boat conformation have been given by Mathieson (1962).

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The Crystal Structure of 2,8-Dihydroxy-5,6,11,12,4b,10b-hexahydrochrysene[*]

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(*Received* 1 *March* 1962)

Crystals of $C_{18}H_{16}(OH)_2$ are monoclinic with two centrosymmetric molecules in special positions in a unit cell of dimensions

$$a=17{\cdot}27,\ b=5{\cdot}13,\ c=7{\cdot}93\ \text{Å};\ \beta=105{\cdot}3^\circ,$$

space group $P2_1/a$. The structure has been determined using two-dimensional Patterson and electron-density syntheses and methods involving Fourier and optical transforms, and refined by diagonal least-squares calculations using anisotropic temperature factors. An analysis of the thermal vibrations is attempted.

Introduction

The interest of the structure of $C_{18}H_{16}(OH)_2$ lies in the configuration of atoms about the bond shared between the benzene and reduced rings. The substance is of biological interest owing to its outstanding oestrogenic activity as reported by Ramage & Robinson (1933). The preparation is described by Dodds, Golberg, Lawson & Robinson (1939).

Experimental

The crystals of $C_{18}H_{16}(OH)_2$ were kindly supplied by Sir Charles Dodds of the Courtauld Institute of Biochemistry, Middlesex Hospital. They are small transparent monoclinic parallelepipeds with [010] parallel to the needle axis of the crystal. The faces (001) and (100) are inclined to each other at an angle of approximately 105°. $(11l)$ and $(\bar{1}1l)$ faces are also present.

The optic axial plane is parallel to (010), *i.e.* the β-vibration direction lies along the symmetry axis b and the γ-vibration direction makes an angle of

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[*] This paper is based on a thesis accepted by the University of London in fulfilment of the requirements of the degree of Doctor of Philosophy.

approximately 32° with the a-axis in the acute angle. The crystals show positive birefringence. The optic angle of 37° in glycerine has been measured by C. H. Carlisle (private communication).

The density of the crystal is 1·29 g.cm.$^{-3}$ as measured in a modified gradient column, described by Low & Richards (1952). A mixture of Cd borotungstate solution and water was used for the gradient column and suitable mixtures of bromoform and xylene to calibrate the column.

From the small number of crystals available those chosen for the X-ray investigation had rather irregular dimensions of the order of 0·1 × 0·3 × 0·1 mm.^{3}. The small size and the chemical composition of the crystals made it unnecessary to apply absorption corrections when using Cu K radiation.

The unit-cell dimensions and space group were determined from rotation and oscillation photographs and intensity data were collected from $h0l$, $h1l$, $h2l$, $0kl$, $1kl$ and $hk0$ Weissenberg film packs (Robertson, 1943). The blackening of the reflections was estimated by visual comparison with an intensity scale. The intensities were reproducible to an accuracy of about 10% for the b-axis and a-axis photographs, whereas the c-axis photographs, owing to the shape of the crystal, have regions that cannot be used for intensity estimation by eye. 72% of the reflections observable with Cu K radiation for the $h0l$, $h1l$, $0kl$ and $hk0$ zones were recorded.

Crystal data

2,8-dihydroxy-5,6,11,12,4b,10b-hexahydrochrysene.
$C_{18}H_{16}(OH)_2$.
M.W. = 266·35.
Monoclinic,

$$a = 17{\cdot}27 \pm 0{\cdot}1,\ b = 5{\cdot}13 \pm 0{\cdot}02,\ c = 7{\cdot}93 \pm 0{\cdot}02\ \text{Å};\quad \beta = 105{\cdot}3 \pm 0{\cdot}5°.$$

Volume of unit cell = 677·97 Å^3.
Density,
calculated ($Z = 2$) = 1·304 g.cm.$^{-3}$,
measured = 1·29 g.cm.$^{-3}$ (N.T.P.).
Total number of electrons per unit cell = $F(000) = 284$.
Systematic absences
$0k0$: $k = 2n+1$,
$h0l$: $h = 2n+1$; space group $P2_1/a$.

Structure analysis

The Patterson map $P(U, W)$ showed clearly the direction of the molecule, which must lie in a $(2k1)$ plane. The assignment of the space group $P2_1/a$ to the structure implies that the two molecules in the unit cell are located in special positions, *i.e.* the centres of symmetry, and must therefore themselves be centrosymmetric and hence in the *trans* configuration. From the stereochemistry of the molecule it follows that the length must lie along $[\bar{1}02]$ as shown in Fig. 1. From the Patterson map $P(U, V)$ not much information could be gained apart from the approximate angle the molecule makes with [010]. The oxygen–oxygen vectors could not be located uniquely on either of the Patterson projections, which thus allowed equally for the two enantiomorphous structures A and B shown in Fig. 1.

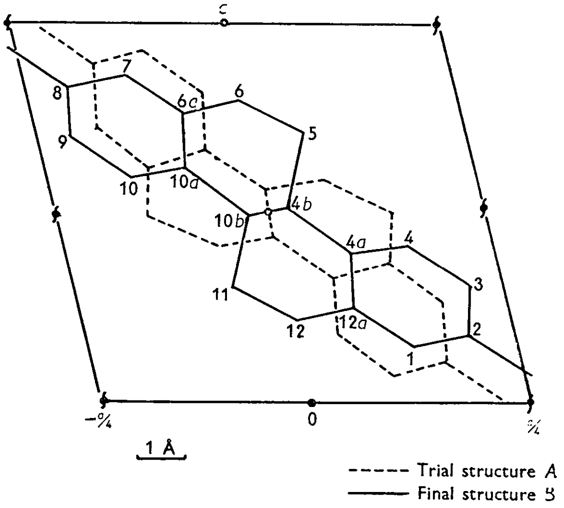

Fig. 1. ($h0l$) Projection,
- - - - - trial structure A,
——— final structure B.

