N(3) have two shorter and two longer N···F contacts, whereas at N(5) all three N···F distances are almost equal. Around the NH_3^+ parts of the pairs N(1)–N(2) and N(3)–N(4) the number of fluorine atoms at possible hydrogen bond distances is greater than three; this might allow the existence of bifurcated hydrogen bonds among some of them.

The two shortest nitrogen contacts between two different $N_2H_5^+$ cations are: N(2)···N(5) = 3·09, N(2)···N(4) = 3·10 Å. These may correspond to weak NH···N interactions.

As can be seen in Fig. 2 the fluorine atoms F(1), F(2) and F(5) are each linked to two different $N_2H_5^+$ cations, with one longer (> 2·80 Å) and one shorter contact (< 2·80 Å). Fluorine F(6) has two $N_2H_5^+$ ions at nearly equal distances. In the vicinity of F(3) there are three $N_2H_5^+$ cations at rather long distances. The F(4) atom is surrounded by three cations with two short N···F distances and one longer.

By inspection of the powder diffraction patterns the analogous vanadium compound $(N_2H_5)_3VF_6$, has been found to be isomorphous with $(N_2H_5)_3CrF_6$.

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The Crystal Structure of [2.2]Metacyclophane-1,9-diene

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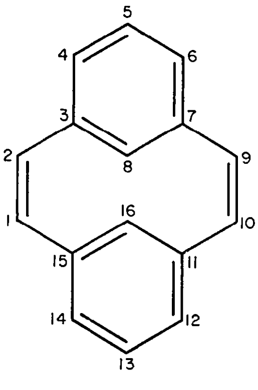
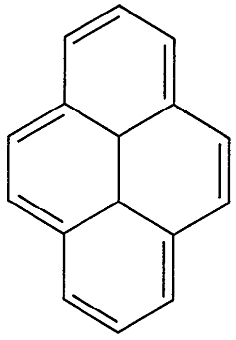
Crystals of the title compound, $C_{16}H_{12}$, are monoclinic, $P2_1/a$, with $a = 13{\cdot}25$ (1), $b = 5{\cdot}640$ (5), $c = 7{\cdot}350$ (5) Å, $\beta = 95{\cdot}39$ (5)°, $Z = 2$. 833 of a possible 931 independent reflexions in the range $\sin\theta/\lambda \leq 0{\cdot}59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures and refined by block-diagonal least-squares methods to a final R index of 0·054. The molecule has crystallographic inversion symmetry and non-crystallographic, but fairly precise, mirror symmetry. The phenyl rings are parallel, but displaced stepwise to avoid too close mutual contact, and they suffer severe boat-distortion. The distance between the carbon positions 8 and 16 of opposing phenyl rings is 2·57 Å. The length of the double bonds in the inter-phenyl bridges is 1·341 (3) Å.

Introduction

The title compound (I) is one of a number of cyclophanes prepared by Professor Boekelheide and his associates. Many of these compounds are highly strained, and it is of interest to compare the chemical and geometrical consequences of such strain. (I) is somewhat unstable, undergoing (in solution) a light-mediated transformation to the corresponding dihydropyrene (II) and ultimately to pyrene (Mitchell & Boekelheide, 1970). The structure analysis was under-



(I)



(II)

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taken in order to examine the molecular geometry which allows this transformation.

Experimental

Crystal data: F.W. 204·3, $V = 547$ Å^3, $D_m = 1{\cdot}24$ g.cm^{-3} (by flotation), $D_x = 1{\cdot}24$ g.cm^{-3}, $\mu = 5{\cdot}4$ cm^{-1} (Cu $K\alpha$). The wavelength assumed for Cu $K\alpha_1$ was 1·54050 Å. The space group was determined from precession and Weissenberg photographs. Systematic absences: $h0l$ for h odd, $0k0$ for k odd. Molecular symmetry: inversion centre.

The material supplied was recrystallized from a cyclohexane–benzene solution, yielding dark green plates. The specimen used for all measurements was a fragment of such a plate, of dimensions 0·2 × 0·5 × 0·7 mm. This was mounted on a four-circle diffractometer with the longest dimension (corresponding to **b**) parallel to the φ axis. In order to reduce the decomposition which appeared to occur in air, it was enclosed in a thin-walled Lindemann-glass capillary. The relative intensities were measured in the θ–2θ scan mode (scans of 2° for $2\theta < 100°$, 3° otherwise) using nickel-filtered Cu $K\alpha$ radiation with pulse-height discrimination. Background intensities were measured at the beginning and end of each scan. The intensity of a standard reflexion was measured periodically, for use in subsequent scaling operations; a decrease in intensity of about 6% occurred during the course of the measurements. Reflexions were considered to be unobserved if their net counts were less than 7 (deca-) counts or 0·15 corresponding background count. In the range explored ($2\theta < 130°$), 833 of 931 accessible reflexions were observed above background. Absorption corrections were not applied.

Structure determination

The approximate structure was readily deduced by symbolic-addition procedures, using the program of Ahmed, Hall, Pippy & Huber (1966). The structure was then refined by block-diagonal least-squares methods, using the program of Ahmed *et al.* (1966). This program minimizes $\sum w\Delta F^2$. The weighting scheme, chosen to ensure reasonable constancy of $w\Delta F^2$ with F_o and $\sin^2\theta$, was $w = w_1 w_2$, where

$$\begin{aligned} w_1 &= F_o/3 && \text{for } F_o \le 3 \\ &= 3/F_o && \text{for } F_o > 3 \\ w_2 &= 1{\cdot}87 \sin\theta && \text{for } \sin\theta < 0{\cdot}54\,. \\ &= 1 && \text{for } \sin\theta \ge 0{\cdot}54 \end{aligned}$$

(The nominal threshold value of F_o is 0·6.)

