transition metal analogues, Nb^V and Ta^V, do not. Iyer & Smith (1967) have noted similarly that there is no structural resemblance between the rare-earth double oxides of Pa^V and the analogous compounds of Nb^V and Ta^V.

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The Crystal Structure of 8,16-Oxido-*cis*-[2.2]metacyclophane

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The crystal structure of 8,16-oxido-*cis*-[2.2]metacyclophane, $C_{16}H_{14}O$, is orthorhombic, space group probably $Cmc2_1$, with $a=8{\cdot}78$, $b=16{\cdot}04$, $c=8{\cdot}42$ Å, $Z=4$. The structure was deduced from the three-dimensional Patterson synthesis and refined by block-diagonal least squares to a final agreement residual of 0·057. The molecule has nearly *mm* symmetry, and is folded to a dihedral form so that the angle between the slightly boat-shaped six-membered rings is 99·6°. The bond angle subtended by the oxygen atom is 101·4°, while the mean value of those in the methylene bridges is 119·0°. The strain implied by these values is consistent with the tendency of the compound to transform into the corresponding pyrene derivative, with ejection of the hetero atom.

Introduction

Although several *trans*-[2.2]metacyclophanes have been reported (Lindsay, Stokes, Humber & Boekelheide, 1961), the title compound (I) is the first reported example of a *cis*-[2.2]metacyclophane (Hess, Bailey & Boekelheide, 1967; Renfroe, Gurney & Hall, 1967). Steric strain is inferred for such compounds from their known tendency (on heating, or treatment with acid) to transform into the corresponding pyrene derivatives, with ejection of the hetero atoms (Boekelheide, 1967). The crystal structure analysis was undertaken in order to determine the geometrical characteristics of such strain. It was realized from the beginning that the ac-

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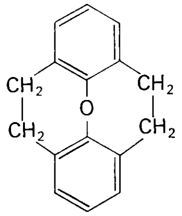
curacy of the analysis would be limited by intense thermal motion, with a consequent low yield of measurable reflections at high Bragg angles. Attempts to cool the specimen resulted in a phase change, with twinning. It was therefore necessary to accept the low accuracy inherent in the room-temperature determination.



(I)

Experimental

Crystal data: Orthorhombic

Formula $C_{16}H_{14}O$, F.W. 222·3

$a=8{\cdot}78\pm0{\cdot}01$, $b=16{\cdot}04\pm0{\cdot}02$, $c=8{\cdot}42\pm0{\cdot}01$ Å

$Z=4$, $V=1185{\cdot}8$ Å^3

$D_x=1{\cdot}245\pm0{\cdot}005$ g.cm^{-3}, $D_m=1{\cdot}24\pm0{\cdot}02$ g.cm^{-3}

$\mu=7{\cdot}0$ cm^{-1} (Cu $K\alpha$).

[Assumed wavelengths 1·54050 (Cu $K\alpha_1$); 1·54434 (Cu $K\alpha_2$)].

Space group $Cmc2_1$, $C2cm$, or $Cmcm$ (from precession photographs. Systematic absences: hkl for $h+k$ odd, $h0l$ for l odd). $Cmc2_1$ is consistent with the deduced structure.

Molecular symmetry: m.

The material supplied consisted of white translucent plates (010) of irregular outline. They appeared to possess surface charges, and readily adhered to probes. (This behavior suggested that the structure must lack a centre of symmetry.) The specimen used was a plate of approximate dimensions (initially) 0·05 × 0·2 × 0·3 mm. During the eight days of data collection it suffered some decomposition, losing about half its original scattering power. The cell constants and relative intensities were measured with the General Electric XRD 5 spectrogoniometer and goniostat equipped with a scintillation counter. Copper $K\alpha$ radiation was used, and reasonable monochromatization was achieved with a $K\beta$ filter and a reverter (pulse-height analyser). The θ–2θ scan method was used, with precomputed goni-o stat settings, and manual operation. Of the 744 accessible reflections (those for which $2\theta\le160°$) significant counts were recorded for 448. The range of observed intensities was about 1 to 6000. Absorption corrections were considered to be unnecessary and were not made.

