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## 6H,12H,18H-5,11,17-Trithiatribenzo[a,e,i]cyclododecene

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**Abstract.**  $C_{21}H_{18}S_3$ , monoclinic,  $P2_1/n$ ,  $a=7.839$  (3),  $b=19.556$  (9),  $c=11.464$  (4) Å,  $\beta=90.12$  (10)°,  $Z=4$ ,  $D_x=1.385$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha, \lambda=1.5418 \text{ Å})=37.4$  cm<sup>-1</sup>. The structure was solved by direct methods and Fourier techniques. An  $R$  of 0.07 was obtained for 2402 observed reflexions after least-squares refinement. Both  $S^{II}-C(sp^3)$  and  $S^{II}-C(sp^2)$  mean bond lengths (1.838 and 1.771 Å) indicate single bonds in agreement with literature data.

**Introduction.** Intensities were collected on a Stoe semi-automatic two-circle diffractometer [for details see Kálmán, Simon, Schwartz & Horváth (1974)]. 411 of the 2813 independent reflexions had  $I-2.5\sigma(I) < 0$  and were taken as unobserved with values of  $I_o = \frac{1}{2}\sigma(I)$ . The phase problem for 331 reflexions with  $E \geq 1.50$  was solved with *MULTAN* (Germain, Main & Woolfson 1971). The  $E$  map computed from the solution with the best ABSFOM = 1.18 revealed the positions of 18 non-

hydrogen atoms. A further cycle of structure factor and Fourier calculations gave the missing six non-hydrogen atoms ( $R=0.214$ ). Block-diagonal refinement of the atomic coordinates with isotropic and anisotropic thermal parameters resulted in a final  $R$  of 0.07 for the observed reflexions (0.083 for all 2813). The H atoms were located geometrically and then refined isotropically in the last two cycles. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the parameters of the H atoms and the C-H distances in Table 2, the bond distances and angles in Fig. 1.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31227 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates ( $\times 10^5$ ) and anisotropic thermal parameters ( $\times 10^4$ )

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form

$$\exp[-b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl].$$

	$x$	$y$	$z$	$b_{11}$	$b_{12}$	$b_{13}$	$b_{22}$	$b_{23}$	$b_{33}$
S(1)	7208 (17)	6514 (7)	-22950 (12)	129 (2)	-14 (1)	-1 (2)	27 (0)	4 (1)	60 (1)
S(2)	32144 (16)	19084 (7)	-2540 (12)	120 (2)	4 (1)	-11 (2)	21 (0)	2 (1)	75 (1)
S(3)	31530 (18)	24997 (7)	-33125 (11)	151 (2)	-32 (1)	23 (3)	28 (0)	-11 (1)	56 (1)
C(1)	27025 (67)	9016 (28)	-30484 (44)	141 (8)	-4 (6)	27 (9)	23 (1)	1 (4)	57 (4)
C(11)	16761 (63)	2879 (25)	-10407 (43)	118 (8)	2 (5)	11 (9)	19 (1)	11 (4)	61 (4)
C(12)	21801 (72)	-4012 (30)	-10974 (49)	153 (9)	-9 (6)	63 (10)	25 (1)	-12 (4)	77 (4)
C(13)	29706 (74)	-7091 (31)	-1763 (57)	150 (9)	7 (7)	45 (12)	24 (2)	14 (5)	109 (5)
C(14)	32255 (77)	-3489 (32)	8458 (53)	161 (10)	17 (7)	28 (12)	30 (2)	41 (5)	90 (5)
C(15)	26976 (70)	3202 (31)	9121 (45)	147 (9)	-10 (7)	36 (10)	32 (2)	0 (4)	55 (4)
C(16)	19040 (63)	6437 (26)	-74 (45)	118 (8)	0 (5)	21 (9)	19 (1)	4 (4)	65 (4)
C(2)	13560 (65)	13926 (28)	1210 (43)	127 (8)	-4 (6)	33 (9)	25 (1)	-6 (4)	53 (4)
C(21)	23339 (61)	27432 (26)	-3272 (42)	111 (7)	-0 (5)	1 (9)	20 (1)	-4 (4)	56 (3)
C(22)	25335 (70)	31721 (30)	6114 (46)	145 (9)	-8 (6)	1 (10)	27 (1)	-14 (4)	61 (4)
C(23)	19673 (76)	38428 (31)	5745 (51)	164 (10)	-3 (7)	25 (11)	29 (2)	-30 (5)	79 (4)
C(24)	11997 (75)	40791 (28)	-4186 (53)	175 (10)	11 (6)	65 (12)	18 (1)	-12 (5)	102 (5)
C(25)	9891 (69)	36585 (28)	-13686 (48)	134 (8)	8 (6)	9 (10)	23 (1)	2 (4)	71 (4)
C(26)	15482 (58)	29830 (25)	-13508 (41)	98 (7)	0 (5)	12 (8)	19 (1)	-4 (4)	56 (3)
C(3)	12221 (65)	25403 (25)	-24170 (43)	119 (8)	-1 (5)	28 (9)	19 (1)	-14 (4)	63 (4)
C(31)	24184 (62)	19309 (26)	-44053 (41)	118 (8)	8 (5)	21 (9)	24 (1)	-6 (4)	51 (3)
C(32)	20596 (74)	21993 (34)	-55005 (44)	161 (9)	26 (7)	18 (10)	37 (2)	10 (5)	48 (4)
C(33)	14792 (76)	17874 (34)	-63788 (46)	175 (10)	45 (7)	-22 (10)	39 (2)	-8 (5)	47 (4)
C(34)	19937 (73)	11103 (35)	-61844 (46)	141 (9)	0 (7)	-11 (10)	44 (2)	-30 (5)	55 (4)
C(35)	15697 (72)	8194 (32)	-50994 (49)	147 (9)	-9 (7)	6 (10)	30 (2)	-23 (5)	69 (4)
C(36)	21986 (60)	12367 (28)	-42034 (42)	94 (7)	0 (5)	-3 (8)	28 (1)	-9 (4)	49 (3)

