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The Crystal Structure of 2,11,20-Trithia[3.3.3](1,2,4)(1,3,5)cyclophane and Molecular Structures of Unsymmertically Tris-bridged [2.2.2](1,2,4)(1,3,5) and [2.2.2](1,2,4)(1,2,5)Cyclophanes, Estimated by Molecular Conformational Analysis†

Yasushi KAI, Takashi MIZUMA,†† Noritake YASUOKA,††† and Nobutami KASAI*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565
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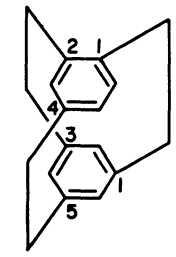
The crystal structure of 2,11,20-trithia[3.3.3](1,2,4)(1,3,5)cyclophane has been determined by the X-ray diffraction method and compared with the molecular structures of unsymmetrically tris-bridged [2.2.2](1,2,4)(1,3,5) and [2.2.2](1,2,4)(1,2,5)cyclophanes, estimated by molecular conformational analysis.

In a series of recent synthetic studies of layered cyclophane compounds with more than two ethano bridges holding two benzene rings,[1-4] a new type of unsymmetrically tris-bridged [2.2.2]cyclophanes (**1** and **2**) has been reported by Nakazaki and his co-workers.[5]

The molecular structures of **1** and **2** are expected to have unusually deformed benzene rings with a new mode of overlapping structures among the various kinds of layered cyclophane compounds. In the synthetic paths to **1** and **2**, trithia[3.3.3]cyclophanes (**3** and **4**) are the intermediate products, followed by the preparation of trisulfones and their pyrolysis.



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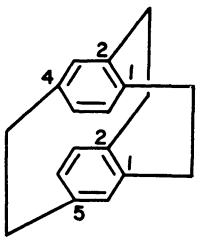

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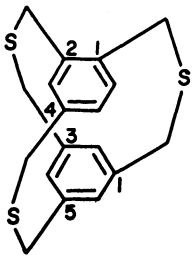

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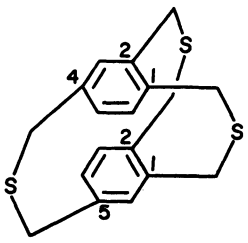

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As a first step in structural studies of these unsymmetrically tris-bridged [2.2.2]cyclophanes, the crystal structure of **3** has been determined by the X-ray diffraction method. The crystals of **1** and **2** were of a poor quality for the X-ray experiment. The molecular structures of **1** and **2**, therefore, have been estimated by the intramolecular-strain-energy-minimization method with semi-empirical potential functions by Boyd,[6] and have been compared with the molecular structure of **3**.

Experimental

Crystal Data. $C_{18}H_{18}S_3$, *F.W.* 330.5, monoclinic, space group $P2_1/c$, $a=15.466(4)$, $b=13.068(5)$, $c=8.409(2)$ Å, $\beta=115.39(2)°$, $V=1535.4(8)$ Å^3, $D_m=1.43$ (by flotation), $D_c=1.430$ g cm^{-3}, $Z=4$.

The three-dimensional X-ray data were collected using a crystal with dimensions of $0.3\times0.3\times0.35$ mm by the use of Zr-filtered Mo $K\alpha$ radiation on a Rigaku automated four-circle diffractometer. The θ-2θ scan method was employed at a rate of 4° min^{-1}. The backgrounds were measured for 5 s before and after each scan. A total of 3384 (2513 non-zero) reflections was collected up to $2\theta=54°$. Usual *Lp* corrections were made but no absorption correction was employed [μ(Mo $K\alpha$) = 4.5 cm^{-1}].

The structure was solved by the direct method (*MULTAN* 74)[7] and refined anisotropically by the block-diagonal least-squares procedure (*HBLS*-V).[8] After the *R* value had converged to 0.113, all the H atoms located on the difference Fourier map were included in the refinement with the isotropic temperature factors. The weighting scheme used was $w=[\sigma^2(F_o)+a|F_o|+b|F_o|^2]^{-1}$ and $w=c$ for non-zero and zero reflections respectively. The final *R* value was 0.098 for non-zero reflections (0.149 for all), and $R_w=0.138$, with $a=0.0796$, $b=0.0017$, and $c=0.1320$. The atomic scattering factors for the S and C atoms were taken from the "International Tables for X-Ray Crystallography," Vol. IV,[9] and those for the H atom from Stewart *et al.*[10] The final atomic coordinates are listed in Table 1.††††

Results and Discussion

Molecular Structure of 2,11,20-Trithia[3.3.3](1,2,4)-(1,3,5)cyclophane (3). The perspective view of the molecule are shown in Fig. 1 by the *ORTEP* drawings,[12] together with the atomic numberings. The bond distances and angles are listed in Table 2.