Structure determination

Packing considerations indicated that the probable space group was $Cmc2_1$, and a trial structure in this space group was deduced from the three-dimensional Patterson synthesis. Refinement was begun by means of Fourier syntheses, and completed with block-diagonal least-squares analysis. The program used was that of Ahmed, written in FORTRAN IV for the IBM system 360 computer. The quantity minimized is $\Sigma\, w(F_o-F_c)^2$. The matrices used are 3 × 3 for the posi-

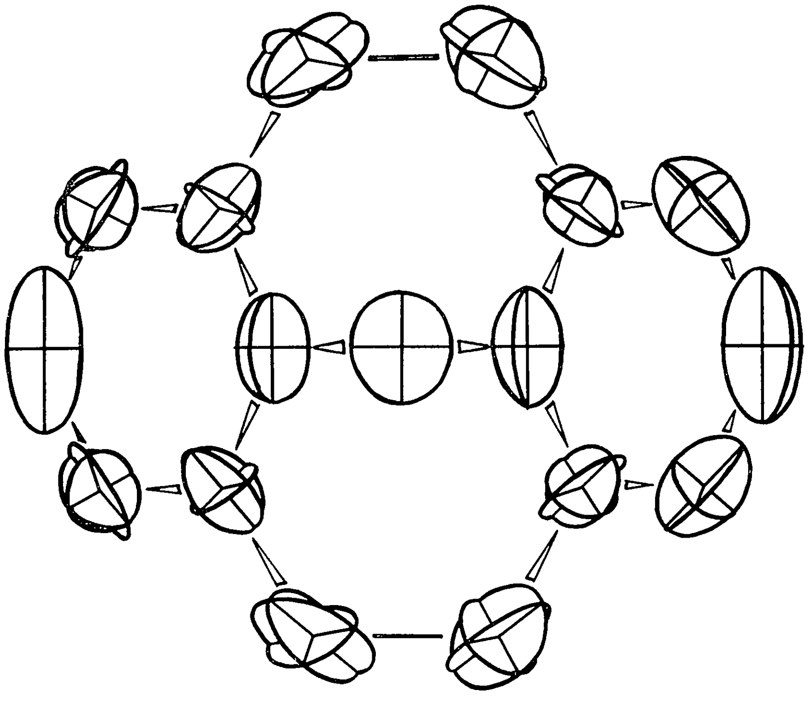


Fig. 1. Thermal ellipsoid plot of the molecule, viewed normal to its mean plane. 50% probability ellipsoids are represented.

tion parameters and 6 × 6 for the thermal parameters of each atom in a general position. The scale of F_o and the overall isotropic temperature factor are refined with a 2 × 2 matrix (Cruickshank, 1961). Schomaker's correction is applied to the shifts of the thermal parameters (Hodgson & Rollett, 1963). The weighting scheme used was $\sqrt{w}=8/F_o$ for $F_o \geq 8$; $\sqrt{w}=F_o/8$ for $F_o < 8$. The nominal minimum observable value of F_o was 2·0. Refinement was rather slow, and it was necessary to prevent oscillation of parameters by applying a factor of 0·5 to all shifts. The scattering curves of Hanson, Herman, Lea & Skillman (1964) were used throughout. In the later stages of refinement the contribution of the hydrogen atoms was included in the structure factor calculations, assuming reasonable positions, and isotropic thermal motion. No attempt was made to refine the parameters of these atoms, however. At the same time a systematic extinction correction was derived in the manner of Pinnock, Taylor & Lipson (1956) and used to correct the intensities of the five strongest reflections. The greatest correction was about 40% of the uncorrected intensity. However, the weighting scheme used was such that these corrections were of little importance in the refinement. Unacceptable discrepancies between F_o and F_c were found for 9 weak reflections. These reflections (identified in Table 3) were omitted from the least-squares totals in the final cycles. Refinement was terminated when all shifts (after the damping factor of 0·5 had been applied) were less than one quarter of the corresponding e.s.d. The final parameters are given in Table 1.

Thermal motion

It is apparent from Table 1 that there is very intense thermal motion in the structure and that there must therefore be significant systematic errors in the observed bond lengths. Examination of the thermal ellipsoid plot (Fig. 1) suggests that at least some of the thermal motion occurs in rigid-body modes, and an analysis has therefore been carried out in the manner described by Cruickshank (1956). (It was assumed, without evidence, that the centre of libration coincided with the

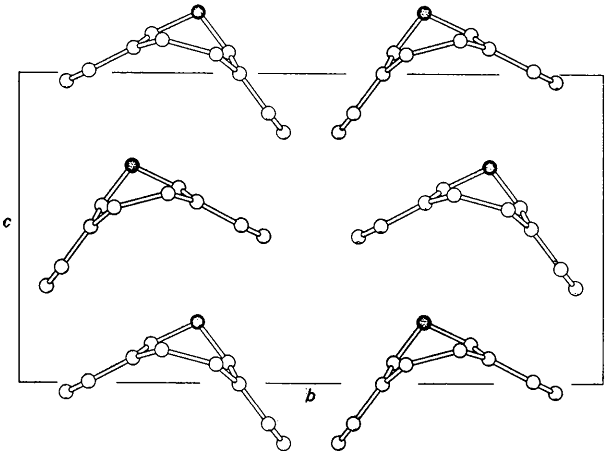


Fig. 2. The structure viewed along **a**. Light outlines represent molecules on the mirror plane at $x=0$; heavy represent those on the mirror plane at $x=\frac{1}{2}$.

