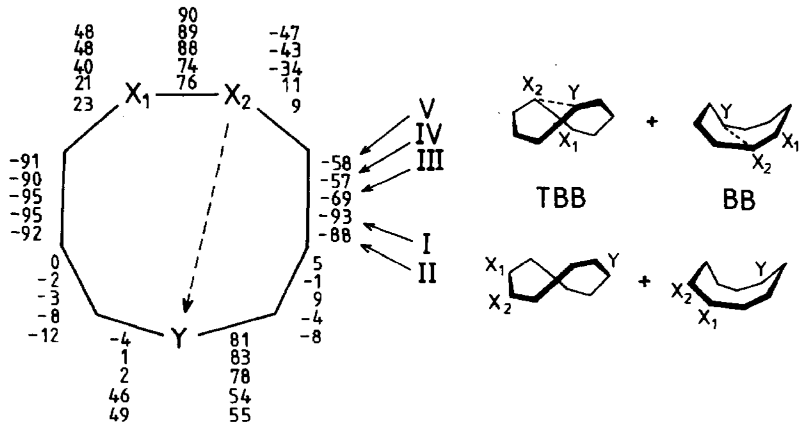


Fig. 2. Conformations of the heterocycles I–V. Endocyclic torsion angles (°) are given.

nular donor–acceptor interaction) 9-membered cycle, e.g. of cyclononane. The YCCC moieties of the cycle are highly rigid because of the two central C atoms being members of benzene rings. Thus only the 5-membered "subcycle" $X^1C...Y...CX^2$ should be considered as conformationally flexible. It is hardly reasonable to describe the latter in terms of canonical forms, but, anyhow, stability of a general configuration of this low-membered cycle is not surprising.

Considering the conformation of the 9-membered heterocycle as an assembly of all endocyclic torsion angles (Fig. 2) it should be noted, first of all, that there is a relative rigidity of the $YCCCX^1$ moiety (within each group of molecules I, II and III–V) and, on the contrary, a flexibility (also within two groups) of the $YCCC^2$ moiety, whose conformation depends on the realization and strength of the $X^2 \rightarrow Y$ interaction. The junction of these moieties is also flexible. Among six torsion angles essentially changing with the alteration of the heterocycle conformation the least contribution to a change of the cycle strain seems to be introduced by the deformation of the CX^1X^2C angle. Its deviation from the optimum value of 90° is small and, as can be seen from the structures of acyclic molecules $(Ph_2CHSe)_2$ [10] and $Se_4(NC_5H_{10})_2$ [11] with corresponding angles of 82 and 76° (the SeSeSeSe angle in the second case), such deviations may be caused even by the crystal field. Two endocyclic CYCC angles of the same type change in the opposite sense on going from the structures I and II to the structures III–V, which is supposedly due to compensation of the corresponding energy changes. When the $X^2 \rightarrow Y$ interaction becomes somewhat stronger without changing the cycle conformation type (III → V), the angles mentioned also change in the opposite sense, indicating a general increase of the strain in this part of the cycle. The same conclusion concerning the torsion angles CCX^1X^2, CCX^2X^1 and $CCCX^2$ can be made. Thus the total strain of the heterocycle with a secondary transannular interaction is naturally higher.

Evidently, the absence of the donor–acceptor interaction in the molecules I and II can not be caused only by the weaker acceptor properties of the YMe_2 group relative to the YPh_2 group. The structures are known in which the $Se \rightarrow Se$ interaction is observed, e.g. with H-substituents at the Si atom [12]. On the other

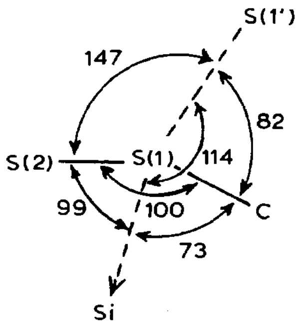


Fig. 3. Coordination of the S(1) atom in structure V (angles in degrees).

hand, the difference between the S → Si interaction parameters in the structures IV (Me-substituents at the Si atom) and V (Ph-substituents) is small (Table 1). Therefore, in the series I–V an interesting feature is observed: the discreteness of "conformational energy levels" of the heterocycle "modulates" a continuous increase in the strength of a possible transannular interaction, and as a result this interaction is displayed only on reaching a certain threshold, the interaction arises and the conformation changes jumpwise in a quite consistent manner.

In the crystal structure V with the strongest $X^2 \rightarrow Y$ interaction the short intermolecular contact S(1)...S(1′) $(-x, 2-y, -z)$ of 3.456(1) Å is observed which may have two explanations. This contact can be accidental, and a certain shortening of the non-bonded distance relative to the doubled Van der Waals radius of the S atom (3.60 Å [7]) can be caused, to some extent, by participation of the S(1) atoms in intramolecular S → Si interactions shifting electron density from the line of contact. The second possibility is a specific, though weak, interaction between sulphur atoms. Arguments can be given in favour of both possibilities. In particular, the S(1) atom coordination (Fig. 3) is considered as distorted tetrahedral, but it is not excluded that the shortening of the S(1)...S(1′) distance is simply due to the deviation of the S(1′) atom by ca. 30° from a position symmetric relative to the S(1)–S(2) and S(1)–C bonds, i.e. due to the realization of the contact not along the direction of the lone electron pairs of S(1) and S(1′) atoms.

