Acta Cryst. (1972). B**28**, 1255

The Crystal Structure of 2,11,20-Trithia[3.3.3](1,3,5)cyclophane

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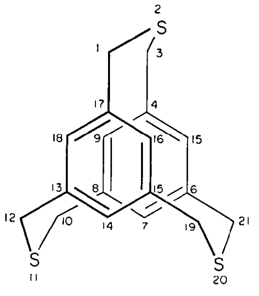
(*Received* 10 *September* 1971)

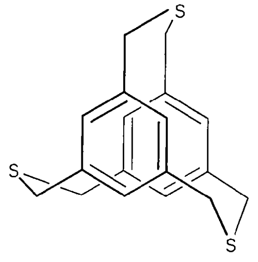
Crystals of 2,11,20-trithia[3.3.3] (1,3,5)cyclophane, $C_{18}H_{18}S_3$, are monoclinic, probably $P2_1/c$, with $a=13{\cdot}19$ (2), $b=33{\cdot}35$ (5), $c=7{\cdot}06$ (1) Å, $\beta=93{\cdot}18$ (5)°, $Z=8$. A subset of weak reflexions is ignored, and the crystal structure is described in terms of a unit cell for which b is halved, and for which the space group is $C2/c$. Three-dimensional intensity data were recorded with a four-circle diffractometer and scintillation counter. The approximate structure was deduced from the Patterson synthesis and refined by block-diagonal least-squares analysis to a final R index of 0·064. Although the structure is necessarily disordered, the essential features of the molecule are revealed. The phenyl rings are parallel, and overlap each other quite precisely with an interplanar separation of 3·19 Å. There is some evidence of rapid flipping of one of the C–S–C linkages.

Introduction

2,11,20-Trithia[3.3.3] (1,3,5)cyclophane is one of a number of thia-bridged cyclophanes prepared by Professor Boekelheide and associates, and used in the synthesis of corresponding C=C bridged cyclophanes (Boekelheide & Hollins, 1970; Mitchell & Boekelheide, 1970; Boekelheide & Lawson, 1970). The material has also been prepared by Vögtle (1970), who reports that the nuclear magnetic resonance (n.m.r.) spectrum consists only of two sharp peaks, assigned to the aromatic and to the methylenic protons. The implied equivalence of the methylenic protons is difficult to reconcile with any static model of the molecule, for which the two conformational isomers (*a*) and (*b*) seem possible. Interconversion of these isomers can occur if one or more of the bridges can be induced to flip from one stable position to another, and if such flipping occurred rapidly enough, equivalence of the protons would be inferred. The conformation in the crystal is found to be exclusively (*a*), but the diffraction effects are consistent with temperature-dependent flipping of one of the bridges.



(*a*)



(*b*)

Experimental

Crystal data

$C_{18}H_{18}S_3$; F.W. 330·5; Monoclinic, $a=13{\cdot}19$ (2), $b=33{\cdot}35$ (5), $c=7{\cdot}06$ (1) Å, $\beta=93{\cdot}18$ (5)°; $V=3102$ Å^{-3}; $D_m=1{\cdot}39$ (2); $Z=8$, $D_x=1{\cdot}41$; $\mu=40{\cdot}2$ cm^{-1}, λ(Cu $K\alpha$) = 1·5418 Å.

The absences noted on Weissenberg and precession photographs are consistent with the space group $P2_1/c$. However, it was found that the reflexions could be divided into two subsets, conveniently designated as 'strong' and 'weak'. Reflexions in the latter subset were invariably very weak or absent, and because this subset includes the systematic absences characteristic of $P2_1/c$, the space group assignment must be regarded as tentative. (At the working temperature of 20 °C it was not possible to distinguish between $P2_1/a$ and $P2_1/c$, there being no observable $h0l$ reflexions with either h or l odd. However, a few very weak reflexions with h odd appeared on a precession photograph of this zone taken at −180 °C.) Reflexions in the 'strong' subset (for which the intensity distribution was more typical) can be indexed for a monoclinic cell identical with that specified above except that the b axis is halved. The space group characteristic of this subset is Cc or $C2/c$. The approximate structure to be described is consistent with $C2/c$.

The crystalline material consisted of colourless needles, elongated along **c**. The specimen used for data collection was a fragment of such a needle, of dimensions 0·04 × 0·04 × 0·18 mm, mounted about the long axis. The intensities were measured with a Picker four-circle diffractometer and scintillation counter, using nickel-filtered Cu $K\alpha$ radiation and pulse-height discrimination. The θ–2θ scan method was used, with 20-second background counts at the beginning and end of each scan. The scan range was 2° for $2\theta < 100°$, and 3° otherwise. Reflexions were regarded as observed only if the net count exceeded 7 (deca)counts and 10 % of the corresponding background count. Within the re-

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gion explored ($2\theta \le 130°$; $\sin \theta/\lambda \le 0{\cdot}59$), 837 of a possible 1328 reflexions were observed. The intensities were corrected for absorption, using a program of Ahmed (1970); corrections ranged from 1·23 to 1·43.

No attempt was made to measure all the reflexions of the weak subset. However, this subset was partially characterized by the following procedures.

(1) All independent reflexions with $2\theta \le 50°$ were measured. Of 399 accessible reflexions in the weak subset, 147 were observed above background, and their average intensity was 22 (deca)counts. Of 129 accessible reflexions in the strong subset, 121 were observed, and their average intensity was 1730 (deca)counts.

(2) Precession photographs of the *h*0*l* and 0*kl* zones were taken both at room temperature and at −180°C. There was no obvious change in the intensities of the strong subset, but those of the weak subset were about five times more intense at the lower temperature. The distribution of relative intensity within each subset did not appear to change appreciably with temperature. The effect of temperature on the weak subset was found to be completely reversible. These reflexions are invariably sharp when observed, and are indistinguishable in shape and size from those of the strong subset.

(3) The intensities of 002 (a strong reflexion of the strong subset) and 012 (one of the strongest reflexions of the weak subset) were measured diffractometrically at nominal temperatures of −180, 20, and 80°C. The net counts recorded at these temperatures were: 002: 32,200, 32,800 and 31,400 (deca)counts; 012: 1030(11), 190(5) and 7(3) (deca)counts.

Structure determination

The space group $C2/c$ was assumed for the approximate structure defined by the strong subset of reflexions. This assumption demands that the molecule occupies either a centre of symmetry or a twofold axis. The molecule cannot have a centre of symmetry and (as it turns out) does not have a twofold axis. Any structure conforming to this space group must therefore be disordered.

A reasonable trial structure, disordered by twofold rotation, was deduced from the Patterson synthesis and refined by block-diagonal least squares. The program used was that of Ahmed, Hall, Pippy & Huber (1966), which minimizes the quantity $\sum w\Delta F^2$. The weighting scheme (chosen to ensure reasonable constancy of the weighted residual as a function of F_o and 2θ) was $w = w_1 w_2$ where

$$\begin{aligned} w_1 &= (F_o/25)^2 && \text{for } F_o < 25 \\ &= 25/F_o && \text{for } F_o \ge 25 \\ w_2 &= 2{\cdot}5 \sin^2\theta && \text{for } \sin^2\theta < 0{\cdot}4 \\ &= 1 && \text{for } \sin^2\theta \ge 0{\cdot}4\,. \end{aligned}$$

(The nominal minimum value of F_o is 8.)