Table 1(*a*). *Final parameters (and e.s.d.'s) of non-hydrogen atoms*

$(0,0,0;\ \frac{1}{2},\frac{1}{2},0)+(x,y,z;\ \bar{x},y,z;\ x,\bar{y},\frac{1}{2}+z;\ \bar{x},\bar{y},\frac{1}{2}+z)$

$$\text{T.F.}=\exp\{-2\pi^2(U_{11}a^{*2}h^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+U_{22}b^{*2}k^2+2U_{23}b^*c^*kl+U_{33}c^{*2}l^2)\}$$

(The numbering system is arbitrary. B_i are the principal-axis B's.)

	x (× 10^4)	y (× 10^4)	z (× 10^4)	U_{11} (× 10^4)	U_{12} (× 10^4)	U_{13} (× 10^4)	U_{22} (× 10^4)	U_{23} (× 10^4)	U_{33} (× 10^4)	B_1 (Å^2)	B_2 (Å^2)	B_3 (Å^2)
O(1)	0	3063	1978	969	0	0	746	−66	487	7·65	6·01	3·72
		3	6	36			26	26	23			
C(2)	0	2272	1251	1115	0	0	475	120	604	8·80	5·34	3·18
		4	8	60			37	33	44			
C(3)	1389	1952	819	553	171	−206	698	−36	836	7·83	5·62	3·02
	5	3	6	27	29	35	26	26	31			
C(4)	1363	1195	74	879	287	−114	768	−33	1028	9·40	7·56	4·16
	6	3	8	37	35	42	27	30	37			
C(5)	0	810	−282	1887	0	0	609	−61	855	14·90	6·86	4·70
		4	10	94			43	50	61			
C(6)	0	3589	657	942	0	0	421	−188	541	7·44	5·36	2·24
		3	7	51			33	32	41			
C(7)	1385	3776	−24	654	−190	−67	592	−74	780	6·44	6·36	3·19
	5	3	6	29	29	35	21	24	29			
C(8)	1358	4282	−1319	877	−231	82	554	−30	1019	8·65	7·27	3·42
	6	3	7	34	27	38	25	29	38			
C(9)	0	4541	−1945	2087	0	0	419	90	747	16·48	6·08	3·12
		4	10	99			37	38	54			
C(10)	2834	2450	1076	800	221	−279	1015	−96	1184	11·24	7·76	4·68
	6	4	8	38	36	36	35	39	44			
C(11)	2829	3378	613	951	−257	−181	1195	−68	1219	10·78	10·07	5·72
	7	4	8	43	41	48	43	42	49			

centre of gravity of the equally-weighted non-hydrogen atoms.) The results are given in Table 2. It is clear from the smallness of the cross term in the tensor that the principal axes of libration are very close to the crystallographic axes. The axis of greatest libration is almost parallel to **b**, and thus about 13° from the axis of least moment of inertia. This seems physically reasonable; however, the agreement between observed and calculated U_{ij}'s is not good. The r.m.s. deviation is 0·0145 Å^2, compared with a mean e.s.d. for the observed elements of 0·0040 Å^2, and thus the hypothesis of pure rigid-body motion is not well supported. The reason may be systematic errors in the thermal parameters, or, quite probably, the presence of non-rigid modes of motion. In any case the bond lengths have not been corrected for rigid-body libration. The corrections would only be of the order of one e.s.d., and it is considered that errors resulting from non-rigid motion could be much greater than this.

Table 1(*b*). *Assumed parameters for hydrogen atoms*

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B (Å^2)
H(4)	2258	920	−50	4·4
H(5)	0	370	−908	5·4
H(8)	2305	4470	−1692	4·4
H(9)	0	4860	−2850	5·4
H(10*a*)	3702	2176	398	5·9
H(10*b*)	3142	2427	2245	5·9
H(11*a*)	3602	3506	−242	5·9
H(11*b*)	3078	3746	1570	5·9

Assessment of results

The agreement between F_o and F_c (Table 3) is reasonable, and there can be no doubt of the essential correctness of the structure. A difference Fourier synthesis of the cell contents projected along **c** reveals no detail inconsistent with the proposed structure. The agreement residual ($R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$) is 0·057, for