Careful inspection of the $h0l$ weighted reciprocal lattice showed two sets of 'fringes'. These were interpreted as arising from the two pairs of rings related by the centre of symmetry (Woolfson, 1953). The directions and spacings of the two sets of fringes indicate that the configuration of the molecule B (full lines) on Fig. 1 is present. This conclusion is supported by the failure of the structure A (broken lines) to refine by Fourier methods, and by the very good agreement between weighted reciprocal lattice and optical transform obtained with the aid of a diffractometer for structure B (full lines).

An attempt to fix the signs for reflections in the orthogonal $hk0$ zone by a systematic application of Sayre relations (Vand & Pepinsky, 1956) proved unsuccessful. Although the range of U-values is satisfactory, the fall off in their magnitudes is irregular, which leads to an excessively large number of sign permutations within the acceptable probability range.

Refinement of structure

The three principal zones and the $h1l$ reflections were refined by least squares methods using programmes developed by H. J. Milledge and D. Milledge (1961). Diagonal terms only were included in the least-squares refinements and unit weights were used for all reflections. Anisotropic temperature factors were applied for all carbon and oxygen atoms to McWeeny's scattering factors (1951). Contributions from the hydrogen atoms (see Table 6) were included in the calculations using isotropic temperature factors, but their positional and thermal parameters were not refined. Fig. 2 shows the electron density map $\varrho(x0z)$.

For convenience, the chemical numbering of the carbon atoms has been re-adjusted as follows:

2, 8 = C(1)
3, 9 = C(2)
4, 10 = C(3)
4a, 10a = C(4)
4b, 10b = C(5)
5, 11 = C(6)
6, 12 = C(7)
6a, 12a = C(8)
1, 7 = C(9)

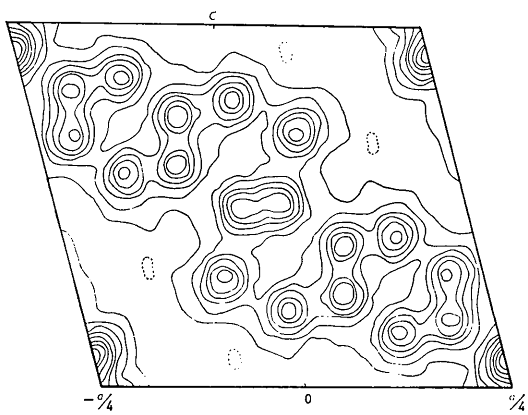

Fig. 2. Electron density synthesis $\varrho(x0z)$.

The directions and magnitudes of the principal axes of the vibration ellipsoids were inferred from difference maps and the magnitudes refined by least squares. Owing to the limitation imposed by the available computing programmes, only seven independent anisotropic temperature factors could be refined, and consequently the atoms C(2) and C(9), C(3) and C(7), C(4) and C(8) were given the same anisotropic vibration ellipsoids in pairs. The direction cosines of the angles between the axes of the ellipsoids and the crystal axes are given in Table 1(*a*). They were taken to be the same for all atoms, although this is perhaps not the best choice of axes with respect to atoms C(4), C(8), C(5) and C(5′). Table 1(*b*) gives alternative direction cosines for these atoms in more reasonable agreement with the geometry of the surrounding atoms (Ehrenberg, 1960). They were used in one

Table 1. *Cosines of angles between axes of vibration ellipsoids and cell axes*

(*a*)

	a	*b*	*c**	
B_x	+0·420	−0·738	+0·521	
B_y	+0·830	+0·068	−0·551	
B_z	−0·370	−0·670	−0·638	for all atoms

(*b*)

	a	*b*	*c**	
B_x	+0·275	−0·730	+0·629	
B_y	+0·870	−0·068	−0·435	
B_z	−0·370	−0·670	−0·638	for C(4) and C(8)

	a	*b*	*c**	
B_x	+0·446	−0·740	+0·484	
B_y	+0·814	+0·034	−0·586	
B_z	−0·370	−0·670	−0·638	for C(5) and C(6) remaining atoms as in (*a*)

(*c*) Values of the components of vibration ellipsoid tensor

$$T = \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$$

(i) Corresponding to (*a*) above

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Oxygen	+0·0053	+0·0732	+0·0272	+0·0080	+0·0145	+0·0009
C(1)	+0·0044	+0·0548	+0·0215	−0·0027	+0·0086	−0·0024
C(2), C(9)	+0·0048	+0·0585	+0·0230	−0·0037	+0·0089	−0·0028
C(3), C(7)	+0·0049	+0·0598	+0·0237	−0·0035	+0·0090	−0·0027
C(4), C(8)	+0·0039	+0·0419	+0·0180	−0·0021	+0·0048	−0·0013
C(5)	+0·0040	+0·0488	+0·0192	−0·0017	+0·0076	−0·0018
C(6)	+0·0044	+0·0530	+0·0215	+0·0030	+0·0082	+0·0002

(ii) Corresponding to (*b*) above

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Oxygen	+0·0054	+0·0754	+0·0280	+0·0091	+0·0150	+0·0013
C(1)	+0·0045	+0·0551	+0·0215	−0·0033	+0·0086	−0·0026
C(2), C(9)	+0·0049	+0·0608	+0·0237	−0·0032	+0·0097	−0·0027
C(3), C(7)	+0·0050	+0·0603	+0·0239	−0·0028	+0·0091	−0·0024
C(4), C(8)	+0·0039	+0·0429	+0·0191	−0·0020	+0·0057	−0·0008
C(5)	+0·0040	+0·0502	+0·0193	+0·0013	+0·0076	−0·0026
C(6)	+0·0044	+0·0530	+0·0215	+0·0070	+0·0079	−0·0001