**Discussion.** Study of the conformational behaviour of the title compound (Ollis, Stoddart & Nógrádi, 1975)

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature parameters ( $\text{\AA}^2$ ) for the H atoms

	x	y	z	B	C-H $\text{\AA}$
H(12)	207 (10)	-64 (4)	-184 (7)	4.4 (18)	1.00 (8)
H(13)	341 (11)	-115 (4)	-29 (7)	6.0 (21)	0.96 (8)
H(14)	387 (9)	-55 (3)	145 (6)	3.4 (16)	0.95 (7)
H(15)	289 (8)	56 (3)	159 (6)	2.7 (15)	0.92 (7)
H(2A)	103 (8)	145 (3)	84 (6)	2.4 (14)	0.87 (6)
H(2B)	39 (7)	151 (3)	-39 (5)	1.2 (11)	0.99 (6)
H(22)	315 (8)	301 (4)	132 (6)	3.1 (15)	0.99 (7)
H(23)	207 (8)	417 (4)	119 (6)	2.6 (15)	0.96 (7)
H(24)	69 (9)	449 (4)	-45 (6)	4.0 (17)	0.90 (7)
H(25)	24 (11)	378 (5)	-207 (8)	6.2 (24)	1.03 (9)
H(3A)	100 (8)	208 (3)	-217 (5)	1.4 (13)	0.95 (6)
H(3B)	54 (11)	278 (5)	-266 (7)	6.4 (23)	0.77 (9)
H(32)	229 (9)	266 (3)	-567 (6)	2.7 (15)	0.95 (7)
H(33)	119 (11)	201 (4)	-710 (7)	5.3 (19)	0.97 (8)
H(34)	64 (9)	81 (4)	-672 (6)	3.1 (16)	0.96 (7)
H(35)	131 (7)	33 (3)	-487 (5)	1.0 (12)	1.01 (6)
H(1A)	333 (7)	119 (3)	-255 (5)	1.5 (12)	0.94 (6)
H(1B)	335 (9)	54 (4)	-308 (6)	3.7 (17)	0.87 (7)

showed that in solution it was present in an asymmetrical helix conformation in rapid ring-inversion equilibrium with its mirror image. It was postulated that the source of the energy barrier of this ring inversion ( $\Delta G^\ddagger = 9.3 \pm 0.2 \text{ kcal mol}^{-1}$ ) was mainly the transannular interaction between the S atoms and  $\text{CH}_2$  groups. The X-ray analysis was carried out in order to compare its conformation in solution with that in the crystal, to obtain accurate bond distances and angles for force-field calculation of the conformations, and finally to extend our previous investigations (Argay, Kálmán, Nahlovski & Ribár, 1975) concerning the nature of C-S bonds.