The hydrogen atoms were assumed to lie in reason-

Table 1. *Final atomic parameters and their e.s.d.'s*

These are referred to a unit cell for which $b = 16{\cdot}68$ Å, and the space group is $C2/c$. S(2) is treated as a half-atom. The quantities given are fractional coordinates $\times 10^4$ for non-hydrogen, $\times 10^3$ for hydrogen atoms [equivalent positions $(0,0,0;\ \frac{1}{2},\frac{1}{2},0) \pm (x,y,z;\ x,\bar{y},\frac{1}{2}+z)$]; $U_{ij} \times 10^4$ Å², for non-hydrogen atoms (T.F. $= \exp[-2\pi^2(U_{11}a^{*2}h^2 + + + 2U_{12}a^*b^*hk + +)]$; r.m.s. displacements D_i along the principal axes of the vibration ellipsoids, in Å; isotropic Debye–Waller factors B, in Å² (hydrogen atoms only).

Atom		x	y	z	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
S(2)		598(3)	4263(2)	2589(5)	885(20)	-65(14)	254(18)	360(14)	-8(16)	1066(24)
S(20)	[S(11')]	1918(1)	617(1)	3702(2)	583(7)	145(8)	92(6)	626(7)	276(8)	756(8)
C(3)	[C(1')]	262(6)	3868(4)	589(14)	1025(54)	165(37)	592(50)	552(38)	369(41)	1402(70)
C(4)	[C(17')]	322(4)	2975(4)	374(8)	690(33)	116(28)	232(25)	562(32)	202(27)	542(30)
C(5)	[C(18')]	1180(4)	2549(3)	894(7)	638(31)	-40(27)	188(23)	462(27)	68(24)	448(28)
C(6)	[C(13')]	1196(4)	1715(3)	910(6)	508(26)	-17(23)	133(19)	504(25)	-17(21)	273(22)
C(7)	[C(14')]	319(4)	1309(3)	319(7)	574(30)	6(25)	84(20)	537(30)	-89(23)	364(25)
C(8)	[C(15')]	-562(4)	1719(4)	-190(6)	554(30)	50(27)	33(20)	785(38)	2(24)	250(23)
C(9)	[C(16')]	-550(4)	2552(4)	-186(8)	678(35)	216(31)	151(25)	790(39)	211(28)	446(30)
C(10)	[C(19')]	-1545(5)	1283(5)	-585(8)	604(35)	-22(34)	-23(25)	1088(51)	-203(33)	472(32)
C(21)	[C(12')]	2120(4)	1278(3)	1702(8)	467(29)	-24(25)	102(23)	589(31)	-4(26)	537(30)

Atom	D_1	D_2	D_3
S(2)	0.18	0.27	0.34
S(20)	0.19	0.24	0.32
C(3)	0.20	0.26	0.43
C(4)	0.18	0.23	0.31
C(5)	0.18	0.22	0.27
C(6)	0.15	0.22	0.24
C(7)	0.18	0.24	0.24
C(8)	0.16	0.23	0.28
C(9)	0.18	0.23	0.32
C(10)	0.20	0.25	0.34
C(21)	0.20	0.24	0.25

Atom	x	y	z	B
H(3a)	26(6)	412(4)	-29(10)	5.0(1.7)
H(3b)	98(9)	399(7)	118(16)	11.2(3.1)
H(5)	182(4)	281(3)	136(7)	1.5(1.0)
H(7)	34(4)	80(4)	40(8)	3.3(1.3)
H(9)	-112(4)	285(3)	-42(8)	2.9(1.2)
H(10a)	-150(4)	92(3)	-167(8)	3.0(1.2)
H(10b)	-209(5)	161(4)	-80(10)	4.8(1.5)
H(21a)	266(4)	163(4)	207(9)	3.7(1.3)
H(21b)	236(4)	90(3)	81(7)	2.9(1.2)

able positions, and their parameters were refined, assuming isotropic thermal motion. The thermal motion of the non-hydrogen atoms was allowed to vary anisotropically. The atomic scattering-factor curves used were those of Hanson, Herman, Lea & Skillman (1964) for non-hydrogen, and that of Stewart, Davidson & Simpson (1965) for hydrogen. The curve for sulphur was corrected for the real part ($\Delta f'=0{\cdot}3$) of the anomalous scattering (*International Tables for X-ray Crystallography*, 1962). In the final cycle of refinement no coordinate shift of a non-hydrogen atom exceeded one quarter of the corresponding estimated standard deviation. The final parameters are given in Table 1. The observed and calculated structure amplitudes are listed in Table 2. The final agreement index ($R=\sum|\Delta F|/\sum|F_o|$) is 0·064, for observed reflexions only. The agreement is satisfactory and, within the limiting assumptions involved, there can be no doubt of the essential correctness of the proposed structure.

Discussion

Details of the molecular structure are given in Fig. 1 and in Tables 3 and 4. Because of the disorder the aver-

Table 2. *Observed and calculated structure amplitudes* (× 10)

An asterisk denotes the threshold value of an unobserved reflexion. The indexing assumes the subcell for which the *b* axis has been halved, and the space group is *C*2/*c*.

