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CRYSTAL AND MOLECULAR STRUCTURE OF 5-t-BUTYL-5-AZA-2,8-DITHIA-1-STANNA(II)BICYCLO[3.3.$0^{1,5}$]OCTANE. IDENTIFICATION OF TWO DIFFERENT GEOMETRIES ALONG THE DISSOCIATION-INVERSION PATHWAY

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Summary

The crystal and molecular structure of 5-t-butyl-5-aza-2,8-dithia-1-stanna(II)bicyclo[3.3.$0^{1,5}$]octane $[Sn(SC_2H_4)_2NC_4H_9]_2$ have been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions: a 14.104(2), b 21.911(4), c 11.624(2) Å, β 98.73(1)°, $Z = 6$. The final R is 0.040 for the 4279 observed reflections. The unit-cell contains four asymmetric dimers (dimer **a**) and two centrosymmetric dimers (dimer **b**), each dimer forms a four-membered Sn_2S_2 ring in which the sulfur atoms are three-coordinated. The Sn–N distances in the two dimeric forms are significantly different (namely, 2.64 and 2.75 in dimer **a**, 2.97 Å in dimer **b**). The lengthening of the Sn–N distances involves the shortening of the bridging tin–sulfur bonds (2.99 and 2.79 in **a**, 2.71 Å in **b**). The coordination around the three different Sn atoms is hemispherical.

Introduction

In recent years the chemistry of tin(II) compounds have been the subject of increasing interest in both inorganic and organic chemistry [1,2]. In this connection the stereochemical influence of the lone pair [3], the generation of reactive organic stannylenes [4,5], the donor and acceptor behaviour of divalent tin compounds [6], and especially the preparation and structure of monomeric tin(II) compounds [1] have received particular attention. The preparation of monomeric tin(II) compounds of the coordination number two has been made possible by the use of bulky substituents [7–9]. The tendency to autoassociation is also reduced in tin(II) contain-

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ing bicyclic octanes of the general type $Sn(XCH_2CH_2)_2Y$ (X = S, NR; Y = NR, PR) [10–12] and in $Sn(SCH_2CH_2CH_2)_2NMe$ [13]. In these compounds the tin atoms reach the coordination number three in solution. Complexation with chromium hexacarbonyl leads to formation of monomeric four-coordinated tin(II) compounds in solution as well as in the solid state [14]. In the light of this information it seemed of interest to investigate the solid state structure of $Sn(SCH_2CH_2)_2N$-t-Bu to determine the degree of autoassociation and the strength of the tin–nitrogen interaction.

TABLE 1

ATOMIC POSITIONAL ($\times 10^4$) AND EQUIVALENT THERMAL PARAMETERS WITH STANDARD DEVIATIONS

Atom	x	y	z	B_{eq} [a]
Sn(1)	4483(0)	3533(0)	2392(0)	3.15
Sn(2)	777(0)	667(0)	−522(0)	3.22
Sn(3)	2710(0)	4484(0)	2062(1)	3.42
S(1)	3331(1)	3962(1)	3654(2)	3.06
S(2)	3971(2)	2453(1)	2580(2)	4.86
S(3)	−719(1)	568(1)	547(2)	3.48
S(4)	2029(1)	407(1)	1114(2)	3.26
S(5)	2800(2)	3970(1)	714(2)	3.86
S(6)	4421(2)	5213(1)	2208(2)	4.36
N(1)	5309(4)	3278(2)	4527(5)	2.52
N(2)	790(4)	1651(3)	1238(5)	2.88
N(3)	2785(4)	5412(3)	−64(5)	3.09
C(1)	4285(5)	4210(3)	4804(6)	3.07
C(2)	4083(6)	2437(3)	4172(8)	4.11
C(3)	−214(6)	844(3)	1988(7)	3.50
C(4)	2441(5)	1180(3)	1500(6)	3.23
C(5)	3430(6)	4360(4)	−344(7)	3.94
C(6)	4129(7)	5902(4)	1329(8)	4.82
C(7)	4826(5)	3663(3)	5360(6)	2.97
C(8)	5090(6)	2616(3)	4748(7)	3.79
C(9)	−11(6)	1531(3)	1915(7)	3.34
C(10)	1709(5)	1554(3)	2036(6)	3.17
C(11)	2858(7)	4896(4)	−906(7)	4.40
C(12)	3707(6)	5752(4)	75(8)	4.48
C(13)	6374(5)	3393(4)	4677(7)	3.76
C(17)	703(6)	2266(3)	629(7)	3.61
C(21)	1913(6)	5794(4)	−433(7)	3.86
C(14)	6803(7)	3056(4)	3681(8)	4.96
C(15)	6537(7)	4084(5)	4528(9)	5.53
C(16)	6885(7)	3177(5)	5869(9)	5.71
C(18)	624(7)	2796(4)	1508(8)	4.68
C(19)	−189(6)	2251(4)	−281(7)	4.62
C(20)	1562(6)	2369(4)	33(7)	4.12
C(22)	1019(7)	5408(5)	−347(8)	5.43
C(23)	1874(7)	6044(5)	−1696(9)	5.82
C(24)	1910(7)	6332(5)	409(9)	5.66