The scattering-factor curve used for carbon was that of Hanson, Herman, Lea & Skillman (1964), and for hydrogen, that of Stewart, Davidson & Simpson (1965). The temperature factors of the carbon atoms were allowed to vary anisotropically, while those of the hydrogen atoms (initially located in a difference Fourier synthesis) were constrained to be isotropic. During refinement it became apparent that the strongest reflexions were suffering slightly from extinction,

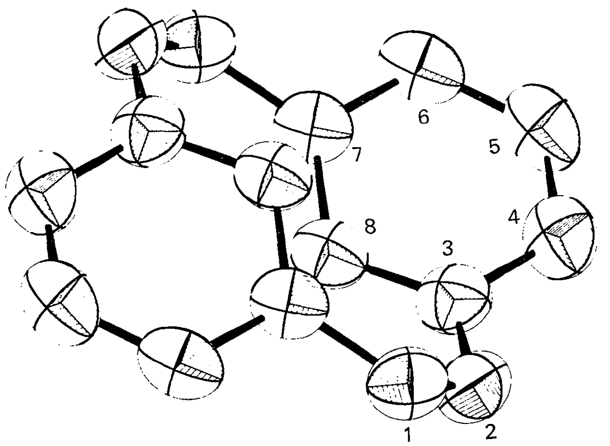

Fig. 1. The thermal motion ellipsoids of 50% probability.

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

Quantities given are: fractional coordinates (× 10^5) for carbon atoms, (× 10^3) for hydrogen atoms [equivalent positions $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,z)$]; U_{ij} (× 10^4) Å^2 for carbon atoms {T. F. = $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)]$; r.m.s. displacements D_i along principal axes of vibration ellipsoids, in Å (× 10^2); isotropic Debye-Waller factors for hydrogen atoms, in Å^2.

	X	Y	Z	U11	U12	U13	U22	U23	U33
C(1)	-11310(15)	30579(39)	12081(31)	527(11)	98(9)	90(10)	561(12)	-16(10)	741(13)
C(2)	-2572(17)	31632(39)	22771(31)	728(13)	55(10)	16(11)	551(13)	-93(10)	641(13)
C(3)	6295(15)	15820(38)	21969(29)	561(11)	-57(9)	-72(9)	523(11)	-40(10)	629(12)
C(4)	10840(16)	5590(45)	37899(30)	534(11)	-95(10)	-97(9)	759(15)	-8(11)	595(12)
C(5)	16973(15)	-14060(46)	36986(31)	465(10)	-22(10)	-124(9)	812(15)	160(12)	678(13)
C(6)	17722(13)	-25515(39)	20606(31)	383(9)	14(9)	-40(9)	567(11)	148(11)	797(14)
C(7)	13211(13)	-15621(37)	4384(29)	388(9)	45(8)	11(8)	550(11)	41(9)	681(12)
C(8)	9006(14)	7091(37)	5273(28)	443(10)	-69(9)	-8(9)	518(11)	59(10)	656(12)

	D1	D2	D3
C(1)	21	25	27
C(2)	22	25	28
C(3)	21	24	27
C(4)	20	26	29
C(5)	19	26	31
C(6)	19	23	30
C(7)	19	24	26
C(8)	20	23	27

	X	Y	Z	B
H(1)	-168(2)	413(5)	146(3)	6.0(0.6)
H(2)	-26(2)	425(4)	328(3)	5.5(0.5)
H(4)	93(2)	112(5)	491(3)	5.6(0.5)
H(5)	201(2)	-206(5)	483(3)	6.6(0.6)
H(6)	210(2)	-411(5)	203(3)	5.5(0.5)
H(8)	64(2)	168(4)	-68(3)	4.6(0.5)

and these were corrected by the empirical method of Pinnock, Taylor & Lipson (1956). The structure amplitudes of six reflexions were thereby increased by 1 to 6%. In addition, some 22 weak reflexions, for which the calculated structure amplitudes were below the estimated threshold, were arbitrarily assigned zero weight. The final parameters are given in Table 1. In the last refinement cycle no parameter shift of a carbon atom exceeded one quarter of the corresponding e.s.d.

Assessment of analysis

The agreement between observed and calculated structure amplitudes (Table 2) is satisfactory, and there can be no doubt of the essential correctness of the proposed structure. The final agreement residual ($R=\sum|\Delta F|/\sum|F_o|$) is 0·054, for observed reflexions only. The final difference Fourier synthesis is, with two exceptions, reasonably featureless, with the residual density lying between the limits ±0·17 e.Å^{-3}. The exceptions are two well-formed peaks, one of height 0·36 e.Å^{-3} and with coordinates 0·024, −0·006, 0·083, and the other of height 0·23 e.Å^{-3}, at 0·005, 0·132, 0·244. (These positions are indicated in Fig. 2.) The first lies 0·02 Å from the non-crystallographic mirror plane of the molecule, 0·70 Å from the centre of symmetry, and 1·1 Å from the nearest carbon atom [C(8)]. The second lies 1·6 Å from the first, and 0·8 Å from C(3); its height and position may be perturbed by the proximity of this atom. A possible explanation of these anomalies is that a second molecular species is present as an impurity. As mentioned in the introduction, 15,16-dihydropyrene (II) is known to be a reaction product of I. Moreover, I is said to be colourless, while solutions of II are deep green (Mitchell, *et al.* 1970). The deep green colour of both the original and recrystallized specimen material is thus consistent with the presence of II. If II were to replace I at a small proportion of sites, occupying roughly the same space, many atoms would overlap and would not be distinguished. However, the atoms terminating the central bond of II could be expected to be resolved near the centre of

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

An asterisk denotes the theshold value of an unobserved reflexion. A minus sign preceding $10F_o$ means that the reflexion was omitted from the refinement.