L	FO	FC
H= 0, K= 0		
2	1465	1462
4	72*	-43
6	56*	-9
8	87	65
H= 2, K= 0		
0	829	801
2	426	384
4	312	324
6	224	-252
8	80*	17
H= -2, K= 0		
2	1780	1815
4	1640	1666
6	289	268
8	82*	14
H= 4, K= 0		
0	256	252
2	636	-646
4	81*	-37
6	247	264
H= -4, K= 0		
2	529	521
4	740	734
6	240	252
8	153	172
H= 6, K= 0		
0	282	255
2	570	571
4	247	-261
6	277	-274
H= -6, K= 0		
2	176	-170
4	228	-241
6	354	414
H= 8, K= 0		
0	673	-672
2	83*	-59
4	236	-223
6	227	-250
H= -8, K= 0		
2	332	328
4	230	228
6	107	-59
H= 10, K= 0		
0	89*	25
2	520	-517
4	335	-334
6	73*	13
H= -10, K= 0		
2	265	270
4	315	-322
6	83*	-21
H= 12, K= 0		
0	352	-370
2	55*	85
4	84*	16
H= -12, K= 0		
2	260	-279
4	123	115
H= 14, K= 0		
0	86*	-78
2	162	-143
H= -14, K= 0		
2	53	-22
H= 1, K= 1		
0	214	200
1	767	-780
2	839	839
3	136	-143
4	329	-328
5	87*	3
6	159	-154
7	159	171
8	62*	13
H= -1, K= 1		
1	853	-823
2	250	233
3	579	-563
4	165	-155
5	146	-146
6	329	349
7	57*	14
8	83*	4
H= 3, K= 1		
0	1661	-1671
1	68	56
2	157	-180
3	269	262
4	278	254
5	50	65
6	57*	66
7	54*	4
8	76*	-26
H= -3, K= 1		
1	519	524
2	451	420
3	66*	-4
4	509	514
5	674	-665
6	57*	23
7	257	-253
8	81*	-15
H= 5, K= 1		
0	874	874
1	169	-205
2	251	-286
3	74*	33
4	174	-172
5	123	103
6	97*	77
7	68*	-45
H= -5, K= 1		
1	148	-117
2	164	-157
3	115	-107
4	461	-463
5	91*	73
6	57*	97
7	156	-199
H= 7, K= 1		
0	147	-167
1	428	417
2	289	283
3	217	-203
4	130	127
5	210	-204
6	251	-251
7	78*	-18
H= -7, K= 1		
1	70*	-21
2	534	-551
3	81*	-8
4	265	264
5	55*	36
6	56*	40
7	65*	-6
H= 9, K= 1		
0	58	68
1	389	-393
2	490	-503
3	240	-235
4	56*	-50
5	93*	-16
6	82	33
H= -9, K= 1		
1	237	240
2	99	112
3	215	-213
4	55*	56
5	135	-125
6	180	-174
7	73*	-25
H= 11, K= 1		
0	151	156
1	278	-272
2	56	37
3	148	-127
4	51*	-73
5	80	-15
H= -11, K= 1		
1	327	331
2	247	-244
3	145	131
4	166	-146
5	88*	66
6	74*	6
H= 13, K= 1		
0	183	-182
1	93*	29
2	90*	62
3	84*	33
4	73*	63
H= -13, K= 1		
1	158	218
2	92	-46
3	347	344
4	143	138
H= 15, K= 1		
0	77*	65
1	74*	-57
H= -15, K= 1		
1	76*	-21
2	109	95
H= 0, K= 2		
0	564	-548
1	355	-316
2	1253	-1226
3	375	-360
4	363	-358
5	448	442
6	57*	14
7	110	80
8	82*	37
H= 2, K= 2		
0	1016	-1010
1	1575	1626
2	317	298
3	114	104
4	323	310
5	171	-175
6	160	-174
7	55*	31
8	66	-67
H= -2, K= 2		
1	509	472
2	1724	-1710
3	62*	32
4	207	-196
5	87*	-78
6	114	-111
7	96*	-99
8	82*	-45
H= 4, K= 2		
0	347	343
1	472	-465
2	304	-313
3	237	228
4	82*	-17
5	204	207
6	97*	100
7	119	-73
H= -4, K= 2		
1	131	110
2	378	378
3	191	-193
4	494	-481
5	162	-160
6	458	-464
7	54*	-105
8	77*	-65
H= 6, K= 2		
0	344	344
1	194	183
2	219	244
3	80*	38
4	174	-174
5	96*	-102
6	56*	61
7	51	51
H= -6, K= 2		
1	560	-574
2	69*	-14
3	144	124
4	86	-86
5	304	307
6	97*	1
7	89	15
H= 8, K= 2		
0	458	-447
1	214	210
2	143	127
3	103	96
4	273	284
5	125	-157
6	136	136
H= -8, K= 2		
1	159	-164
2	290	288
3	173	190
4	278	288
5	251	-246
6	93*	72
7	79*	54
H= 10, K= 2		
0	214	218
1	514	-515
2	94	90
3	101	-94
4	55*	37
5	89*	24
H= -10, K= 2		
1	133	-139
2	161	163
3	209	-216
4	182	-171
5	53*	-22
6	104	97
H= 12, K= 2		
0	56*	90
1	172	126
2	216	234
3	100	-59
4	87	16
H= -12, K= 2		
1	105	92
2	55*	-68
3	262	264
4	89	27
5	75	13
H= 14, K= 2		
0	87*	6
1	85*	-22
2	127	-102
3	90	62
H= -14, K= 2		
1	86*	57
2	188	177
3	79*	0
H= 1, K= 3		
0	516	-488
1	47	-34
2	588	562
3	254	-250
4	105	-116
5	369	-357
6	57*	-2
7	96*	-12
8	79*	16
H= -1, K= 3		
1	1441	-1409
2	1084	-1034
3	560	533
4	158	-178
5	247	243
6	57*	38
7	56*	-44
8	81*	-29
H= 3, K= 3		
0	156	189
1	157	-214
2	99	85
3	113	-79
4	212	216
5	383	-381
6	57*	-67
7	171	-166
H= -3, K= 3		
1	483	499
2	302	304
3	236	232
4	259	-255
5	376	-386
6	152	-204
7	55*	72
8	100	-77
H= 5, K= 3		
0	382	376
1	1318	-1309
2	68*	-55
3	543	-531
4	201	-211
5	167	204
6	97*	15
7	87*	33
H= -5, K= 3		
1	227	226
2	363	343
3	418	-414
4	84*	-12
5	168	176
6	115	-122
7	115	101
H= 7, K= 3		
0	72*	30
1	560	581
2	79*	76
3	131	-138
4	115	86
5	111	-84
6	133	108
7	86	41
H= -7, K= 3		
1	584	582
2	108	-92
3	437	452
4	240	237
5	56	81
6	108	117
7	95	-90
H= 9, K= 3		
0	85*	-18
1	59	-92
2	90*	6
3	146	133
4	209	230
5	120	109
6	54	71
H= -9, K= 3		
1	398	411
2	241	228
3	181	-173
4	109	106
5	55*	19
6	86*	10
H= 11, K= 3		
0	211	224
1	95*	35
2	136	108
3	153	-154
4	50*	-75
5	78*	-4