[a] B_{eq} (Å^2) $= 4/3\Sigma\Sigma B_{ij}\vec{a}_i\vec{a}_j$.

Experimental

The synthesis of the title compound has been described elsewhere [11]. Single crystals were obtained by recrystallization from benzene. The space group ($P2_1/c$) was unequivocally established by Weissenberg photographs. The unit-cell parameters were obtained by least-squares refinement from the setting angles of 15 reflections: a 14.104(2), b 21.911(4), c 11.624(2) Å, β 98.73(1)°, $Z = 6$ ($Sn_2S_4N_2C_{16}H_{34}$), D_{calc} 1.74 g cm^{-3}.

The intensities were collected in the ω-scan mode (width 1.2°) with a Syntex $P2_1$ diffractometer, using monochromatic Mo-K_α radiation (λ 0.71069 Å) to $2\theta_{max} = 47°$. 5216 independent intensities were measured, of which 4279 were considered as observed using the criterion $I \geq 2.5\sigma(I)$. The structure was solved by the heavy-atom method: the positions of the three different Sn atoms (in the asymmetric part of the unit-cell) were derived from a Patterson map, and those of other atoms by the DIRDIF-program. The full-matrix least-squares refinement of the positional and thermal parameters were carried out by the SHELX 76-program. The thermal parameters were treated anisotropically except for the nine methyl groups. The weighting scheme was $w = 1/(\sigma|F| + 0.00202F^2)$. The atomic factors used were those included in the SHELX 76-program. The final R index is 0.040 for the set of observed reflections, R_w is 0.048. The positional parameters from the final least-squares cycle are listed in Table 1.

TABLE 2

BOND LENGTHS (Å) WITH e.s.d.'s IN PARENTHESES

Dimer a			
S(1)–Sn(1)	2.530(2)	S(5)–Sn(3)	2.559(2)
S(2)–Sn(1)	2.494(2)	S(6)–Sn(3)	2.499(2)
S(5)–Sn(1)	2.991(2)	S(1)–Sn(3)	2.789(2)
N(1)–Sn(1)	2.636(5)	N(3)–Sn(3)	2.745(6)
S(1)–C(1)	1.829(7)	S(5)–C(5)	1.834(8)
S(2)–C(2)	1.833(9)	S(6)–C(6)	1.834(9)
C(1)–C(7)	1.514(10)	C(5)–C(11)	1.516(11)
C(2)–C(8)	1.528(12)	C(6)–C(12)	1.524(12)
C(7)–N(1)	1.520(8)	C(11)–N(3)	1.508(9)
C(8)–N(1)	1.513(8)	C(12)–N(3)	1.485(9)
C(13)–N(1)	1.508(9)	C(21)–N(3)	1.497(9)
Dimer b			
S(3)–Sn(2)	2.615(2)		
S(4)–Sn(2)	2.458(2)		
S(3)–Sn(2)	2.709(2)		
N(2)–Sn(2)	2.971(6)		
S(3)–C(3)	1.821(7)		
S(4)–C(4)	1.825(7)		
C(3)–C(9)	1.538(10)		
C(4)–C(10)	1.523(10)		
C(9)–N(2)	1.494(9)		
C(10)–N(2)	1.490(9)		
C(17)–N(2)	1.519(9)		

