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The Crystal Structure of the Diolefin of [2.2]Paracyclophane*

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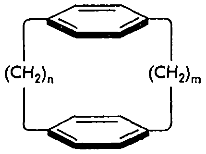
The diolefin of [2·2]paracyclophane ($C_{16}H_{12}$) forms monoclinic crystals with

$$a_0 = 6{\cdot}866,\ b_0 = 11{\cdot}636,\ c_0 = 7{\cdot}640\ \text{Å},\ \beta = 116{\cdot}9^\circ,$$

and two molecules in the unit cell in space group $P2_1/c$. The structure has been refined by full matrix three-dimensional least-squares methods, and the final parameters include small corrections for molecular libration. The aromatic rings are bent into a boat form about 14° at each end, and the bonds to the α-carbons are bent an additional 15° from the plane of the edge of each aromatic ring. The ring deformation may also be described as a folding of 16° about a line between the *p*-substituted atoms. The exocyclic single bond distance is 1·51 Å, at least 0·02 Å longer than normal. The lengthening is attributed in part to the orthogonality of the π-systems in the molecule and in part to intramolecular strain. Other distances are normal. The distribution of strain in the molecule is discussed.

Introduction

The [*n*.*m*]paracyclophane system (I) represents an interesting class of strained organic compounds (Cram & Steinberg, 1951; Robertson, 1953). Dewhirst & Cram (1958) prepared a number of *p*-cyclophanes and *p*-cyclophane derivatives, and studied their spectroscopic properties; included in this group was the diolefin of [2.2]*p*-cyclophane (1,2,9,10-tetradehydro[2.2]paracyclophane) (Fig. 1).



(I)

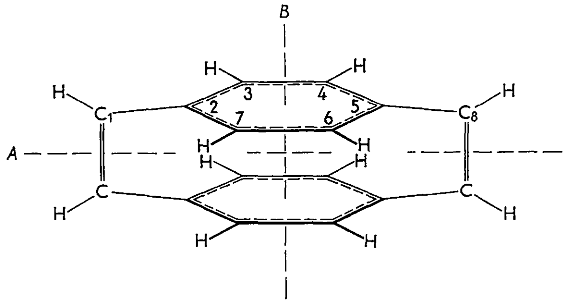


Fig. 1. Schematic drawing of molecule showing atomic numbering and reference axes.

The first crystallographic work on the cyclophanes was done by Brown (1953), who determined the structures of the parent compound, [2.2]*p*-cyclophane or di-*p*-xylylene, and of the corresponding *meta* compound. The structure of [2.2]*p*-cyclophane was independently investigated by Lonsdale, Milledge & Rao (1960). The structure of [3.3]*p*-cyclophane has been determined by Gantzel & Trueblood (1963) and that of 4,12-dimethyl[2.2]metacyclophane has been studied precisely by Hanson (1962). The aromatic rings in all of these compounds are bent, indicating a substantial amount of steric strain due to the close non-bonded intramolecular contacts. For comparison, it appeared worth while to determine the precise structure of the diolefin of [2.2]*p*-cyclophane.

Experimental

Drs Dewhirst & Cram kindly provided a sample of the diolefin of [2.2]*p*-cyclophane (230–231 °C) for crystallographic examination. The substance crystallized from benzene mainly in the form of colorless, diamond-shaped plates which showed optical extinction along the longer diagonal, later established as the [010] direction. Rotation, Weissenberg, and precession photographs of crystals mounted about the **a**, **b**, **c**, and [101] directions established the symmetry as monoclinic, and extinctions (*h*0*l*, *l* odd; 0*k*0, *k* odd) indicated the space group to be $P2_1/c$ (C^5_{2h}). All photographs were taken at room temperature (22 ± 3 °C).

The lattice constants, determined from Weissenberg photographs taken with copper radiation (Cu $K\alpha$; $\lambda = 1{\cdot}5418$ Å) and calibrated with cerium oxide ($a_0 = 5{\cdot}411$ Å) were:

$$a_0 = 6{\cdot}866 \pm 0{\cdot}010,\ b_0 = 11{\cdot}636 \pm 0{\cdot}010,$$
$$c_0 = 7{\cdot}640 \pm 0{\cdot}010\ \text{Å},\ \beta = 116{\cdot}9 \pm 0{\cdot}1^\circ.$$

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The experimental density is 1·25 g.cm^{-3}; that calculated for two molecules in the unit cell is 1·246. Thus the centers of the molecules are constrained to lie on centers of symmetry.

Multiple-film Weissenberg photographs were taken with unfiltered copper radiation about **b** for $k=0$ through 6, and about **c** for $l=0$ through 3. The **b**-axis crystal was approximately cylindrical, with dimensions of $0{\cdot}12\times0{\cdot}09\times0{\cdot}54$ mm; the **b** direction was slightly off the cylinder axis. The **c** crystal was a rectangular parallelepiped of width 0·30 mm and thickness 0·16 mm. Since the linear absorption coefficient for copper radiation is 6·46 cm^{-1}, the maximum difference in the intensity between $\theta=0°$ and $\theta=90°$ due to absorption for the zero layer of the **b** crystal was less than 5%, and of the **c** crystal 9%. No absorption corrections were applied.

The intensities were estimated visually, using calibrated intensity strips prepared with the same crystal. Of the 1215 reflections in the copper sphere, 780 were observed and an additional 305 were accessible but were below the minimum observable value. Scaling of the data was done by means of an iterative relaxation technique (R. A. Sparks, unpublished) for finding the best single set of multipliers for each layer about each axis. A Wilson (1942) plot indicated the overall temperature factor to be about 5 Å^2. The intensity of reflections observed about more than one axis showed an average deviation from the mean of about 10%.

The $|F|_h^2$ values were modified (Patterson, 1935) by dividing each of them by the quantity

$$\sum_i f_i^2 \exp\left(-2B\sin^2\theta/\lambda^2\right)$$

and a sharpened, modified three-dimensional Patterson function was calculated with the use of $(\sin\theta/\lambda)^4\exp(-19\sin^2\theta/\lambda^2)$ as a modification function (Waser, 1944; Donohue & Trueblood, 1952). Most of the calculations were carried out on SWAC (Sparks, Prosen, Kruse & Trueblood, 1956) but the final two least-squares cycles and the analyses of the thermal motion and the molecular geometry were done on an IBM 7090.

Three appropriately located coplanar 1·4 Å vectors, in conjunction with a strong 3·0 Å vector perpendicular to the plane defined by the 1·4 Å vectors, fixed the approximate positions of the six unique carbons in the aromatic ring. The Patterson vectors due to the other two unique carbons were more difficult to locate, and a Fourier synthesis phased with the six known carbons was calculated. The other two carbon atoms appeared with heights of about 4 e.Å^{-3}; no other peaks above 1 e.Å^{-3} were observed. The discrepancy index, R, was 50% with only the six ring carbons included in the structure factor calculation, and 35% with all eight unique carbon atoms included. This, in conjunction with the Fourier map, indicated the trial structure to be at least promising.

Refinement

The form factors of McWeeny for hydrogen (1951) and graphite carbon (1954), averaged over different orientations, were used in all calculations. In the initial least-squares refinements on SWAC, size limitations precluded calculating the full matrix for more than seven unique atoms with nine parameters per atom. Consequently in the refinement of the carbon atoms, one atom was fixed for each cycle, although no given atom was ever constrained on successive cycles. The weighting system used was one which gave maximum weight to reflections at about $4F_{\min}$; for those with $F_o>3{\cdot}2$, $\sqrt{w}=3{\cdot}2/F_o$, while for those with $F_o<3{\cdot}2$, $\sqrt{w}=F_o/3{\cdot}2$. When convergence was apparent, a difference synthesis was calculated; it revealed clearly the six hydrogen atoms, as broad maxima of average height 0·5 e.Å^{-3}. These atoms were included (at 1·09 Å from the corresponding carbon, in the direction of the maximum in the difference map) in the structure factor calculations for two more least-squares cycles of refinement of the carbon parameters. The hydrogen positions were then refined by one least-squares cycle; a considerable improvement in the bond angles resulted.

Finally two cycles of full-matrix refinement of both the carbon and hydrogen parameters simultaneously were done on an IBM 7090 (ACA Program 317, Gantzel, Sparks & Trueblood, unpublished). The function minimized is $\Sigma w(F_o-F_c)^2$. The hydrogen atoms were given isotropic temperature factors of 5·0 Å^2; otherwise the parameters used were those from the SWAC refinements. The weighting system, however, was changed to one with constant weight for $F_o<3{\cdot}2$ (Hughes, 1941). Only about one-third of the ninety-seven parameters changed by as much as σ in the first cycle; six changed by nearly 2σ and one by about 3σ (B_{23} of C4). The average shift in the second cycle was about $\sigma/4$, and the largest shift ($0{\cdot}8\sigma$) was in one of the hydrogen positions. Thus, in spite of the difference in weighting schemes and the need to constrain some atoms in the SWAC calculations, the two refinements converged to essentially the same structure.

