The Crystal Structure of Benzil

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The crystal structure of benzil at room temperature has been determined from X-ray diffraction data. A complete three-dimensional analysis has been carried out, and the anisotropic thermal parameters as well as the atomic coordinates have been refined on an electronic computer. Some data at a lower temperature have also been obtained, but the results from these are being reserved until further work has been done. A preliminary investigation of the molecular thermal motion has been made and corrections have been applied to the bond lengths, the standard deviations of which are estimated to be < 0.01 Å.

Introduction

The unit cell and space group of benzil, $C_6H_5.CO.CO.C_6H_5$, were first determined by Becker & Rose (1923) who obtained $a = 8.15$ and $c = 13.46$ Å in the trigonal space group D_3^4 and D_3^6. These values were improved somewhat by Allen (1927). Later, benzil crystals were found to give a marked diffuse scattering pattern (Lonsdale & Smith, 1941) which became very much reduced at low temperatures. The most prominent feature of this diffuse pattern was a set of streaks along layer lines. In order to interpret this effect fully, it was necessary to know the structure of the crystals, and for this reason the present work was undertaken.

Groth (1919) reported that both left and right handed crystals were obtained from solution; the absolute configuration of the specimens used in this work is not known. He also mentioned that no stable polymorphic modification exists up to the melting point (95°); apparently there is no form of benzil corresponding to the centrosymmetrical dibenzyl (Jeffrey, 1947) owing to the steric hindrance of the oxygen atoms, but it is an interesting speculation that such a metastable form might be prepared under suitable conditions of temperature and pressure.

Experimental

The specimen used in this study was a roughly equidimensional crystal, about 0.2 mm across. Oscillation and Weissenberg photographs were taken about a, c and [11.0], and as many reflexions as it was possible to obtain with Cu $K\alpha$ radiation were recorded by the multiple-film technique. The relative intensities were measured with a microphotometer, using a reference intensity scale prepared from the same specimen. A satisfactorily consistent set of data for 539 independent reflexions was derived from about

15,000 observed intensities, and the comparison of each reflexion with the same appearing on different photographs, as well as with the symmetrically equivalent ones, confirmed that their standard deviation $\sigma(I_0)/I_0$, has the maximum value of 0.092. The relative values thus obtained were corrected for the Lorentz and polarization factors and then put on the absolute scale by Wilson's method. The overall temperature factor estimated from this statistical method was $B = 5.94$. No correction was made for absorption on account of the small size and nearly spherical shape of the specimen.

Experiments at low temperatures were carried out by placing the same specimen in a stream of cold air produced by forced evaporation of liquid air. The temperature around the specimen was controlled by the velocity of the stream and was kept at -92 ± 3 °C during the exposures. Though some oscillation photographs were taken about c by this means, our attempt at obtaining a complete set of intensity data corresponding to those at room temperature failed because the crystal developed minute cracks. Further experiments to collect low temperature data are in hand.

In order to make an accurate determination of the lattice constants, diffraction photographs of the crystalline powder were also taken with a quadruple Guinier focusing camera (de Wolff, 1948), with silicon powder as a standard calibrating substance.

Unit cell and space group

The lattice constants at 20 °C deduced from the powder photographs mentioned above are

$$a = 8.376 \pm 0.009, \quad c = 13.700 \pm 0.008 \text{ Å}.$$

There are three molecules of $C_{14}H_{10}O_2$ in the unit cell, which requires a density of 1.256 g.cm^{-3}. Des Cloizeaux (1869) found 1.23 experimentally, and our own determination by flotation in sodium iodide solution gave

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1·225. These low values indicate some imperfections in the crystals. The constants at − 92 °C were measured from the oscillation photographs about c:

$$a = 8{\cdot}267 \pm 0{\cdot}006, \quad c = 13{\cdot}407 \pm 0{\cdot}026 \text{ Å}.$$

Hence the linear expansion coefficients α between the limits − 92 and 20 °C are given by

$$\alpha_a = \varDelta a/a \cdot \varDelta T = 118.10^{-6}, \quad \alpha_c = 195.10^{-6}.$$

The 00l reflexions are absent for $l = 3n \pm 1$, no other systematic absences being observed. The space group of the crystals is therefore confirmed as one of the enantiomorphic pair $P3_121$ and $P3_221$.

