

0.006 (4) Å] but the two ring mean planes of each cation are separated by 0.030 Å. The bond lengths and angles in the cation agree well with the values for (4,4'-bipyH<sub>2</sub>)<sub>2</sub>(Sb<sub>2</sub>Cl<sub>10</sub>) (Lipka, 1980) and for the protonated ring in (4,4'-bipyH)[Ce(4,4'-bipy)(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] (Bukowska-Strzyzewska & Tosik, 1978), in particular as regards the increase in the ring angle at N compared with that in unprotonated 4,4'-bipy. The dihedral angle of zero between the C<sub>5</sub>N ring planes contrasts with the angles of 3.1° in (4,4'-bipyH<sub>2</sub>)<sub>2</sub>(Sb<sub>2</sub>Cl<sub>10</sub>) and *ca* 22° in the unstable form of the latter compound (Lipka, 1983). The dihedral angles for the neutral and monoprotonated molecules in (4,4'-bipyH)<sub>2</sub>[μ-(4,4'-bipy)Nd<sub>2</sub>(NO<sub>3</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>].2(4,4'-bipy) and [Ho(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].2(4,4'-bipy) range from zero to 36° (Weakley, 1984) and the dication can clearly adapt in the same way to the local requirements of crystal packing because of negligible resistance to

torsion about the central C—C bond. The title compound, unlike the (Sb<sub>2</sub>Cl<sub>10</sub>)<sup>4-</sup> and (Cu<sub>2</sub>Cl<sub>6</sub>)<sup>2-</sup> salts, contains hydrogen bonds [N(1)···O(1) 2.77 Å].

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## Structures of 9,9-Dimethoxy-1-methyl-7-phenylsulfonylbicyclo[4.3.0]nonan-2-one (I) and 10,10-Dimethoxy-8-phenylsulfonylbicyclo[5.3.0]decan-2-one (II)

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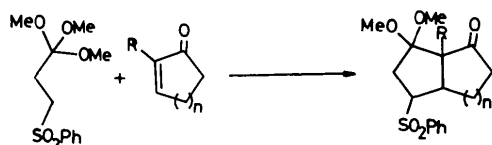
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**Abstract.** (I): C<sub>18</sub>H<sub>24</sub>O<sub>5</sub>S, *M<sub>r</sub>* = 352.45, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 12.861 (2), *b* = 14.554 (3), *c* = 9.412 (1) Å, β = 97.08 (1)°, *V* = 1748.3 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.34 g cm<sup>-3</sup>, *Cu Kα*, λ = 1.54178 Å, μ = 18.3 cm<sup>-1</sup>, *F*(000) = 752, *T* = 291 K, *R* = 0.041 for 2801 observed reflections. (II): C<sub>18</sub>H<sub>24</sub>O<sub>5</sub>S, *M<sub>r</sub>* = 352.45, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.326 (2), *b* = 19.182 (3), *c* = 7.227 (2) Å, *V* = 1708.7 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.37 g cm<sup>-3</sup>, *Cu Kα*, λ = 1.54178 Å, μ = 18.7 cm<sup>-1</sup>, *F*(000) = 752, *T* = 291 K, *R* = 0.045 for 1537 observed reflections. The ring fusions are *cis* and the phenylsulfonyl substituents are orientated in the *exo* position. The five-membered rings in both compounds exhibit envelope conformations, the six-membered ring in (I) has a chair conformation, and the seven-membered ring in (II) exhibits a twist-chair conformation.

**Introduction.** Natural and non-natural cyclopentanoids constitute an area of growing interest. In a previous communication (De Lombaert, Nemery, Roekens, Carretero, Kimmel & Ghosez, 1986) we reported a new two-step sequence that provides highly functionalized fused cyclopentanone derivatives from trimethyl 3-phenylsulfonylorthopropionate and the corresponding enone.



(I) *R* = Me, *n* = 2

(II) *R* = H, *n* = 3

This method is highly diastereoselective since cyclopentannulated products (I and II) are obtained as a single crystalline diastereoisomer (overall yield 50–68%). However, the unambiguous stereochemical assignment of the three chiral centres of the products has not been possible by NMR techniques. Therefore X-ray analysis was undertaken in order to establish the relative configurations of (I) and (II).