H= -11, K= 3		
1	169	-172
2	55*	-76
3	56	-90
4	53*	24
5	215	207
6	99	99
H= 13, K= 3		
0	53*	-61
1	120	127
2	69*	-25
3	127	77
H= -13, K= 3		
1	53*	75
2	100	59
3	117	88
4	79*	41
H= 15, K= 3		
0	85	-10
1	129	-122
H= -15, K= 3		
1	74*	-36
2	71*	32
H= 0, K= 4		
0	1149	-1141
1	155	-131
2	169	-110
3	729	-710
4	88	-62
5	209	231
6	98*	24
7	95*	-84
8	79*	57
H= 2, K= 4		
0	66	18
1	1131	1128
2	58*	69
3	372	-355
4	104	-102
5	441	-449
6	58	85
7	122	-115
H= -2, K= 4		
1	384	370
2	371	-330
3	474	464
4	78*	-93
5	54	68
6	97*	-28
7	210	-194
8	78*	-71
H= 4, K= 4		
0	490	-479
1	905	-878
2	248	-245
3	74	-78
4	110	128
5	94*	-17
6	115	-50
7	119	-95
H= -4, K= 4		
1	555	571
2	98	83
3	548	-539
4	82*	-78
5	92*	-82
6	58*	19
7	155	141
H= 6, K= 4		
0	205	-199
1	452	-449
2	104	-83
3	401	-404
4	51*	-87
5	97*	-32
6	115	64
7	116	129
H= -6, K= 4		
1	370	-398
2	577	-574
3	330	322
4	88*	-36
5	202	192
6	96*	15
7	86*	-35
H= 8, K= 4		
0	80*	38
1	82*	62
2	87*	27
3	365	369
4	161	155
5	95*	-79
6	65*	21
H= -8, K= 4		
1	397	386
2	187	-189
3	489	490
4	274	-272
5	169	-193
6	141	-132
7	76*	-22
H= 10, K= 4		
0	52*	41
1	286	-280
2	95*	65
3	56*	50
4	94*	16
5	139	112
H= -10, K= 4		
1	238	-232
2	93*	-10
3	55*	-70
4	55*	13
5	129	117
6	133	-115
H= 12, K= 4		
0	105	60
1	211	195
2	98	-53
3	89	-67
4	80	-40
H= -12, K= 4		
1	165	-181
2	95*	-30
3	149	145
4	87*	-24
5	76*	38
H= 14, K= 4		
0	85*	-68
1	82*	-35
2	77*	62
H= -14, K= 4		
1	182	159
2	81*	9
3	115	-103
H= 1, K= 5		
0	77	44
1	52*	-13
2	375	-393
3	455	-448
4	80*	-39
5	91*	13
6	98*	59
7	219	202
H= -1, K= 5		
1	963	-936
2	283	-288
3	679	654
4	153	153
5	122	86
6	153	-201
7	111	-49
8	87	-33
H= 3, K= 5		
0	552	541
1	251	259
2	137	-129
3	814	821
4	119	-87
5	54	-3
6	98*	-10
7	59*	-55
H= -3, K= 5		
1	541	536
2	167	-139
3	258	259
4	187	-192
5	137	-153
6	57*	-38
7	92*	61
H= 5, K= 5		
0	660	-619
1	67*	-25
2	73*	11
3	81*	-93
4	94	96
5	227	224
6	108	11
7	83*	24
H= -5, K= 5		
1	473	-463
2	78	-72
3	413	-412
4	117	100
5	134	128
6	97*	-1
7	160	155
H= 7, K= 5		
0	76*	1
1	533	576
2	83*	-13
3	176	-164
4	141	-135
5	96*	-74
6	105	76
H= -7, K= 5		
1	184	-159
2	81*	27
3	131	140
4	299	-293
5	96*	27
6	93	-103
7	156	-150
H= 9, K= 5		
0	112	-96
1	90*	13
2	237	229
3	216	230
4	56*	62
5	124	69
6	75*	-29
H= -9, K= 5		
1	373	393
2	90*	43
3	353	-342
4	168	-168
5	94*	-100
6	88	-70
H= 11, K= 5		
0	95*	-28
1	96*	57
2	96*	-47
3	150	-162
4	87*	3
5	84	52
H= -11, K= 5		
1	302	-319
2	138	121
3	95*	-63
4	91*	78
5	138	122
H= 13, K= 5		
0	91*	67
1	89*	92
2	86*	31
3	78*	61
H= -13, K= 5		
1	90	96
2	89*	8
3	84*	4
4	75*	-48
H= 0, K= 6		
0	1076	-1065
1	90	-100
2	276	251
3	315	-312
4	136	147
5	199	207
6	58*	72
7	137	124
H= 2, K= 6		
0	56*	6
1	465	443
2	65	-47
3	74*	-54
4	296	-292
5	118	96
6	102	104
7	147	145
H= -2, K= 6		
1	66	64
2	555	541
3	498	497
4	265	-260
5	121	91
6	58*	-19
7	91*	-69
H= 4, K= 6		
0	106	-94
1	66*	48
2	325	331
3	654	652
4	122	111
5	169	170
6	96	-105
7	84*	-10
H= -4, K= 6		
1	287	305
2	415	-423
3	475	-469
4	87*	3
5	95*	39
6	210	217
7	216	215
H= 6, K= 6		
0	73*	-48
1	218	223
2	354	-361
3	223	-237
4	126	121
5	96*	72
6	91*	11
7	74*	51
H= -6, K= 6		
1	776	-769
2	169	155
3	85*	21
4	170	167
5	97*	15
6	99	-85
7	81*	-46
H= 8, K= 6		
0	394	391
1	86	80
2	90*	-46
3	233	238
4	146	-135
5	117	-94
6	124	-99
H= -8, K= 6		
1	123	130
2	239	-249
3	92*	-52
4	95	-65
5	190	-205
6	87*	-25
H= 10, K= 6		
0	54*	-115
1	104	-77
2	56*	-31
3	55*	61
4	111	96
5	111	92
H= -10, K= 6		
1	126	-118
2	180	-178
3	148	-140
4	157	170
5	87	-71
6	74*	6
H= 12, K= 6		
0	54*	54
1	93	92
2	100	-109
3	65*	-65
4	74*	-39
H= -12, K= 6		
1	199	-204
2	93*	81
3	89*	35
4	82*	-28
H= 14, K= 6		
0	80*	0
1	77*	-1
2	81	54
H= -14, K= 6		
1	137	131
2	87	-86
H= 1, K= 7		
0	833	814
1	214	218
2	651	-665
3	267	-265
4	315	313
5	55*	83
6	97	109
7	105	137
H= -1, K= 7		
1	185	-175
2	956	918
3	291	291
4	449	442
5	94*	46
6	138	-140
7	50	-72
H= 3, K= 7		
0	636	624
1	153	169
2	241	238
3	305	306
4	233	-236
5	96*	-16
6	56*	-48
7	84*	18
H= -3, K= 7		
1	266	258
2	161	-169
3	78*	23
4	221	196
5	55*	-16
6	156	158
7	87*	30
H= 5, K= 7		
0	392	-389
1	81	71
2	152	188
3	119	135
4	252	257
5	56*	56
6	51*	-1
7	76*	-16
H= -5, K= 7		
1	211	-217
2	77*	-33
3	92	-91
4	284	289
5	96	93
6	180	183
7	82*	29
H= 7, K= 7		