A final difference-Fourier synthesis was calculated as a check on the refinement. It contained one positive and four negative regions of density 0·25–0·3 e.Å^{-3}, which is about $2{\cdot}5\sigma(\varrho)$. None exceeded 3σ, and since none was in a chemically meaningful location they were considered merely random fluctuations. The final structure factors are listed in Table 1. The final value of R was 12·0% including all reflections, 10·0% including observed reflections only, and 9·6% if the six strongest (marked with E in Table 1) are omitted. The value of F_o listed for the unobserved reflections (marked with U in Table 1) is $F_{\min}/\sqrt{3}$, and this value was used in the least-squares refinements (Hamilton, 1955). Among the unobserved reflections, only one had F_c greater than $1{\cdot}5F_{\min}$; for this reflec-

Table 1. *Observed and calculated structure factors*

The three columns listed are, respectively, l, F_o and F_c. The letter E following a value of F_o means that this was one of the six strongest intensities, which are suspected of suffering from extinction. The letter U following a value of F_o means 'Unobserved'; for such reflections, the F_o listed is $F_{\min}/\sqrt{3}$, where $F_{\min}$ is the minimum observable structure amplitude in that region of reciprocal space

H= 0, K= 0		
2	34.44	-37.14
4	8.36	7.37
6	12.00	-11.78
8	0.82	-0.48
H= 0, K= 1		
1	28.10E	36.10
2	17.99	21.47
3	5.42	-4.83
4	1.06	0.39
5	4.69	-4.24
6	1.35	-0.97
7	2.99	-2.67
8	0.90U	-0.64
H= 0, K= 2		
0	30.37E	38.67
1	10.69	12.27
2	45.51E	-55.56
3	14.51	15.82
4	14.08	13.68
5	2.99	-2.89
6	0.90U	-0.34
7	0.61U	-0.23
8	1.69	1.97
H= 0, K= 3		
1	48.37E	-48.08
2	26.26	25.91
3	3.97	4.32
4	3.58	-3.63
5	5.27	5.23
6	1.16	0.18
7	4.89	4.81
8	0.82	-0.76
H= 0, K= 4		
0	17.12	-18.33
1	5.70	5.77
2	14.26	-14.90
3	3.53	-3.37
4	14.18	12.59
5	2.28	-2.08
6	1.74	1.74
7	0.47U	0.24
8	0.67U	0.50
H= 0, K= 5		
1	1.35	1.31
2	3.53	-3.20
3	14.41	14.37
4	10.59	-10.36
5	5.52	-5.97
6	3.44	3.85
7	0.61U	-0.42
8	0.68	-0.61
H= 0, K= 6		
0	17.46	17.81
1	0.82	-0.09
2	6.10	6.42
3	11.85	-11.65
4	1.45	0.93
5	3.24	3.65
6	5.37	-6.18
7	0.67U	-0.32
H= 0, K= 7		
1	5.70	5.11
2	4.40	-2.00
3	4.84	4.72
H= 0, K= 8		
0	6.58	5.96
1	1.00U	-0.34
2	7.40	-8.40
3	1.26	1.36
6	0.73U	-0.34
H= 0, K= 9		
1	6.77	-6.24
2	2.99	3.14
3	1.69	-1.61
H= 0, K= 10		
0	4.06	4.14
1	4.59	-4.54
2	6.43	-7.39
3	4.21	4.74
H= 0, K= 11		
1	2.32	2.18
2	0.90U	0.68
3	0.61U	0.46
5	0.73U	-0.53
6	0.73U	-0.67
H= 0, K= 12		
0	6.48	6.27
1	5.32	-5.31
2	0.61U	0.41
3	2.41	2.30
H= 0, K= 13		
1	0.73U	0.72
2	0.67U	0.59
3	1.00U	0.88
H= 0, K= 14		
0	2.23	-1.41
1	1.88	-1.93
2	1.26	-1.19
H= 1, K= 0		
-8	1.74	-1.34
-6	4.74	-4.61
-4	6.63	6.77
-2	24.62	25.97
0	35.45E	34.64
2	12.33	-12.74
4	6.82	-6.28
6	1.26	-0.70
8	3.19	-2.72
H= 1, K= 1		
-9	0.73U	1.13
-8	3.39	3.18
-7	2.51	-2.06
-6	1.98	1.51
-5	1.93	-1.56
-4	13.01	-12.73
-3	1.06	-0.78
-2	19.35	-23.48
-1	43.53E	52.71
0	15.09	-14.83
1	33.23	-33.70
2	16.44	18.03
3	11.07	10.03
4	3.82	2.80
5	6.87	-6.23
6	6.10	5.45
7	1.06	0.27
8	1.79	-1.69
H= 1, K= 2		
-9	0.73U	0.07
-8	0.73U	0.69
-7	7.50	6.94
-6	2.13	-2.36
-5	9.29	-9.04
-4	2.66	2.60
-3	10.64	-11.40
-2	25.35	-29.93
-1	27.38	-36.83
0	11.12	11.95
1	25.15	27.30
2	3.82	-4.36
3	2.18	-1.60
4	2.99	3.36
5	8.31	7.89
6	3.77	3.63
7	1.26	0.27
8	1.69	-1.41
H= 1, K= 3		
-9	0.82	0.97
-8	2.51	2.59
-7	1.16	1.28
-6	1.16	0.62
-5	3.09	2.69
-4	5.22	-5.08
-3	15.33	-15.83
-2	2.61	2.90
-1	11.85	-13.10
0	6.28	-6.43
1	22.06	-18.90
2	12.19	12.39
3	15.19	14.16
4	11.90	-9.90
5	1.06	1.26
6	5.52	5.53
7	2.46	2.76
8	1.45	-2.00
H= 1, K= 4		
-8	0.56U	-0.15
-7	1.45	1.73
-6	0.82	0.85
-5	2.91	-2.63
-4	14.41	13.39
-3	16.01	15.88
-2	25.35	-31.38
-1	8.36	8.86
0	9.82	9.61
1	12.87	10.58
2	4.30	-4.45
3	17.37	-17.12
4	0.82	0.66
5	1.06	-1.13
6	2.76	3.07
7	0.73U	-0.51
H= 1, K= 5		
-8	0.78U	-0.58
-7	0.73U	-0.48
-6	2.41	-3.12
-5	5.62	5.66
-4	9.24	7.80
-3	2.23	2.94
-2	15.86	16.53
-1	7.40	7.39
0	1.60	-1.66
1	5.32	-4.66
2	0.82	0.80
3	3.04	3.09
4	11.75	-11.14
5	6.96	-7.17
6	1.16	0.90
7	1.45	1.56
H= 1, K= 6		
-8	1.74	-2.32
-7	1.98	-2.07
-6	0.73U	-0.75
-5	0.78U	0.25
-4	6.58	6.79
-3	3.19	2.91
-2	0.90U	0.30
-1	3.58	3.54
0	13.73	12.57
1	3.53	-3.43
2	0.78U	0.59
3	0.78U	-0.63
4	6.68	-6.94
5	0.78U	0.48
6	1.93	-1.90
7	0.73U	-0.72
H= 1, K= 7		
-8	0.78U	0.97
-7	0.73U	-0.11
-4	0.67U	0.46
-3	5.27	-5.13
-2	5.17	-5.10
-1	12.14	12.18
0	10.89	-9.81
1	3.58	-4.09
2	6.87	7.90
3	8.66	9.19
6	0.67U	0.55
H= 1, K= 8		
-7	0.73U	-0.22
-6	0.73U	1.01
-5	0.78U	1.09
-3	7.11	-7.15
-2	0.90U	0.22
-1	5.42	-5.01
0	4.30	-3.87
1	3.92	-3.42
2	5.90	6.67
3	7.78	8.44
4	0.67U	0.43
H= 1, K= 9		
-6	0.73U	-0.02
-4	0.67U	0.93
-3	6.53	-7.08
-2	1.55	-1.19
-1	4.40	4.90
0	6.38	-6.13
1	11.22	-12.27
2	4.26	5.15
3	10.21	11.13
4	0.67U	0.26
H= 1, K= 10		
-7	0.73U	0.51
-3	0.73U	0.21
-2	5.42	5.82
-1	2.66	2.93
0	7.35	-7.12
1	2.66	-1.77
2	0.78U	-0.91
3	1.88	-1.47
4	0.67U	-0.04
5	0.78U	-0.17
H= 1, K= 11		
-6	0.73U	0.43
-4	0.67U	0.95
-3	2.99	3.15
-2	4.40	4.44
-1	6.92	6.92
0	0.73U	-0.59
1	9.53	-10.04
2	1.98	0.46
3	1.60	1.59
H= 1, K= 12		
-5	0.78U	0.27
-3	2.03	-2.04
-2	3.97	4.12
-1	4.11	4.47
0	0.73U	0.16
1	0.73U	0.08
2	1.55	-2.14
3	2.76	-2.72
H= 1, K= 13		
-3	1.74	-1.60
-2	0.90U	0.30
-1	1.93	1.88
0	0.73U	0.80
1	0.73U	-0.21
2	1.06	1.22
3	0.78U	1.40
H= 1, K= 14		
-3	3.44	-3.62
-2	4.50	-4.18
-1	3.19	2.60
0	2.18	1.97
1	0.73U	-0.34
2	2.51	2.24
H= 2, K= 0		
-8	3.19	3.07
-6	8.08	-7.13
-4	13.59	13.32
-2	32.50	-32.08
0	9.77	-8.87
2	24.09	21.67
4	5.47	-5.30
6	2.99	3.07
H= 2, K= 1		
-9	0.97	-0.59
-8	1.69	1.20
-7	3.44	2.76
-6	6.28	-5.39
-5	8.03	-6.79
-4	4.55	-3.96
-3	12.38	12.83
-2	0.47U	-0.35
-1	23.22	-26.85
0	11.90	11.03
1	12.43	11.34
2	9.67	8.52
3	1.26	-0.41
4	6.87	7.09
5	3.82	3.48
6	1.55	-0.76
7	4.50	-3.51
H= 2, K= 2		
-9	1.06	0.82
-8	0.73U	0.45
-7	0.73U	-0.41
-6	4.55	-4.05
-5	7.50	-6.98
-4	9.67	9.31
-3	5.03	-4.76
-2	5.22	-4.48
-1	7.88	7.80
0	7.93	-6.74
1	2.28	2.20