In the crystal structure of **3**, no conformational disorder of the sulfide bridges is found, in contrast with the crystal structures of related compounds, 2,11,20-trithia[3.3.3](1,3,5)cyclophane (**5**),[13] and *syn*-2,11-dithia-9,18-dimethyl[3.3]cyclophane (**6**).[14] The conformational disorder observed in **5** and **6** was inter-

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†† Present address: Fuji-FACOM Coorporation, 23-5 Nishi Shimbashi, 3-Chome, Minato-ku, Tokyo 105.

††† Present address: Institute for Protein Research, Osaka University, Yamadaoka, Suita, Osaka 565.

†††† Tables of observed and calculated structure factors and anisotropic thermal parameters are deposited as Document No. 8342 at the Chemical Society of Japan.

TABLE 1. FRACTIONAL ATOMIC COORDINATES OF THE **3** MOLECULE WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a) S and C atoms with equivalent temperature factors.[11]

Atom	x	y	z	B_{eq}/Å^2
S(2)	0.48268(12)	0.60850(15)	0.8016(3)	4.32
S(11)	0.14673(14)	0.37512(14)	0.0391(3)	4.32
S(20)	0.04427(11)	0.61177(14)	0.4316(3)	3.73
C(1)	0.3724(5)	0.5682(5)	0.8135(8)	3.8
C(3)	0.4414(5)	0.6905(6)	0.6085(10)	4.8
C(4)	0.3496(5)	0.6605(5)	0.4574(8)	3.6
C(5)	0.2654(5)	0.7056(5)	0.4427(8)	3.4
C(6)	0.1774(4)	0.6738(5)	0.3156(8)	3.0
C(7)	0.1739(5)	0.5972(5)	0.1994(8)	3.3
C(8)	0.2564(5)	0.5486(5)	0.2126(8)	3.3
C(9)	0.3449(5)	0.5810(5)	0.3420(8)	3.6
C(10)	0.2509(5)	0.4573(6)	0.0973(8)	4.1
C(12)	0.1811(5)	0.2914(6)	0.2326(8)	4.0
C(13)	0.2259(5)	0.3510(5)	0.4036(8)	3.2
C(14)	0.3223(5)	0.3400(5)	0.5145(9)	3.6
C(15)	0.3660(5)	0.4069(5)	0.6514(8)	3.6
C(16)	0.3167(4)	0.4868(5)	0.6819(7)	3.0
C(17)	0.2170(4)	0.4913(5)	0.5826(7)	2.8
C(18)	0.1736(5)	0.4233(5)	0.4465(8)	3.2
C(19)	0.1526(5)	0.5686(6)	0.6165(8)	3.7
C(21)	0.0878(5)	0.7086(5)	0.3261(9)	3.8

b) H atoms with isotropic temperature factors.

Atom	x	y	z	B/Å^2
H(1A)	0.334(6)	0.626(6)	0.803(11)	4(2)
H(1B)	0.395(7)	0.545(8)	0.919(12)	6(3)
H(3A)	0.493(7)	0.688(7)	0.566(12)	5(3)
H(3B)	0.440(6)	0.759(7)	0.629(12)	5(3)
H(5)	0.266(5)	0.765(6)	0.511(9)	3(2)
H(7)	0.107(6)	0.570(6)	0.106(10)	3(2)
H(9)	0.413(6)	0.549(7)	0.349(11)	4(2)
H(10A)	0.248(7)	0.482(8)	0.007(14)	6(3)
H(10B)	0.308(6)	0.410(7)	0.139(11)	4(2)
H(12A)	0.232(6)	0.242(7)	0.240(11)	4(2)
H(12B)	0.115(8)	0.259(9)	0.225(15)	8(3)
H(14)	0.352(7)	0.293(8)	0.497(13)	6(3)
H(15)	0.433(8)	0.408(8)	0.718(14)	7(3)
H(18)	0.093(7)	0.431(8)	0.369(13)	6(3)
H(19A)	0.123(7)	0.546(8)	0.709(13)	6(3)
H(19B)	0.197(7)	0.631(7)	0.696(11)	4(2)
H(21A)	0.099(7)	0.769(7)	0.397(12)	5(3)
H(21B)	0.033(6)	0.712(7)	0.222(12)	5(2)