Table 2

H	K	L	F OBS	F CALC
2	0	0	2.39	2.64
4	0	0	6.47	7.91
6	0	0	3.99	-4.39
8	0	0	1.77	1.74
10	0	0	(.35)	0.27
12	0	0	2.45	2.63
14	0	0	1.99	2.13
16	0	0	1.16	1.99
18	0	0	1.74	-1.45
20	0	0	(.30)	-0.93
-20	0	1	(.33)	0.13
-18	0	1	(.41)	-0.23
-16	0	1	4.70	4.13
-14	0	1	2.14	-1.99
-12	0	1	0.55	0.83
-10	0	1	1.22	-1.29
-8	0	1	3.94	3.06
-6	0	1	2.83	-3.52
-4	0	1	2.16	-2.47
-2	0	1	2.67	2.58
0	0	1	5.62	-4.98
4	0	1	10.29	10.29
6	0	1	4.72	-5.01
8	0	1	6.93	6.75
10	0	1	0.53	-1.00
12	0	1	0.40	-0.56
14	0	1	0.14	-0.39
16	0	1	0.61	0.57
18	0	1	0.64	0.50
20	0	1	0.57	0.54
-20	0	2	(.34)	-0.92
-18	0	2	0.59	0.55
-16	0	2	2.54	-2.47
-14	0	2	7.09	-7.07
-12	0	2	1.35	1.05
-10	0	2	3.93	-3.77
-8	0	2	7.84	7.59
-6	0	2	0.99	0.61
-4	0	2	2.66	1.84
-2	0	2	4.56	-5.23
0	0	2	8.19	-7.91
2	0	2	3.17	-2.84
6	0	2	2.34	2.17
8	0	2	2.97	3.03
10	0	2	3.58	-3.45
12	0	2	(.44)	-0.15
14	0	2	0.44	-0.53
16	0	2	1.25	-1.18
18	0	2	1.29	-1.08
-20	0	3	0.60	-0.01
-18	0	3	(.41)	0.16
-16	0	3	0.89	-0.75
-14	0	3	2.14	2.38
-12	0	3	(.40)	0.36
-10	0	3	1.96	-1.71
-8	0	3	3.95	-2.81
-4	0	3	0.50	0.13
-2	0	3	0.76	1.38
0	0	3	3.72	-3.55
2	0	3	6.10	-6.41
4	0	3	1.79	-1.61
6	0	3	2.19	-2.00
8	0	3	2.98	-2.97
10	0	3	(.43)	-0.15
12	0	3	1.08	0.93
14	0	3	(.43)	0.03
16	0	3	(.36)	-0.26
18	0	3	(.26)	0.58
-20	0	4	0.65	-0.11
-18	0	4	(.41)	-0.16
-16	0	4	0.44	-0.45
-14	0	4	1.09	1.27
-12	0	4	1.02	1.01
-10	0	4	3.71	3.02
-8	0	4	4.03	-3.91
-6	0	4	3.74	3.30
-4	0	4	3.48	2.90
-2	0	4	1.52	1.27
0	0	4	0.55	-0.16
2	0	4	8.83	9.06
4	0	4	2.96	2.80
6	0	4	0.39	0.27
8	0	4	0.60	-0.72
10	0	4	0.64	-0.76
12	0	4	0.43	-0.32
14	0	4	(.38)	0.20
16	0	4	(.29)	0.41
-20	0	5	1.46	1.23
-18	0	5	0.38	0.58
-16	0	5	0.75	-0.57
-14	0	5	2.98	2.66
-12	0	5	(.44)	-0.38
-10	0	5	0.96	0.96
-8	0	5	(.40)	0.22
-6	0	5	4.30	3.93
-4	0	5	1.71	-2.09
-2	0	5	(.36)	0.17
0	0	5	0.75	-0.95
2	0	5	1.15	1.22
4	0	5	2.80	-3.41
6	0	5	1.26	1.22
8	0	5	(.45)	-0.16
10	0	5	1.78	1.87
12	0	5	1.10	1.20
14	0	5	(.30)	-0.09
-20	0	6	1.04	-0.92
-18	0	6	(.34)	0.29
-16	0	6	(.41)	0.91
-14	0	6	0.61	0.55
-12	0	6	4.11	-3.97
-10	0	6	0.97	1.92
-8	0	6	1.41	-1.69
-6	0	6	4.13	4.13
-4	0	6	1.83	2.08
-2	0	6	1.16	1.34
0	0	6	(.42)	-0.34
2	0	6	0.72	-0.85
4	0	6	0.62	-0.45
6	0	6	0.75	0.91
8	0	6	(.43)	0.46
10	0	6	1.07	1.21
12	0	6	0.96	-1.13
-18	0	7	0.28	0.14
-16	0	7	0.57	-0.38
-14	0	7	(.41)	0.93
-12	0	7	(.43)	-0.13
-10	0	7	0.88	1.09
-8	0	7	1.66	-1.73
-6	0	7	(.45)	0.41
-4	0	7	5.74	-6.14
-2	0	7	1.21	-1.23
0	0	7	(.45)	-0.20
2	0	7	(.44)	0.36
4	0	7	(.43)	0.27
6	0	7	0.56	-0.50
8	0	7	0.61	-0.53
10	0	7	0.91	-1.01
-18	0	8	(.15)	-0.31
-16	0	8	0.49	-0.53
-14	0	8	(.34)	-0.01
-12	0	8	(.39)	0.34
-10	0	8	(.41)	0.24
-8	0	8	(.43)	0.50
-6	0	8	1.17	-1.30
-4	0	8	0.75	-0.72
-2	0	8	1.88	2.57
0	0	8	(.41)	-0.23
2	0	8	(.40)	0.41
4	0	8	0.36	-0.33
6	0	8	(.30)	-0.20
8	0	8	(.21)	-0.02
-14	0	9	(.24)	0.13
-12	0	9	0.59	-0.66
-10	0	9	(.33)	-0.45
-8	0	9	(.35)	0.09
-6	0	9	(.36)	0.10
-4	0	9	1.18	1.67
-2	0	9	(.34)	-0.34
0	0	9	0.65	-0.80
2	0	9	0.40	-0.49
4	0	9	0.30	-0.47
-10	0	10	(.16)	0.68
-8	0	10	0.29	0.27
-6	0	10	(.23)	0.16
-4	0	10	0.42	0.43
-2	0	10	0.18	0.18
3	1	0	2.22	2.24
4	1	0	1.44	1.21
5	1	0	2.89	2.96
6	1	0	7.02	-6.86
7	1	0	4.56	4.72
8	1	0	0.43	-0.45
9	1	0	0.32	0.36
10	1	0	0.68	0.66
11	1	0	0.79	-1.00
12	1	0	(.22)	-0.22
13	1	0	(.24)	0.21
14	1	0	0.72	-0.98
15	1	0	1.16	-1.30
16	1	0	0.96	-1.05
17	1	0	0.72	0.77
18	1	0	0.89	0.73
19	1	0	0.75	0.96
0	2	0	1.55	-1.98
8	2	0	(.20)	-0.45
9	2	0	0.59	-0.62
10	2	0	0.94	-0.99
11	2	0	0.67	0.59
12	2	0	0.73	0.74
13	2	0	1.51	1.69
14	2	0	2.02	-1.63
15	2	0	0.41	0.39
16	2	0	0.55	0.53
17	2	0	0.21	0.23
18	2	0	1.34	-1.05
19	2	0	0.40	-0.60
1	3	0	2.12	2.10
2	3	0	1.88	2.02
3	3	0	1.33	1.03
4	3	0	0.83	-0.90
5	3	0	0.78	-0.88
6	3	0	0.90	-1.08
7	3	0	0.65	-0.48
8	3	0	0.39	0.38
9	3	0	0.23	-0.03
10	3	0	(.24)	0.26