The conformation of the twisted dodecene ring (Fig. 2) can be described by the 12 torsion angles (Table 3) (Klyne & Prelog, 1960). In the dodecene ring there are three kinds of torsion angles. The values around  $0^\circ$  are in agreement with the fixed planarity of the benzene rings, while those containing a  $\text{C}_m\text{-S}$  torsion axis provide nearly maximum ( $180^\circ$ ) spatial separations of these rings. The other six angles in which the torsion

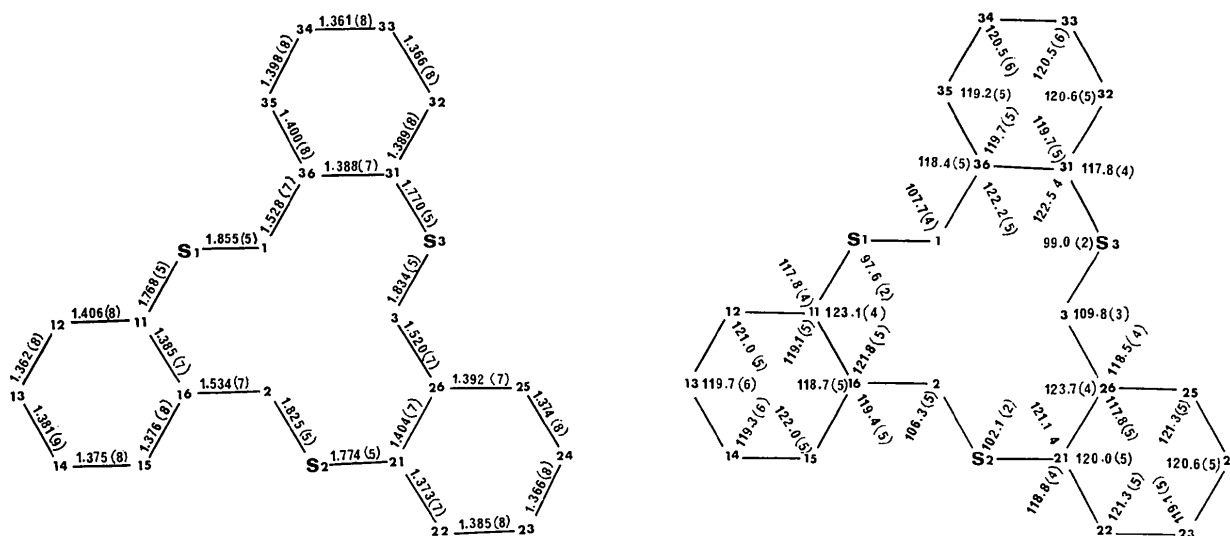


Fig. 1. Bond distances and angles with their e.s.d.'s and the atomic numbering. The bare numbers are for C atoms.

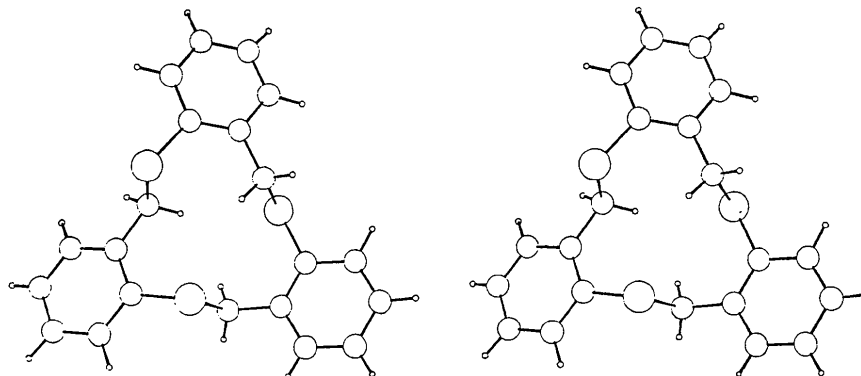


Fig. 2. An ORTEP stereo drawing of the title compound.

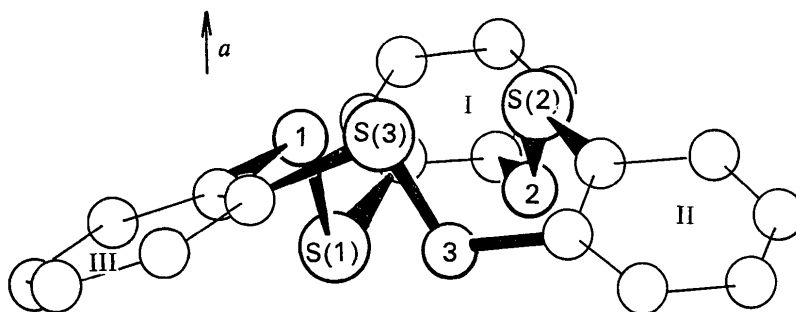


Fig. 3. A side-view of the molecule.