H	FO	FC
K= 0, L= 0		
2	252	248
4	485	-537
6	15	8
8	19	-21
10	56	54
12	22	22
14	63	-62
K= 1, L= 0		
1	375	-385
2	403	-407
3	217	247
4	385	394
5	254	269
6	54	53
7	55	52
8	168	-164
9	6*	0
10	57	-54
11	35	-34
12	69	-67
13	13	-12
14	6*	4
15	5	5
K= 2, L= 0		
0	276	-277
1	76	-79
2	-52	22
3	312	-328
4	19	-19
5	257	-261
6	144	-147
7	75	77
8	45	44
9	77	73
10	43	42
11	37	-37
12	13	13
13	33	-30
14	18	19
K= 3, L= 0		
1	5*	0
2	202	207
3	96	-87
4	80	79
5	13	16
6	33	-31
7	17	-18
8	73	-69
9	97	-97
10	26	-23
11	30	-32
12	57	55
13	39	33
K= 4, L= 0		
0	73	-71
1	43	-42
2	43	-45
3	6*	-4
4	22	23
5	72	68
6	29	27
7	60	62
8	7*	0
9	28	28
10	21	23
11	6*	1
12	7	-4
K= 5, L= 0		
1	60	61
2	48	52
3	7*	-4
4	10	12
5	23	-22
6	61	-64
7	7*	3
8	14	-17
9	22	17
10	41	38
K= 6, L= 0		
0	25	24
1	35	-38
2	26	27
3	30	-32
4	7	4
5	21	21
6	7	3
K= 0, L= 1		
0	373	372
2	284	-288
4	18	-26
6	110	-111
8	76	78
10	154	157
12	17	-13
14	24	24
-2	560	580
-4	337	-366
-6	81	-95
-8	41	36
-10	141	-141
-12	39	-40
-14	20	19
K= 1, L= 1		
0	183	186
1	236	237
2	267	273
3	193	203
4	64	67
5	68	67
6	40	-42
7	25	21
8	73	74
9	6*	-4
10	84	-79
11	26	24
12	64	-62
13	7*	-5
14	59	56
15	27	-29
-1	299	-292
-2	593	625
-3	387	-383
-4	65	54
-5	45	61
-6	353	-359
-7	35	43
-8	67	73
-9	6*	4
-10	107	105
-11	7*	0
-12	33	-34
-13	49	-45
-14	18	-20
-15	16	-13
K= 2, L= 1		
0	146	-146
1	34	-34
2	39	-34
3	72	-74
4	57	-58
5	60	61
6	59	61
7	71	72
8	-10	-2
9	82	81
10	97	-91
11	31	30
12	16	16
13	68	-62
14	10	10
-1	113	113
-2	6*	-4
-3	25	-19
-4	264	250
-5	160	166
-6	77	-93
-7	164	173
-8	111	-113
-9	71	-67
-10	92	92
-11	33	-31
-12	59	60
-13	31	32
-14	17	18
K= 3, L= 1		
0	91	87
1	110	-101
2	44	40
3	115	-107
4	32	-32
5	81	-79
6	6	4
7	34	-33
8	51	-50
9	7	-10
10	14	-10
11	41	-40
12	41	40
13	6*	1
-1	104	102
-2	84	-78
-3	115	122
-4	60	-60
-5	12	9
-6	15	-13
-7	75	77
-8	24	-29
-9	25	29
-10	62	60
-11	48	-50
-12	18	16
-13	-7	0
K= 4, L= 1		
0	16	-15
1	76	-71
2	-9	-4
3	19	19
4	61	63
5	24	25
6	23	23
7	25	-24
8	34	-33
9	49	-48
10	6*	6
11	6*	1
12	13	-9
-1	91	-90
-2	48	-47
-3	18	19
-4	31	-31
-5	19	23
-6	35	33
-7	40	-44
-8	14	-18
-9	54	-55
-10	6*	1
-11	27	-26
-12	40	41
K= 5, L= 1		
0	30	-30
1	35	33
2	7*	-2
3	21	20
4	10	-9
5	7	-3
6	33	-32
7	6*	-2
8	24	24
9	33	32
-1	14	13
-2	35	-38
-3	25	-28
-4	47	-52
-5	36	-36
-6	18	19
-7	13	-10
-8	43	48
-9	7	-9
-10	13	-10
K= 6, L= 1		
0	11	10
1	6*	2
2	17	17
3	6*	5
4	19	-21
5	5*	2
6	5*	2
-1	19	22
-2	11	-7
-3	30	33
-4	6*	0
-5	8	-6
-6	5	2
K= 0, L= 2		
0	156	-149
2	101	96
4	290	-284
6	230	-226
8	128	128
10	73	73
12	31	35
14	30	35
-2	310	-305
-4	224	-228
-6	25	-30
-8	140	137
-10	6*	-4
-12	73	-72
-14	25	25
K= 1, L= 2		
0	163	165
1	219	-212
2	76	74
3	101	94
4	104	-100
5	108	101
6	70	70
7	51	-57
8	17	20
9	44	-47
10	31	-29
11	15	-18
12	86	88
13	20	-22
14	34	33
-1	115	-114
-2	38	38
-3	-11	-4
-4	12	8
-5	21	-12
-6	122	-123
-7	5*	5
-8	41	-40
-9	53	-49
-10	44	45
-11	13	-11
-12	56	-57
-13	18	18
-14	54	-55
-15	8	-7
K= 2, L= 2		
0	204	197
1	126	112
2	83	74
3	72	66
4	38	-34
5	74	-76
6	26	22
7	110	108
8	56	-52
9	162	164
10	-9	0
11	35	-36
12	35	35
13	76	-75
-1	36	-38
-2	62	58
-3	56	-55
-4	74	66