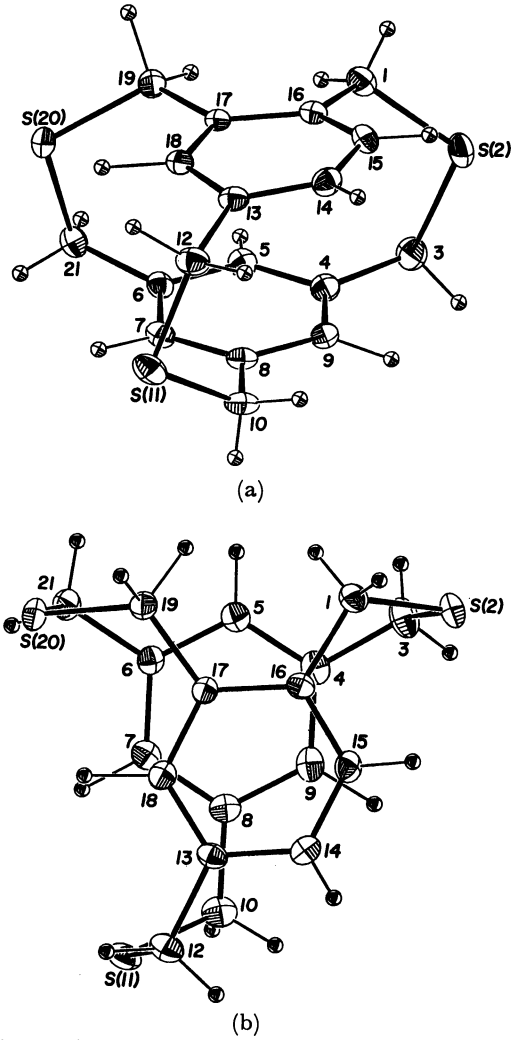
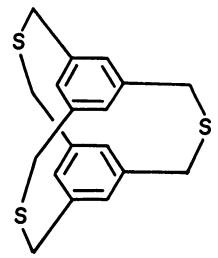


Fig. 1. Molecular structures of **3** with the numbering scheme of the atoms. Thermal ellipsoids for non-hydrogen atoms are drawn at the 30% probability level. H atoms are shown as spheres with arbitrary temperature factor of 1.0 Å^2. a) Side view of the molecule. b) Projection of the molecule onto the mean plane of (1, 3, 5) benzene.



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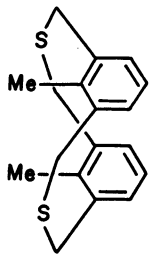

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preted in terms of a temperature-modulated flipping of the sulfide bridges[13] between two positions related by the local 2-fold symmetry. The lack of local 2-fold symmetry in **3** may be an important factor in preventing the sulfide bridges from flipping in the crystal structure.

The structures of the two benzene rings in this molecule are different from each other. The benzene ring with three sulfide bridges symmetrically on its 1, 3, and 5 positions [abbreviated as (1,3,5)benzene hereafter] is planar within a maximum deviation of 0.015 Å. On the other hand, the other benzene ring, with three sulfide bridges unsymmetrically on its 1, 2, and 4 positions [(1,2,4)benzene], deviates from a plane to boat structure. The C(14), C(15), C(17), and C(18) atoms make a base plane within a 0.003 Å deviation, with the C(13) and C(16) atoms as the bow and/or stern atoms. The dihedral angles between the base plane and the bow and/or stern planes [C(14), C(13), and C(18)] and [C(15), C(16), and C(17)] are both 6.4°, a value of which is much smaller than the corresponding angles (12—14°) of the boat-form benzene rings in [2.2]paracyclophane[15] and its derivatives.[16,17] In the **5** molecule, the two benzene rings are both planar and are parallel to each other within a 1° deviation. In the **3** molecule, the mean plane of the (1,3,5)benzene ring makes an angle of 6.8° with the base plane of the (1,2,4)-benzene ring. The distances of the carbon atoms in (1,3,5)benzene from the base plane of (1,2,4)benzene lie between 2.902 and 3.238 Å, the average of which [3.077 Å] is shorter than the corresponding distance of **5**, 3.192 Å.