11	3	0	0.72	-0.79
12	3	0	2.02	-2.16
13	3	0	(.24)	-0.04
14	3	0	0.40	-0.55
15	3	0	(.22)	0.08
16	3	0	0.19	0.14
17	3	0	(.19)	0.03
18	3	0	0.14	0.20
0	4	0	(.23)	-0.13
1	4	0	1.11	1.12
2	4	0	1.74	-1.73
3	4	0	2.92	-1.97
4	4	0	1.29	1.07
5	4	0	(.24)	-0.02
6	4	0	1.54	1.38
7	4	0	0.48	-0.35
8	4	0	0.41	0.39
9	4	0	0.34	0.34
10	4	0	0.23	0.30
11	4	0	0.10	0.60
12	4	0	0.31	0.26
13	4	0	0.97	1.03
14	4	0	0.55	0.38
15	4	0	0.27	-0.03
16	4	0	0.19	0.06
17	4	0	0.10	-0.12
1	5	0	1.41	1.38
2	5	0	0.53	-0.13
3	5	0	0.40	0.05
4	5	0	1.50	1.51
5	5	0	0.16	-0.35
6	5	0	(.23)	0.13
7	5	0	(.22)	0.08
8	5	0	0.21	0.25
9	5	0	0.20	0.22
10	5	0	(.20)	-0.20
11	5	0	(.19)	0.20
12	5	0	0.16	-0.21
13	5	0	(.13)	0.22
14	5	0	(.09)	0.16
0	6	0	1.65	-1.31
1	6	0	0.44	0.34
2	6	0	(.18)	-0.09
3	6	0	0.39	-0.32
4	6	0	(.17)	0.08
5	6	0	(.17)	-0.16
6	6	0	(.15)	0.05
7	6	0	(.14)	-0.23
8	6	0	(.12)	0.00
9	6	0	0.18	-0.16
0	1	1	3.23	3.20
0	1	2	9.16	8.63
0	1	3	8.46	-8.08
0	1	4	(.31)	-0.39
0	1	5	0.69	0.69
0	1	6	(.41)	-0.48
0	1	7	(.41)	0.19
0	1	8	(.38)	-0.26
0	1	9	0.46	0.55
0	2	1	5.12	5.70
0	2	2	1.61	2.39
0	2	3	2.88	-2.50
0	2	4	0.77	-0.93
0	2	5	(.38)	-0.14
0	2	6	0.41	-0.55
0	2	7	0.56	-0.58
0	2	8	0.82	0.81
0	2	9	0.55	-0.52
0	3	1	(.32)	0.03
0	3	2	2.21	-2.45
0	3	3	1.39	-1.40
0	3	4	(.41)	0.44
0	3	5	(.41)	0.37
0	3	6	1.95	-1.81
0	3	7	(.36)	0.07
0	3	8	0.51	0.29
0	4	1	0.77	0.55
0	4	2	0.80	-0.80
0	4	3	1.15	0.88
0	4	4	0.41	-0.38
0	4	5	0.55	0.40
0	4	6	0.35	-0.49
0	4	7	(.28)	0.04
0	5	1	1.00	-0.86
0	5	2	(.40)	0.41
0	5	3	1.37	-0.96
0	5	4	(.35)	-0.13
0	5	5	(.30)	0.38
0	5	6	0.33	0.29
0	6	1	0.29	0.27
0	6	2	0.56	0.26
0	6	3	(.23)	0.14
-1	1	9	0.72	0.70
-1	1	8	0.96	-0.70
-1	1	7	(.41)	0.28
-1	1	6	0.98	-0.82
-1	1	5	(.35)	0.33
-1	1	4	0.42	-0.45
-1	1	3	2.00	-1.82
-1	1	2	5.84	-5.79
-1	1	1	6.94	-6.68
1	1	1	14.61	14.97
1	1	2	10.44	9.32
1	1	3	5.42	5.09
1	1	4	1.20	-1.41
1	1	5	(.37)	0.15
1	1	6	(.39)	0.48
1	1	7	(.41)	-0.30
1	1	8	0.36	-0.63
1	1	9	0.53	0.55
-2	1	9	0.62	-0.68
-2	1	8	1.03	-1.12
-2	1	7	1.22	1.23
-2	1	6	0.38	-0.56
-2	1	5	0.90	1.25
-2	1	4	0.72	1.02
-2	1	3	(.24)	-0.01
-2	1	2	0.96	0.77
-2	1	1	4.47	5.00
2	1	0	10.65	-10.21
2	1	1	22.70	22.01
2	1	2	0.73	-0.05
2	1	3	6.02	-5.17
2	1	4	1.56	1.42
2	1	5	0.63	0.56
2	1	6	(.41)	0.02
2	1	7	(.41)	0.45
2	1	8	(.36)	0.21
2	1	9	0.35	-0.27
-3	1	10	(.15)	-0.19
-3	1	9	0.71	-0.20
-3	1	8	(.38)	-1.52
-3	1	7	1.64	1.87
-3	1	6	(.39)	-0.07
-3	1	5	3.40	2.79
-3	1	4	0.50	0.76
-3	1	3	0.70	1.47
-3	1	2	1.52	0.77
-3	1	1	5.40	4.76
3	1	0	2.64	2.23
3	1	1	6.86	6.70
3	1	2	10.73	-9.09
3	1	3	3.52	-3.12
3	1	4	3.82	-4.31
3	1	5	1.20	1.30
3	1	6	0.56	0.96
3	1	7	(.41)	-0.68
3	1	8	(.34)	0.05
3	1	9	0.36	0.52
-4	1	10	(.16)	0.45
-4	1	9	0.78	-0.77
-4	1	8	(.40)	0.25
-4	1	7	0.57	-0.85
-4	1	6	2.66	2.02
-4	1	5	(.35)	0.22
-4	1	4	4.52	-4.02
-4	1	3	0.57	-0.12
-4	1	2	0.67	-1.23
-4	1	1	0.65	-1.29
4	1	0	1.74	1.23
4	1	1	(.22)	-0.22
4	1	2	4.00	-3.82
4	1	3	(.30)	0.27
4	1	4	2.73	-2.73
4	1	5	1.78	1.64
4	1	6	0.71	0.59
4	1	7	(.40)	-0.20
4	1	8	0.32	-0.40
4	1	9	(.17)	0.13
-5	1	10	(.18)	-0.22
-5	1	9	(.32)	0.03
-5	1	8	1.24	1.31
-5	1	7	2.39	2.63
-5	1	6	2.79	-2.87
-5	1	5	2.42	-2.41
-5	1	4	4.31	-4.09
-5	1	3	0.26	0.39
-5	1	2	3.83	-3.84
-5	1	1	2.36	-3.23
5	1	0	3.20	2.75
5	1	1	0.77	0.93
5	1	2	1.01	-0.39
5	1	3	4.05	3.97
5	1	4	0.62	0.23
5	1	5	3.49	1.62
5	1	6	0.58	-0.66
5	1	7	(.38)	-0.41
5	1	8	(.30)	0.30
-6	1	10	(.19)	0.13
-6	1	9	0.34	-0.16
-6	1	8	1.30	-1.38
-6	1	7	(.41)	-0.05
-6	1	6	4.62	4.64
-6	1	5	3.47	-3.37
-6	1	4	0.63	-0.11
-6	1	3	1.02	0.52
-6	1	2	1.84	2.17
-6	1	1	(.25)	-0.38
6	1	0	7.27	-6.84
6	1	1	0.52	-0.35
6	1	2	4.67	3.78
6	1	3	0.72	1.05
6	1	4	1.00	-0.63
6	1	5	0.99	0.87
6	1	6	0.41	-0.41
6	1	7	(.37)	-0.02
6	1	8	(.27)	-0.14
-7	1	10	(.18)	-0.03
-7	1	9	(.32)	-0.27
-7	1	8	(.39)	-0.27
-7	1	7	0.93	-0.98
-7	1	6	1.63	-1.77
-7	1	5	2.47	2.18