Results and discussion

Selections of bond lengths and bond angles are given in Tables 2 and 3. The packing in the unit-cell (Fig. 1) shows that [Sn$(SCH_2CH_2)_2$N-t-Bu]$_2$ exists as two independent dimers characterized by different bond lengths and bond angles. In both forms the dimerisation takes place through intermolecular Sn–S interactions, with formation of Sn_2S_2 rings. The sulfur atoms (S(1), S(3) and S(5)) involved in

TABLE 3

SELECTED BOND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Dimer a			
S(1)–Sn(1)–S(2)	94.7(1)	S(5)–Sn(3)–S(6)	97.5(1)
N(1)–Sn(1)–S(5)	151.0(1)	N(3)–Sn(3)–S(1)	148.4(1)
S(1)–Sn(1)–S(5)	75.1(1)	S(1)–Sn(3)–S(5)	78.4(1)
S(2)–Sn(1)–S(5)	98.5(1)	S(1)–Sn(3)–S(6)	87.8(1)
N(1)–Sn(1)–S(1)	76.3(1)	N(3)–Sn(3)–S(5)	76.5(1)
N(1)–Sn(1)–S(2)	79.0(1)	N(3)–Sn(3)–S(6)	76.8(1)
Sn(1)–S(1)–Sn(3)	92.8(1)	Sn(1)–S(5)–Sn(3)	87.7(1)
C(1)–S(1)–Sn(1)	93.9(2)	C(5)–S(5)–Sn(3)	96.9(2)
C(1)–S(1)–Sn(3)	113.1(2)	C(5)–S(5)–Sn(1)	99.7(3)
C(2)–S(2)–Sn(1)	97.1(2)	C(6)–S(6)–Sn(3)	93.8(3)
S(1)–C(1)–C(7)	110.1(5)	S(5)–C(5)–C(11)	111.7(6)
S(2)–C(2)–C(8)	111.7(5)	S(6)–C(6)–C(12)	112.2(6)
C(1)–C(7)–N(1)	114.4(5)	C(5)–C(11)–N(3)	112.7(6)
C(2)–C(8)–N(1)	111.8(6)	C(6)–C(12)–N(3)	114.9(6)
C(7)–N(1)–C(8)	107.5(5)	C(11)–N(3)–C(12)	107.6(6)
C(7)–N(1)–Sn(1)	107.8(4)	C(11)–N(3)–Sn(3)	106.5(4)
C(7)–N(1)–C(13)	111.7(5)	C(11)–N(3)–C(21)	111.6(6)
C(8)–N(1)–Sn(1)	106.9(4)	C(12)–N(3)–Sn(3)	105.4(4)
C(8)–N(1)–C(13)	111.4(5)	C(12)–N(3)–C(21)	114.7(6)
C(13)–N(1)–Sn(1)	111.3(4)	C(21)–N(3)–Sn(3)	110.6(4)
Dimer b			
S(3)–Sn(2)–S(4)	98.6(1)		
N(2)–Sn(2)–S′(3)	136.8(1)		
S(3)–Sn(2)–S′(3)	84.1(1)		
S(4)–Sn(2)–S′(3)	78.1(1)		
N(2)–Sn(2)–S(3)	69.7(1)		
N(2)–Sn(2)–S(4)	72.9(1)		
Sn(2)–S(3)–Sn′(2)	95.9(1)		
C(3)–S(3)–Sn(2)	100.3(2)		
C(3)–S(3)–Sn′(2)	110.3(2)		
C(4)–S(4)–Sn(2)	98.0(2)		
S(3)–C(3)–C(9)	108.9(5)		
S(4)–C(4)–C(10)	112.9(5)		
C(3)–C(9)–N(2)	111.3(6)		
C(4)–C(10)–N(2)	113.7(6)		
C(9)–N(2)–C(10)	107.6(6)		
C(9)–N(2)–Sn(2)	108.0(4)		
C(9)–N(2)–C(17)	112.8(5)		
C(10)–N(2)–Sn(2)	103.8(4)		
C(10)–N(2)–C(17)	114.7(5)		
C(17)–N(2)–Sn(2)	109.3(4)		

TABLE 4

SOME TORSION ANGLES (°)