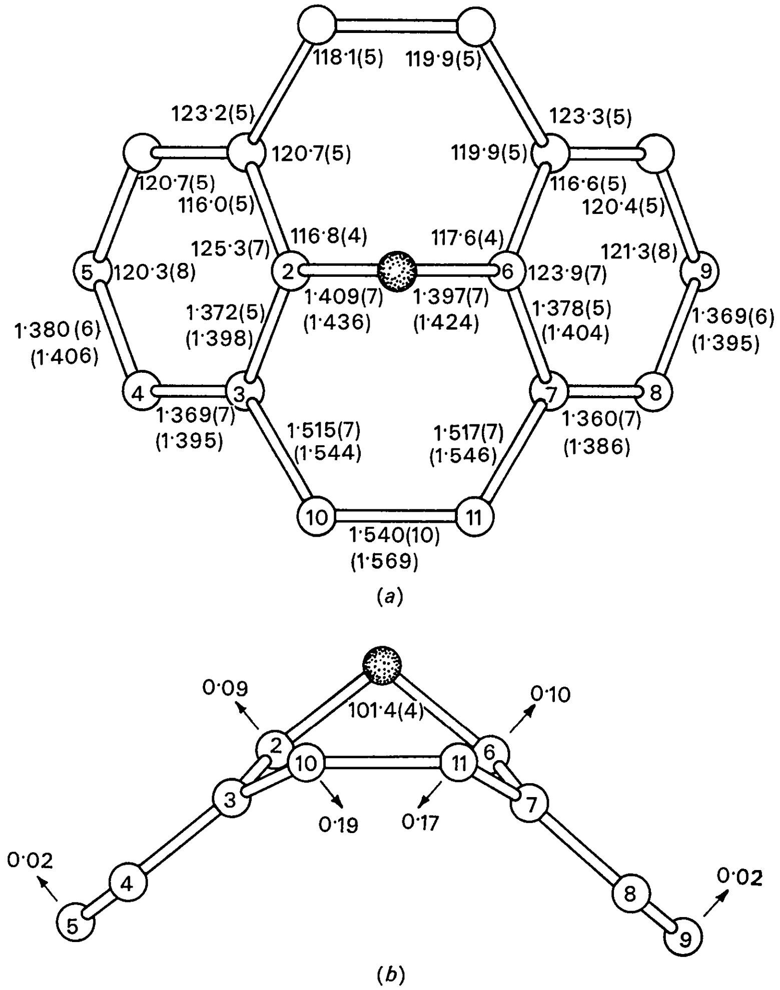


Fig. 3. Molecular geometry: Bond lengths and angles and their e.s.d.'s. The bond lengths in parentheses have been modified as described in the text. Arrows indicate the deviations (Å) of certain atoms from the planes defined by C(3)–C(4) and C(7)–C(8).

observed reflections only. The e.s.d.'s of coordinates range from 0·004 to 0·009 Å, depending on atom type and intensity of thermal motion. Good agreement between chemically equivalent bond lengths and angles (Fig. 3) suggests that these e.s.d.'s are realistic at least in so far as they apply to random errors of intensity measurement. As indicated in the previous section, however, the thermal motion is such that there are probably significant systematic errors in the bond lengths.

Table 2. *Rigid-body thermal parameters and their e.s.d.'s*

$$\mathbf{T}=\begin{pmatrix}609 & 0 & 0\\ & 521 & -66\\ & & 548\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \mathbf{L}=\begin{pmatrix}11{\cdot}2 & 0 & 0\\ & 37{\cdot}6 & 0{\cdot}2\\ & & 27{\cdot}6\end{pmatrix}(^\circ)^2$$

$$\sigma(\mathbf{T})=\begin{pmatrix}46 & - & -\\ & 40 & 41\\ & & 66\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \sigma(\mathbf{L})=\begin{pmatrix}3{\cdot}5 & - & -\\ & 4{\cdot}9 & 2{\cdot}8\\ & & 2{\cdot}7\end{pmatrix}(^\circ)^2$$

Table 3. *Observed and calculated structure factors*

An asterisk indicates an unobserved reflection, for which the threshold value is given. A dash indicates that the reflection was omitted from the least-squares totals. All *F* values have been multiplied by 10.