-7	1	4	4.30	3.59
-7	1	3	7.00	7.47
-7	1	2	2.38	-2.76
-7	1	1	0.61	0.70
7	1	0	5.27	4.71
7	1	1	3.20	-3.22
7	1	2	3.95	-3.62
7	1	3	1.16	-1.07
7	1	4	(.37)	-0.37
7	1	5	(.42)	0.44
7	1	6	0.60	-0.67
7	1	7	0.33	0.51
7	1	8	(.24)	0.05
-8	1	10	(.16)	0.10
-8	1	9	(.31)	-0.20
-8	1	8	(.30)	0.20
-8	1	7	0.41	0.56
-8	1	6	0.56	0.29
-8	1	5	1.28	-1.37
-8	1	4	1.74	-1.86
-8	1	3	3.65	-3.85
-8	1	2	7.00	6.68
-8	1	1	0.28	-0.18
8	1	0	0.40	-0.42
8	1	1	2.68	2.65
8	1	2	0.94	-1.06
8	1	3	1.51	1.58
8	1	4	2.29	-2.23
8	1	5	0.71	-0.78
8	1	6	0.94	0.86
8	1	7	0.31	0.37
8	1	8	(.18)	-0.28
-9	1	10	(.14)	-0.20
-9	1	9	0.30	0.43
-9	1	8	0.37	0.48
-9	1	7	(.41)	-0.25
-9	1	6	(.40)	0.60
-9	1	5	(.65)	-0.68
-9	1	4	2.21	-2.25
-9	1	3	2.96	-1.84
-9	1	2	5.74	-5.64
-9	1	1	1.61	1.70
9	1	0	0.30	0.37
9	1	1	1.43	-1.18
9	1	2	1.37	1.19
9	1	3	1.76	1.77
9	1	4	1.72	1.98
9	1	5	0.58	-0.52
9	1	6	0.74	-0.88
9	1	7	(.28)	0.31
-10	1	9	(.30)	-0.02
-10	1	8	(.37)	0.10
-10	1	7	1.95	-1.98
-10	1	6	1.35	1.34
-10	1	5	0.54	0.80
-10	1	4	(.37)	0.09
-10	1	3	1.01	0.95
-10	1	2	1.98	2.49
-10	1	1	1.21	-1.23
10	1	0	0.73	0.65
10	1	1	0.35	0.42
10	1	2	0.53	0.32
10	1	3	0.98	0.97
10	1	4	2.06	-2.00
10	1	5	0.89	1.02
10	1	6	0.33	0.25
10	1	7	(.24)	0.19
-11	1	9	(.28)	0.49
-11	1	8	0.72	-0.84
-11	1	7	1.21	-1.26
-11	1	6	1.15	0.96
-11	1	5	1.11	1.09
-11	1	4	2.33	2.47
-11	1	3	1.13	0.95
-11	1	2	1.10	0.96
-11	1	1	1.15	1.15
11	1	0	0.94	-1.02
11	1	1	(.37)	0.23
11	1	2	(.40)	0.22
11	1	3	0.92	-0.87
11	1	4	0.41	-0.27
11	1	5	1.07	-1.26
11	1	6	(.31)	0.29
11	1	7	(.17)	0.53
-12	1	9	(.27)	-0.66
-12	1	8	(.35)	0.18
-12	1	7	(.40)	-0.15
-12	1	6	0.70	0.85
-12	1	5	(.41)	-0.12
-12	1	4	1.46	1.53
-12	1	3	5.52	-5.55
-12	1	2	(.37)	0.16
-12	1	1	1.95	1.78
12	1	0	(.38)	-0.20
12	1	1	0.55	0.89
12	1	2	(.41)	-0.31
12	1	3	0.82	-0.83
12	1	4	(.40)	0.06
12	1	5	(.35)	0.16
12	1	6	(.27)	-0.19
-13	1	9	(.24)	0.67
-13	1	8	(.33)	-0.20
-13	1	7	(.38)	0.41
-13	1	6	0.99	1.09
-13	1	5	0.58	-0.61
-13	1	4	2.05	-2.15
-13	1	3	4.45	-4.12
-13	1	2	0.67	0.83
-13	1	1	0.67	0.62
13	1	0	(.40)	0.01
13	1	1	0.57	0.72
13	1	2	(.41)	0.06
13	1	3	(.41)	-0.31
13	1	4	0.36	0.24
13	1	5	(.31)	0.03
13	1	6	0.34	0.67
-14	1	9	(.21)	-0.42
-14	1	8	(.31)	0.43
-14	1	7	(.37)	-0.10
-14	1	6	(.40)	-0.04
-14	1	5	1.08	1.27
-14	1	4	0.58	-0.46
-14	1	3	2.36	-2.52
-14	1	2	3.08	2.98
-14	1	1	(.41)	0.24
14	1	0	1.00	-0.97
14	1	1	1.36	1.56
14	1	2	(.41)	-0.14
14	1	3	(.39)	-0.29
14	1	4	(.35)	0.26
14	1	5	(.27)	-0.03
-15	1	9	(.13)	-0.36
-15	1	8	(.28)	-0.11
-15	1	7	(.35)	-0.17
-15	1	6	(.40)	-0.40
-15	1	5	(.41)	-0.15
-15	1	4	0.71	0.73
-15	1	3	1.29	1.26
-15	1	2	3.39	3.54
-15	1	1	0.72	-0.88
15	1	0	1.17	-1.30
15	1	1	0.82	-0.67
15	1	2	(.40)	0.22
15	1	3	(.37)	0.02
15	1	4	(.31)	-0.17
15	1	5	(.20)	0.02
-16	1	8	(.24)	0.09
-16	1	7	(.32)	0.02
-16	1	6	(.37)	0.36
-16	1	5	(.40)	-0.45
-16	1	4	0.82	-0.68
-16	1	3	(.41)	0.08
-16	1	2	0.82	-0.90
-16	1	1	1.08	1.05
16	1	0	1.00	-1.04
16	1	1	1.85	1.90
16	1	2	0.52	-0.52
16	1	3	(.32)	-0.30
16	1	4	(.25)	0.00
-17	1	8	(.20)	0.36
-17	1	7	(.29)	-0.29
-17	1	6	(.34)	-0.12
-17	1	5	(.37)	0.05
-17	1	4	(.39)	0.20
-17	1	3	0.80	-0.76
-17	1	2	0.70	-0.63
-17	1	1	1.65	-1.91
17	1	0	0.55	0.77
17	1	1	0.51	0.45
17	1	2	0.75	0.84
17	1	3	(.28)	-0.20
17	1	4	(.18)	-0.27
-18	1	7	(.26)	-0.33
-18	1	6	0.98	0.84
-18	1	5	0.34	-0.41
-18	1	4	(.37)	0.33
-18	1	3	(.39)	0.02
-18	1	2	0.93	0.22
-18	1	1	0.90	0.79
18	1	0	0.79	0.73
18	1	1	0.47	0.27
18	1	2	(.28)	-0.08
18	1	3	(.21)	-0.02
-19	1	7	(.19)	0.11
-19	1	6	0.59	0.55
-19	1	5	0.82	-0.14
-19	1	4	(.33)	0.41
-19	1	3	(.35)	0.17
-19	1	2	(.35)	0.04
-19	1	1	(.34)	0.11
19	1	0	0.83	0.97
19	1	1	0.56	-0.59
19	1	2	(.22)	-0.02
-20	1	6	0.82	0.82
-20	1	5	0.90	-0.59
-20	1	4	(.29)	-0.29
-20	1	3	(.31)	0.05
-20	1	2	(.31)	-0.09
-20	1	1	(.43)	-0.59
20	1	0	0.37	-0.84
20	1	1	(.22)	-0.36