Derivation of an approximate structure

As there are only three molecules in the unit cell which has a sixfold general position, the molecules must lie with their mid points on the crystallographic twofold axis, as shown in Fig. 1 (Allen, 1927; Knaggs & Lonsdale, 1939). Lines joining the corresponding atoms in the two halves of the molecule are all perpendicular to the twofold axis, which bisects the central carbon–carbon bond. Therefore the (11$\bar{2}$0) Harker section may be expected to show near the origin peaks corresponding to C(O)–C(O'), O–O' and

possibly C(1)–C(1') distances in the molecule. Moreover, if the two halves of the molecule are planar, as might be surmised from the probably partial double-bond character of the C(O)–C(1) bond, the C(1)–C(2) and C(4)–C(5) bonds as well as the line joining C(3) and C(6), and their counterparts in the
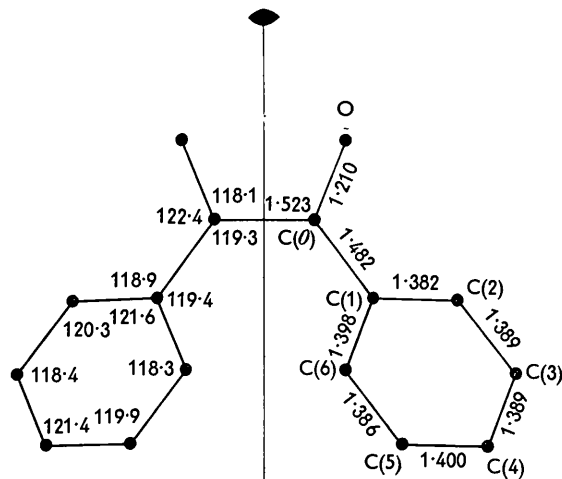

Fig. 1. Formal diagram of benzil molecule, showing bond-lengths (Å) and inter-bond angles (°), uncorrected for thermal vibrations.
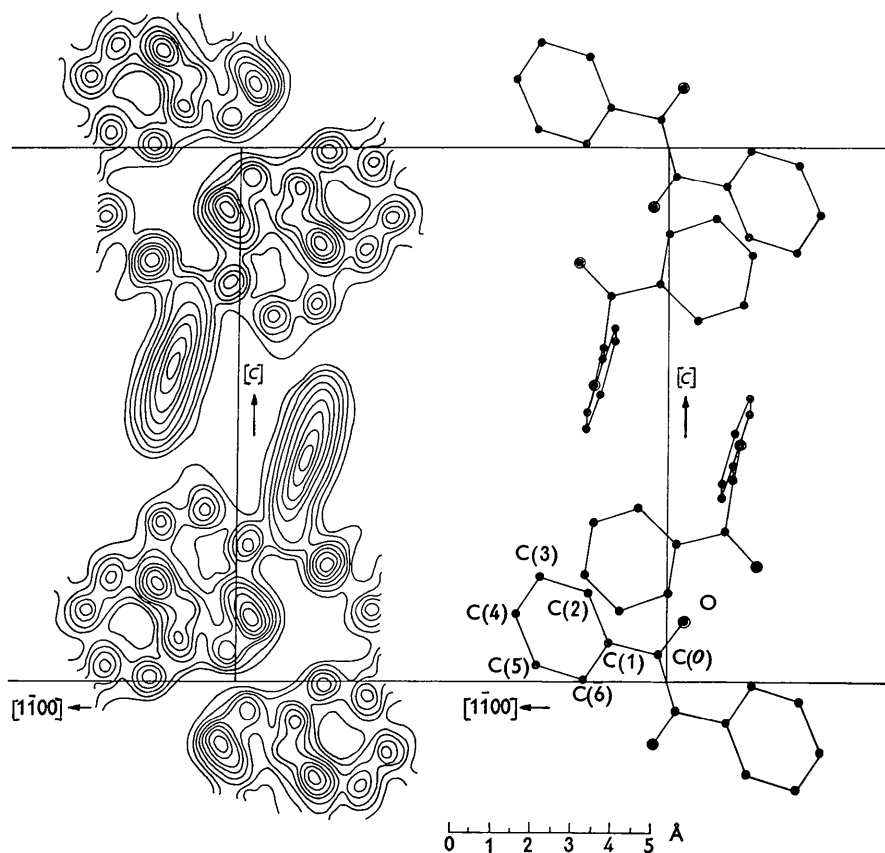