The C–S–C angles about the S(2), S(11), and S(20) atoms are 103.9(3), 103.1(3), and 103.5(3)° respectively. The C–S distances range from 1.817(8) to 1.840(8) Å [av. 1.827 Å]. The S–C–C angles, distributed in the

TABLE 2. SELECTED BOND LENGTHS AND BOND ANGLES IN THE **3** MOLECULE WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å	Bond length	l/Å
S(2)–C(1)	1.829(7)	S(2)–C(3)	1.817(8)
S(11)–C(10)	1.820(8)	S(11)–C(12)	1.840(8)
S(20)–C(19)	1.820(7)	S(20)–C(21)	1.833(7)
C(1)–C(16)	1.510(9)	C(3)–C(4)	1.495(10)
C(4)–C(5)	1.386(9)	C(4)–C(9)	1.403(9)
C(5)–C(6)	1.385(9)	C(6)–C(7)	1.383(9)
C(6)–C(21)	1.496(9)	C(7)–C(8)	1.386(9)
C(8)–C(9)	1.400(9)	C(8)–C(10)	1.516(7)
C(12)–C(13)	1.517(10)	C(13)–C(14)	1.387(9)
C(13)–C(18)	1.388(9)	C(14)–C(15)	1.371(9)
C(15)–C(16)	1.379(9)	C(16)–C(17)	1.406(8)
C(17)–C(18)	1.375(9)	C(17)–C(19)	1.528(9)
C–H 0.81—1.14(8—12), av. 0.99(10)			
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
C(1)–S(2)–C(3)	103.9(3)	C(10)–S(11)–C(12)	103.1(4)
C(19)–S(20)–C(21)	103.5(3)	S(2)–C(1)–C(16)	114.5(5)
S(2)–C(3)–C(4)	116.5(5)	C(3)–C(4)–C(5)	118.6(6)
C(3)–C(4)–C(9)	122.1(6)	C(5)–C(4)–C(9)	119.0(6)
C(4)–C(5)–C(6)	121.1(6)	C(5)–C(6)–C(7)	119.3(6)
C(5)–C(6)–C(21)	119.5(6)	C(7)–C(6)–C(21)	120.3(6)
C(6)–C(7)–C(8)	121.3(6)	C(7)–C(8)–C(9)	118.9(6)
C(7)–C(8)–C(10)	120.8(6)	C(9)–C(8)–C(12)	120.0(6)
C(4)–C(9)–C(8)	120.3(6)	S(11)–C(10)–C(8)	115.9(5)
S(11)–C(12)–C(13)	112.0(5)	C(12)–C(13)–C(14)	120.4(6)
C(12)–C(13)–C(18)	121.1(6)	C(14)–C(13)–C(18)	118.3(6)
C(13)–C(14)–C(15)	119.9(6)	C(14)–C(15)–C(16)	121.8(6)
C(1)–C(16)–C(15)	118.8(6)	C(1)–C(16)–C(17)	122.8(6)
C(15)–C(16)–C(17)	118.3(6)	C(16)–C(17)–C(18)	119.1(6)
C(16)–C(17)–C(19)	123.6(5)	C(18)–C(17)–C(19)	117.3(5)
C(13)–C(18)–C(17)	121.7(6)	S(20)–C(19)–C(17)	118.7(5)
S(20)–C(21)–C(6)	111.1(5)		
S–C–H 96—116 (5—8), av. 106(6)			
C–C(sp^3)–H 104—118 (5—8), av. 110(6)			
C–C(sp^2)–H 116—122 (4—8), av. 119(6)			
H–C(sp^3)–H 90—117 (7—9), av. 107(8)			

range from 111.1(5) to 118.7(5)° [av. 114.8°], are greater than the tetrahedral angle of 109.5°.