2	10.84	10.18
3	5.75	6.59
4	7.11	-7.48
5	4.50	4.37
6	3.97	3.93
7	1.60	-1.67
H= 2, K= 3		
-9	2.66	-2.29
-8	3.34	2.98
-7	1.74	1.75
-6	2.56	-2.40
-5	1.26	-1.52
-4	3.39	3.89
-3	2.99	3.31
-2	1.93	2.07
-1	12.48	12.82
0	20.56	-17.52
1	7.40	-6.90
2	5.57	-5.33
3	2.32	-2.24
4	3.48	3.74
5	0.82	0.55
6	1.06	0.47
7	0.47U	0.12
H= 2, K= 4		
-9	0.73U	-0.60
-8	1.69	-1.95
-7	2.61	2.96
-6	2.13	2.23
-5	1.55	1.74
-4	2.41	-2.30
-3	11.17	11.36
-2	12.48	13.76
-1	5.37	-5.70
0	6.87	-5.97
1	14.56	-14.04
2	1.35	1.28
3	6.58	-6.95
4	8.03	-7.50
5	1.16	1.14
6	4.94	4.94
7	0.73U	0.61
H= 2, K= 5		
-9	1.45	-2.09
-8	0.90U	1.03
-7	3.34	3.54
[illegible]	0.90U	0.41
-4	2.41	2.46
-3	7.01	-7.29
-2	14.46	14.48
-1	17.32	16.67
0	12.91	-12.56
1	13.68	-11.70
2	1.16	1.44
3	1.26	0.66
4	5.57	-6.46
5	1.16	-1.14
6	0.90U	1.04
7	0.90U	1.23
H= 2, K= 6		
-8	0.90U	-0.86
-7	0.90U	0.21
-6	3.39	3.87
-5	4.69	-4.88
-4	7.64	-7.73
-3	3.19	2.81
-2	6.53	6.58
-1	0.82	0.47
0	6.00	-5.19
1	13.35	11.47
2	4.26	4.56
3	1.98	-1.61
4	4.89	-5.51
5	2.23	-1.80
6	2.76	3.09
H= 2, K= 7		
-8	0.90U	-0.52
-3	6.10	-5.91
-2	3.44	3.65
-1	5.37	5.01
0	0.84U	0.68
1	1.69	-1.59
2	15.67	15.93
3	3.97	4.24
5	0.90U	-0.89
H= 2, K= 8		
-8	0.90U	-0.57
-7	0.90U	0.48
-6	0.90U	0.36
-5	0.90U	-0.66
-3	5.17	-5.15
-2	1.26	1.35
-1	4.26	-3.49
0	3.77	-3.52
1	9.04	8.84
2	8.76	9.08
3	0.90U	0.40
5	0.90U	0.57
6	0.90U	1.31
H= 2, K= 9		
-7	0.90U	1.48
-5	0.90U	-2.21
-4	0.61U	1.29
-3	2.51	2.42
-2	1.88	-2.05
-1	1.93	-2.07
0	6.53	-6.14
1	0.97	-0.10
2	1.26	1.29
3	2.41	2.75
4	0.61U	-0.83
5	0.90U	-0.12
H= 2, K= 10		
-7	0.90U	0.83
-6	0.90U	1.31
-3	0.61U	-1.15
-2	2.99	3.00
-1	2.41	-2.61
0	7.40	-6.80
1	5.80	-5.62
2	2.56	2.90
H= 2, K= 11		
-6	0.90U	0.07
-5	0.90U	1.42
-3	3.44	4.49
-2	0.67U	0.45
-1	1.35	-1.48
0	0.84U	-1.62
1	3.97	-3.76
2	4.26	-4.21
3	0.90U	-0.28
H= 2, K= 12		
-5	0.90U	-0.18
-4	0.61U	0.32
-3	2.13	-2.08
-2	3.14	2.60
-1	5.95	5.68
0	3.44	-3.41
1	0.73U	0.29
2	1.35	0.92
3	0.90U	-0.40
H= 2, K= 13		
-3	1.20	-1.36
-2	2.76	2.57
-1	1.79	1.54
0	4.94	4.18
1	0.73U	-0.16
2	1.06	0.78
H= 2, K= 14		
-3	1.45	-1.42
-2	0.61U	0.15
-1	2.91	2.76
0	0.73U	0.79
1	0.73U	0.68
H= 3, K= 0		
-8	4.30	4.25
-6	6.63	-6.23
-4	10.84	9.94
-2	19.54	-20.55
0	13.88	12.52
2	7.35	6.73
4	2.81	-2.51
6	0.97	-0.71
H= 3, K= 1		
-9	2.18	-1.16
-8	3.34	-2.87
-7	2.23	1.89
-6	2.41	2.16
-5	1.79	1.55
-4	6.48	5.99
-3	9.04	-8.67
-2	20.70	21.25
-1	1.26	-0.96
0	9.34	-8.28
1	12.09	10.42
2	4.35	3.77
3	4.21	-3.58
4	3.82	-3.37
5	1.79	2.08
6	0.47U	-0.46
H= 3, K= 2		
-9	3.09	-2.75
-8	4.74	4.19
-7	0.56U	-0.47
-6	6.05	-6.08
-5	3.53	3.20
-4	11.75	10.87
-3	16.16	17.17
-2	13.93	-13.91
-1	2.46	-2.02
1	3.92	-3.55
2	2.46	2.41
3	3.29	2.98
4	2.03	-1.97
5	2.81	-3.52
6	1.35	1.19
H= 3, K= 3		
-9	2.46	-2.08
-8	1.35	-1.06
-7	2.76	2.84
-6	2.76	3.54
-5	3.39	-3.68
-4	2.41	-2.75
-3	9.19	8.69
-2	10.21	9.82
-1	7.55	-7.29
0	27.28	-23.26
1	0.82	0.69
2	9.96	9.20
3	6.05	-6.62
4	1.69	-1.70
5	4.79	4.74
6	0.82	0.73
H= 3, K=		
-9	0.73U	0.32
-8	2.91	2.58
-7	2.41	2.65
-6	7.60	-7.71
-5	2.76	-2.80
-4	8.85	8.72
-3	3.92	-4.37
-2	4.94	5.24
-1	15.28	-14.64
0	4.40	-4.38
1	0.97	-0.74
2	1.16	-0.96
3	4.55	4.80
4	2.18	-2.31
5	0.82	0.02
6	1.35	1.37
H= 3, K= 5		
-9	2.23	-2.10
-8	1.79	1.99
-7	1.88	1.87
-6	0.61U	-0.56
-5	6.82	-7.07
-4	6.82	-7.45
-3	10.93	11.24
-2	0.90U	-0.56
-1	0.97	1.04
0	6.87	-5.93
1	0.97	0.97
2	5.28	5.81
3	3.97	-4.91
4	0.67U	0.15
5	3.19	3.53
6	0.73U	0.16
H= 3, K= 6		
-9	0.73U	-0.04
-7	0.56U	-0.67
-6	4.50	-4.59
-5	3.19	-3.46
-4	1.79	1.28
-3	1.16	-0.76
-2	3.82	4.17
-1	6.43	6.31
0	1.45	-0.77
1	7.35	6.69
2	1.45	0.82
3	2.99	-3.12
4	0.73U	0.39
5	0.73U	-0.37
6	0.73U	-0.31
H= 3, K= 7		
-8	0.73U	0.21
-4	0.73U	-0.58
-3	3.82	-3.50
-2	7.69	7.87
-1	0.73U	0.14
0	9.96	9.03
1	0.73U	-0.57
2	2.66	-2.81
3	0.90U	1.27
H= 3, K= 8		
-8	0.73U	1.03
-7	0.67U	-0.46
-6	0.73U	1.29
-3	0.73U	0.56
-2	4.84	-5.43
-1	5.08	5.11
0	0.73U	-1.10
1	0.73U	0.16
2	0.97	1.02
3	3.92	-4.87
H= 3, K= 9		
-8	0.73U	1.35
-7	0.73U	1.00
-4	0.73U	-0.57
-3	7.35	-6.57
-2	0.90U	-1.21
-1	0.73U	0.97
0	3.87	-3.51
1	1.45	-1.15
2	3.29	-3.51
3	0.90U	1.30
H= 3, K= 10		
-8	0.73U	-0.87
-7	0.73U	0.35
-6	0.73U	0.77
-4	0.73U	1.62
-3	4.45	-4.54
-2	1.45	-1.72
-1	5.17	-4.46
0	3.39	2.38
1	3.44	-3.22
2	0.78U	-0.36
3	0.90U	1.01
H= 3, K= 11		
-6	0.73U	0.34
-3	0.73U	0.57
-2	0.90U	-0.23
-1	3.44	3.39
0	3.39	-3.15
1	0.73U	0.88
2	1.88	1.87
3	1.98	-2.26
H= 3, K= 12		
-5	0.56U	0.88
-3	0.73U	-0.15
-2	0.48	0.94
-1	2.32	2.25
0	1.93	1.62
1	2.76	2.17
2	0.78U	-0.68
H= 3, K= 13		
-4	0.73U	0.58
-3	1.35	1.13
-2	3.53	3.29
-1	1.98	-1.52
0	2.03	1.73
1	1.45	1.03
H= 3, K= 14		
-2	0.90U	-1.83
-1	0.73U	0.63
H= 4, K= 0		
-8	6.77	6.75
-6	1.06	0.61
-4	7.25	6.71
-2	0.67U	0.88
0	11.80	-10.10
2	1.93	-2.14
4	2.76	-2.50
H= 4, K= 1		
-9	0.97	-0.18
-8	0.67U	-0.49
-7	3.53	3.31
-6	4.30	3.87
-5	2.99	2.70
-4	7.35	8.18
-3	2.11	-1.88
-1	1.55	1.11
0	3.39	-2.76
1	2.61	-2.09
2	3.48	-3.39
3	3.34	-3.64
4	2.03	-1.81
5	2.18	1.84
H= 4, K= 2		
-9	3.19	-2.67
-8	4.26	4.17
-7	3.44	3.11
-6	7.30	-7.23
-5	6.05	6.17
-4	0.67U	0.43
-3	7.16	6.37
-2	1.74	-1.28
-1	8.08	-7.53
0	2.41	2.27
1	1.55	1.41
2	3.44	3.18
3	4.64	-5.73
4	0.78U	0.59
5	0.56U	0.29
H= 4, K= 3		
-9	0.82	0.87
-8	0.82	-0.66
-7	5.65	-5.98
-6	2.66	2.80
-5	0.82	-0.16
-3	10.89	-10.25
-2	1.55	-1.33
-1	8.90	8.57
0	1.06	-0.68
1	3.48	3.31
2	0.73U	0.22
3	2.18	2.49
4	1.06	-1.52
5	0.48	-0.21
H= 4, K= 4		
-9	0.67U	-0.51
-8	1.06	0.80
-7	1.16	0.70
-6	7.40	-8.11
-5	3.97	-4.89
-4	4.59	5.01
-3	4.21	-4.34
-2	2.37	-2.50
-1	2.37	-1.75
0	5.08	4.72
1	7.11	6.78
2	0.82	-0.58
3	0.73U	0.97
4	1.35	1.56
5	0.67U	-0.27
H= 4, K= 5		
-9	0.67U	0.61
-8	0.67U	-0.66
-7	4.40	-5.18
-6	0.61U	0.25
-5	9.91	11.37
-4	12.53	-11.98
-3	4.06	-3.83
-2	3.87	4.27
-1	6.33	5.97
0	0.84U	0.65
1	6.33	-6.45
2	5.08	5.50
3	0.73U	0.72
4	0.73U	0.53
5	1.74	-1.56
H= 4, K= 6		
-9	0.67U	0.67
-8	0.67U	1.14
-7	0.61U	-0.09
-6	0.61U	1.05
-5	1.88	-2.27
-4	8.36	9.12
-3	0.73U	-0.76
-2	2.32	-2.40
-1	2.95	3.11
0	2.32	-2.60
1	1.16	-1.20
2	3.82	-3.74
3	2.41	2.59
4	1.60	1.52