Fig. 2. (11$\bar{2}$0) electron density projection, together the corresponding molecular arrangement.

other half of the molecule, will also be parallel to the Harker section and to the direction of the central C(O)–C(O') bond.

With these expectations in mind, the (11$\bar{2}$0) Harker section was calculated, and after several trials a reasonable way of assigning the interatomic distances to the peaks near the origin was found. From the atomic coordinates estimated from this molecular orientation, the $h0\bar{h}l$ structure factors were calculated, and after minor adjustments, reasonably good agreement between the observed and calculated structure factors was obtained. From these values, the (11$\bar{2}$0) electron density projection was computed; this is shown in Fig. 2 together with the corresponding molecular arrangement. In this, however, there are some serious overlaps between atoms in projection, and it was obvious that further refinement in two dimensions would be fruitless. Accordingly, the three-dimensional refinement described below was commenced.

Three-dimensional refinement (room temperature)

In the sphere of reflexion for Cu $K\alpha$ radiation there are 758 independent planes, of which 219 did not give observable spots on the longest exposed photographs. The remaining 539 were used to refine the atomic coordinates and anisotropic temperature parameters by least squares on a Ferranti Pegasus computer, using the program compiled by Cruickshank & Pilling (1961). Seven cycles of structure factor calculations and least-squares refinement were carried out, the value of the residual R falling from 22·3% to 7·8%. Hydrogen atoms with initial temperature factor $B = 6·0$ were included in the structure factor calculations, but only their isotropic temperature factors were refined. After the seventh cycle, the refinement was judged to be effectively complete, the largest shifts in both coordinates and temperature parameters being less than their corresponding stan-

dard deviations. The intensities of twelve of the low order planes were found to be diminished either by extinction or by underestimation, and in the later stages of the refinement the observed values were replaced by the calculated for these structure amplitudes in order to reduce errors which might arise from this cause. The final refined values of the positional and thermal parameters are listed in Table 1.

The values of the observed and calculated structure amplitudes and their phase angles are given in Table 2. The structure amplitudes of the unobserved planes were calculated and found in every case to have very small values; these were not used at all in the refinement or in the calculation of the residual R.

Description of the structure

The molecules pack together in the crystal with only van der Waals forces; viewed along c (Fig. 3) they appear as groups of helical chains around the 3_1 axis, the chains being close-packed. Each molecule has a twofold symmetry axis perpendicular to the C(O)–C(O') bond, coinciding with the twofold axis in the unit cell, so that three molecules of benzil occupy the sixfold general positions in space groups $P3_121$ and $P3_221$. The bond lengths and inter-bond angles and their standard deviations are given in Table 3, and shown in Fig. 1.

The equation of the mean plane of the benzene ring referred to standard rectangular axes, a^*, b and c, is

$$0\cdot9485x' - 0\cdot0700y - 0\cdot3090z = 1\cdot3208$$

and the individual atoms are displaced from this plane by the following amounts: C(1) +0·0010; C(2) −0·0011; C(3) 0·0000; C(4) +0·0011; C(5) −0·0012; C(6) +0·0002, and C(O) +0·0278 Å.