-5	129	-128
-6	21	14
-7	9	-8
-8	84	-84
-9	21	24
-10	29	29
-11	44	-42
-12	39	38
-13	-7	0
-14	17	-17
K= 3, L= 2		
0	5*	4
1	5	-1
2	51	-45
3	123	-119
4	82	87
5	23	23
6	8	11
7	154	156
8	130	-130
9	7*	3
10	7*	-2
11	64	-65
12	43	41
13	12	13
-1	68	70
-2	29	-29
-3	102	103
-4	40	-41
-5	46	48
-6	68	67
-7	7*	1
-8	7	-8
-9	59	65
-10	15	-17
-11	18	21
-12	46	46
-13	37	-35
K= 4, L= 2		
0	35	-36
1	84	-85
2	35	35
3	97	-98
4	88	88
5	7*	-6
6	65	-67
7	7	-9
8	30	-30
9	35	-36
10	32	32
11	5*	0
-1	25	21
-2	42	40
-3	84	84
-4	13	-13
-5	68	70
-6	7*	-6
-7	8	-8
-8	20	17
-9	28	-24
-10	31	-34
-11	7	12
-12	17	13
K= 5, L= 2		
0	47	-44
1	8	9
2	74	75
3	7	6
4	13	12
5	28	-27
6	27	-24
7	34	-31
8	11	12
9	9	6
-1	25	-23
-2	67	-68
-3	36	-36
-4	7	-4
-5	16	-14
-6	7*	-4
-7	8	-6
-8	27	26
-9	16	-17
K= 6, L= 2		
0	17	-14
1	10	8
2	25	-26
3	19	-21
4	20	-23
5	5	-6
-1	24	24
-2	48	-49
-3	6*	0
-4	14	-14
-5	16	-19
K= 0, L= 3		
0	5*	2
2	142	-134
4	154	-146
6	67	69
8	55	54
10	44	-44
12	28	-26
14	33	-29
-2	114	102
-4	86	-82
-6	91	-83
-8	74	72
-10	56	52
-12	32	29
-14	44	42
K= 1, L= 3		
0	91	-76
1	23	22
2	90	-80
3	237	227
4	101	-94
5	47	-49
6	32	-35
7	121	-124
8	22	-23
9	51	-54
10	71	75
11	-8	0
12	65	69
13	39	39
-1	312	-300
-2	164	-156
-3	24	26
-4	90	-88
-5	169	169
-6	53	-55
-7	65	67
-8	44	46
-9	13	-10
-10	63	66
-11	41	-42
-12	36	-32
-13	12	-12
-14	44	-41
K= 2, L= 3		
0	180	167
1	154	133
2	107	-103
3	62	-67
4	67	-62
5	48	-47
6	22	22
7	71	72
8	40	43
9	20	-21
10	62	66
11	50	-52
12	17	-16
13	6	-5
-1	68	-78
-2	177	172
-3	139	-143
-4	29	-28
-5	41	40
-6	67	-67
-7	26	-27
-8	67	-68
-9	69	-72
-10	7*	-2
-11	26	-28
-12	33	31
-13	14	9
-14	26	-26
K= 3, L= 3		
0	7	12
1	13	13
2	44	46
3	17	-19
4	58	59
5	134	132
6	94	-95
7	52	51
8	26	-23
9	14	-12
10	45	45
11	6*	-4
12	-5	-1
-1	72	71
-2	74	79
-3	99	-95
-4	57	-53
-5	86	-88
-6	55	-53
-7	15	17
-8	54	60
-9	18	18
-10	19	18
-11	6*	2
-12	-6	3
-13	20	-17
K= 4, L= 3		
0	43	-44
1	143	-139
2	80	80
3	24	-26
4	26	-24
5	105	103
6	59	-59
7	42	40
8	29	30
9	19	-20
10	6	-5
-1	-10	4
-2	8	-5
-3	147	143
-4	84	81
-5	87	88
-6	17	-21
-7	7*	-2
-8	16	-15
-9	24	-23
-10	9	9
-11	6*	7
K= 5, L= 3		
0	101	100
1	19	-19
2	82	80
3	7*	-5
4	47	-49
5	25	-24
6	12	-12
7	36	-38
8	10	-9
-1	7	-5
-2	49	-49
-3	24	20
-4	24	-23
-5	23	27
-6	16	15
-7	6*	9
-8	7	-7
-9	14	-14
K= 6, L= 3		
0	6*	-5
1	25	-27
2	18	-20
3	5	-5
-1	16	-17
-2	35	-34
-3	6*	6
-4	37	-39
K= 0, L= 4		
0	15	-12
2	52	53
4	93	92
6	73	75
8	37	-34
10	68	-52
12	14	-13
-2	139	129
-4	199	185
-6	70	-74
-8	62	-65
-10	14	9
-12	7*	1
-14	50	43
K= 1, L= 4		
0	51	-45
1	73	69
2	28	-27
3	-7	2
4	13	9
5	11	-12
6	6	-3
7	7	-10
8	47	-49
9	7*	-1
10	7*	-2
11	27	25
12	16	17
-1	41	-36
-2	143	-131
-3	68	-61
-4	17	-15
-5	55	63
-6	43	44
-7	67	70
-8	7*	-5
-9	13	15
-10	62	64
-11	7	6
-12	41	42
-13	17	-14
-14	21	-17
K= 2, L= 4		
0	80	-73
1	24	20
2	82	-77
3	33	-33
4	14	-10
5	52	-54
6	36	-35
7	78	-78
8	22	24
9	8	-7
10	44	47
11	12	14
12	6	-5
-1	33	28
-2	25	23
-3	61	-60
-4	30	-27
-5	42	42
-6	8	-9
-7	111	111
-8	7*	-7
-9	23	-23
-10	31	-36
-11	75	-73
-12	15	13
-13	-11	3
K= 3, L= 4		
0	-8	1
1	16	12
2	37	38
3	7	-5
4	26	-25
5	8	-10
6	7*	1