In the above table of $|F_o|$, F_c (given relative to one asymmetric unit) reflections *hkl* common to more than one layer are repeated twice to show the spread of the data even after scaling.

cycle of least-squares calculations, but no significant improvement was observed in the subsequent difference map, probably due to the fact that these particular atoms do not show large thermal anisotropy. Table 1(*c*) gives the values of the components of the vibration ellipsoid tensor corresponding to (*a*) and (*b*) above. The structure refinement was therefore completed with the original set of vibration directions. The observed and calculated structure factors are given in Table 2. The discrepancy factors are:

$$R(h0l)=10{\cdot}73,\ R(hk0),\ R(0kl)=11{\cdot}70,$$
$$R(h1l)=11{\cdot}82\%\,.$$

The recommendations for changes in coordinates and temperature factors did not lead to any further systematic improvement in the *R*-factors, so that it must be concluded that the intensity data are not sufficiently accurate to allow further refinement.

Discussion

The discrepancy factors obtained are sufficiently low to leave no doubt that the structure of the molecule and its position in the unit cell are correctly determined. The final coordinates in fractions of the cell constants and the final *B*-coefficients with their respective standard deviations are given in Tables 3 and 4. The *x* and *z* coordinates of the hydrogen atoms were obtained from a difference map. The *y* coordinates could not be derived in a similar manner owing to overlap on the (100) and (001) projections and they were calculated by taking the carbon–hydrogen bond to be 1 Å.