Table 3. The observed ( $\varphi$ ) and idealized ( $\varphi_0$ ) torsion angles of the dodecene ring

The types of torsion axes are given in the second column.

Angle	Axis	$\varphi$	$\varphi_0$	$\Delta\varphi$
C(11)–S(1)–C(1)–C(36)	S–C <sub>m</sub>	179.7°	180°	–0.3°
S(1)–C(1)–C(36)–C(31)	C <sub>m</sub> –C <sub>φ</sub>	110.4	90	20.4
C(1)–C(36)–C(31)–S(3)	C <sub>φ</sub> –C <sub>φ</sub>	–4.7	0	–4.7
C(36)–C(31)–S(3)–C(3)	C <sub>φ</sub> –S	–73.4	–90	16.6
C(31)–S(3)–C(3)–C(26)	S–C <sub>m</sub>	–182.8	–180	–2.8
S(3)–C(3)–C(26)–C(21)	C <sub>m</sub> –C <sub>φ</sub>	–83.1	–90	6.9
C(3)–C(26)–C(21)–S(2)	C <sub>φ</sub> –C <sub>φ</sub>	6.5	0	6.5
C(26)–C(21)–S(2)–C(2)	C <sub>φ</sub> –S	–84.9	–90	5.1
C(21)–S(2)–C(2)–C(16)	S–C <sub>m</sub>	–189.9	–180	–9.9
S(2)–C(2)–C(16)–C(11)	C <sub>m</sub> –C <sub>φ</sub>	–92.0	–90	–2.0
C(2)–C(16)–C(11)–S(1)	C <sub>φ</sub> –C <sub>φ</sub>	–0.8	0	–0.8
C(16)–C(11)–S(1)–C(1)	C <sub>φ</sub> –S	96.3	90	6.3

axis is either a C<sub>φ</sub>–S or a C<sub>φ</sub>–C<sub>m</sub> bond, despite significant deviations, approach 90°. If we accept the ideal 90° for these angles then good agreement is obtained between the sums of the absolute values of the observed ( $\sum\varphi = 1079.1^\circ$ ) and the ideal ( $\sum\varphi_0 = 1080^\circ \equiv 6\pi$ ) torsion angles. It is noticeable that the sequence (with an equal difference of 90°) of the ideal torsion angles shows a  $3\pi$  unit of a 'saw-tooth'-like function in both *clockwise* and *anticlockwise* directions if the zero point of this function is fixed to the conformational angle: C(3)–C(26)–C(21)–S(2) = 0°. Naturally, the sequence of experimental torsion angles does not show such a perfect regularity.

As seen from the side-view of the molecule (Fig. 3) the plane (0.9919X – 0.1172Y – 0.0482Z = 2.0775) formed by C(1), S(2), and S(3) is nearly parallel (3.9°) to that of C(2), C(3), and S(1). These planes, which are almost perpendicular to **a**, can be regarded as an upper and a lower slice of the sandwich-like molecule. The best planes of the three benzene rings make the following angles with that of the upper slice [C(1), S(2),

S(3)] 29.8°, 29.9°, and 13.8°, respectively. The angles between the planes of the benzene rings are: I/II 1.3°, I/III 28.4°, and II/III 27.8° which show that only rings I and II are parallel. The molecule in the crystal, as in solution, shows no symmetry.

The average S<sup>II</sup>–C length of 1.771 Å agrees well with those found recently in 2,2'-diaminodiphenyl disulphide (Lee & Bryant, 1970) indicating S<sup>II</sup>–C(sp<sup>2</sup>) single bonds in accordance with the expected value (Truter, 1962). The mean S<sup>II</sup>–C(sp<sup>3</sup>) length of 1.838 Å is similar to the mean of the S<sup>II</sup>–C(sp<sup>3</sup>) distances (1.843 Å) given by Jones, Bernal, Frey & Koetzle (1974) and near the average of the S<sup>II</sup>–C(sp<sup>3</sup>) lengths (1.818 Å) observed in various thiazoline derivatives (Argay, Kálmán, Nahlovski & Ribár, 1975). Thus the most probable S<sup>II</sup>–C(sp<sup>3</sup>) single bond is somewhat longer than the expected 1.81 Å given by Truter (1962). The average C–S–C bond angle of 99.6° is in agreement with literature data.

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