7	7*	3
8	42	43
9	13	12
10	21	-22
11	27	-26
-1	56	52
-2	38	39
-3	56	-56
-4	24	25
-5	155	-156
-6	97	-98
-7	33	-34
-8	26	-23
-9	47	47
-10	47	46
-11	7	-9
-12	10	9
K= 4, L= 4		
0	7*	2
1	41	-43
2	7*	4
3	47	46
4	30	-27
5	67	68
6	18	23
7	45	42
8	9	-7
9	9	10
-1	39	-39
-2	59	-62
-3	31	27
-4	33	34
-5	10	9
-6	38	41
-7	17	-21
-8	36	-33
-9	6*	-3
-10	-6*	4
K= 5, L= 4		
0	74	71
1	9	-6
2	20	-20
3	13	12
4	19	-19
5	6*	-2
6	5	-3
-1	9	-6
-2	39	39
-3	48	47
-4	25	-24
-5	43	43
-6	8	8
-7	5	-2
K= 0, L= 5		
0	148	146
2	61	-58
4	62	-60
6	79	81
8	7*	-1
10	14	-11
-2	86	88
-4	44	43
-6	14	-12
-8	97	-92
-10	11	-12
-12	6*	1
K= 1, L= 5		
0	15	17
1	43	-45
2	38	37
3	79	79
4	135	132
5	79	75
6	19	-22
7	7	-7
8	95	-102
9	7*	-6
10	12	11
11	10	-13
-1	53	-54
-2	43	43
-3	-7	-3
-4	6*	-3
-5	12	12
-6	38	42
-7	7*	9
-8	7*	-4
-9	7*	-2
-10	22	-25
-11	-6	2
-12	41	40
-13	8	12
K= 2, L= 5		
0	25	-20
1	6*	-7
2	18	20
3	12	-14
4	53	-47
5	43	-41
6	72	-73
7	38	40
8	36	36
9	33	35
10	32	34
-1	20	-20
-2	23	-20
-3	27	29
-4	25	-22
-5	62	64
-6	7*	-2
-7	60	61
-8	51	49
-9	17	21
-10	6*	3
-11	37	-33
-12	9	-10
K= 3, L= 5		
0	19	22
1	7*	4
2	14	16
3	47	-50
4	19	-20
5	35	-37
6	9	-11
7	15	-15
8	22	-22
9	45	-43
-1	23	23
-2	21	-20
-3	7*	3
-4	13	-16
-5	14	-12
-6	28	-28
-7	7*	-1
-8	15	-18
-9	22	20
-10	27	22
-11	5*	2
K= 4, L= 5		
0	8	-6
1	31	-30
2	7*	-2
3	20	-18
4	21	21
5	26	24
6	-7	-1
7	33	32
-1	10	-10
-2	26	-27
-3	-7	-3
-4	25	-26
-5	34	-33
-6	13	13
-7	39	-41
-8	6*	0
-9	5*	-4
K= 5, L= 5		
0	6*	-4
1	6	-4
2	6*	-3
3	6	-4
-1	6*	-2
-2	6*	3
-3	13	13
-4	19	-18
-5	15	16
K= 0, L= 6		
0	52	-48
2	222	-223
4	7*	4
6	72	74
8	18	19
10	24	27
-2	132	136
-4	7*	-1
-6	42	-43
-8	31	-32
-10	24	-19
-12	11	15
K= 1, L= 6		
0	36	-33
1	78	76
2	58	58
3	66	64
4	59	57
5	23	-24
6	55	-58
7	24	-25
8	6*	0
9	9	-9
-1	42	-43
-2	74	79
-3	72	-74
-4	55	56
-5	8	-11
-6	43	-45
-7	7*	2
-8	24	-29
-9	7*	3
-10	20	-20
-11	6*	4
K= 2, L= 6		
0	7*	6
1	9	-8
2	32	33
3	7*	8
4	20	-18
5	76	76
6	11	9
7	53	53
8	25	25
9	22	-24
-1	28	-30
-2	-11	3
-3	38	-40
-4	47	49
-5	34	35
-6	7*	7
-7	46	47
-8	16	-12
-9	12	-13
-10	-7	2
-11	20	-19
K= 3, L= 6		
0	49	48
1	10	-10
2	7*	-3
3	7*	-5
4	52	-51
5	6*	1
6	27	-28
7	30	-28
-1	23	24
-2	17	19
-3	13	13
-4	15	-16
-5	15	14
-6	20	-20
-7	48	48
-8	8	-5
-9	27	26
K= 4, L= 6		
0	11	9
1	25	-25
2	17	18
3	7	4
4	5*	6
5	5*	1
-1	23	-21
-2	12	-9
-3	10	9
-4	11	-13
-5	13	12
-6	5*	-2
-7	5*	3
K= 0, L= 7		
0	101	-103
2	43	-42
4	9	10
6	6*	1
-2	7*	6
-4	18	21
-6	22	-21
-8	20	21
-10	15	18
K= 1, L= 7		
0	44	-44
1	26	24
2	11	-11
3	27	-28
4	32	-29
5	24	-24
6	9	11
7	14	-13
-1	45	43
-2	9	-11
-3	17	-21
-4	52	60
-5	32	-32
-6	18	-16
-7	9	-5
-8	47	-51
-9	6*	1
K= 2, L= 7		
0	15	15
1	8	-5
2	23	24
3	28	30
4	14	14
5	24	25
6	14	14
-1	7*	-4
-2	28	-28
-3	29	-31
-4	22	20
-5	44	-46
-6	32	35
-7	7	8
-8	26	-25
K= 3, L= 7		
0	20	17
1	8	-8
2	18	-19
3	23	22
4	6	-6
-1	17	-15
-2	20	21
-3	13	14
-4	6	5
-5	6*	0
-6	8	8
K= 0, L= 8		
0	22	20
2	6*	-2
4	18	-18
-2	12	10
-4	6*	2
-6	10	-12
K= 1, L= 8		
0	19	-19
1	-8	3
2	32	-32
3	19	12
4	8	-8
-1	6	-3
-2	13	-14
-3	6*	7
-4	6*	5
-5	6	4
-6	5*	6
K= 2, L= 8		
0	5*	-3
1	-5	2
2	21	-18
-1	5*	0
-2	5*	1
-3	5*	4
-4	6	-7