**Experimental.** Parallelepiped crystals from ethyl acetate–cyclohexane. Crystal dimensions: (I) 0.24 × 0.25 × 0.34 mm, (II) 0.14 × 0.16 × 0.34 mm. Huber 424 + 511 diffractometer, graphite-monochromated Cu K $\alpha$  radiation. Unit cell from: (I) 25 reflections in range 12 ≤ 2 $\theta$  ≤ 26°, (II) 22 reflections in range 8 ≤ 2 $\theta$  ≤ 22°. Data collection: (I) 3150 ± hkl (−15 ≤ h ≤ 15, 0 ≤ k ≤ 17, 0 ≤ l ≤ 11), (II) 1795 hkl (0 ≤ h ≤ 14, 0 ≤ k ≤ 22, 0 ≤ l ≤ 8) independent reflections with sin $\theta$ / $\lambda$  ≤ 0.60 Å<sup>−1</sup>. 2801 (I), 1537 (II) reflections

Table 1. Atomic coordinates (×10<sup>4</sup>) and equivalent temperature factors (Å<sup>2</sup>) for compound (I)

$$B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B <sub>eq</sub>
C(1)	2393 (2)	−1290 (1)	3663 (2)	3.41 (3)
C(2)	1702 (2)	−1825 (2)	4617 (2)	4.26 (4)
C(3)	633 (2)	−1483 (2)	4795 (3)	6.13 (6)
C(4)	66 (2)	−1055 (2)	3442 (3)	5.96 (6)
C(5)	714 (2)	−275 (2)	2989 (3)	4.95 (5)
C(6)	1774 (2)	−609 (1)	2602 (2)	3.47 (3)
C(7)	2522 (2)	226 (1)	2500 (2)	3.25 (3)
C(8)	3530 (2)	31 (2)	3464 (2)	4.03 (4)
C(9)	3207 (2)	−653 (1)	4570 (2)	3.46 (3)
C(10)	2960 (3)	−1990 (2)	2833 (3)	5.12 (5)
O(11)	2023 (2)	−2517 (1)	5212 (2)	5.99 (4)
S(12)	2694	424	670 (1)	3.31 (1)
O(13)	3306 (1)	−309 (1)	169 (2)	4.48 (3)
O(14)	1670 (1)	590 (1)	−92 (2)	4.82 (3)
C(15)	3431 (2)	1451 (1)	671 (2)	3.26 (3)
C(16)	3035 (2)	2260 (2)	1169 (2)	4.17 (4)
C(17)	3609 (2)	3063 (2)	1129 (3)	5.13 (5)
C(18)	4552 (2)	3043 (2)	573 (3)	5.24 (5)
C(19)	4932 (2)	2250 (2)	78 (3)	4.91 (5)
C(20)	4383 (2)	1437 (2)	124 (2)	3.99 (4)
O(21)	2641 (1)	−241 (1)	5587 (1)	3.86 (3)
C(22)	3173 (3)	455 (2)	6470 (3)	5.60 (6)
O(23)	4139 (1)	−1065 (1)	5201 (2)	4.66 (3)
C(24)	4093 (3)	−1627 (2)	6443 (3)	5.48 (5)

Table 2. Atomic coordinates (×10<sup>4</sup>) and equivalent temperature factors (Å<sup>2</sup>) for compound (II)