0	82*	42
1	84*	89
2	96	-107
3	110	-115
4	232	-242
5	94*	-43
6	83*	-33
H= -7, K= 7		
1	229	-227
2	548	554
3	164	123
4	156	-155
5	56*	-13
6	89*	-46
H= 9, K= 7		
0	105	-120
1	53*	27
2	206	156
3	161	153
4	218	-156
5	85*	-20
H= -9, K= 7		
1	161	147
2	151	-154
3	120	-90
4	55*	-67
5	50*	-28
6	187	152
H= 11, K= 7		
0	287	-258
1	56*	-12
2	155	-202
3	90*	-48
4	81*	52
H= -11, K= 7		
1	167	-179
2	151	188
3	52*	9
4	87*	20
5	77*	43
H= 13, K= 7		
0	131	83
1	65*	75
2	80*	-15
3	71*	0
H= -13, K= 7		
1	66*	21
2	52	-57
3	79*	-14
H= 0, K= 8		
0	331	-334
1	452	-445
2	458	455
3	75*	15
4	222	232
5	56*	-8
6	57*	56
7	60*	-3
H= 2, K= 8		
0	261	252
1	265	-261
2	231	-230
3	61*	-65
4	264	-262
5	56*	20
6	121	76
7	123	92
H= -2, K= 8		
1	68*	-6
2	868	890
3	124	-116
4	218	-218
5	269	-283
6	56*	-8
7	65*	-21
H= 4, K= 8		
0	72*	-12
1	74*	50
2	504	492
3	144	144
4	52*	-20
5	56*	-3
6	52*	-66
7	76*	-41
H= -4, K= 8		
1	96	52
2	510	-515
3	64*	26
4	139	120
5	56*	-70
6	240	233
7	115	-89
H= 6, K= 8		
0	81*	-21
1	63*	33
2	349	-351
3	52*	-77
4	235	282
5	54*	56
6	57	40
H= -6, K= 8		
1	63*	12
2	421	419
3	50*	-19
4	138	138
5	56*	36
6	148	-133
7	58	-74
H= 8, K= 8		
0	431	451
1	51*	56
2	54*	-8
3	158	-174
4	248	-229
5	68*	-65
6	51	-58
H= -8, K= 8		
1	90	57
2	163	-173
3	55	-106
4	56*	7
5	52*	9
6	80*	25
H= 10, K= 8		
0	132	-140
1	96*	-118
2	56*	-27
3	53*	-4
4	160	123
5	72*	14
H= -10, K= 8		
1	170	177
2	188	-173
3	54*	-30
4	178	171
5	81*	17
H= 12, K= 8		
0	51*	30
1	89*	-64
2	118	-104
3	78*	-42
H= -12, K= 8		
1	59	93
2	122	148
3	118	100
4	75*	-4
H= 14, K= 8		
0	72*	63
H= -14, K= 8		
1	72*	27
H= 1, K= 9		
0	542	-497
1	109	96
2	729	-714
3	106	110
4	259	259
5	186	177
6	54*	49
7	95	-46
H= -1, K= 9		
1	411	402
2	54	-73
3	281	-270
4	51*	-28
5	97*	30
6	156	-152
7	82*	-13
H= 3, K= 9		
0	253	308
1	226	228
2	163	160
3	212	-204
4	283	-293
5	57*	-36
6	123	-104
7	75	57
H= -3, K= 9		
1	75*	-11
2	638	-629
3	151	-157
4	382	-384
5	57*	4
6	53*	-23
7	75*	7
H= 5, K= 9		
0	285	-286
1	82*	31
2	128	133
3	247	260
4	135	151
5	95*	-27
6	85*	-30
H= -5, K= 9		
1	81*	-51
2	85*	-64
3	163	179
4	55	114
5	56*	61
6	110	-118
7	113	-95
H= 7, K= 9		
0	88*	47
1	117	-113
2	176	-185
3	55*	10
4	55*	-34
5	85	-16
6	127	144
H= -7, K= 9		
1	167	-182
2	414	412
3	55*	-31
4	56*	-65
5	53	-72
6	82*	-53
H= 9, K= 9		
0	55*	-7
1	56*	-41
2	264	270
3	138	-92
4	89*	-22
5	111	-107
H= -9, K= 9		
1	240	-241
2	235	-245
3	55*	84
4	92*	13
5	83*	-16
H= 11, K= 9		
0	118	-139
1	134	-146
2	89*	29
3	83*	50
4	148	152
H= -11, K= 9		
1	149	139
2	126	137
3	67*	23
4	80*	-8
H= 13, K= 9		
0	209	199
1	77*	15
2	71*	11
H= -13, K= 9		
1	79*	-25
2	76*	38
H= 0, K= 10		
0	515	-505
1	77*	-48
2	85	36
3	534	546
4	183	154
5	110	-106
6	52*	-44
7	163	-166
H= 2, K= 10		
0	314	316
1	324	-330
2	141	-131
3	85*	-59
4	55*	-51
5	167	-154
6	50*	74
H= -2, K= 10		
1	232	-231
2	82*	64
3	88*	-83
4	352	-339
5	97*	-32
6	91*	-52
7	158	156
H= 4, K= 10		
0	198	193
1	83*	-33
2	356	349
3	435	-435
4	145	-134
5	212	-213
6	163	-144
H= -4, K= 10		
1	204	-202
2	102	-87
3	235	232
4	95*	18
5	113	56
6	88*	-20
H= 6, K= 10		
0	88*	-73
1	226	-227
2	170	-173
3	95*	87
4	128	105
5	102	97
6	76*	54
H= -6, K= 10		
1	599	621
2	388	405
3	55*	-55
4	199	195
5	53*	-53
6	122	-95
H= 8, K= 10		
0	204	205
1	112	127
2	55*	-58
3	195	-197
4	114	-72
5	79	65
H= -8, K= 10		
1	55*	53
2	95*	45
3	55*	8
4	53*	27
5	166	153
H= 10, K= 10		
0	124	-110
1	174	165
2	127	139
3	110	73
4	103	65
H= -10, K= 10		
1	54	57
2	106	-75
3	50*	47
4	157	162
5	160	133
H= 12, K= 10		
0	84*	44
1	62*	-41
2	81	-103
H= -12, K= 10		
1	83*	15
2	117	102
3	127	-113
H= 1, K= 11		
0	154	-130
1	94	76
2	86*	-1
3	91*	65
4	100	58
5	95*	-55
6	87*	72
H= -1, K= 11		
1	510	515
2	268	273
3	313	-306
4	56*	-39
5	56*	-89
6	173	-74
H= 3, K= 11		
0	116	114
1	169	-166
2	109	-102
3	668	-666
4	56*	-64
5	218	-206
6	123	121
H= -3, K= 11		
1	233	-236
2	88*	-16
3	228	-234
4	56*	-63
5	153	170
6	130	132
H= 5, K= 11		
0	281	-290
1	288	-287
2	134	133
3	135	-51
4	109	107
5	185	-185
6	75*	-76
H= -5, K= 11		
1	350	340
2	139	-146
3	152	205
4	149	145
5	109	-102
6	81*	-11
H= 7, K= 11		
0	129	114
1	452	-513
2	100	-137
3	55*	65
4	51*	75
5	139	123
H= -7, K= 11		
1	280	267
2	135	-153
3	56*	56
4	215	-206
5	98	-80
H= 9, K= 11		
0	136	115
1	55*	53