symmetry, as is the larger of the two extraneous peaks. The hypothesis of minor disorder is by no means demonstrated, but it seems plausible. The possible effects on the observed molecular dimensions of I should not be entirely overlooked.

The thermal motion of the structure is appreciable, and as the molecule seems likely to behave as a rigid body, an appropriate analysis was undertaken, using the procedure of Schomaker & Trueblood (1968). The results, summarized in Table 3, are reasonably consistent with rigid-body behaviour, although no particularly interesting pattern emerges. The bond lengths have been appropriately corrected. Observed differences between chemically-equivalent bond lengths (4 pairs) are not significant either before or after the correction for thermal motion. This result suggests that the nominal e.s.d.'s are realistic.

Table 3. *Rigid-body thermal parameters*

$$\mathbf{T}(\sigma\mathbf{T}) = \begin{bmatrix} 393\ (12) & -14\ (11) & -71\ (9) \\ & 443\ (13) & 3\ (10) \\ & & 576\ (10) \end{bmatrix} \times 10^{-4}\text{Å}^2$$

$$\mathbf{L}(\sigma\mathbf{L}) = \begin{bmatrix} 121\ (10) & -6\ (5) & 16\ (7) \\ & 82\ (7) & -70\ (6) \\ & & 99\ (12) \end{bmatrix} \times 10^{-1}(°)$$

(Centre of libration at molecular centre of symmetry.)

Principal axes of **T**:

Eigenvalue	Direction cosines		
0·060 Å^2	0·324	−0·044	−0·945
0·044	0·133	−0·987	0·092
0·037	0·937	0·155	0·314

Principal axes of **L**

Eigenvalue	Direction cosines		
16·7 (°)^2	0·327	−0·615	0·717
11·6	0·943	0·264	−0·203
1·9	0·064	−0·743	−0·667*

* 22·5° from normal to molecular plane of symmetry. R.m.s. discrepancy between observed and calculated U_{ij} = 0·003 Å^2. All directions referred to the orthogonal axes $x' \| \mathbf{a}$, $y' \| \mathbf{b}$, $z' \| \mathbf{c}^*$.

Structure

The molecular geometry is summarized in Tables 4 and 5, and in Figs. 1 and 2. The molecule has fairly precise $2/m$ symmetry, and all bond lengths are close to their normal values. C(8) and C(8′) are constrained to lie only 2·57 Å apart; their proximity obviously favours the formation of a covalent bond, with conversion of I to II. The mutual repulsion of these atoms causes severe boat deformation of the phenyl rings. Judged by the criteria of distance and ring deformation, the repulsion is greater than has yet been observed in metacyclophanes (Hanson & Huml, 1969). The repulsion must, of course, be balanced by tension in the bridges. Nevertheless there is no indication of any elongation of the double bonds; the observed length of 1·341 (3) Å is not significantly different from the mean value for double bonds of 1·337 (6) Å (*International Tables for X-ray Crystallography*, 1962) or the value of 1·339 Å cited for *trans*-but-2-ene (Sutton, 1965). No significantly elongated double bond has yet been observed in cyclophane molecules (Coulter & Trueblood, 1963; Hanson *et al.*, 1969; Hanson, 1971). Single bonds in [2.2]cyclophanes are, in contrast, commonly found to have 'stretched' lengths of 1·57 to 1·59 Å, (Hanson, 1962; Mathew, 1968; Hanson & Huml, 1971; Bernstein & Trueblood, 1971; Hope, Bernstein & Trueblood, 1972), compared with the nominal paraffinic value of 1·541 (3) Å (*International Tables for X-ray Crystallography*, 1962) and a comparable value of 1·531 (4) Å found in [3.3]paracyclophane (Gantzel & Trueblood, 1965).