H	FO	FC
K=	0, L=	0
2	99	103
4	90	36
6	288	294
8	188	197
10	29*	27
K=	1, L=	0
1	302	306
3	126	121
5	26	22
7	87	82
9	33*	2
11	20*	0
K=	2, L=	0
0	850	843
2	357	338
4	219	201
6	70	79
8	39-	19
10	28*	4
K=	3, L=	0
1	146	156
3	500	519
5	41	51
7	56-	24
9	33*	7
11	19*	23
K=	4, L=	0
0	519	548
2	79	63
4	340	349
6	64	71
8	49	70
10	27	29
K=	5, L=	0
1	51	57
3	425	425
5	86	90
7	53	84
9	32*	12
K=	6, L=	0
0	310	312
2	57	43
4	54	72
6	28*	17
8	34*	7
10	25*	2
K=	7, L=	0
1	81	69
3	191	190
5	37	30
7	67	57
9	30*	19
K=	8, L=	0
0	22*	4
2	219	219
4	27*	12
6	28*	7
8	33*	13
10	21*	1
K=	9, L=	0
1	183	174
3	96	88
5	28*	10
7	64	54
9	25*	11
K=	10, L=	0
2	90	88
4	176	168
6	39	36
8	30	36
10	39	51
K=	11, L=	0
1	100	97
3	28*	24
5	27*	20
7	33*	5
9	22*	20
K=	12, L=	0
0	110	109
2	103	103
4	95	95
6	66	63
8	41	41
K=	13, L=	0
1	48	51
3	176	172
5	84	71
7	29*	30
K=	14, L=	0
0	40	34
2	32	39
4	34*	13
6	39	47
8	19*	1
K=	15, L=	0
1	74	82
3	34*	30
5	31*	19
7	24	17
K=	16, L=	0
0	122	114
2	40	26
4	95	94
6	24*	24
K=	17, L=	0
1	32*	4
3	37	37
5	28	27
K=	18, L=	0
0	30	36
2	25*	1
4	24*	13
K=	19, L=	0
1	23*	6
3	38	34
K=	20, L=	0
0	30	24
2	19*	10
K=	1, L=	1
1	976	973
3	387	396
5	128	140
7	308	311
9	34-	17
11	20*	22
K=	2, L=	1
0	398	419
2	187	185
4	294	290
6	27*	29
8	35*	22
10	28*	20
K=	3, L=	1
1	813	828
3	376	385
5	27-	7
7	121	120
9	33*	32
11	26	19
K=	4, L=	1
0	507	491
2	173	178
4	370	360
6	57	57
8	36	53
10	35	35
K=	5, L=	1
1	332	339
3	168	165
5	55	28
7	55	59
9	32*	22
K=	6, L=	1
0	486	485
2	29	38
4	41	45
6	54	57
8	61	55
10	25*	27
K=	7, L=	1
1	138	136
3	132	137
5	34	54
7	38	47
9	30*	9
K=	8, L=	1
0	434	441
2	107	100
4	148	131
6	31	23
8	33*	29
10	20*	11
K=	9, L=	1
1	112	112
3	94	92
5	61	56
7	36	23
9	27	26
K=	10, L=	1
0	72	72
2	110	104
4	119	128
6	35*	1
8	31*	12
K=	11, L=	1
1	160	158
3	187	190
5	27*	16
7	32*	34
9	31-	20
K=	12, L=	1
0	158	155
2	55	56
4	77	88
6	34*	17
8	26	30
K=	13, L=	1
1	98	104
3	68	69
5	64	69
7	29*	33
K=	14, L=	1
0	33	37
2	80	81
4	62	69
6	30*	15
8	19*	8
K=	15, L=	1
1	35*	23
3	75	74
5	71	73
7	24	30
K=	16, L=	1
0	34	45
2	56	65
4	60	66
6	24*	7
K=	17, L=	1
1	57	52
3	55	59
5	24*	6
K=	18, L=	1
0	30*	22
2	28*	19
4	50	43
K=	19, L=	1
1	24*	13
3	44	37
K=	20, L=	1
0	20*	6
2	18*	13
K=	0, L=	2
0	1470	1442
2	414	427
4	459	464
6	83	94
8	75	74
10	40	34
K=	1, L=	2
1	428	427
3	326	342
5	103	96
7	28*	30
9	33*	12
11	17*	17
K=	2, L=	2
0	1344	1345
2	221	216
4	171	137
6	79	80
8	72	67
10	26*	9
K=	3, L=	2
1	99	98
3	325	328
5	70	65
7	45-	5
9	32*	7
K=	4, L=	2
0	820	883
2	117	114
4	105	111
6	88	83
8	70	75
10	26*	19
K=	5, L=	2
1	186	177
3	26*	22
5	65	65
7	46	60
9	31*	2
K=	6, L=	2
0	303	294
2	180	189
4	112	118
6	43	50
8	38	48
10	23*	17
K=	7, L=	2
1	372	369
3	130	132
5	55	56
7	117	119
9	29*	5
K=	8, L=	2
0	414	404
2	90	86
4	81	78
6	63	64
8	40	46
10	19*	12
K=	9, L=	2
1	73	80
3	89	91
5	41	41
7	41-	26
9	26*	25
K=	10, L=	2
0	51	53
2	105	97
4	154	159
6	35*	29
8	29*	34
K=	11, L=	2
1	107	106
3	117	118