The atoms C(1), C(O), O and C(O') lie approximately in a plane whose equation is

$$0\cdot9791x' - 0\cdot0417y - 0\cdot1989z = 1\cdot4607$$

Table 1. *Atomic parameters*

The values of B quoted below are defined by the temperature factor exponent

$$\exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \ldots)\right]$$

used in the structure amplitude calculations

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(O)	0·2270	0·1927	0·0525	5·11	5·24	7·22	3·12	−0·08	0·11
C(1)	0·2313	0·0224	0·0766	4·26	4·71	6·61	2·42	0·03	0·52
C(2)	0·2841	0·0025	0·1693	5·86	7·17	7·20	4·02	0·11	−0·34
C(3)	0·2862	−0·1570	0·1947	7·74	8·04	9·72	5·42	1·89	1·01
C(4)	0·2339	−0·2946	0·1249	8·57	6·19	10·65	4·50	2·25	2·63
C(5)	0·1798	−0·2752	0·0311	7·80	5·07	10·79	3·58	−0·32	2·37
C(6)	0·1783	−0·1156	0·0061	5·38	5·09	7·17	2·68	−0·11	1·31
O	0·2588	0·3111	0·1125	9·20	6·02	8·76	4·97	−2·12	−1·72
H(2)	0·3240	0·1116	0·2222	B(isotropic) = 4·88					
H(3)	0·3275	−0·1735	0·2669	B(isotropic) = 9·08					
H(4)	0·2351	−0·4193	0·1435	B(isotropic) = 9·08					
H(5)	0·1391	−0·3845	−0·0217	B(isotropic) = 9·08					
H(6)	0·1373	−0·0983	−0·0661	B(isotropic) = 4·88					

Table 2. *Observed and calculated structure amplitudes and phase angles*

H	K	L	F(OBS)	F(CAL)	α
0	0	3	18.0*	21.1	180
0	0	6	7.6	8.1	0
0	0	12	1.1	0.8	0
0	0	15	1.2	1.0	0
1	0	-17	1.2	0.9	60
1	0	-14	1.6	1.7	60
1	0	-13	2.1	2.2	300
1	0	-12	3.5	4.0	0
1	0	-11	0.9	0.9	240
1	0	-10	2.3	2.6	300
1	0	-8	1.7	1.5	60
1	0	-7	14.5	13.3	300
1	0	-6	7.7	8.6	180
1	0	-5	11.0	11.2	60
1	0	-4	34.7	36.4	300
1	0	-3	36.7	39.2	0
1	0	-2	53.9*	66.4	60
1	0	-1	7.8	7.7	120
1	0	0	25.4	26.0	0
1	0	1	12.7	11.9	60
1	0	2	38.3*	43.1	120
1	0	4	8.1	8.1	60