5	0.73U	-1.27
H= 4, K= 7		
-8	0.67U	-0.81
-7	0.61U	-0.53
-3	7.30	-7.53
-2	9.77	9.54
-1	0.67U	0.98
0	7.06	-6.89
1	4.84	-4.88
2	0.73U	-0.72
3	2.61	2.79
4	0.73U	-0.27
H= 4, K= 8		
-8	0.67U	1.21
-7	0.61U	-0.70
-6	0.61U	-0.04
-3	3.87	3.76
-2	3.92	-4.10
-1	1.16	0.02
0	0.73U	-0.12
1	5.62	-5.58
2	2.32	2.09
3	0.73U	-0.28
H= 4, K= 9		
-7	0.61U	-1.15
-6	0.61U	1.19
-5	0.67U	-0.93
-4	0.67U	-0.53
-3	7.30	-6.88
-2	3.14	3.30
-1	4.69	4.91
0	3.77	-4.19
1	0.67U	0.86
2	0.73U	-0.80
3	1.55	1.50
H= 4, K= 10		
-5	0.67U	0.44
-3	0.73U	-0.20
-2	3.19	3.34
-1	2.13	-2.01
0	3.48	3.33
1	1.88	1.94
2	1.60	-1.30
3	0.73U	-0.39
H= 4, K= 11		
-4	0.61U	-0.73
-3	0.73U	0.71
-2	1.93	-1.61
-1	6.19	5.48
0	1.88	1.98
1	2.41	-2.28
2	0.73U	0.95
H= 4, K= 12		
-5	0.67U	0.96
-3	1.26	-1.07
-2	0.68	0.65
-1	1.16	-1.05
0	0.73U	0.36
1	3.82	3.87
H= 4, K= 13		
-3	2.32	-2.07
-2	1.16	-1.09
-1	0.67U	-0.28
H= 5, K= 0		
-8	5.57	5.44
-6	2.23	2.65
-4	1.69	1.77
-2	1.69	-1.42
0	17.02	-14.78
2	0.67U	-0.69
4	1.88	2.10
H= 5, K= 1		
-9	2.86	1.82
-8	1.98	-1.68
-7	1.26	0.26
-6	1.88	2.03
-5	4.45	3.87
-4	2.51	-2.41
-3	1.16	-1.18
-2	6.28	5.89
-1	6.00	-4.92
0	1.45	0.94
1	4.02	-4.01
2	2.56	-2.68
3	1.06	0.74
4	0.97	-0.32
H= 5, K= 2		
-9	0.73U	-1.15
-8	0.73U	-0.34
-7	0.73U	-0.17
-6	2.61	-2.54
-5	1.26	0.86
-4	3.39	-3.35
-3	0.73U	-0.87
-2	10.49	10.31
-1	9.24	8.68
0	3.48	-2.80
1	5.95	-5.50
2	3.53	4.27
3	1.06	-0.28
4	1.16	-1.49
H= 5, K= 3		
-9	0.97	-1.03
-8	1.88	-2.06
-7	5.12	-5.63
-6	3.34	4.09
-5	1.74	-1.96
-4	6.87	-6.78
-3	0.47U	0.34
-2	7.35	7.42
-1	9.96	9.89
0	0.82	-0.50
1	4.94	4.94
3	0.73U	-0.13
4	1.06	0.25
H= 5, K= 4		
-9	0.68	-0.09
-8	2.41	-2.57
-7	1.69	1.59
-6	1.16	1.19
-5	1.55	-1.64
-4	6.68	-7.66
-3	2.32	-2.16
-2	9.91	9.84
-1	2.66	2.22
0	1.16	-1.29
1	2.28	-2.23
2	4.74	5.55
3	0.97	1.30
4	3.92	-3.98
H= 5, K= 5		
-9	0.90U	0.58
-8	0.90U	-0.43
-7	1.16	0.58
-6	2.71	2.86
-5	4.21	5.22
-4	5.47	-6.04
-3	6.48	-6.70
-2	1.60	1.48
-1	0.61U	-0.27
0	1.69	-1.86
1	1.35	-1.13
2	1.79	1.93
3	0.73U	-0.50
4	0.97	0.83
H= 5, K= 6		
-8	0.90U	0.94
-7	1.35	1.39
-6	7.21	7.98
-5	2.18	-2.52
-4	4.26	-4.72
-3	0.73U	1.19
-2	1.45	-1.65
-1	4.45	-4.88
0	7.25	-7.72
1	3.19	3.46
2	0.90U	1.42
3	0.73U	0.83
H= 5, K= 7		
-3	6.72	-6.53
-2	0.78U	-0.15
-1	0.67U	-0.61
0	1.55	-1.32
1	1.88	-2.13
3	0.73U	0.75
H= 5, K= 8		
-3	4.94	4.84
-2	2.56	2.58
-1	4.21	-4.18
0	1.26U	0.77
1	2.18	2.11
2	0.90U	0.53
3	0.73U	-1.33
H= 5, K= 9		
-3	0.73U	-0.63
-2	0.90U	0.64
-1	6.82	6.12
0	1.26U	-0.43
1	0.67U	-0.31
2	0.90U	-1.28
H= 5, K= 10		
-3	0.73U	1.26
-2	3.82	3.50
-1	0.97	-1.09
0	1.26U	0.39
1	0.67U	0.31
2	0.90U	-0.87
H= 5, K= 11		
-3	1.26	-1.04
-2	0.90U	-0.51
-1	0.67U	0.91
0	1.26U	1.30
H= 5, K= 12		
-3	1.74	-1.56
-2	0.90U	-0.22
-1	0.67U	0.43
H= 6, K= 0		
-8	1.16	-0.99
-6	4.69	4.95
-4	5.37	-5.47
-2	2.56	2.51
0	9.87	-9.17
2	4.98	4.78
H= 6, K= 1		
-9	1.60	-1.12
-8	2.76	-2.20
-7	1.79	1.75
-6	1.26	-0.54
-5	1.45	-1.03
-4	3.44	2.91
-3	3.63	3.04
-2	7.30	7.03
-1	7.60	-7.27
0	2.51	-1.60
1	2.41	2.63
2	1.26	-1.24
3	0.73U	-0.17
H= 6, K= 2		
-9	2.37	-2.02
-8	0.73U	-1.33
-7	0.73U	-0.89
-6	2.13	2.37
-5	1.69	-1.21
-4	2.76	-2.45
-3	9.67	9.74
-2	6.77	6.25
-1	1.26	0.94
0	3.67	-3.34
1	1.55	-1.91
2	1.69	2.22
3	0.82	-1.23
H= 6, K= 3		
-9	0.68	-0.77
-8	1.88	-1.63
-7	0.73U	-0.03
-6	1.16	0.28
-5	1.74	-2.26
-4	1.16	-0.86
-3	5.90	5.84
-2	4.50	4.83
-1	1.16	-0.99
0	3.34	-3.08
1	3.44	4.13
2	0.68	0.10
3	2.71	-3.18
H= 6, K= 4		
-9	0.73U	0.67
-8	0.97	0.76
-7	1.06	1.34
-5	2.56	-2.91
-4	2.91	-3.39
-3	1.55	-1.53
-2	3.29	3.43
-1	2.76	-2.77
0	1.16	1.55
1	0.73U	-0.37
2	0.73U	-0.70
3	0.82	2.02
H= 6, K= 5		
-8	0.82	-0.14
-7	0.90U	0.54
-6	1.93	2.23
-5	2.91	-3.52
-4	4.06	-5.05
-3	1.45	-0.43
-2	3.34	-3.63
-1	2.28	-2.00
0	1.60	0.10
1	0.73U	2.99
2	0.73U	0.94
H= 6, K= 6		
-8	1.26	1.12
-7	0.90U	0.49
-5	1.35	1.18
-4	2.91	-3.80
-3	3.19	-3.46
-2	0.90U	-0.59
-1	1.16	1.08
0	1.26U	-0.29
1	0.73U	0.02
2	0.73U	-0.67
H= 6, K= 7		
-3	0.73U	0.49
-2	0.90U	-0.04
-1	1.74	-1.59
0	3.87	3.13
1	0.73U	0.27
H= 6, K= 8		
-3	0.73U	0.66
-2	3.34	2.62
-1	2.91	2.25
0	1.26U	-1.83
1	0.73U	-0.72
H= 6, K= 9		
-3	2.41	1.95
-2	0.90U	-0.51
-1	0.48	-0.51
0	1.16	1.16
H= 6, K= 10		
-3	0.73U	0.07
-2	0.90U	0.78
-1	1.55	-1.19
H= 6, K= 11		
-3	0.73U	-1.07
H= 7, K= 0		
-8	0.67U	-0.09
-6	1.60	1.51
-4	1.16	0.39
-2	0.67U	-0.70
0	1.55	1.85
H= 7, K= 1		
-9	0.73U	-1.31
-8	0.73U	-0.69
-7	2.46	2.00
-6	1.60	1.60
-5	1.26	-1.48
-4	4.02	3.22
-3	2.91	2.83
-2	2.03	-1.36
-1	3.19	-2.83
0	0.67U	-0.22
1	2.66	2.41
H= 7, K= 2		
-8	0.73U	0.24
-7	1.16	-1.15
-6	0.73U	0.94
-5	4.26	4.55
-4	1.45	-1.14
-3	0.73U	-0.43
-2	0.73U	-0.54
-1	0.73U	-0.19
0	1.60	1.43
1	0.97	-1.32
H= 7, K= 3		
-8	1.69	-1.75
-7	0.97	0.11
-6	1.06	0.41
-5	1.35	-1.89
-4	1.16	1.10
-3	0.73U	0.33
-2	2.13	-2.35
-1	1.16	-0.97
0	2.13	1.69
1	0.48	0.87
H= 7, K= 4		
-8	0.73U	-0.16
-7	1.45	-1.82
-6	0.73U	-0.48
-5	0.73U	-0.11
-4	1.06	-1.54
-3	2.81	-2.93
-2	0.73U	0.25
-1	1.69	1.55
0	0.73U	0.40
1	0.82	0.66
H= 7, K= 5		
-8	0.90U	-1.24
-7	1.16	-1.65
-6	0.97	0.58
-5	0.90U	-0.13
-4	1.55	-2.41
-3	0.73U	1.10
-2	0.73U	-0.18
-1	0.73U	-0.29
0	1.08U	0.96
1	0.48	-0.53
H= 7, K= 6		
-7	1.26	1.42
-5	0.90U	0.20
-4	1.74	1.74
-3	0.73U	-0.28
-2	0.73U	0.12
-1	0.73U	0.59
0	1.26U	-0.10
H= 7, K= 7		
-3	2.41	1.84
-2	1.16	1.39
-1	2.32	-1.55
0	1.26U	-1.65
H= 7, K= 8		
-3	1.88	1.11
-2	2.46	-1.88
-1	0.73U	0.34
H= 7, K= 9		
-3	0.73U	0.07
H= 8, K= 0		
-6	1.60	1.87
-4	1.60	-1.56
-2	1.74	1.43
H= 8, K= 1		
-7	0.73U	-0.19
-6	0.82	0.88
-5	0.73U	0.33
-4	2.56	-2.56
-3	0.61U	-0.81
-2	0.47U	-0.39
-1	2.32	2.10
H= 8, K= 2		
-7	0.73U	0.49
-6	0.73U	0.73
-5	0.73U	-0.70
-4	1.26	-1.42
-3	3.39	-2.78
-2	1.55	1.04
-1	1.55	1.09
H= 8, K= 3		
-7	0.68	-0.51
-6	0.97	1.30
-5	0.68	-0.49
-4	1.93	-2.29
-3	0.73U	0.06
-2	1.06	0.89
-1	0.73U	0.37
H= 8, K= 4		
-7	0.73U	-0.31
-6	0.73U	0.77
-5	0.73U	0.94
-4	0.73U	-0.04
-3	0.73U	-0.22
-2	1.45	-1.01
H= 8, K= 5		
-6	0.90U	0.84
-5	0.90U	0.84
-4	0.90U	1.22
-3	0.73U	-0.20
-2	0.73U	0.08
H= 8, K= 6		
-5	0.90U	1.09
-4	0.90U	0.93
-3	0.73U	-0.03