Dimer a	
S(2)–Sn(1)–S(1)–C(1)	113.9
Sn(1)–S(1)–C(1)–C(7)	−64.9
S(1)–C(1)–C(7)–N(1)	60.5
C(1)–C(7)–N(1)–C(8)	−134.3
C(7)–N(1)–C(8)–C(2)	79.1
N(1)–C(8)–C(2)–S(2)	66.9
C(8)–C(2)–S(2)–Sn(1)	−56.1
C(2)–S(2)–Sn(1)–S(1)	−50.9
S(5)–Sn(3)–S(6)–C(6)	109.0
Sn(3)–S(6)–C(6)–C(12)	−65.3
S(6)–C(6)–C(12)–N(3)	62.2
C(6)–C(12)–N(3)–C(11)	−133.9
C(12)–N(3)–C(11)–C(5)	78.5
N(3)–C(11)–C(5)–S(5)	68.4
C(11)–C(5)–S(5)–Sn(3)	−60.1
C(5)–S(5)–Sn(3)–S(6)	−47.5
Dimer b	
S(3)–Sn(2)–S(4)–C(4)	−101.1
Sn(2)–S(4)–C(4)–C(10)	69.8
S(4)–C(4)–C(10)–N(2)	−62.4
C(4)–C(10)–N(2)–C(9)	134.6
C(10)–N(2)–C(9)–C(3)	−81.4
N(2)–C(9)–C(3)–S(3)	−68.6
C(9)–C(3)–S(3)–Sn(2)	68.9
C(3)–S(3)–Sn(2)–S(4)	35.0

those four-membered cycles are three-coordinated. The Sn_2S_2 ring is non-planar in dimer **a**, whereas it must be perfectly planar (by crystallographic symmetry $\bar{1}$ in 0,0,0) in dimer **b**. The t-butyl groups are in *trans* disposition in both dimers.

The conformations of the eight-membered rings are characterized by the torsion angles given in Table 4. The three different cycles adopt boat-chair conformations. A boat-boat conformation has been observed in the corresponding chromium complex

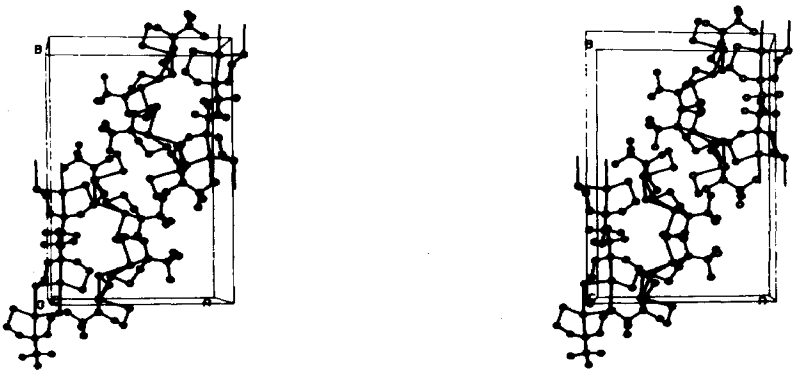


Fig. 1. Stereoscopic view of the molecular packing (PLUTO drawing).

[14]. The torsion angles can be compared with those found in similar eight-membered rings [17], but a significant difference is observed in the C–C–N–C torsion angles of the chair sections compared with the values found in $Me_2Sn(SCH_2CH_2)_2NMe$ [18]. The greatest differences between dimers **a** and **b** appear in the torsion angles S–Sn–S–C, C–C–S–Sn and C–S–Sn–S; these angles are obviously very sensitive to the detail of the coordination around the tin atoms.

Dimer a

The structure of this dimer is illustrated in Fig. 2. Both tin atoms (Sn(1) and Sn(3) are four-coordinate, with a severely distorted ψ-trigonal bipyramidal arrangement (with the Sn^{II} lone pair in equatorial position). However the angles N(1)–Sn(1)–S(5) and N(3)–Sn(3)–S(1) of 151.0 and 148.4° are in the range expected for ψ-trigonal bipyramidal coordination in tin(II) compounds, reflecting the stereochemical effect of the lone pair [1,8]. A similar geometry is observed around the isoelectronic Sb atom, in the compound $ClSb(SCH_2CH_2)_2O$ [15], where the Cl–Sb–O angle is 152.0°.