$$B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B <sub>eq</sub>
C(1)	6352 (3)	2104 (2)	−1886 (6)	2.83 (6)
C(2)	6927 (4)	1496 (3)	−2762 (7)	3.70 (8)
C(3)	6517 (5)	784 (3)	−2169 (9)	4.58 (10)
C(4)	6998 (5)	578 (3)	−311 (10)	4.88 (10)
C(5)	6879 (5)	1106 (3)	1241 (8)	4.44 (9)
C(6)	7547 (4)	1777 (3)	967 (8)	4.12 (8)
C(7)	7003 (3)	2341 (2)	−165 (6)	3.19 (7)
C(8)	7817 (3)	2870 (2)	−989 (6)	3.20 (7)
C(9)	7385 (3)	3123 (3)	−2882 (7)	3.46 (7)
C(10)	6280 (3)	2761 (2)	−3066 (6)	3.05 (7)
O(11)	7707 (3)	1555 (2)	−3755 (6)	5.01 (7)
S(12)	8184 (1)	3568 (1)	522 (2)	3.45 (2)
O(13)	8366 (3)	3275 (2)	2334 (5)	4.50 (6)
O(14)	9054 (3)	3945 (2)	−349 (6)	4.68 (6)
C(15)	7063 (4)	4139 (2)	701 (6)	3.40 (7)
C(16)	6212 (4)	3976 (3)	1883 (7)	3.71 (8)
C(17)	5361 (4)	4430 (3)	2031 (8)	4.33 (9)
C(18)	5366 (5)	5057 (3)	1062 (8)	4.77 (10)
C(19)	6217 (5)	5226 (3)	−64 (8)	4.60 (9)
C(20)	7083 (4)	4763 (3)	−258 (8)	4.10 (8)
O(21)	5437 (2)	3150 (2)	−2215 (5)	3.61 (5)
C(22)	5133 (5)	3780 (3)	−3098 (9)	4.43 (10)
O(23)	6079 (2)	2658 (2)	−4961 (4)	3.65 (5)
C(24)	5105 (5)	2284 (4)	−5388 (8)	4.71 (10)

Table 3. Bond distances (Å) in the rings

Compound (I)	Compound (II)
C(1)–C(2)	1.549 (3)
C(1)–C(6)	1.555 (3)
C(1)–C(9)	1.570 (3)
C(2)–C(3)	1.491 (4)
C(2)–O(11)	1.201 (3)
C(3)–C(4)	1.521 (4)
C(4)–C(5)	1.501 (4)
C(5)–C(6)	1.533 (3)
C(6)–C(7)	1.560 (3)
C(7)–C(8)	1.515 (3)
C(8)–C(9)	1.534 (3)
C(1)–C(2)	1.505 (6)
C(1)–C(7)	1.548 (6)
C(1)–C(10)	1.525 (6)
C(2)–C(3)	1.516 (7)
C(2)–O(11)	1.205 (6)
C(4)–C(3)	1.520 (9)
C(4)–C(5)	1.518 (8)
C(5)–C(6)	1.540 (7)
C(6)–C(7)	1.513 (6)
C(7)–C(8)	1.547 (6)
C(8)–C(9)	1.547 (6)
C(9)–C(10)	1.534 (5)

Table 4. Endocyclic torsion angles (°) ( $\sigma \leq 1^\circ$ )

Compound (I)	
Five-membered ring	
C(1)–C(6)–C(7)–C(8)–C(9)–	23, 0, −24, 39, −38
Six-membered ring	
C(1)–C(2)–C(3)–C(4)–C(5)–	−18, 36, −58, 63, −46, 23
C(6)–	
Compound (II)	
Five-membered ring	
C(1)–C(7)–C(8)–C(9)–C(10)–	−35, 20, 3, −26, 39
Seven-membered ring	
C(1)–C(2)–C(3)–C(4)–C(5)–	95, −81, 52, −68, 86, −40, −36
C(6)–C(7)–	

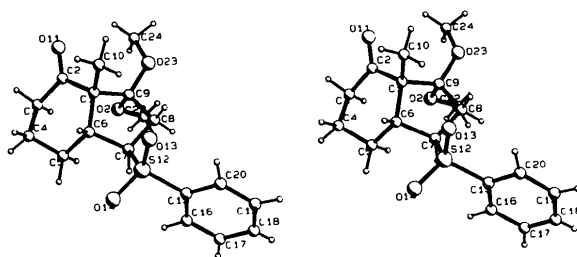


Fig. 1. Stereoscopic view of compound (I) and atom numbering.