5	42	39
7	32*	33
9	20*	10
K=	12, L=	2
0	63	61
2	75	71
4	159	159
6	36	60
8	35	36
K=	13, L=	2
1	56	47
3	27*	29
5	34*	22
7	34	19
K=	14, L=	2
0	44	47
2	68	78
4	96	92
6	29*	31
K=	15, L=	2
1	35*	16
3	93	91
5	49	48
7	21*	16
K=	16, L=	2
0	51	43
2	33*	26
4	57	62
6	22*	23
K=	17, L=	2
1	36	43
3	29*	35
5	23*	4
K=	18, L=	2
0	28*	27
2	27*	14
4	24	22
K=	19, L=	2
1	24*	11
3	20*	20
K=	20, L=	2
0	45	41
K=	1, L=	3
1	127	126
3	295	293
5	155	149
7	132	125
9	34	24
K=	2, L=	3
0	298	296
2	140	135
4	259	258
6	45	52
8	34*	34
10	26	22
K=	3, L=	3
1	303	305
3	111	102
5	91	80
7	116	114
9	31*	26
K=	4, L=	3
0	394	391
2	227	234
4	37	47
6	64	57
8	35	40
10	24*	15
K=	5, L=	3
1	286	285
3	122	120
5	49	55
7	108	108
9	29*	23
K=	6, L=	3
0	425	412
2	137	134
4	33-	20
6	77	70
8	59	60
10	20*	12
K=	7, L=	3
1	300	309
3	139	138
5	36	20
7	35*	44
9	31	34
K=	8, L=	3
0	322	321
2	42	40
4	69	72
6	53	49
8	31*	30
K=	9, L=	3
1	153	154
3	197	198
5	58	40
7	58	63
9	23*	3
K=	10, L=	3
0	190	188
2	71	76
4	67	72
6	51	78
8	43	41
K=	11, L=	3
1	87	91
3	202	205
5	62	65
7	36	49
K=	12, L=	3
0	71	82
2	45	50
4	65	72
6	32*	30
8	24	18
K=	13, L=	3
1	62	59
3	35*	41
5	64	61
7	26*	23
K=	14, L=	3
0	53	62
2	35*	33
4	53	55
6	28*	10
K=	15, L=	3
1	34*	9
3	90	92
5	38	42
7	17*	26
K=	16, L=	3
0	32*	32
2	31*	31
4	29	39
6	20*	15
K=	17, L=	3
1	30*	32
3	27*	20
5	27	34
K=	18, L=	3
0	27*	40
2	25*	20
4	19*	18
K=	19, L=	3
1	31	22
K=	0, L=	4
0	369	368
2	224	229
4	131	140
6	28*	52
8	33*	20
10	22*	14
K=	1, L=	4
1	118	121
3	151	142
5	28*	16
7	39*	3
9	29*	1
K=	2, L=	4
0	216	206
2	201	201
4	138	142
6	28*	22
8	33*	22
10	22*	11
K=	3, L=	4
1	235	228
3	82	76
5	48	55
7	45	49
9	29*	15
K=	4, L=	4
0	436	445
2	78	81
4	79	89
6	42	40
8	53	54
10	20*	13
K=	5, L=	4
1	306	307
3	37	25
5	74	72
7	63	70
9	27*	12
K=	6, L=	4
0	134	136
2	91	91
4	28*	23
6	27*	30
8	31*	19
K=	7, L=	4
1	79	79
3	89	95
5	41	43
7	51	53
9	24*	8
K=	8, L=	4
0	179	174
2	112	110
4	256	263
6	44	38
8	35	54
K=	9, L=	4
1	107	114
3	28*	29
5	35*	14
7	57	45
9	19*	12
K=	10, L=	4
0	164	158
2	88	87
4	127	130
6	34	24
8	36-	16
K=	11, L=	4
1	129	136
3	39	45
5	54	44
7	39	33
K=	12, L=	4
0	132	134
2	69	76
4	52	60
6	35	34
8	18*	23
K=	13, L=	4
1	83	86
3	40	48
5	31*	15
7	43	44
K=	14, L=	4
0	57	45
2	34*	25
4	52	48
6	24*	16
K=	15, L=	4
1	32*	18
3	31*	11
5	26*	2
K=	16, L=	4
0	37	33
2	30*	21
4	31	29
K=	17, L=	4
1	28*	25
3	24*	19
K=	18, L=	4
0	24*	12
2	22*	21
K=	19, L=	4
1	16*	3
K=	1, L=	5
1	108	101
3	56	53
5	85	84
7	50	45
9	26*	13
K=	2, L=	5
0	192	184
2	81	83
4	88	94
6	42	29
8	31*	26
K=	3, L=	5
1	159	156
3	41	40
5	65	67
7	77	68
9	25*	13
K=	4, L=	5
0	232	227
2	72	73
4	89	100
6	61	58
8	33	43
K=	5, L=	5
1	63	61
3	136	131
5	55	47
7	68	62
9	24	17
K=	6, L=	5
0	204	198
2	119	120
4	76	85
6	48	41
8	33	27
K=	7, L=	5
1	49	43
3	184	184
5	71	67
7	32*	37
9	19*	19
K=	8, L=	5
0	44	39
2	47	41
4	39	38
6	33*	7
8	25*	18
K=	9, L=	5
1	28*	24
3	192	196
5	41	43
7	29*	26
K=	10, L=	5
0	74	81
2	51	54
4	35*	54
6	34*	12