The angular deviation of the C(3)–C(4) bond from the plane defined by the C(4), C(5), and C(9) atoms, that of the C(6)–C(21) bond from the plane defined by the C(5), C(6), and C(7) atoms, and that of the C(8)–C(10) bond from the plane defined by the C(7), C(8), and C(9) atoms are 5.9, 9.5, and 3.4° respectively. The corresponding angular deviations of the C(1)–C(16), C(17)–C(19), and C(12)–C(13) bonds are 2.7, 0.2, and 4.1° respectively. These angles are much smaller than the corresponding angles (11—15°) in [2.2]paracyclophane[15] and related compounds.[16,17]

The above results suggest that the intramolecular strain of the **3** molecule may be much smaller than the layered cyclophanes with ethano bridges and a little greater than those of the symmetrically tris-bridged analogue (**5**) and the di-bridged related compound (**6**).

Estimated Molecular Structures of Unsymmetrically Tris-bridged [2.2.2](1,2,4)(1,3,5) and [2.2.2](1,2,4)(1,2,5)-Cyclophanes. The molecular structures of [2.2.2](1,2,4)(1,3,5)cyclophane (**1**) and [2.2.2](1,2,4)(1,2,5)-cyclophane (**2**) were obtained by the conformational analysis of Boyd's *MOLBD*-3 program.[6] The starting molecular models were generated by Mansfield's *MOLGEN* program[18] using the standard structural parameters. The starting molecular models were refined through the energy-minimization procedure by means of the *MOLBD*-3 program to converged structures with strain energies of 39.1 (**1**) and 28.3 kcal mol^{-1} (**2**).†††† The calculated molecular structures of **1** and **2** are shown in Fig. 2. The molecular structures thus obtained give quite reasonable results, with a significantly greater strain energy in **1** than in **2**. The strain energy of [2.2]-paracyclophane was reported by Boyd to be 35.1 kcal mol^{-1}.[6]

The additional strain energy in **1** compared with that in **2** is based on the difference in bridging positions between the facing benzene rings. In the **2** molecule, the bridging from the 1, 2, and 4 positions of one benzene ring to the 1, 2, and 5 positions of the other benzene ring is done by sliding and rotating two benzene

†††† 1 cal=4.186 J.