The tin–sulfur distances to the non-bridging sulfur atoms Sn(1)–S(2) and Sn(3)–S(6) are very short in comparison to those found in other tin(II) compounds of the same coordination number (see Table 11 of ref. 1), but they are comparable with the non-bridging Sn–S bond in the trimeric $[Sn(SC_6H_3\text{-i-}Pr_2\text{-}2,6)_2]_3$ [8]. The tin–sulfur bond lengths to the bridging sulfur atoms Sn(1)–S(1) and Sn(3)–S(5) are slightly larger, but still shorter than the corresponding bond lengths in $[Sn(SC_6H_3\text{-i-}Pr_2\text{-}2,6)_2]_3$. The apical tin–nitrogen interaction strongly influences the bridging tin–sulfur (also apical) bond lengths: a short intramolecular bond Sn(1)–N(1) (2.636 Å) is associated with a long intermolecular distance Sn(1)–S(5) (2.991 Å), whereas a longer Sn(3)–N(3) (2.745) bond is associated with a short Sn(3)–S(1) bond (2.789 Å).

Dräger noted a similar tendency in compounds of the type ClA $(SCH_2CH_2)_2X$ (A = As, Sb; X = O, S) in which increasing A–X interactions cause a lengthening of the apical A–Cl bond length [15].

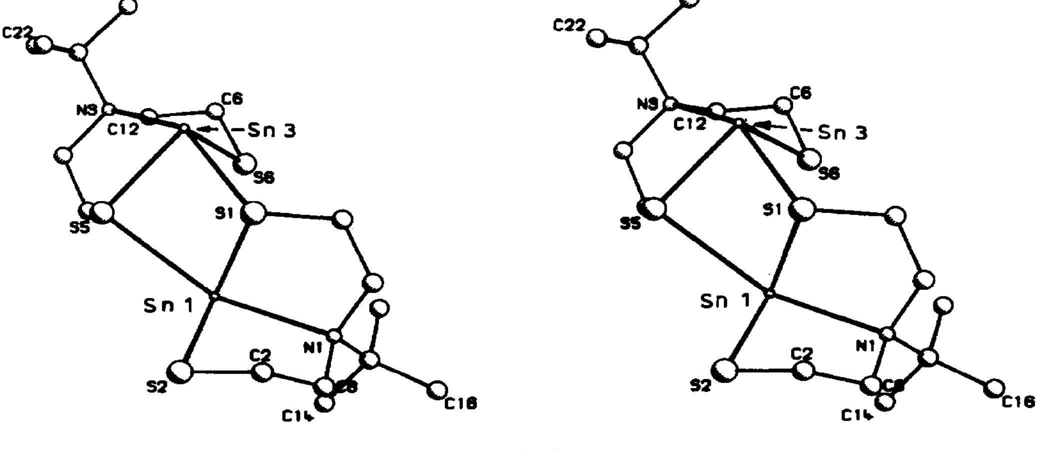


Fig. 2. Stereoview of the dimer **a** (with atom numbering).

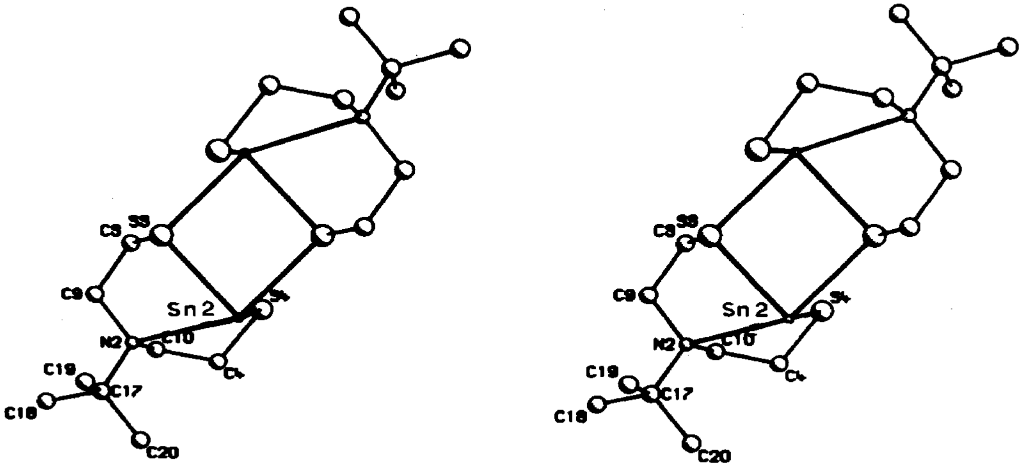


Fig. 3. Stereoview of the dimer **b** (with atom numbering).