The hydrogen atoms have been located with a nominal precision of 0·02 to 0·03 Å. It is found that all are slightly displaced from positions of coplanarity with the three nearest carbon atoms (Table 5). For the

Table 4. *Intramolecular distances and angles*

	Distance (uncorrected)	Distance (corrected for thermal motion)	Mean
C(1)–C(2)	1·338 (3) Å	1·341 Å	
C(2)–C(3)	1·481 (3)	1·484	1·483 Å
C(1)–C(7′)	1·477 (3)	1·482	
C(3)–C(4)	1·391 (3)	1·392	1·396
C(6)–C(7)	1·399 (3)	1·400	
C(4)–C(5)	1·380 (3)	1·383	1·383
C(5)–C(6)	1·378 (3)	1·383	
C(3)–C(8)	1·400 (3)	1·404	1·404
C(7)–C(8)	1·401 (3)	1·405	
C(8)···C(8′)	2·567 (4)		
C(1)–H(1)	0·98 (3)	0·96 (1)	
C(2)–H(2)	0·96 (3)		
C(4)–H(4)	0·92 (3)		
C(6)–H(6)	0·99 (3)		
C(5)–H(5)	0·97 (3)		
C(8)–H(8)	1·07 (2)		
C(8)···H(8′)	2·46 (2)		

	Angle
C(1)–C(2)–C(3)	126·6 (2)°
C(2)–C(1)–C(7′)	125·3 (2)
C(2)–C(3)–C(8)	121·1 (2)
C(8)–C(7)–C(1′)	121·5 (2)
C(2)–C(3)–C(4)	119·9 (2)
C(6)–C(7)–C(1′)	119·8 (2)
C(4)–C(3)–C(8)	117·8 (2)
C(6)–C(7)–C(8)	117·7 (2)
C(3)–C(4)–C(5)	120·2 (2)
C(5)–C(6)–C(7)	119·8 (2)
C(4)–C(5)–C(6)	120·7 (2)
C(3)–C(8)–C(7)	119·9 (2)
C–C–H	115 to 122°

hydrogen atoms attached to the phenyl rings the displacement is invariably towards the centre of the molecule (Fig. 2). Similar displacements have been observed for other cyclophanes (Coulter *et al.*, 1963; Gantzel *et al.*, 1965; Bernstein *et al.*, 1971; Hope *et al.*, 1972), and various explanations have been proposed. We find the effect easiest to understand in terms of the resistance to twisting of the aromatic bonds, a concept which can also be used to explain the asymmetrical boat deformation found for the aromatic rings of all [2.2]metacyclophanes (Hanson *et al.*, 1969). Stereochemical requirements ensure that the bridge atoms will lie well out of the ring planes, necessitating some bending of the bond to the ring, and some rotation of the bridgehead atom. Efficient overlap of orbitals is maintained (*i.e.* torsional stresses are relieved) by a corresponding rotation of adjacent atoms. The hydrogen atoms thus tend to move to the same side of the ring planes as the bridge atoms. The greatest displacement (0·2 Å) is found for H(8), bringing this atom (in apparent defiance of van der Waals forces) to within 2·46 Å of C(8′). A corresponding displacement is *not* found when this hydrogen atom is replaced by a methyl group, as in 4,12-dimethyl[2.2]metacyclophane (Hanson, 1962). In this case the effect of the rotation of the ring carbon atom must be just balanced by that of increased van der Waals repulsion, as the relatively bulky methyl group is found to be accurately coplanar with the three nearest carbon atoms.

Table 5. *Distances of some atoms from specified planes, and some dihedral angles*

Specific planes are defined by atoms in bold type. Distances are in Å × 10^3.

Plane	Atoms and distances
1	**C(3)**, 0; **C(4)**, 0; **C(6)**, 0; **C(7)**, 0; C(5), −79; C(8), −226; C(1′), 479; C(2), 498.
2	**C(3)**, (0); **C(4)**, (0); **C(5)**, (0); H(4), 72.
3	**C(5)**, (0); **C(6)**, (0); **C(7)**, (0); H(6), 57.
4	**C(4)**, (0); **C(5)**, (0); **C(6)**, (0); H(5), 105.
5	**C(4)**, (0); **C(8)**, (0); **C(7)**, (0); H(8), 196.
6	**C(1)**, (0); **C(2)**, (0); **C(3)**, (0); H(2), 128.
7	**C(2)**, (0); **C(1)**, (0); **C(7′)**, (0); H(1), 77.