Bond lengths and bond angles are shown in Fig. 3 and Table 5. The carbon–carbon distances in the benzene ring have the accepted values and those found for the reduced ring are slightly larger than

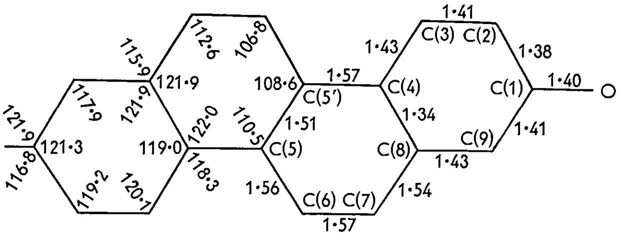

Fig. 3. Bond lengths (Å) and bond angles (degrees).

Table 5. *Bond lengths and bond angles*

Bond lengths between atoms	Bond lengths
Oxygen–C(1)	1·40 Å
C(1)–C(2)	1·38
C(2)–C(3)	1·41
C(3)–C(4)	1·43
C(4)–C(8)	1·34
C(8)–C(9)	1·43
C(9)–C(1)	1·41
C(4)–C(5′)	1·57
C(5′)–C(5)	1·51
C(5)–C(6)	1·56
C(6)–C(7)	1·57
C(7)–C(8)	1·54

Angles between atoms	Angles
Oxygen–C(1)–C(2)	116·8°
Oxygen-C(1)–C(9)	121·9
C(2)–C(1)–C(9)	121·3
C(1)–C(2)–C(3)	119·2
C(2)–C(3)–C(4)	120·1
C(3)–C(4)–C(8)	119·0
C(8)–C(4)–C(5′)	122·0
C(3)–C(4)–C(5′)	118·8
C(4)–C(5′)–C(5)	110·5
C(5′)–C(5)–C(6)	108·6
C(5)–C(6)–C(7)	106·8
C(6)–C(7)–C(8)	112·6
C(7)–C(8)–C(4)	121·9
C(7)–C(8)–C(9)	115·9
C(4)–C(8)–C(9)	121·9
C(8)–C(9)–C(1)	117·9

Table 3. *Atomic coordinates and standard deviations*

	x/a	σ	y/b	σ	z/c	σ
Oxygen	0·25140	0·00026	0·45000	0·00184	0·08350	0·00059
Carbon (1)	0·19553	0·00039	0·44162	0·00233	0·18394	0·00087
Carbon (2)	0·20848	0·00041	0·25900	0·00273	0·31619	0·00089
Carbon (3)	0·15330	0·00042	0·23900	0·00280	0·41910	0·00091
Carbon (4)	0·08667	0·00037	0·41420	0·00213	0·39099	0·00083
Carbon (5)	0·97426	0·00034	0·61998	0·00219	0·49440	0·00085
Carbon (6)	0·93234	0·00039	0·67407	0·00232	0·29809	0·00088
Carbon (7)	0·99970	0·00041	0·76000	0·00273	0·20933	0·00091
Carbon (8)	0·07243	0·00037	0·57620	0·00213	0·25300	0·00083
Carbon (9)	0·12882	0·00041	0·61002	0·00239	0·15125	0·00092

Table 4. *Temperature factors and standard deviations*

	B_x	σ	B_y	σ	B_z	σ
Oxygen	7·25	+0·41316	3·25	+0·14488	8·27	+0·33401
Carbon (1)	6·12	+0·51382	3·80	+0·18594	5·34	+0·32218
Carbon (2), (9)	6·60	+0·54152	4·18	+0·28417	5·62	+0·47958
Carbon (3), (7)	6·71	+0·55248	4·38	+0·29368	5·78	+0·49287
Carbon (4), (8)	4·62	+0·42341	4·13	+0·26525	4·13	+0·37954
Carbon (5)	5·39	+0·48574	3·42	+0·25795	4·83	+0·41188
Carbon (6)	5·42	+0·49360	3·89	+0·26491	5·76	+0·46423

Table 6. *Deviations of atoms from the mean plane of the benzene ring*

Atoms	Deviations from plane	
Oxygen	+0·0060	
C(1)	−0·0041	
C(2)	−0·0080	
C(3)	+0·0069	
C(9)	−0·0008	
C(4)	−0·0322	atoms common to both rings
C(8)	+0·0740	
C(5′)	+0·0215	
C(5)	−0·4085	
C(6)	+0·4885	
C(7)	+0·1098	

normal. The common bond between C(4) and C(8) of 1·34 Å is remarkably short.

Table 6 gives the deviations of all the atoms from the mean plane of the benzene ring. The oxygen atom and the four carbon atoms C(1), C(2), C(3) and C(9) of the benzene ring remote from the reduced ring are planar within the accuracy of the determination, whereas the two carbon atoms common to the two rings deviate markedly from the plane in opposite directions.

The molecules are linked by OH... OH... bonds of length 2·87 Å forming parallel chains throughout the crystal. The accuracy of the structure determination is not sufficient to decide the position of the H atom on these bonds, or whether disorder (two H/2 positions) occurs. The H coordinates assumed are shown in Table 7. All intermolecular distances smaller than 4 Å are shown in Fig. 4. The closest contact between neighbouring molecules is 3·65 Å.

The standard deviations were calculated from the least-squares refinement by means of the expression:

Table 7. *Atomic coordinates of hydrogen atoms, placed so that bond lengths are approximately* 1 Å, *in reasonable positions*

The difference Fourier (*h*0*l*) projection confirmed the *x*/*a*, *z*/*c* co-ordinates

	x/*a*	*y*/*b*	*z*/*c*
H(0)	0·25	0·62	0
H(2)	0·25	0·099	0·366
H(3)	0·174	0·086	0·498
H(5)	0·970	0·792	0·414
H(6)	0·887	0·725	0·344
H(6′)	0·891	0·810	0·215
H(7)	0·970	0·920	0·144
H(7′)	0·029	0·905	0·304
H(9)	0·113	0·800	0·089