2	53*	66
3	89*	-26
4	80*	-71
H= -9, K= 11		
1	153	-171
2	98	-73
3	362	355
4	85*	-58
5	131	126
H= 11, K= 11		
0	87*	-63
1	66*	-15
2	81*	-14
3	135	127
H= -11, K= 11		
1	122	103
2	84*	20
3	78*	50
H= 0, K= 12		
0	115	141
1	153	126
2	50*	-57
3	300	297
4	56*	6
5	149	-134
6	188	-184
H= 2, K= 12		
0	165	118
1	367	-376
2	304	-331
3	222	206
4	56*	-15
5	278	273
6	107	108
H= -2, K= 12		
1	121	-131
2	135	-145
3	137	-135
4	96*	51
5	53*	-28
6	82*	11
H= 4, K= 12		
0	256	-250
1	427	470
2	154	-160
3	56*	17
4	55*	-56
5	88*	-36
6	52	26
H= -4, K= 12		
1	262	[illegible]
2	135	-97
3	259	241
4	56*	52
5	55	85
6	78*	26
H= 6, K= 12		
0	307	-321
1	211	200
2	135	136
3	225	235
4	51*	27
5	80*	38
H= -6, K= 12		
1	120	140
2	265	-272
3	105	-111
4	197	-207
5	108	-83
H= 8, K= 12		
0	95*	-28
1	95*	21
2	53*	-36
3	160	-146
4	81	-32
H= -8, K= 12		
1	217	-243
2	94*	-16
3	251	-242
4	318	-326
5	99	116
H= 10, K= 12		
0	98	-44
1	204	209
2	125	90
3	76*	6
H= -10, K= 12		
1	88*	53
2	86*	55
3	81*	14
4	75	-37
H= 12, K= 12		
0	73*	-53
H= -12, K= 12		
1	72*	50
H= 1, K= 13		
0	125	-114
1	129	-114
2	311	328
3	151	148
4	55*	-46
5	185	206
6	75*	-60
H= -1, K= 13		
1	299	308
2	103	110
3	218	-213
4	168	-166
5	150	-154
6	76*	38
H= 3, K= 13		
0	92*	-22
1	93*	-31
2	55*	-53
3	139	120
4	54*	-2
5	320	337
H= -3, K= 13		
1	193	-208
2	194	185
3	96*	-66
4	54*	22
5	124	135
6	73*	61
H= 5, K= 13		
0	144	163
1	559	578
2	96*	6
3	262	277
4	126	-104
5	111	-65
H= -5, K= 13		
1	55*	-27
2	96	101
3	121	117
4	52*	33
5	126	-104
H= 7, K= 13		
0	95*	54
1	95*	-91
2	118	-116
3	126	95
4	96	97
H= -7, K= 13		
1	252	-268
2	127	-111
3	316	-315
4	132	104
5	73*	-30
H= 9, K= 13		
0	95	95
1	89*	35
2	124	-114
3	128	-114
H= -9, K= 13		
1	179	-172
2	97*	15
3	82*	-47
4	119	120
H= 11, K= 13		
0	94	40
1	74*	0
H= -11, K= 13		
1	95	115
2	85	-76
H= 0, K= 14		
0	175	191
1	242	237
2	218	-216
3	96*	-4
4	93*	14
5	157	-156
H= 2, K= 14		
0	59	-83
1	253	-236
2	96*	62
3	95*	16
4	276	275
5	120	146
H= -2, K= 14		
1	95*	-29
2	365	-384
3	125	-122
4	97	67
5	83*	78
H= 4, K= 14		
0	188	172
1	135	114
2	95*	-14
3	132	-76
4	87	-58
5	93	-41
H= -4, K= 14		
1	95*	-73
2	121	98
3	103	97
4	90*	-22
5	79*	24
H= 6, K= 14		
0	95*	50
1	94*	13
2	183	194
3	88*	76
4	94	-45
H= -6, K= 14		
1	95*	82
2	94	84
3	91*	-11
4	103	-48
5	108	-104
H= 8, K= 14		
0	228	-215
1	209	-198
2	85*	8
3	78*	-47
H= -8, K= 14		
1	117	-80
2	165	138
3	82*	-49
4	102	114
H= 10, K= 14		
0	78*	56
1	118	109
H= -10, K= 14		
1	77*	45
2	74*	39
H= 1, K= 15		
0	96*	-47
1	96*	0
2	230	238
3	185	185
4	107	-55
5	110	-101
H= -1, K= 15		
1	96*	-3
2	95*	-41
3	107	103
4	176	-170
5	80	12
H= 3, K= 15		
0	236	-237
1	105	-105
2	95*	-14
3	91*	-65
4	106	93
H= -3, K= 15		
1	168	-183
2	59	117
3	92*	75
4	86*	71
5	119	134
H= 5, K= 15		
0	268	270
1	93*	89
2	91*	-50
3	134	-123
4	77*	-91
H= -5, K= 15		
1	123	102
2	121	43
3	89*	18
4	130	-138
H= 7, K= 15		
0	89*	-51
1	111	-47
2	92	52
3	106	67
H= -7, K= 15		
1	145	143
2	95	-93
3	81*	-42
4	114	125
H= 9, K= 15		
0	79*	62
1	118	84
2	155	-152
H= -9, K= 15		
1	77	-4
2	74*	12
H= 0, K= 16		
0	427	454
1	147	153
2	93*	33
3	160	-132
4	81*	-81
H= 2, K= 16		
0	95*	-44
1	94*	63
2	92*	90
3	88*	-4
4	114	92
H= -2, K= 16		
1	94*	76
2	92*	9
3	97	-105
4	234	230
H= 4, K= 16		
0	92*	46
1	92*	-76
2	180	-170
3	117	-105
4	73*	-36
H= -4, K= 16		
1	92*	-2
2	151	137
3	85*	-13
4	138	83
H= 6, K= 16		
0	130	67
1	86*	-48
2	127	119
3	85	68
H= -6, K= 16		
1	67*	2
2	84*	-63
3	78*	14
H= 8, K= 16		
0	163	-145
1	75	-92
H= -8, K= 16		
1	77*	-52
2	73*	56
H= 1, K= 17		
0	108	93
1	128	-107
2	133	120
3	82*	59
4	71	-64
H= -1, K= 17		
1	184	-163
2	100	-87
3	82	28
4	72*	13
H= 3, K= 17		
0	162	-157
1	88*	-64
2	85*	-40
3	78*	31
H= -3, K= 17		
1	89*	17
2	86*	84
3	121	124
H= 5, K= 17		
0	119	109
1	83*	-27
2	78*	-68
H= -5, K= 17		
1	84	19
2	80	13
3	73*	-23
H= 7, K= 17		
0	92	-73
1	80	117
H= -7, K= 17		
1	74*	113
H= 0, K= 18		
0	86*	19
1	84*	19
2	81*	-1
3	175	-160
H= 2, K= 18		
0	84*	-107
1	133	147
2	79*	106
3	71*	-20
H= -2, K= 18		
1	132	109
2	79*	-33
3	72*	-19
H= 4, K= 18		
0	79*	-2
1	132	-123
2	80	-102
H= -4, K= 18		
1	79*	56
2	118	85
H= 6, K= 18		
0	100	97
H= 1, K= 19		
0	76*	48
1	75*	-16
H= -1, K= 19		
1	155	-149
H= 3, K= 19		
0	76	-52
1	71*	9
H= -3, K= 19		
1	72*	51