tion, (651), F_c was about 2·5 times the estimated $F_{\min}$.

The final position parameters and their standard deviations, estimated from the inverse of the matrix of the normal equations, are given in Table 2. The numbering of the carbon atoms is indicated in Fig. 1; the hydrogen atoms have been numbered to correspond

Table 2. *Final position parameters**

Carbon parameters and e.s.d.'s × 10^4; hydrogen parameters and e.s.d.'s × 10^3

	Before libration correction			After libration correction					
Atom	x	y	z	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C1	4003	1069	2337	4016	1071	2344	6	3	5
C2	2759	0036	2462	2770	0035	2472	5	3	5
C3	2808	−0994	1512	2820	−0999	1519	6	3	6
C4	0997	−1710	0729	1003	−1717	0734	6	3	6
C5	−0894	−1409	0877	−0896	−1415	0883	6	3	5
C6	−0721	−0570	2221	−0723	−0572	2231	6	4	5
C7	1093	0156	2999	1097	0156	3011	6	3	5
C8	−3106	−1732	−0749	−3115	−1736	−0748	6	3	6
H1	555	123	339	557	123	340	8	5	8
H3	400	−114	119	402	−115	120	7	4	6
H4	098	−232	−018	098	−233	−018	9	5	8
H6	−197	−033	244	−198	−033	245	7	4	6
H7	107	084	377	107	084	378	7	4	7
H8	−387	−236	−058	−388	−237	−058	7	4	6

* For details of the libration correction see text and Table 4.

Table. 3. *Final temperature factor parameters*

Carbon values (dimensionless) × 10^4; hydrogen values in Å^2. The e.s.d. is given below each value

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Atom	B
C1	280	89	279	−46	188	−36	H1	4·8
	(9)	(3)	(9)	(8)	(14)	(9)		(1·0)
C2	287	75	218	22	124	27	H3	3·9
	(9)	(3)	(7)	(8)	(13)	(7)		(0·9)
C3	296	73	314	49	227	27	H4	4·9
	(9)	(3)	(9)	(8)	(15)	(9)		(1·2)
C4	383	63	275	58	249	37	H6	3·2
	(11)	(3)	(9)	(8)	(15)	(8)		(0·8)
C5	350	65	244	−15	236	54	H7	4·0
	(10)	(2)	(8)	(8)	(14)	(8)		(0·9)
C6	375	91	235	−19	310	32	H8	3·2
	(11)	(3)	(8)	(9)	(15)	(8)		(0·8)
C7	388	78	222	−8	249	−5		
	(11)	(3)	(7)	(9)	(14)	(8)		
C8	350	74	308	−61	312	−2		
	(11)	(3)	(9)	(9)	(16)	(9)		

to the carbon atoms to which they are attached. Table 3 lists the final anisotropic thermal parameters for the carbons and the corresponding isotropic values for the hydrogens. Examination of the averaged intra-atomic correlation coefficients (Cramer, 1955) revealed that, excluding correlations due to the non-

Table 4. *Rigid-body thermal parameters*

(For the molecule centered at the origin)

$$\mathbf{T}\dagger=\begin{pmatrix}509 & 27 & 2\\ & 390 & 43\\ & & 481\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \omega\dagger=\begin{pmatrix}12\cdot9 & 4\cdot6 & 3\cdot0\\ & 17\cdot4 & 5\cdot6\\ & & 14\cdot9\end{pmatrix}(^\circ)^2$$

$$\sigma(T)=\begin{pmatrix}17 & 12 & 12\\ & 15 & 12\\ & & 15\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \sigma(\omega)=\begin{pmatrix}1\cdot6 & 1\cdot0 & 1\cdot0\\ & 1\cdot7 & 1\cdot0\\ & & 1\cdot5\end{pmatrix}(^\circ)^2$$

Principal axes:

		Direction cosines relative to		
	Eigenvalue	**a**	**b**	**c***
T	0·0520 Å^2	0·8627	0·3146	0·3960
	0·0492	0·4746	−0·2332	−0·8487
	0·0368	0·1746	−0·9201	0·3505

		Direction cosines relative to		
	Eigenvalue	**a**	**b**	**c***
ω	24·4 (°)^2	0·4264	0·7162	0·5524
	10·9	0·6296	0·2034	−0·7498
	9·9	0·6494	−0·6675	0·3643

† Referred to the directions of the orthogonal axes **a**, **b**, **c***.