1	0	5	23.5*	30.3	300
1	0	6	4.8	4.1	180
1	0	7	15.4	17.1	240
1	0	8	2.7	3.2	120
1	0	9	5.7	6.0	180
1	0	10	6.6	6.7	120
1	0	13	1.6	1.3	240
2	0	-14	2.2	2.5	60
2	0	-13	1.7	2.1	300
2	0	-12	3.1	2.7	0
2	0	-11	0.7	1.1	240
2	0	-10	7.2	7.2	300
2	0	-8	4.7	5.1	240
2	0	-7	5.8	5.1	120
2	0	-6	3.2	3.5	180
2	0	-5	9.1	9.0	60
2	0	-4	14.4	14.3	300
2	0	-3	2.6	2.7	0
2	0	-2	26.5*	31.5	60
2	0	-1	65.0*	82.7	120
2	0	0	54.7*	61.0	180
2	0	1	43.4	45.6	240
2	0	3	2.6	2.5	0
2	0	4	8.7	9.7	60
2	0	5	7.7	7.4	300
2	0	6	3.2	3.4	180
2	0	7	2.8	2.1	240
2	0	8	2.1	2.1	120
2	0	9	2.3	2.6	180
2	0	10	2.1	2.1	60
2	0	11	4.4	5.1	300
2	0	12	4.8	4.5	180
2	0	13	3.6	4.2	60
2	0	14	1.9	2.3	300
2	0	15	1.5	0.7	180
3	0	-15	1.0	0.9	180
3	0	-13	1.6	1.7	120
3	0	-12	1.6	1.2	0
3	0	-11	1.6	1.2	60
3	0	-10	1.3	1.4	300
3	0	-9	1.2	0.5	0
3	0	-7	6.3	5.1	300
3	0	-6	11.6	11.1	180
3	0	-4	30.1	31.4	120
3	0	-3	29.1	31.2	180
3	0	-2	26.3	27.2	240
3	0	-1	2.8	2.5	120
3	0	0	3.5	2.5	0
3	0	1	11.8	12.1	240
3	0	2	26.3*	29.5	300
3	0	3	10.6	10.3	180
3	0	4	13.7	12.1	240
3	0	5	14.2	15.8	120
3	0	6	11.6	9.7	0
3	0	7	4.5	4.2	240
3	0	8	4.1	3.8	120
3	0	10	2.9	2.8	240
3	0	12	0.8	0.2	0
3	0	14	1.2	0.2	300
3	0	15	1.6	1.4	180
4	0	-11	1.4	1.3	240
4	0	-10	3.2	3.1	120
4	0	-9	7.2	6.6	180
4	0	-8	4.5	4.2	60
4	0	-7	3.6	2.9	300
4	0	-6	1.6	1.5	180
4	0	-5	9.2	8.2	240
4	0	-4	1.6	1.4	120
4	0	-3	15.0	14.8	180
4	0	-2	28.5*	32.8	240
4	0	-1	5.7	5.2	360
4	0	0	31.8*	36.8	0
4	0	1	3.2	2.1	240
4	0	2	12.2	11.4	300
4	0	3	8.2	8.5	180
4	0	4	7.0	7.7	240
4	0	6	4.2	4.1	180
4	0	7	7.1	7.4	240
4	0	8	2.1	2.4	120
4	0	9	3.5	3.7	180
4	0	10	1.2	1.5	60
4	0	11	1.6	1.8	120
5	0	-11	2.6	2.4	240
5	0	-10	1.2	1.3	300
5	0	-9	3.8	3.8	180
5	0	-7	7.6	6.0	300
5	0	-6	12.9	14.3	180
5	0	-5	1.1	1.1	60