8	20*	11
K=	11, L=	5
1	57	64
3	35*	9
5	32*	31
7	43	37
K=	12, L=	5
0	121	120
2	35*	39
4	32*	21
6	39	23
K=	13, L=	5
1	43	47
3	32*	11
5	28*	14
K=	14, L=	5
0	82	90
2	31*	25
4	28*	10
6	24	28
K=	15, L=	5
1	64	69
3	28*	8
5	21*	20
K=	16, L=	5
0	41	38
2	26*	29
4	25	20
K=	17, L=	5
1	32	26
3	22	15
K=	18, L=	5
0	26	15
K=	0, L=	6
0	94	97
2	56	53
4	80	75
6	34*	42
8	31*	15
K=	1, L=	6
1	73	78
3	62	50
5	27*	17
7	32*	29
9	20*	8
K=	2, L=	6
0	137	143
2	69	79
4	48	41
6	45	33
8	28*	17
K=	3, L=	6
1	99	108
3	145	144
5	35*	32
7	54	34
9	19*	13
K=	4, L=	6
0	174	170
2	61	71
4	121	122
6	34*	30
8	29*	20
K=	5, L=	6
1	92	91
3	67	66
5	35*	20
7	30*	25
K=	6, L=	6
0	126	132
2	52	46
4	106	105
6	32*	16
8	31	31
K=	7, L=	6
1	85	96
3	27*	7
5	34*	13
7	36	31
K=	8, L=	6
0	94	86
2	55	57
4	100	110
6	31*	26
8	20*	27
K=	9, L=	6
1	27*	32
3	54	53
5	48	39
7	24*	15
K=	10, L=	6
0	35*	42
2	43	27
4	53	48
6	28*	15
K=	11, L=	6
1	34*	21
3	33*	7
5	29*	8
7	18*	9
K=	12, L=	6
0	33*	48
2	32*	28
4	36	29
6	22*	5
K=	13, L=	6
1	56	69
3	29*	12
5	24*	9
K=	14, L=	6
0	34	42
2	28*	34
4	24*	15
K=	15, L=	6
1	31	30
3	30	26
K=	16, L=	6
0	39	41
2	21*	30
K=	1, L=	7
1	28*	17
3	75	73
5	34*	29
7	28*	17
K=	2, L=	7
0	78	81
2	78	73
4	113	113
6	31*	14
8	22*	12
K=	3, L=	7
1	57	50
3	104	90
5	44	52
7	33	41
K=	4, L=	7
0	81	86
2	49	48
4	48	53
6	31*	7
8	20*	17
K=	5, L=	7
1	55	55
3	85	82
5	32*	15
7	36	21
K=	6, L=	7
0	46	43
2	41	38
4	39	34
6	29*	9
K=	7, L=	7
1	87	94
3	45	38
5	31*	7
7	44	44
K=	8, L=	7
0	51	57
2	46	40
4	32*	27
6	26*	14
K=	9, L=	7
1	34*	20
3	37	40
5	28*	11
K=	10, L=	7
0	33*	30
2	32*	18
4	29*	22
6	21*	7
K=	11, L=	7
1	31*	10
3	29*	29
5	24*	17
K=	12, L=	7
0	30*	33
2	29*	22
4	24*	17
K=	13, L=	7
1	28*	16
3	32	28
K=	14, L=	7
0	25*	21
2	23*	15
K=	15, L=	7
1	20*	14
K=	0, L=	8
0	78	79
2	57	53
4	75	70
6	27*	23
K=	1, L=	8
1	35*	28
3	64	66
5	31*	24
7	21*	3
K=	2, L=	8
0	48	48
2	34*	5
4	32*	24
6	27*	20
K=	3, L=	8
1	47	38
3	73	71
5	38	30
7	20*	8
K=	4, L=	8
0	35*	20
2	34*	28
4	69	71
6	25*	11
K=	5, L=	8
1	41	41
3	70	57
5	28*	28
7	17*	14
K=	6, L=	8
0	89	90
2	33*	24
4	30*	18
6	23*	13
K=	7, L=	8
1	33*	16
3	31*	22
5	26*	7
K=	8, L=	8
0	75	75
2	31*	23
4	28*	12
6	18*	18
K=	9, L=	8
1	31*	4
3	28*	4
5	21*	5
K=	10, L=	8
0	29*	23
2	28*	19
4	23*	7
K=	11, L=	8
1	31	30
3	24*	21
K=	12, L=	8
0	24*	12
2	23*	18
K=	13, L=	8
1	20*	5
K=	1, L=	9
1	46	43
3	30*	13
5	24*	12
K=	2, L=	9
0	32*	27
2	31*	18
4	27*	29
6	18*	9
K=	3, L=	9
1	32*	2
3	39	45
5	23*	10
K=	4, L=	9
0	31*	32
2	43	49
4	60	57
K=	5, L=	9
1	30*	28
3	48	44
5	27	21
K=	6, L=	9
0	29*	5
2	28*	14
4	24*	23
K=	7, L=	9
1	28*	26
3	25*	15
K=	8, L=	9
0	27*	12
2	29*	5
4	19*	2
K=	9, L=	9
1	38	40
3	20*	22
K=	10, L=	9
0	22*	13
2	20*	17
K=	11, L=	9
1	18*	12
K=	0, L=	10
0	35	49
2	24*	14
4	18*	10
K=	1, L=	10
1	25*	11
3	22*	3
K=	2, L=	10
0	26*	17
2	24*	9
4	17*	9
K=	3, L=	10
1	24*	16
3	20*	23
K=	4, L=	10
0	24*	26
2	22*	19
K=	5, L=	10
1	22*	14
3	29	30
K=	6, L=	10
0	21*	15
2	19*	14
K=	7, L=	10
1	18*	13