Table 5. *Approximate molecular axes*†

(For the molecule centered at the origin)

Axis	Direction cosines relative to a	b	c*	Description
A	0·7014	0·6022	0·3814	Approximately parallel to C1–C8 line
B	−0·0431	0·5699	−0·8206	Normal to plane of C3, C4, C6, C7
C	−0·7109	0·5513	0·4367	Normal to plane of C1, C8, and their centrosymmetric counterparts

† See Fig. 1 also. Axis *A* is normal to *B* and *C*, but they are at 90·7° (rather than 90°) to one another, being defined by the actual geometry of the molecule.

orthogonality of the axes, the correlation between the scale factor and the principal temperature parameters was the largest, and B_{11} and B_{22} showed a significant inverse correlation. The former effect was expected in view of the obvious interdependence of the scale factor and the temperature parameters; the latter effect was also observed by Sparks (1958) in anthracene, and may be due to neglect of weak reflections.

The anisotropic thermal parameters of the carbon atoms were used in a determination (Cruickshank, 1956*a*, *b*) of translational and librational tensors for the molecule considered as a rigid body. The results

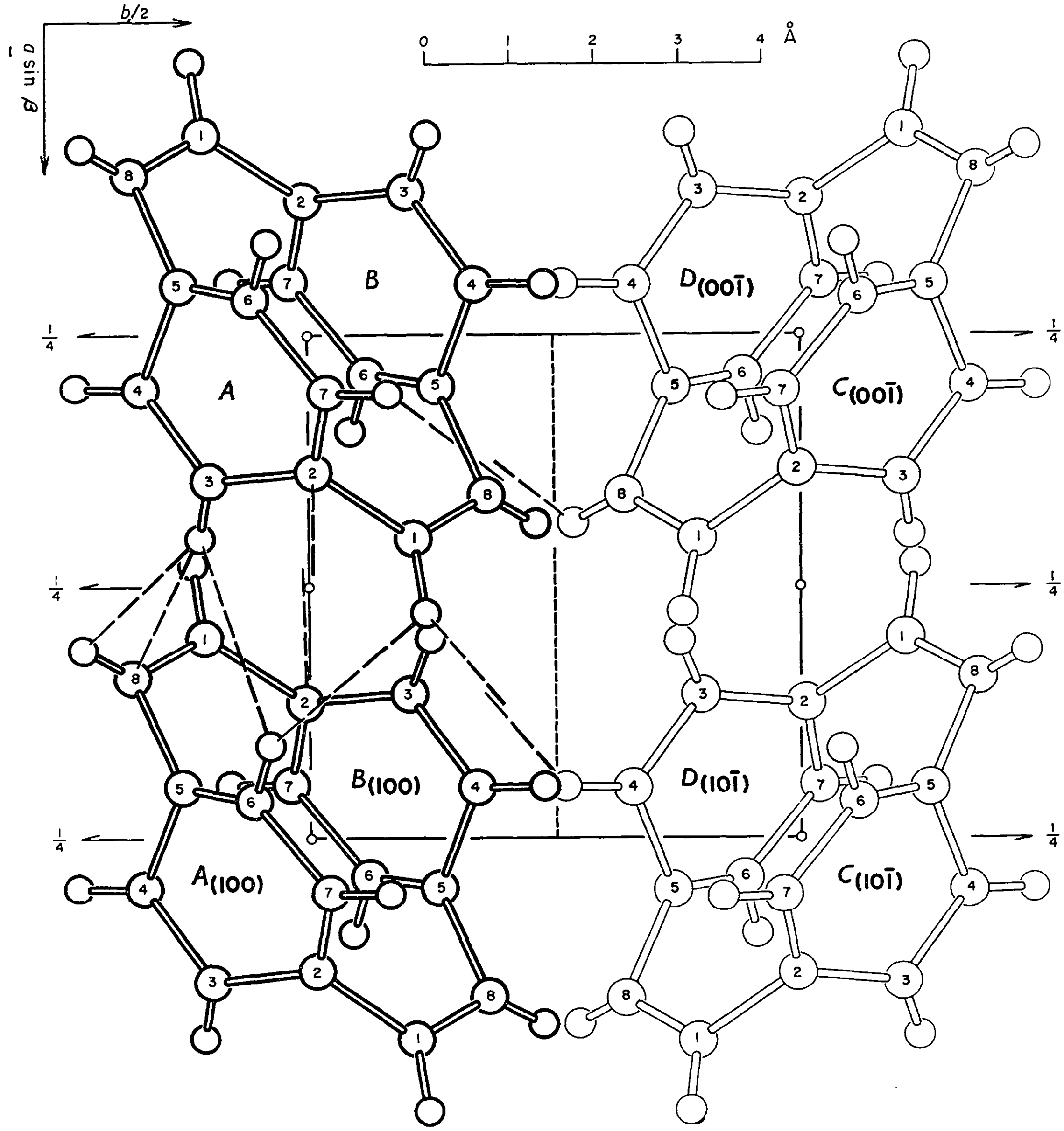

Fig. 2. Arrangement of molecules in one unit cell. Asymmetric units are identified as in Table 6. Some of the contacts in Table 6 are shown.

are given in Table 4. The fit seems quite good, as is reasonable for this rather rigid molecule; the r.m.s. discrepancy between the observed and derived U_{ii} or U_{ij} is only about 5% of the average U_{ii} and the largest discrepancy only about 10%. The overall translational motion is not markedly anisotropic. On the other hand, the r.m.s. amplitude of libration is about 50% greater around one axis than about the other two, and while not unusually large, is sufficient to lead to bond length corrections averaging about 0·005 Å (Cruickshank, 1956*b*, 1961). Both the uncorrected and corrected position parameters are given in Table 2. The axis of maximum libration is about 20° from the long axis of the molecule (axis *A* in Fig. 1 and Table 5) and is nearly normal to axis *B*.

Crystal and molecular structure

The arrangement of the molecules in the unit cell is shown in Fig. 2 and the closest intermolecular approaches are given in Table 6. The packing is determined by the H · · · H and H · · · C contacts, and none of these approaches the sum of the usually accepted van der Waals radii (about 2·4 and 2·9 Å respectively). The shortest C · · · C contact is about 0·3 Å greater than twice the van der Waals radius ascribed to aromatic carbon. This looseness of packing is consistent with the significant librational motion of the molecule, and it is clear that any distortions in the molecule must be ascribed to *intra-* rather than *inter*-molecular potentials.

The molecular geometry is presented in Figs. 3 to 5 and Tables 7 to 9. The most striking feature is the deformation of the aromatic rings into a boat shape, perhaps best illustrated by the side profile of the molecule in Fig. 4. Carbon atoms 2 and 5 are 0·166

Table 6. *Shortest intermolecular distances**

From atom X at position *A*	To atom Y at position	Distance
H1	H4 *D* (100)	2·71 Å
H1	H6 *A* (100)	2·78
H3	H6 *A* (100)	2·65
H3	H8 *A* (100)	2·77
H3	H8 *C* $(1\bar{1}0)$	2·82
H6	H7 *B* (001)	2·72
H7	H8 *D*	2·74
H3	C8 *A* (100)	3·03 Å
H4	C5 *C* $(0\bar{1}\bar{1})$	3·06
H4	C6 *C* $(0\bar{1}\bar{1})$	3·03
H8	C1 *D* $(0\bar{1}0)$	3·10
H8	C3 *C* $(\bar{1}\bar{1}\bar{1})$	3·02
C2	C2 *B* (101)	3·69 Å

* Position *A* is (x, y, z); *B* is $(-x, -y, -z)$; *C* is $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; and *D* is $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$. Positions equivalent by translation are identified by the numbers in parentheses.

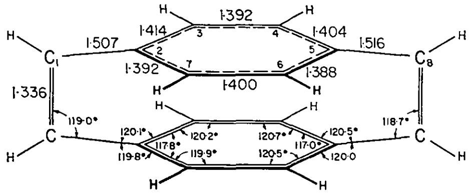

Fig. 3. Bond distances and angles. Values involving hydrogen atoms are given in Table 7.

Table 7. *Bond distances and bond angles*†*

Bond	Distance		Angle	Value
C1–C8	1·336	(1·330) Å	C8*B*–C1–C2	118·7°
			C5–C8–C1*B*	119·0
C1–C2	1·507	(1·502)		
C5–C8	1·516	(1·511)	C1–C2–C3	120·0
			C1–C2–C7	120·5
C2–C3	1·414	(1·409)	C8–C5–C4	119·8
C3–C4	1·392	(1·388)	C8–C5–C6	120·1
C4–C5	1·404	(1·398)		
C5–C6	1·388	(1·383)	C3–C2–C7	117·0
C6–C7	1·400	(1·396)	C4–C5–C6	117·8
C7–C2	1·392	(1·386)		
			C2–C3–C4	120·5
C1–H1	1·02		C3–C4–C5	119·9
C3–H3	0·98		C5–C6–C7	120·2
C4–H4	0·99		C6–C7–C2	120·7
C6–H6	0·99			
C7–H7	1·00		C8*B*–C1–H1	120
C8–H8	0·95		C1*B*–C8–H8	121
			C2–C1–H1	121
			C5–C8–H8	120
			C2–C3–H3	120
			C2–C7–H7	119
			C5–C4–H4	121
			C5–C6–H6	123
			C4–C3–H3	119
			C3–C4–H4	117
			C7–C6–H6	116
			C6–C7–H7	119

* Values in parentheses are before correction for libration; angles did not change significantly. The e.s.d.'s are: C–C, 0·006–0·007 Å, including an arbitrary estimate of 0·004 Å as the standard error in the libration correction; C–H, 0·05 Å; C–C–C, 0·4°; C–C–H, 5°.