H	K	L	F(OBS)	F(CAL)	α
5	0	-4	12.2	12.5	300
5	0	-3	14.7	15.4	0
5	0	-2	3.8	2.8	60
5	0	-1	1.2	1.5	300
5	0	0	2.4	2.0	180
5	0	1	1.0	1.3	60
5	0	2	1.3	1.3	120
5	0	3	2.8	2.8	180
5	0	4	1.6	1.3	60
5	0	5	2.0	1.0	120
5	0	7	7.7	7.6	240
5	0	9	6.5	6.0	180
5	0	10	4.5	4.3	60
5	0	11	1.2	1.2	120
6	0	-13	1.2	1.2	120
6	0	-12	1.0	1.2	0
6	0	-11	1.2	1.0	240
6	0	-10	3.6	3.0	300
6	0	-9	1.1	1.1	0
6	0	-8	3.6	3.4	240
6	0	-6	1.2	1.7	180
6	0	-5	4.1	3.6	60
6	0	-2	10.0	10.4	60
6	0	-1	12.6	13.9	120
6	0	0	0.9	0.2	0
6	0	1	5.3	5.2	60
6	0	2	1.1	0.8	300
6	0	3	3.0	2.7	0
6	0	4	3.1	2.8	240
6	0	5	1.6	1.1	120
6	0	6	1.7	1.4	0
6	0	7	1.5	1.7	60
6	0	9	1.1	1.1	180
6	0	10	3.5	2.8	60
6	0	11	1.7	2.1	300
6	0	13	1.6	1.4	60
7	0	-9	1.5	1.1	0
7	0	-8	2.8	2.5	60
7	0	-7	1.2	1.5	300
7	0	-6	2.6	2.0	0
7	0	-5	1.7	2.1	60
7	0	-4	6.5	7.1	120
7	0	-3	6.1	7.0	180
7	0	-2	3.2	3.7	60
7	0	-1	4.6	5.0	120
7	0	0	3.4	4.1	0
7	0	1	3.0	2.8	60
7	0	2	1.3	1.1	300
7	0	3	1.9	2.0	0
7	0	4	2.7	2.7	240
7	0	5	5.1	5.5	120
7	0	6	8.8	9.0	0
7	0	7	3.1	2.5	240
7	0	8	1.6	1.6	120
7	0	9	0.8	0.3	0
8	0	-8	1.9	1.8	60
8	0	-7	1.2	1.0	120
8	0	-4	0.8	0.0	120
8	0	-3	1.2	1.4	130
8	0	-2	1.8	1.1	240
8	0	-1	3.3	3.8	300
8	0	0	2.1	2.6	180
8	0	1	1.1	1.1	60
8	0	2	1.2	1.0	0
8	0	4	3.0	2.9	60
8	0	5	1.1	1.0	300
8	0	7	0.8	1.3	240
8	0	8	0.8	0.8	120
9	0	-4	1.5	1.4	300
9	0	-3	0.7	0.2	0
9	0	0	0.9	0.6	60
1	1	0*	28.9*	32.6	172
1	1	1	34.7*	38.5	60
1	1	2	19.4	18.3	339
1	1	3	16.0	15.0	274
1	1	4	10.9	10.7	321
1	1	5	27.1	25.8	1
1	1	6	14.5	13.5	176
1	1	7	2.6	2.0	297
1	1	8	8.1	8.0	293
1	1	9	6.4	7.2	113
1	1	10	6.3	7.4	26
1	1	11	3.6	3.7	280
1	1	12	5.1	5.0	110
1	1	13	1.2	1.3	333
1	1	14	1.6	1.0	45
2	1	-13	0.8	1.1	80
2	1	-12	4.2	4.5	104
2	1	-11	1.7	2.5	26
2	1	-10	6.6	7.1	341
2	1	-9	5.8	5.7	322
2	1	-8	8.5	8.1	313
2	1	-7	6.0	5.0	124
2	1	-6	8.9	9.3	95
2	1	-5	12.2	11.9	339
2	1	-4	16.1	17.2	152
2	1	-3	14.0	14.1	203
2	1	-2	7.0	6.3	136
2	1	-1	28.7	30.2	354
2	1	0	12.1	9.4	139
2	1	1	23.5	25.7	198
2	1	2	5.9	5.8	30
2	1	3	17.3	17.0	152
2	1	4	8.3	7.3	206
2	1	5	8.5	8.1	128
2	1	6	14.7	13.8	346
2	1	7	5.8	5.2	99
2	1	8	4.9	5.1	346