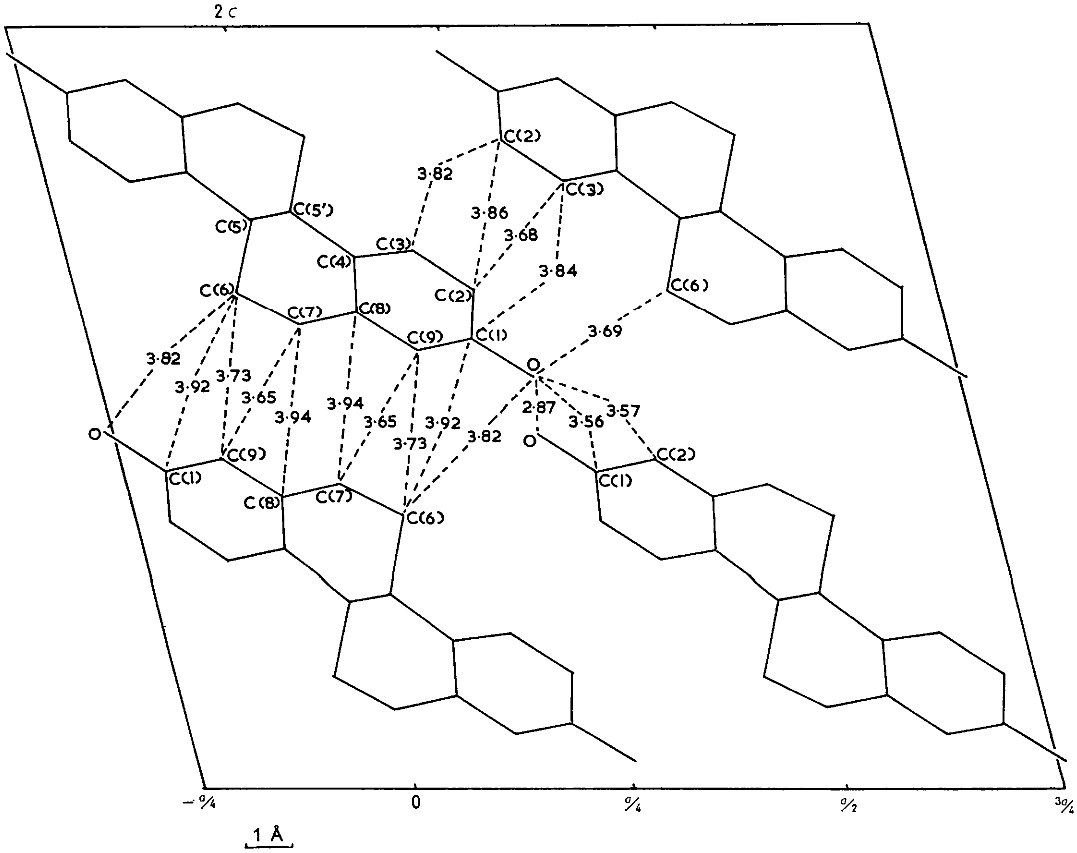

Fig. 4. Intermolecular contacts.

$$\sigma_{xi}^2 = \Sigma(w\Delta F)^2/(n-s)\ \{\Sigma w\Delta F\,.\,w(\partial F/\partial x)/\Sigma(w\,.\,(\partial F/\partial x))^2\}$$

where

σ_{xi} is the s.d. of the x coordinate of the ith atom,
n = number of reflections,
s = number of variable parameters,
w = weight.

The values for the final coordinates are 0·005 Å, 0·010 Å and 0·006 Å for x, y and z respectively. The greater error in the y direction is explained by the comparative sparsity of data contributing to the determination of the y coordinates. From the standard deviations of the coordinates the standard deviations of the bond lengths are derived by the expression

$$\sigma(l)^2 = [(\sigma_{x1}^2 + \sigma_{x2}^2)\cos^2\alpha + (\sigma_{y1}^2 + \sigma_{y2}^2)\cos^2\beta + (\sigma_{z1}^2 + \sigma_{z2}^2)\cos^2\gamma]$$

where

$\sigma(l)$ is the s.d. of the bond length,
σ_{x_1}, σ_{x_2} the s.d. of the x coordinates of atom 1 and atom 2 *etc.*,
$\cos\alpha$, $\cos\beta$, $\cos\gamma$ the direction cosines of the bond with respect to a, b and c^*.

All values for $\sigma(l)$ come to less than $1{\cdot}5\times10^{-2}$ Å. The standard deviations of the B-coefficients are of the order of 10%.

Analysis of thermal vibrations

Finally, an attempt was made to interpret the anisotropic temperature factors in terms of translations and librations of the molecule and of intramolecular movements of the atoms resulting in distortion of the molecule (Lonsdale, 1960). The physical interpretation of the thermal factors so obtained is a large translatory motion in the plane of the molecule, normal to the chains of the molecules, which is in accordance with Lonsdale's results for diketopiperazine (1961); the librations are largest about the long axis of the molecule, which is usual for long-chain compounds.

The accuracy of the X-ray data is not sufficient to produce reliable values for the distortional vibrations as these are arrived at as residues.

The early stages of the work described in this paper were carried out at Birkbeck College, London, and it was completed at University College, London.

I wish to thank Prof. Dame Kathleen Lonsdale, F.R.S., Prof. J. D. Bernal, F.R.S., Dr C. H. Carlisle and Dr H. J. Milledge for encouragement and helpful discussions.

The computing was carried out by means of a grant from the Wellcome Trust and with the use of tape-editing equipment purchased by means of a grant from the University of London Central Research Fund.

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Cascade: An Automatic Single-Crystal X-ray Diffractometer

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(*Received* 16 *March* 1962)

An automatic system is described for the measurement of intensities of X-ray reflections from single crystals. It is controlled by a programmable plugboard and punched paper tape output from an IBM 1620 computer. The goniometer used is the G.E. single crystal orienter. A circuit is provided which maximizes the counting rate before the intensity is measured.

1. Introduction

A few years ago the factor limiting the scope and precision of an X-ray crystal structure analysis was the lack of proper computing facilities. Now we have computers which can handle whatever calculations one wishes in an extremely short time and the factor limiting the scope of an X-ray analysis is frequently the collection of data. CASCADE (Colorado Automatic