† *B* refers to an atom at $(-x, -y, -z)$, as in Table 6.

Table 8. *Some non-bonded intramolecular C–C distances*†*

Next-nearest neighbors		Others	
C1–C5*B*	2·46 Å	C1 · · · C4*B*	3·26 Å
C1–C3	2·53	C1 · · · C6*B*	3·24
C1–C7	2·52	C2 · · · C5*B*	2·80
C3–C5	2·42	C2 · · · C4*B*	3·29
C3–C7	2·39	C2 · · · C6*B*	3·27
C5–C7	2·42	C3 · · · C6*B*	3·14
		C3 · · · C5*B*	3·29
C8–C2*B*	2·45	C3 · · · C7*B*	3·43
C8–C4	2·53	C3 · · · C8*B*	3·22
C8–C6	2·52	C4 · · · C7*B*	3·14
C4–C2	2·44	C4 · · · C6*B*	3·44
C4–C6	2·39	C5 · · · C7*B*	3·26
C2–C6	2·43	C7 · · · C8*B*	3·23
		C2 · · · C5	2·81
		C3 · · · C6	2·77
		C4 · · · C7	2·77

* *B* refers to an atom at $(-x, -y, -z)$ as in Table 6.

† All distances less than 3·5 Å are listed.

Table 9. *Some least-squares planes*†

	Plane I	Plane II	Plane III	Plane IV
l_1	−0·7109	0·0431	−0·0607	0·1430
l_2	0·5513	−0·5699	−0·4877	−0·6457
l_3	0·4367	0·8206	0·8709	0·7501

Deviations of atoms (Å)

(Bold type indicates atom was used to define the plane)

	I	II	III	IV
C1	**(0·000)**	−0·886		
C2	0·013	−0·166	0·000	**0·002**
C3	−1·192	**0·002**	−0·001	0·344
C4	−1·193	**−0·002**	0·001	0·343
C5	0·009	−0·178	0·000	**−0·002**
C6	1·198	**0·002**	0·342	**0·004**
C7	1·200	**−0·002**	0·333	**−0·004**
C8	**(0·000)**	−0·918		
H1	−0·09			
H3	−2·05	−0·04	−0·16	
H4	−2·07	−0·10	−0·22	
H6	2·09	−0·08		−0·20
H7	2·08	−0·04		−0·17
H8	0·06			
C1*B*	**(0·000)**			
C8*B*	**(0·000)**			

† l_1, l_2, l_3 are direction cosines relative to **a**, **b**, and **c*** respectively.

and 0·178 Å respectively below the plane of carbons 3, 4, 6, and 7; the dihedral angles between the latter plane and those of atoms 3, 2, and 7 and atoms 4, 5, and 6 are respectively 13·1° and 14·3°. Furthermore, the exocyclic bonds, 2–1 and 5–8 are bent additionally below the planes at each end, by 15·4° and 14·9° respectively. The decrease of the internal angle at the substituted carbon atoms (2 and 5) below 120° is characteristic of all the *p*-cyclophanes and is at least in part due to a folding about the line between C2 and C5. This is illustrated in Fig. 5, which is a view of the molecule from one end (along axis *A* of Fig. 1). The dihedral angle between the two sides (planes of carbons 2, 3, 4, and 5 and carbons 2, 7, 6, and 5) is 16·4°. In part, however, the decrease in the internal angles at C2 and C5 seems characteristic merely of carbon substitution at these atoms. Thus in biphenyl (Robertson, 1961) the internal angle at atom 1 is 117·35° and in 1,8-diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955) the angle is 118·2°; the aromatic rings are planar in these molecules. In [3.3]-*p*-cyclophane the angles are 116·7 and 117·0°, and the deformations are similar to (although smaller than) those in the present compound.

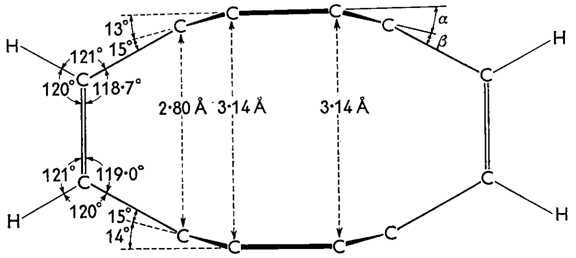

Fig. 4. Profile of the molecule viewed along axis *C* of Table 5.

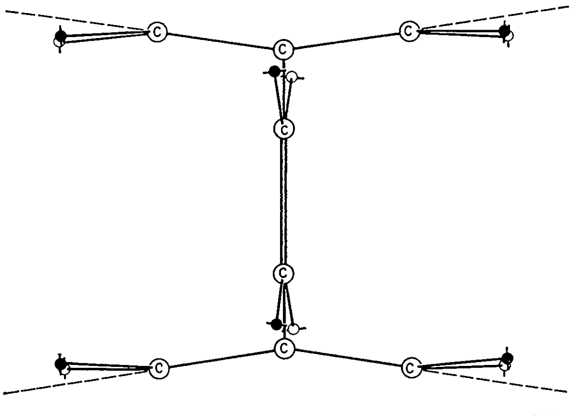

Fig. 5. Profile of the molecule viewed along axis *A* of Fig. 1. The small circles are hydrogen atoms; the shaded ones are nearer. The short lines through each hydrogen atom extend a distance 2σ from the center of the atom and thus represent a reasonable limit of error in the corresponding direction.

An unexpected feature of the structure, found also in [3.3]-*p*-cyclophane, is shown in Fig. 5. The hydrogens of the aromatic ring all lie significantly (more than 2σ) below the plane of the half of the aromatic ring to which they are attached, and indeed also below (by only 1–2σ) the plane of carbons 3, 4, 6, and 7 (Table 9). Prof. D. J. Cram has suggested (1960) that this may result from an increased π-electron density on the outside of the molecule as a consequence of the inter-ring repulsion; the effect would be analogous to that observed in many inorganic systems where significant unshared pair-bonded pair repulsions are manifested (Gillespie & Nyholm, 1957). Evidence for this increased π-density is provided by the enhanced complexing ability of these *p*-cyclophanes with tetracyanoethylene (Cram & Bauer, 1959). It may be noted that H1 and H8 are not significantly out of the plane of C1, C8, and the atoms related to them by the center of symmetry.

The C–H distances average 0·99 Å in the present refinement, about 0·1 Å shorter than the presumed internuclear distance. This sort of effect has been noted in many previous X-ray studies, although by no means in all in which the hydrogen atoms have been located. In any event, it is on the borderline of significance here and does not warrant discussion.

The intramolecular contact distances between atoms of the aromatic rings are 2·80, 3·14 and 3·14 Å for the pairs of atoms which lie on lines essentially normal to the ring planes (Fig. 4). These distances are considerably smaller than those for the normal contact between parallel aromatic molecules, about 3·4 Å (Robertson, 1953), and are comparable to those in [2.2]-*p*-cyclophane itself (Brown, 1953). These unusually close contacts, as well as the deformation of the aromatic rings described above, are indicative of the highly strained condition of this molecule, which,

Table 10. *Some 'single-bond' distances between trigonal carbon atoms**

	Bond distances (Å)					
Molecule	*E–E*	*Ar–E*	*Ar–Ar*	Dihedral angle†	State	Reference
Butadiene	1·483			0°	*V*	Almenningen, Bastiansen & Traettberg (1958)
Biphenyl			1·497	0	*Cr*	Robertson (1961)
			1·492	42	*V*	Almenningen & Bastiansen (1958)
Dimethylfulvene	1·452‡ (1·440§)			0	*Cr*	Norman & Post (1961)
	1·449‡ (1·435§)			0		
1,8-Diphenyl-1,3,5,7-octatetraene		1·468§		5		
	1·440§			0	*Cr*	Drenth & Wiebenga (1955)
	1·438§			0		
Cyclooctatetraene	1·462			57	*V*	Bastiansen, Hedberg & Hedberg (1957)
	1·465			55	*Cr*	Bregman & Post (1961)

* *E* refers to a carbon atom involved in an ethylenic bond, *Ar* to one in an aromatic ring. *Cr* means crystal, *V* vapor. The estimated standard deviations of these determinations are about 0·01 Å or less.

† Range of dihedral angles is only 0–90°, *i.e.* no distinction is made between *cis* and *trans* forms.

‡ Corrected by us for librational effects on basis of published thermal parameters.

§ Uncorrected for librational effects.

of course, results from tying together the two aromatic rings with the two-carbon unsaturated bridges. At first sight it seems surprising that the double-bond distance (1·336 Å) has not been increased from the ethylenic value (1·334, Bartell & Bonham, 1960; 1·337, Allen & Plyler, 1958). However, the ease of out-of-plane deformation of the aromatic ring systems here is sufficient to relieve much of the inter-ring repulsive strain, and, as calculated below, that remaining would lengthen the bond by only about σ. Thus the effect is not detectable.