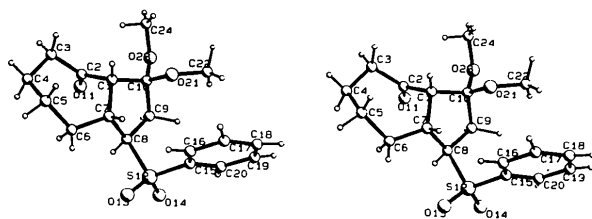


Fig. 2. Stereoscopic view of compound (II) and atom numbering.

with  $I \geq 2.5\sigma(I)$  used in refinement. Standard reflections 221 (I), 131 (II) checked every 50 reflections: no significant deviation. Empirical absorption correction factor between 0.9 and 1.1 (I), 0.97 and 1.26 (II). Structures solved with *SHELXS86* (Sheldrick, 1985). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX76*; Sheldrick, 1976) using *F*. H isotropic with common refined temperature factor [ $B = 6.5$  (I),  $4.4 \text{ \AA}^2$  (II)].  $w = 1/(\sigma^2 + gF^2)$ ,  $g = 0.0002$  (I),  $0.0037$  (II).  $R = 0.041$ ,  $wR = 0.046$  for 2801 observed reflections (I) and  $R = 0.045$ ,  $wR = 0.053$  for 1537 observed reflections (II). Final  $(\Delta/\sigma)_{\max} = 0.07$  (I),  $0.5$  (II);  $S = 2.74$  (I),  $1.0$  (II). Max. and min. heights in final difference Fourier synthesis =  $0.21$  and  $-0.31 \text{ e \AA}^{-3}$  (I),  $0.17$  and  $-0.45 \text{ e \AA}^{-3}$  (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The atomic parameters are summarized in Tables 1 and 2,\* the bond distances in the rings in Table 3, and the endocyclic torsion angles in Table 4. Figs. 1 and 2 give stereoscopic views of the molecules (Motherwell & Clegg, 1978).

\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44111 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## The First Structurally Characterized Monoalkylthioborane. Structure of 1,3,5-Tri(*tert*-butyl)cyclotriborathiane

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(Received 28 January 1987; accepted 20 July 1987)

**Abstract.** C<sub>12</sub>H<sub>33</sub>B<sub>3</sub>S<sub>3</sub>,  $M_r = 306$ , orthorhombic, *Pbca*,  $a = 15.577$  (3),  $b = 18.327$  (4),  $c = 27.791$  (5) Å,  $V = 7933.7$  (26) Å<sup>3</sup>,  $Z = 16$ ,  $D_m$  (by flotation) =  $1.07$  (1),  $D_x = 1.02 \text{ g cm}^{-3}$ ,  $F(000) = 2688$ ,  $\text{Mo } K\alpha_1$ ,  $\lambda = 0.70926 \text{ \AA}$ ,  $\mu = 3.18 \text{ cm}^{-1}$ ,  $T = 293 \text{ K}$ ,  $R = 0.059$ ,  $wR = 0.058$  for 2918 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . There are two crystallographically independent (Bu<sup>t</sup>SBH<sub>2</sub>)<sub>3</sub> molecules per asymmetric unit with no imposed symmetry. The B–S distances range from

In the two compounds the five-membered rings exhibit envelope conformations with C(9) for (I) and C(1) for (II) at the flap. In compound (I), the six-membered ring has a chair conformation flattened in the C(2)–C(1)–C(4) moiety with an approximate mirror plane passing through C(1) and C(4). In compound (II), the seven-membered ring exhibits a twist-chair conformation with a twofold axis passing through C(7) and the middle point of the C(3)–C(4) bond.

The ring fusions in the two compounds are *cis* and the phenylsulfonyl substituents are in *exo* positions.

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1.915 (10) to 1.978 (10) Å. The B–S–B angles range from  $103.3$  (3) to  $110.9$  (3)° and the S–B–S angles from  $102.6$  (4) to  $111.1$  (4)°.

**Introduction.** Recently, we have been exploring the chemical reactivity of early-transition-metal borohydride complexes toward various thiols with the purpose of synthesizing new complexes that contain *M*–S and/or *M*–SR bonds. In a preliminary communication, we have reported (Coucouvanis, Lester, Kanatzidis & Kessissoglou, 1985) on the synthesis and characterization of  $[\text{Zr}_3\text{S}_3(\text{SR})_2(\text{BH}_4)_4]_n(\text{THF})_2$  ( $n =$

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