Discussion

The packing in the structure is illustrated in Fig. 2. The molecules are wedge-shaped, and all point in approximately the same direction. There could therefore be a permanent dipole associated with the crystal (a pyroelectric effect is allowed by the symmetry). The intermolecular distances have normal van der Waals values: there are fourteen such distances less than 4·00 Å, but none less than 3·62 Å.

The molecular geometry is illustrated in Fig. 3. The angle between the six-membered rings is 99·6°, and each is slightly distorted to a boat shape, as shown. There is no clear evidence of strain in the uncorrected lengths of the bridging C–O and C–C bonds. The CH_2–CH_2 distance of 1·540 Å does not differ significantly from the value of 1·533 Å reported for n-butane and n-hexane (Sutton, 1965). However, appropriately corrected distances (assuming the corrections could be estimated) might well give a different impression. An idea of the magnitude of such corrections is given by a comparison of the bond lengths in the six-membered rings of this and other structures. The mean value for benzene is 1·395 Å (*International Tables for X-ray Crystallography*, 1962) and for *trans*-4,12-dimethyl[2.2]-metacyclophane it is 1·399 Å (Hanson, 1962). The corresponding value in the present compound is 1·371 Å. There is no reason to expect such a reduction in the actual distance, and we might reasonably conclude that the observed distance should be increased by 0·026 Å, or 1·9%. If the remaining distances are increased in like manner (and this is clearly a dangerous procedure) the modified values are consistent with significant strain. In particular, the distance CH_2–CH_2 becomes 1·569 Å, a value which is comparable to the 1·573 Å found for *trans*-4,12-dimethyl[2.2]metacyclophane. Although this result confirms reasonable expectations, it must be remembered that the modified distances are not very reliable, and do not by themselves constitute conclusive evidence of strain. Stronger evidence is provided by the differences of some of the bond angles from typical values. The angle C–O–C is 101·4°, quite different from the value of 111·5° found in dimethyl ether (Sutton, 1965). The average value of the angles terminating the CH_2–CH_2 bond is 119·0°, whereas the unstrained tetrahedral value is 109·5°, and the corresponding value in the moderately-strained *trans*-4,12-dimethyl[2.2]metacyclophane is only 111·5°. The deformation of this angle must provide at least some of the driving force for the ejection of the hetero atom in such compounds.

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