Angles: 1,4–6·7°
1,5–18·8

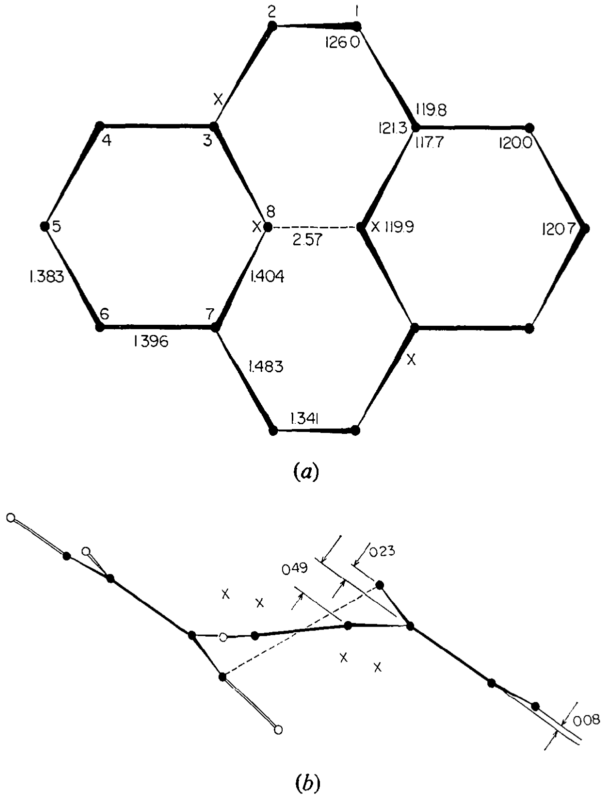

Fig. 2. The molecular geometry. The *X*'s indicate the positions of extraneous peaks in the difference map. (*a*) The view normal to the phenyl ring planes. Mean distances and angles are given in Å and (°). (*b*) The view normal to the molecular plane of symmetry. Mean hydrogen positions are shown for half the molecule.

One further point may be noted concerning the positions of the hydrogen atoms. The distance C(8)–H(8) at 1·07 (2) Å is appreciably longer than the other C–H distances [range, 0·92–0·99 Å; mean, 0·96 (1) Å]. The increased distance may indicate steric constraint on the electron distribution of H(8).

The molecular packing is illustrated in Fig. 3. Inter-

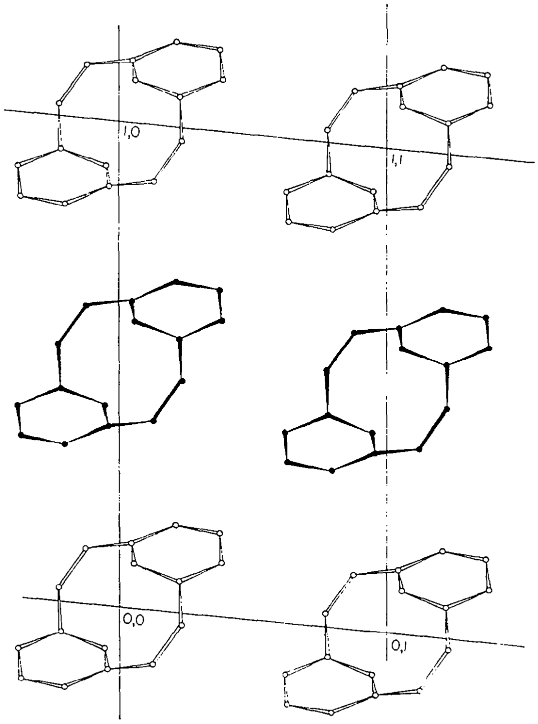

Fig. 3. A part of the structure, viewed along **b**. Molecules in open outline are centred at $y=0$, others at $y=\frac{1}{2}$.

molecular contacts appear to be normal; the shortest (between hydrogen atoms) is 2·68 Å.

Computer programs used in this work are those of Ahmed *et al.* (1966), Gantzel & Trueblood (*MGTLS*, thermal motion analysis) and C. K. Johnson (*ORTEP*, thermal ellipsoid plot). The problem was suggested, and specimen material supplied by Professor V. Boekelheide.

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Hydrogen Bond Studies. LXI.* An X-ray Diffraction Study of the Isotope Effect in Lithium Hydrogen Oxalate Monohydrate, $LiHC_2O_4.H_2O$

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The crystal structures of the normal and deuterated forms of $LiHC_2O_4.H_2O$ have been determined from three-dimensional single-crystal X-ray diffraction data collected at room temperature using an automatic Stoe–Philips four-circle diffractometer. The unit cells in both structures are triclinic with the space group $P1$ and containing one formula unit. The cell dimensions are, for $LiHC_2O_4.H_2O$ $a=5{\cdot}056$ (1), $b=6{\cdot}140$ (1), $c=3{\cdot}411$ (1) Å, $\alpha=95{\cdot}06$ (1), $\beta=98{\cdot}93$ (1), $\gamma=78{\cdot}57$ (1)°, $V=102{\cdot}36$ Å^3 and for $LiDC_2O_4.D_2O$ $a=5{\cdot}055$ (1), $b=6{\cdot}138$ (1), $c=3{\cdot}410$ (1) Å, $\alpha=95{\cdot}05$ (1), $\beta=98{\cdot}62$ (1), $\gamma=78{\cdot}57$ (1)°, $V=102{\cdot}34$ Å^3. The undeuterated structure consists of infinite parallel chains of hydrogen oxalate ions joined by 2·490 (1) Å asymmetric hydrogen bonds. These chains are linked transversely in the plane of the hydrogen oxalate ions by weaker hydrogen bonds, 2·702 (1) and 2·777 (1) Å, *via* the water molecules and by $Li^+\cdots O$ electrostatic forces. The infinite planes so formed are in turn held together by further $Li^+\cdots O$ electrostatic forces. The structure is generally unchanged in the deuterated form except for an increase of 0·016 (1) Å in the shortest $O\cdots O$ hydrogen bond length. The conventional R values obtained from the refinement of the normal and deuterated compound are 0·024 and 0·026 respectively.

Introduction

Deuteration has long been recognized as a most useful device in hydrogen-bond studies, *e.g.* Robertson & Ubbelohde (1939). The majority of observations of the resulting 'isotope effect' have been based, however, on cell parameter measurements combined with the assumption that any isotope effect present would appear only as changes in the hydrogen-bond lengths. More recently a number of complete structural studies of normal and deuterated compounds have been made:

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