age molecule appears as two half-molecules related by twofold rotation. Except for S(2), which appears as two half-atoms, and the adjacent carbon atoms, which are somewhat elongated, the superposition is reasonably precise, and the essential features of the molecule can be observed. The conformation is of type (*a*). The bond lengths not involving S(2) and the adjacent carbon atoms are reasonable, but may be unreliable because of thermal motion (which may be non-rigid) and other systematic effects. The phenyl rings are planar, deviate from parallelism by less than 1°, and are separated by 3·192 Å. The C–C bonds of the bridges are inclined at 6° to the ring planes, indicating moderate strain. Except for the disordered bridge, the molecule has a non-crystallographic mirror plane midway between the phenyl rings. The exception is illustrated in Fig. 1(*b*); S(2) lies 0·2 Å from the median plane, and the long axes of the thermal-motion ellipsoids of the adjacent carbon atoms are inclined at about 40° to this plane.

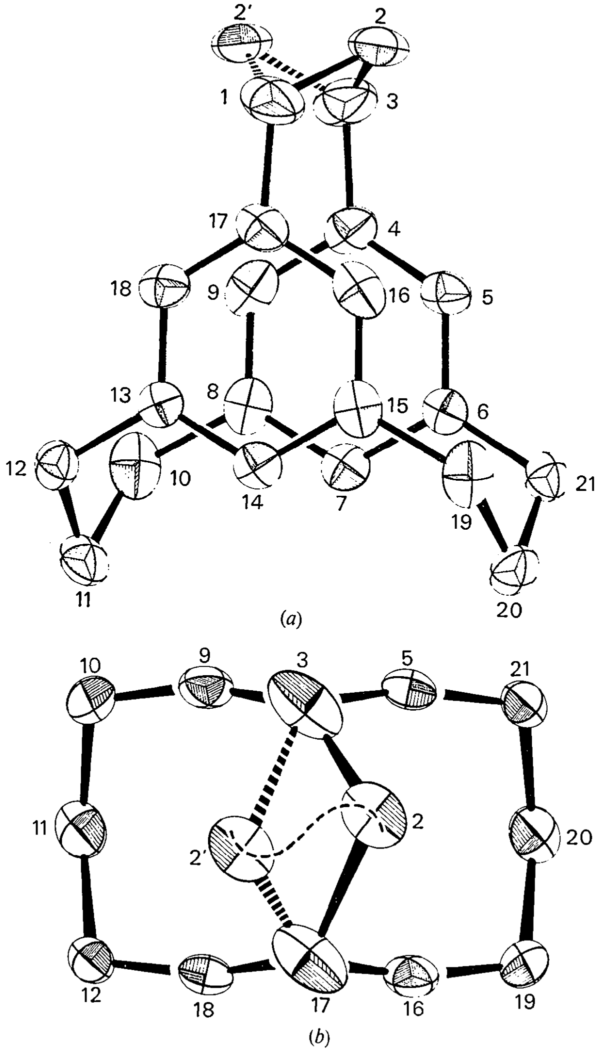

Fig. 1. Thermal ellipsoids of 30% probability, (*a*) viewed along **c**, (*b*) viewed along **b**. Overlapped atoms have been omitted for clarity. The dashed line represents a possible path for S(2) during flipping.

Table 3. *Bond lengths and some angles*

Values in brackets involve the disordered bridge, and are unreliable.

	Distance	Mean
C(4)–C(5)	1·369 (8) Å	1·38 Å
C(5)–C(6)	1·391 (7)	
C(6)–C(7)	1·385 (7)	
C(7)–C(8)	1·378 (8)	
C(8)–C(9)	1·389 (9)	
C(9)–C(4)	1·388 (8)	
C(3)–C(4)	[1·499 (9)]	
C(6)–C(21)	1·502 (7)	1·50
C(8)–C(10)	1·499 (8)	
S(2)—C(1)	[1·882 (10)]	
S(2)—C(3)	[1·599 (10)]	
S(11)–C(10)	1·821 (7)	1·82
S(11)–C(12)	1·823 (6)	

C–H distances range from 0·75 to 1·04 Å.

	Angle	Mean
S(2)—C(1)—C(17)	[117·0 (6)°]	
S(2)—C(3)—C(4)	[119·0 (6)]	
S(11)–C(12)–C(13)	115·6 (4)	115·4°
S(11)–C(10)–C(8)	115·2 (5)	
C(1)—S(2)—C(3)	[108·2 (4)]	
C(10)–S(11)–C(12)	104·7 (3)	

Table 4. *Distances of some atoms from the mean plane of the phenyl ring* [C(4)···C(9)]

The equation of the plane is $0\cdot3224x'+0\cdot0077y'-0\cdot9466z'+0\cdot0779=0$ for an orthogonal coordinate system, in Å, for which $x' \parallel \mathbf{a}$, $y' \parallel \mathbf{b}$, $z' \parallel \mathbf{c}^*$.

	Distance		Distance
C(4)	−0·001 (6) Å	C(3)	−0·161 (10) Å
C(5)	0·004 (5)	C(10)	−0·164 (6)
C(6)	−0·010 (5)	C(21)	−0·161 (5)
C(7)	0·013 (5)	S(2)	−1·374 (4)
C(8)	−0·009 (5)	S(2′)	−1·761 (4)
C(9)	0·003 (5)	S(11)	−1·613 (2)
		S(20)	−1·616 (2)

The simplifying assumptions of the analysis ensure that the observed structure is disordered. However, it does not follow that the true structure is entirely ordered, and various considerations suggest that it is unlikely to be so. Conformational disorder of a similar sulphur bridge has been observed in the crystal structure of the related compound *syn*-2,11-dithia-9,18-dimethyl[3.3]cyclophane (Davis & Bernal, 1971). As mentioned earlier, rapid flipping of all bridges of the present compound is consistent with the otherwise anomalous n.m.r. results. The n.m.r. spectrum of an analogous nitrogen-bridged compound {*N*,*N*′,*N*″-tritosyl-2,11,20-triaza[3.3.3] (1,3,5)cyclophane} has been studied over a range of temperatures by Vögtle &

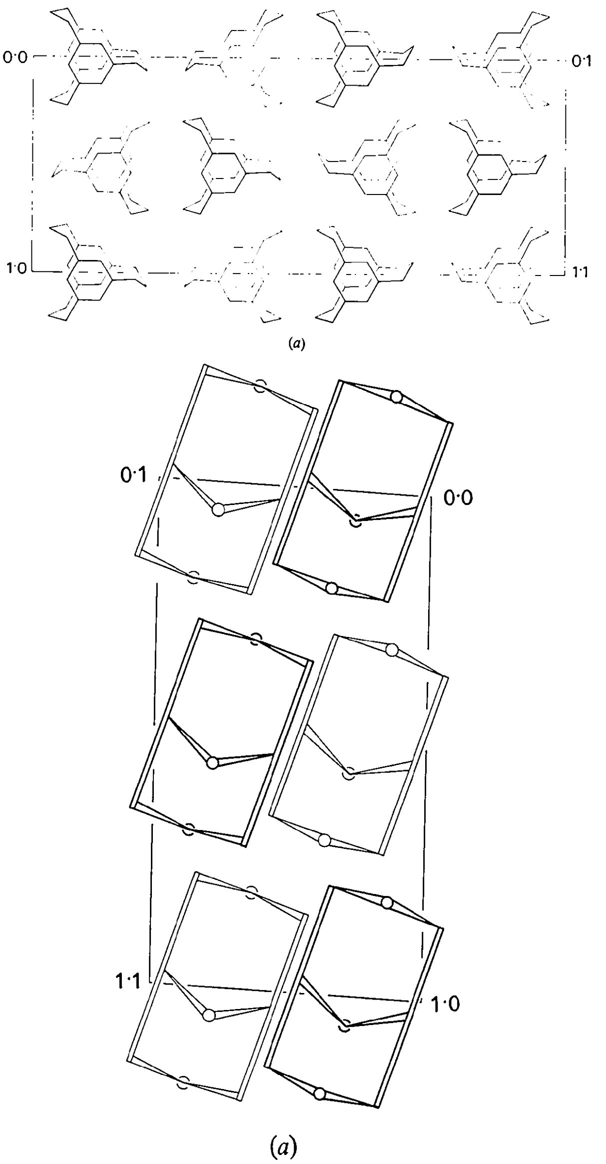

Fig. 2. Schematic representation of a possible ordered, low-temperature structure. (*a*) The projection along **c**. The stronger outlines represent molecules at $z=\frac{3}{4}$, the weaker at $z=\frac{1}{4}$. (*b*) The projection along **b** of the structure from $y=0$ to $y=\frac{1}{2}$. The stronger outlines represent molecules at about $y=\frac{3}{8}$, the weaker at about $y=\frac{1}{8}$.