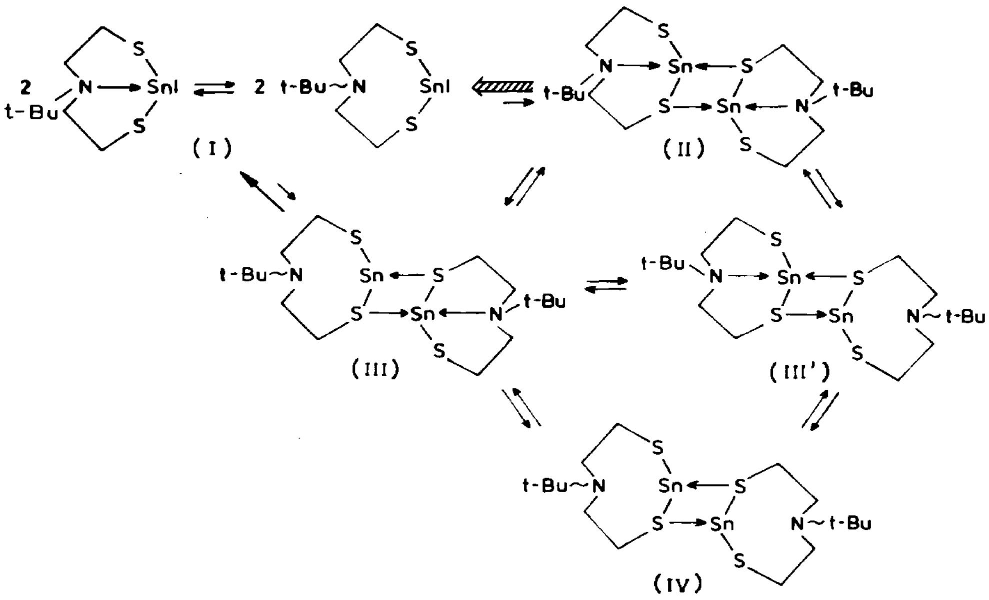
Dimer b

The second dimer is centrosymmetric with a planar Sn_2S_2 ring. Its structure is shown in Fig. 3. The tin atom is bonded to three S atoms in an irregular trigonal pyramidal configuration. The coordination around Sn(2) is completed by a weak intramolecular Sn–N contact. If this contact is taken into account, Sn(2) has also a ψ-trigonal bipyramidal environment. Taking 2.20 Å as a Sn^{II}–N single bond length [1] and 3.20 Å as the limit for nonbonding, the Sn–N distance of 2.97 Å reflects a bond order of only 0.23 compared with 0.56 and 0.46 for the corresponding Sn–N interactions in dimer **a** [16]. This situation involves a short intermolecular Sn–S bridge (Sn(2)–S′(3) 2.709 Å). The bond length (2.458 Å) between Sn(2) and the two-coordinated S(4) is very short, and comparable with the shortest known Sn^{II}–S value which was observed in the monomeric $Sn(SC_6H_2\text{-t-Bu}_3\text{-2,4,6})_2$ (in which the Sn is two-coordinate) [8].

Relevance of results to dynamic processes

We and others have recently interpreted the dynamic behaviour of 5-aza-2,8-dielement-1-stannabicyclo[3.3.$0^{1,5}$]octanes $R_2Sn(XCH_2CH_2)_2NMe$ [19] and $Sn(XCH_2CH_2)_2NR$ [11,20] in solution in terms of a dissociation-inversion and a dimerization process. In this connection it has been shown that for the tin(II) compounds with X = O, the dimers dominate (see Table 1 of ref. 20), whereas the title compound is monomeric in solution [11], though the molecular weight determinations did not exclude the presence of the forms II–IV (Scheme 1) in a fast equilibrium, and the temperature dependent ^{119}Sn NMR spectrum can be better interpreted in terms of such an equilibrium [11]. The second signal at low temperature is perhaps due to one of the dimers II–IV or is possibly an averaged signal for II–IV. In the solid state the dimers are thermodynamically more favored, perhaps because of lattice forces; a similar effect has been observed in cyclic diazastannylenes [9]. Dimer **a** represents a geometry on the route from II to III/III′ and dimer **b** a geometry on the route from III/III′ to IV (see Scheme 1).

SCHEME 1. Processes connecting the equilibrium forms of the title compound.



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