The average C–C distance in the aromatic rings is 1·399 Å, which is not significantly different from that found in benzene (1·397, Stoicheff, 1954; 1·393, Cox, Cruickshank & Smith, 1958). The average deviation of the individual bonds is 0·008 Å, but the average lengths of chemically equivalent bonds are not significantly different. The mean exocyclic C–C single-bond distance is 1·512 Å, which is the same as that in toluene (Keidel & Bauer, 1956) and significantly longer than the single-bond distances between trigonally hybridized carbon atoms in other hydrocarbons. Some comparable precisely determined distances are listed in Table 10. In the absence of precise studies on styrene or its derivatives, it is difficult to know what distance to choose as a standard for comparison with that in the present molecule. Perhaps a reasonable value is the average of the distances in biphenyl and butadiene, 1·49 Å. However, it is noteworthy that in the molecules with longer conjugated systems the distance is appreciably shorter than in either butadiene or biphenyl. The present molecule would have a cyclic conjugated system if it were not constrained so that the π-orbitals of the double bond are orthogonal to those of the aromatic ring. In planar or nearly planar polyenes, the lengths of the 'single' bonds between ethylenic bonds approach 1·44–1·45 Å; even in cyclooctatetraene, in which the planes of adjacent double bonds make an angle of about 57° with one another, the distance is only 1·46 Å. The single bond between ethylenic and aromatic carbons in the one precise study made is about 1·47 Å.

Two factors in the present molecule presumably serve to lengthen the bond: overlap is minimized because the planes of the π-systems are at 90°, and furthermore the presence of three short 1,3-contacts (Table 8) on the same side of the atom (for both atoms 1 and 8) is an uncommon situation for a trigonally hybridized atom. If there is any merit in Bartell's (1960) view of the importance of such contacts in determining bond distances, this alone could cause an increase of perhaps 0·02–0·03 Å in the bonding radius for the olefinic atoms.

Single-bond distances between tetrahedral carbon atoms are lengthened to about 1·56 Å as a consequence of short intramolecular repulsions in cyclobutane (Dunitz & Schomaker, 1952), norbornane, and a similar polycyclic compound (Berndt, 1957; Wong, 1957), and a value of 1·573 with a standard deviation of only 0·002 Å has been reported for the two equivalent single bonds in 4,12-dimethyl[2.2]metacyclophane (Hanson, 1962). With a C–C stretching force constant of 5 md.Å^{-1} (Wilson, Decius & Cross, 1955) the latter stretch corresponds to only about 0·6 kcal.mole^{-1} strain energy in each such bond relative to a standard bond of length 1·533 Å. It seems doubtful that the lengthening of the single bond in the present molecule is as much as 0·05 Å, and it might be as little as 0·02 Å, depending on the standard chosen. This corresponds, with four such bonds per molecule, to between about 0·5 and about 3 kcal.mole^{-1} of strain energy from this cause. These are the only bonds of abnormal length.

On the other hand, the strain due to the angle deformations is appreciably greater. By methods described elsewhere (Gantzel & Trueblood, 1963; Gantzel, 1962) we calculate that the observed geometry corresponds to an angle strain energy of about 38 kcal.mole^{-1}, using the potential function of Whiffen (1955); the potential function of Coulson & Senent (1955) yields a value only slightly smaller. Almost all of this strain arises from the buckling of the benzene rings and the further bending of the C1–C2 and equivalent bonds, *i.e.*, to changes in the angles α and β (Fig. 4) from 0°. The C–C–C angle at C1 is decreased only 3–4° from its normal value (Pauling, 1960). If one uses the assumed potential functions and the condition that $\delta-(\alpha+\beta)$ must equal 90° (where δ is the angle at C1), the values of α, β, and δ which minimize the angle strain when all non-bonded repulsions are ignored can be calculated (see *e.g.* Schomaker, 1951). The strain is then more evenly distributed among the three angles, the calculated angles being $\alpha \sim 8°$, $\beta \sim 12°$, $\delta \sim 110°$ and the total angle-strain energy about 28 kcal.mole^{-1}. Comparison with the angles in the actual molecule shows that, as is reasonable, the inter-ring repulsions increase δ markedly (thereby decreasing the strain in this angle) and thus necessarily increase $(\alpha+\beta)$ also, because of the condition that $\delta-(\alpha+\beta)=90°$.

The magnitude of the inter-ring repulsions can be very roughly estimated with the help of an appropriate potential, such as that of Bartell (1960). The only significant terms are those arising from the C · · · C interactions, and even these are not large. The two shortest contacts, C2 · · · C5′ at 2·80 Å, correspond to just 0·7 kcal.mole^{-1} each, which is just slightly more than *RT*. The four contacts at 3·14 Å each contribute about 0·1 kcal.mole^{-1}; thus the total inter-ring repulsive energy, if this potential is valid here, is only about 2 kcal.mole^{-1}. The corresponding focces parallel to the double bonds amount to about $3{\cdot}6\times10^{-5}$ dynes tending to elongate each bond; this would produce a stretch of only 0·007 Å, not detectable in the present analysis. On the other hand, if the real molecule had the no-repulsion values of α, β, and δ calculated above, the inter-ring distances would be about 2·38 (twice) and 2·58 (four times) instead of the 2·80 and 3·14 actually observed. The shorter distances would correspond to an inter-ring repulsion of some 24 kcal.mole^{-1}. Thus the increase of about 10 kcal.mole^{-1} in the angle strain in the real molecule is much more than compensated by the relief of inter-ring repulsion, which means that the potentials used are consistent at least in this regard.

The effect of changes in the much shorter 1, 3 contacts is difficult to evaluate, for although the energies involved in each amount to between 3 and 5 kcal.mole^{-1} in the range from 2·55 to 2·45 Å, comparable contacts are present in reference compounds. Because the potential curve is so steep at this point, slight differences in distance can make significant changes in the repulsive energy and no detailed discussion is warranted without precise dimensions for reference compounds. As mentioned earlier, these contacts may play a role in stretching the C1–C2 (and C5–C8) bonds and their vertical components may act to stretch the double bond slightly, although the latter effect would be small.

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The Crystal Structure of Trimethyloxosulfonium Perchlorate $[(CH_3)_3SO]^+ClO_4^-$*

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Crystals of $[(CH_3)_3SO]^+ClO_4^-$ display tetragonal symmetry with unit cell dimensions $a = 11\cdot66 \pm 0\cdot01$ Å and $c = 5\cdot99 \pm 0\cdot01$ Å. The space group is $P\bar{4}2_1m$ with $Z = 4$. A satisfactory trial structure was found by use of a three-dimensional Patterson summation and the refinement was carried out by means of three-dimensional difference syntheses and least-squares routine on the IBM 7090.

The $[(CH_3)_3SO]^+$ ion is required crystallographically to have the symmetry *m* but it approximates the symmetry 3*m*. The perchlorate ions are crystallographically of two types, one with required symmetry $\bar{4}$ and the other with required symmetry *mm*2. However, the perchlorate ions of the second type achieve the required symmetry in a statistical (disordered) manner.

Bond distances and angles in the trimethyloxosulfonium ion are:

$$S\text{–}C(1) = 1\cdot78 \pm 0\cdot01 \text{ Å},\; S\text{–}C(2) = 1\cdot76 \pm 0\cdot01 \text{ Å},\; S\text{–}O = 1\cdot45 \pm 0\cdot01 \text{ Å},\; C(1)\text{–}S\text{–}C(1) = 105\cdot8 \pm 0\cdot7^\circ,$$
$$C(1)\text{–}S\text{–}C(2) = 105\cdot7 \pm 0\cdot5^\circ,\; C(1)\text{–}S\text{–}O = 112\cdot1 \pm 0\cdot5^\circ,\; C(2)\text{–}S\text{–}O = 114\cdot8 \pm 0\cdot6^\circ\,.$$

In the ordered perchlorate ions: $Cl\text{–}O = 1\cdot45 \pm 0\cdot01$ Å, $O\text{–}Cl\text{–}O = 111\cdot5 \pm 0\cdot9^\circ$ and $108\cdot8 \pm 0\cdot9^\circ$.

Introduction

The syntheses and properties of members of two series of salts formed by the reaction of dimethyl sulfoxide with esters RX have been reported by Smith & Winstein (1958) and by Smith (1959). One series was reported to involve the ion $[R(CH_3)_2SO]^+$ in which all three alkyl groups are bonded directly to sulfur, and the other series the ion $[(RO)(CH_3)_2S]^+$ in which the R group is separated from sulfur by an oxygen atom. Structure assignments for the two series of salts were made on the basis of proton magnetic resonance studies as well as on chemical evidence. As a check on this structure assignment and in order to determine the bond distances and angles in the interesting $[(CH_3)_3SO]^+$ ion, the present study of the perchlorate was undertaken.

Experimental

Trimethyloxosulfonium perchlorate was prepared by Smith by the reaction of silver perchlorate on the iodide salt in aqueous solution. The substance was purified by recrystallization from water and elementary analyses for carbon, hydrogen, sulfur and chlorine gave results in close agreement with the formula $C_3H_6SClO_5$.

Crystals suitable for the X-ray study were grown by spontaneous evaporation of aqueous solutions. Precession and Weissenberg photographs about the

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* Contribution No. 1546 from the Department of Chemistry, University of California at Los Angeles.