Neumann (1970). At 35 °C the spectrum is comparable to that of the present compound, with a single sharp peak attributable to the methylenic protons. At −57 °C, however, this peak is found to have separated into an *AB* system of two doublets. A reasonable interpretation of this result is that the rate of flipping of the bridges (limited in any case by the inertia of the massive tosyl groups) is sufficiently reduced at the lower temperature to reveal the non-equivalence of the methylenic protons.

Such considerations suggest that rapid, possibly temperature-modulated flipping of the sulphur bridges is a normal condition which will occur unless prevented. Two of the bridges, S(11) and S(20), are stabilized by intermolecular contacts, but there is no obvious reason why S(2) should not flip, and there is in fact some indication that it does so. Experiments with a model suggest that, on flipping, the sulphur atom will not remain on the median plane, but will instead follow a curved path resembling that shown in Fig. 1(*b*). The departure from mirror symmetry, mentioned earlier, is thus consistent with flipping. The end points of the path, lying on the median plane, represent the stable positions of the sulphur atoms, while the observed positions are merely the most probable positions at a given time. In a dynamic situation these need not (and in the present case apparently do not) coincide. The curvilinear motion will be accompanied by cooperative movements of the adjacent carbon atoms (and, to a lesser extent of the remainder of the molecule), resulting in the observed elongation of their thermal motion ellipsoids.

It is thus reasonable to predict that the crystal structure should suffer some degree of disorder. It is in fact difficult to see why there should be any long-range order, such as is suggested by the presence of the subset of weak reflexions. However, it seems likely that at a sufficiently low temperature the flipping of S(2) could be suppressed, and the structure ordered. It might then be as represented in Fig. 2, with space group $P2_1/c$, and the molecules lying on the twofold screw axes. The subset of weak reflexions for this structure would result, for the most part, from the contributions of the sulphur atoms lying closest to the twofold screw axes. With increasing temperature, thermal flipping of these atoms would ensue, with an increasing probability of their occupying alternative positions. The intensities of the reflexions of the weak subset would be thereby reduced. At a sufficiently high temperature (apparently above 80°C), the probability would approach 50%, and the reflexions of the weak subset would vanish. The translational elements of the screw axes would be lost. the *b* dimension would be halved, and the space group would become truly $C2/c$.

Computer programs used in this work are those of Ahmed, Hall, Pippy & Huber (1966), Ahmed (1970) and Johnson (1965). The specimen material was kindly supplied by Professor V. Boekelheide.

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The Crystal and Molecular Structure of the 1:1 Compound Formed between Phosphorus Pentachloride and Tellurium Tetrachloride, Cl_9PTe

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(*Received* 22 *September* 1971)

The compound Cl_9PTe crystallizes in the orthorhombic space group $I2mb$ with $Z=8$ and with cell dimensions $a=12{\cdot}10$, $b=16{\cdot}64$, $c=12{\cdot}52$ Å. The structure contains discrete, approximately tetrahedral $[PCl_4]^+$ cations, and polymeric chain anions in which each tellurium atom is surrounded by a distorted octahedron of chlorine atoms. The chain consists of octahedra linked by sharing two *cis* vertices. Using visually estimated three-dimensional photographically recorded data the structure was refined to a final R of 0·122.

Introduction

The chemical status of the pentahalotellurate(IV) complex anions is by no means clear, even though several compounds have been prepared which apparently, from the elemental analysis, contain these ions. Tellurium tetrachloride is a tetrameric solid (Buss & Krebs, 1970), containing six coordinate tellurium atoms [3 Te–Cl at 2·32 Å (av) and 3 Te–Cl at 2·93 Å (av)]. Under suitable conditions tellurium tetrachloride reacts readily with chloride ions to form the octahedral $[TeCl_6]^{2-}$ ion. Because of the chemical interest in species containing formal lone pairs of electrons, both the hexachloro- and hexabromotellurate(IV) ions have been structurally characterized by X-ray diffraction (Hazell, 1966; Das & Brown, 1966) and subjected to assorted vibrational spectroscopic assaults (see, for example, Adams & Downs, 1970; Adams & Lloyd, 1971 and references therein). It seems plausible that the addition of chloride ions to $TeCl_4$ occurs in a stepwise manner and that the species $[TeCl_5]^-$ should exist. Ultraviolet and visible spectroscopy in acetonitrile solution gave evidence for a species, possibly $[TeCl_5]^-$, formed when equimolar amounts of $TeCl_4$ and $[TeCl_6]^{2-}$ are mixed (Beattie & Chudzynska, 1967). Other studies have also provided evidence for $[TeX_5]^-$ ions ($X=Cl$, Br) (Korewa & Smagowski, 1965; Korewa & Szponar, 1965), but since all these solution reactions are carried out in ionizing and potentially coordinating solvents, it may well be that such pentahalo species are sufficiently solvated to influence the coordination geometry. The reported structure (Aynsley & Hazell, 1963) of uronium pentachlorotellurate (IV) is incorrect (Beattie, Chudzynska, Hulme & Aynsley, 1963).

In contrast to the chloro and bromo species the only known fluorocomplex of Te(IV) is the $[TeF_5]^-$ ion which exists as discrete square pyramidal anions both in solid $KTeF_5$ (Edwards & Mouty, 1969; Mastin, Ryan & Asprey, 1970) and in solution from F-19 nuclear magnetic resonance experiments. The structure of β-Me_2TeI_2 consists of $[Me_3Te]^+$ $[MeTeI_4]^-$, the anion of which is square pyramidal with an axial methyl group (Einstein, Trotter & Williston, 1967).

Solid compounds apparently containing the $[TeX_5]^-$ ion include $[Et_4N]$ $[TeCl_5]$ (Creighton & Green, 1968) and the mixed haloanion in $[Et_4N]$ $[TeCl_2Br_3]$ (Ozin & Vander Voet, 1971). The system PCl_5–$TeCl_4$ has been examined in $AsCl_3$ (Gutmann, 1953) and $POCl_3$ (Groeneveld, 1956; Groeneveld, 1952; Groeneveld & Zuur, 1953) and evidence for the compounds $2PCl_5$, $TeCl_4$; PCl_5, $TeCl_4$ and PCl_5, $2TeCl_4$ presented. Beattie has examined the vibrational spectra of the 1:1 compound Cl_9PTe (Beattie, 1967; Beattie & Chudzynska, 1967) which gave clear cut evidence for the $[PCl_4]^+$ ion. The structure of the anion is not clear but the observation of the chlorine isotope splitting pattern of ν_1 of the cation suggests a relatively simple structure.

An examination of the compound Cl_9PTe was undertaken to establish the structure of the solid and in particular the nature of the anionic species present.