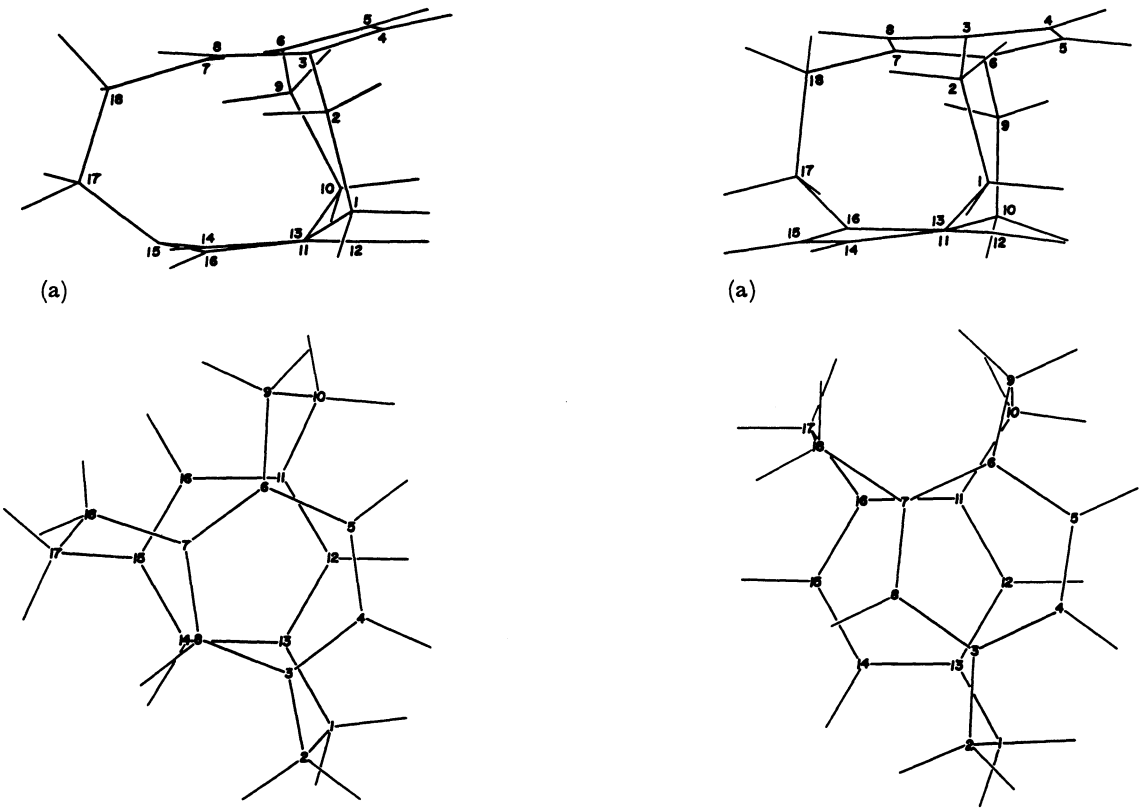

Fig. 2. Molecular structures of **1** and **2** estimated by the molecular conformational analysis by the use of *MOLBD*-3 program. a) Side views of the molecules projected along the C(13)–C(11) bond. b) Projections of the molecules onto the least-squares planes of (1, 3, 5)benzene for **1** and (1, 2, 5) benzene for **2**, respectively.

rings from the eclipsed position without adding an extra strain energy to its molecular structure. In the **1** molecule, however, the deviation of the two benzene rings from the eclipsed position is smaller than that of **2** because of the more constrained bridging positions of 1, 3, and 5 of the second benzene ring. This causes the rather large deformations of the structural parameters from the standard values. Almost all of the difference between the intramolecular strain energies of **1** and **2** [10.2 kcal mol^{-1}] is due to the difference in the strain energies of the angular deformations about C(benzene) connecting to the ethano bridges [2.7 kcal mol^{-1}] and out-of-plane deformations of C(benzene)–C(bridge) from the C(benzene) plane [6.5 kcal mol^{-1}] between **1** and **2**.

In the **1** molecule, the (1,2,4)benzene ring takes an approximately boat form, with the base plane including C(4), C(5), C(7), and C(8) atoms, while the (1,3,5)-benzene ring is roughly planar. The structures of these benzene rings in **1** are similar to those found in trithia-[3.3.3]cyclophane, which has the same bridging structure (**3**). In the **2** molecule, the (1,2,4)benzene ring also takes a boat form, with the base plane including C(4), C(5), C(7), and C(8), while the planality of the (1,2,5)-benzene ring is lower than that of the (1,3,5)benzene ring in **1**. The distances of the atoms in the (1,3,5)-benzene ring from the base plane of the (1,2,4)-benzene ring in **1** range from 2.57 to 3.02 Å [av. 2.82 Å], while

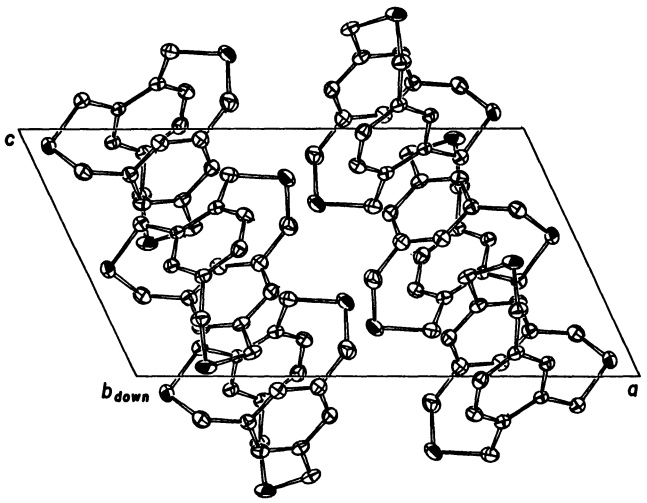

Fig. 3. Crystal structure of **3** projected along the b axis.

the corresponding values in **2** range from 2.52 to 3.01 Å [av. 2.81 Å]. It is noteworthy that the projection of **3** onto the mean plane of (1,3,5)benzene (Fig. 1), which shows an overlapping structure of two benzene rings, is essentially the same as the projection of **1** in Fig. 2.

Crystal Structure of 2,11,20-Trithia[3.3.3](1,3,5)cyclophane (3). The crystal structure of the **3** molecule is shown in Fig. 3. No unusually short contacts were found, the shortest ones being as follows: S(11)–C(13)

[x, 1/2−y, 1/2+z] 3.567 Å, S(11)–C(21) [x, 1/2−y, −1/2+z] 3.583 Å, and S(20)–S(20) [−x, 1−y, 1−z] 3.617 Å.

All the computations were carried out on an ACOS 800 computer at the Computation Center, Osaka University, and on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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