Experimental

Crystal data of V: monoclinic, a 9.936(2), b 13.936(3), c 15.594(4) Å, β 92.54(2)°, V 2157(1) Å^3, d_{calc} 1.314 g cm^{-3}, $Z = 8$ $C_{26}H_{22}S_2Si$, space group $P2_1/n$.

Unit cell parameters and intensities of 5385 reflections were measured with a Syntex $P2_1$ diffractometer at 20°C (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $\theta_{\max}$ 30°). The structure was solved by direct methods and refined by a block–diagonal least squares technique in anisotropic approximation for non-hydrogen atoms and isotropic for H atoms located in the difference Fourier map. Finally, $R = 0.037$ ($R_w = 0.039$) for 3516 unique reflections with $I > 3.5\sigma(I)$. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [13]. Atomic coordinates and thermal parameters are given in Table 3.

Table 3

Atomic coordinates ($\times 10^5$ for Si and S, $\times 10^4$ for C, $\times 10^3$ for H) and thermal parameters B_{eq} (B_{iso} for H atoms) in structure V

Atom	x	y	z	B (Å^2)
Si	409(6)	72352(5)	13246(4)	1.18(1)
S(1)	4324(7)	88394(5)	−2638(4)	1.89(1)
S(2)	9736(7)	79303(5)	−11970(4)	2.01(1)
C(1)	−1374(2)	8654(2)	−191(2)	1.97(6)
C(2)	−1795(2)	7613(2)	−167(2)	1.67(6)
C(3)	−1303(2)	6958(2)	466(1)	1.46(5)
C(4)	−1819(2)	6019(2)	425(2)	1.80(6)
C(5)	−2732(3)	5724(2)	−221(2)	2.29(6)
C(6)	−3169(2)	6364(2)	−841(2)	2.41(7)
C(7)	−2709(2)	7305(2)	−810(2)	2.15(6)
C(8)	1416(2)	6816(2)	−612(2)	1.79(6)
C(9)	2328(2)	6990(2)	163(1)	1.43(5)
C(10)	1840(2)	7170(2)	982(1)	1.26(5)
C(11)	2797(2)	7315(2)	1659(1)	1.45(5)
C(12)	4172(2)	7302(2)	1536(2)	1.69(6)
C(13)	4632(2)	7143(2)	729(2)	1.88(6)
C(14)	3715(2)	6982(2)	50(1)	1.78(6)
C(15)	−317(2)	8422(2)	1832(1)	1.32(5)
C(16)	640(2)	9153(2)	1945(1)	1.54(5)
C(17)	345(2)	10006(2)	2355(1)	1.81(6)
C(18)	−917(3)	10159(2)	2650(2)	2.02(6)
C(19)	−1908(3)	9463(2)	2531(2)	2.01(6)
C(20)	−1605(2)	8606(2)	2127(2)	1.70(6)
C(21)	0(2)	6286(2)	2186(1)	1.49(5)
C(22)	636(2)	5401(2)	2054(2)	2.07(6)
C(23)	710(3)	4700(2)	2685(2)	2.64(7)
C(24)	169(3)	4866(2)	3468(2)	2.85(7)
C(25)	−475(3)	5723(2)	3620(2)	2.67(7)
C(26)	−555(2)	6424(2)	2981(2)	1.91(6)
H(1.1)	−179(3)	899(2)	−70(2)	3.1(6)
H(1.2)	−162(2)	899(2)	30(1)	2.0(5)
H(8.1)	192(2)	648(2)	−103(1)	1.3(5)
H(8.2)	56(2)	650(2)	−51(1)	2.0(5)
H(4)	−154(2)	559(2)	86(1)	1.5(5)
H(5)	−305(3)	511(2)	−20(2)	4.2(7)
H(6)	−374(3)	616(2)	−127(2)	3.3(6)
H(7)	−300(2)	776(2)	−125(2)	2.4(6)
H(11)	250(2)	742(1)	224(1)	0.8(4)
H(12)	477(2)	738(2)	200(1)	1.5(5)
H(13)	555(2)	713(2)	62(1)	1.8(5)
H(14)	399(2)	686(2)	−50(1)	1.1(5)
H(16)	154(2)	905(2)	175(1)	1.7(5)
H(17)	104(2)	1041(2)	143(1)	1.6(5)
H(18)	−116(2)	1070(2)	294(1)	2.2(6)
H(19)	−276(2)	958(2)	270(2)	2.5(6)
H(20)	−232(2)	810(2)	204(1)	1.7(5)
H(22)	106(2)	529(2)	153(1)	2.1(5)
H(23)	117(3)	410(2)	258(2)	3.0(6)
H(24)	23(2)	443(2)	390(1)	2.5(6)
H(25)	−87(2)	583(2)	415(2)	2.6(6)
H(26)	−104(2)	699(2)	311(1)	1.6(5)

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