H	K	L	F(OBS)	F(CAL)	α
2	1	9	1.2	1.2	76
2	1	11	2.0	2.0	143
2	1	12	5.1	5.5	110
2	1	13	2.1	2.2	18
2	1	14	1.5	1.0	276
2	1	15	0.9	0.6	198
3	1	-14	1.2	1.2	225
3	1	-12	1.4	1.4	330
3	1	-11	2.3	1.7	59
3	1	-9	5.7	5.8	69
3	1	-8	1.3	0.7	117
3	1	-7	3.8	3.5	141
3	1	-6	1.6	1.7	48
3	1	-5	12.3	10.9	299
3	1	-4	3.7	2.6	307
3	1	-3	5.8	4.9	124
3	1	-2	30.2	30.7	183
3	1	-1	6.3	5.8	45
3	1	0	9.8	9.0	10
3	1	1	3.1	2.6	144
3	1	2	16.1	14.6	8
3	1	3	8.1	6.2	93
3	1	4	5.3	4.8	8
3	1	5	6.6	6.7	207
3	1	6	11.5	10.9	269
3	1	7	3.9	2.5	164
3	1	8	10.0	10.3	94
3	1	10	2.1	2.1	138
3	1	11	3.5	3.5	207
3	1	12	1.4	1.6	22
3	1	13	1.1	1.4	257
4	1	-15	1.2	0.9	315
4	1	-13	1.1	1.2	275
4	1	-10	2.6	2.1	78
4	1	-9	5.2	5.1	173
4	1	-8	5.6	5.1	36
4	1	-7	11.6	10.7	213
4	1	-6	6.7	5.0	85
4	1	-5	6.1	5.3	240
4	1	-4	6.2	5.6	308
4	1	-3	2.5	1.6	343
4	1	-2	7.7	7.3	106
4	1	-1	3.1	1.6	231
4	1	0	0.9	8.5	322
4	1	1	5.8	5.1	152
4	1	2	0.1	8.5	151
4	1	3	10.6	9.0	327
4	1	4	0.3	8.0	320
4	1	5	1.6	0.9	43
4	1	6	8.1	7.4	196
4	1	8	3.0	2.8	194
4	1	9	6.1	6.5	263
4	1	11	4.0	4.9	213
5	1	-13	1.2	0.2	104
5	1	-10	1.1	0.2	333
5	1	-9	3.3	3.1	274
5	1	-8	4.5	5.2	286
5	1	-7	4.8	4.4	223
5	1	-6	4.8	4.3	154
5	1	-5	7.9	8.3	53
5	1	-4	8.5	8.5	214
5	1	-3	11.7	11.6	292
5	1	-2	8.8	8.7	72
5	1	-1	5.3	5.3	238
5	1	0	3.2	3.4	178
5	1	1	1.9	1.5	118
5	1	2	3.1	3.1	134
5	1	3	8.1	7.2	255
5	1	4	2.1	2.1	109
5	1	5	4.4	4.3	327
5	1	6	4.1	3.6	134
5	1	7	1.4	1.1	285
5	1	8	5.1	5.1	261
5	1	9	2.0	3.1	257
6	1	-11	1.0	0.8	180
6	1	-9	1.3	1.6	287
6	1	-8	1.6	1.5	321
6	1	-7	1.4	0.7	221
6	1	-6	3.4	3.6	331
6	1	-5	4.6	4.0	327
6	1	-4	9.6	9.6	170
6	1	-3	5.3	5.6	238
6	1	-2	5.3	3.1	135
6	1	-1	5.2	5.3	180
6	1	0	3.0	2.8	84
6	1	1	3.0	2.1	265
6	1	2	1.9	1.9	81
6	1	3	3.4	3.5	20
6	1	4	8.8	8.3	203
6	1	5	3.8	3.7	57
6	1	6	4.3	4.1	307
6	1	8	1.7	1.7	343
7	1	-9	1.1	1.1	49
7	1	-5	1.4	1.5	298
7	1	-4	2.6	3.2	28
7	1	-3	3.0	3.4	170
7	1	-2	11.6	11.6	227
7	1	-1	1.8	1.8	229
7	1	0	3.4	3.3	119
7	1	3	1.6	1.9	61
7	1	4	2.2	2.3	116
7	1	5	3.8	3.2	23
7	1	6	2.1	2.3	332
7	1	7	1.0	1.0	197
8	1	-6	2.1	2.2	122
8	1	-5	0.7	0.9	229
8	1	-4	1.2	1.5	352
8	1	-3	1.2	1.2	38

H	K	L	F(OBS)	F(CAL)	α
8	1	-2	0.5	0.8	246
8	1	-1	0.7	1.0	133
8	1	0	1.7	2.0	93
8	1	1	1.2	1.3	42
8	1	2	0.6	0.9	258
8	1	4	1.3	1.4	78
8	1	5	1.2	1.5	42
2	2	0	20.2	17.6	190
2	2	1	19.3	17.4	325
2	2	2	8.7	8.5	60
2	2	3	14.2	13.6	329
2	2	4	6.2	6.1	123
2	2	5	4.9	4.7	159
2	2	6	10.1	9.1	309
2	2	7	9.0	7.2	33
2	2	8	1.4	0.8	60
2	2	9	6.1	6.2	41
2	2	10	3.1	3.6	161
2	2	11	3.5	3.3	102
2	2	12	1.4	1.6	42
2	2	13	1.3	1.3	231
2	2	14	2.2	1.2	152
2	2	15	0.7	1.0	58
3	2	-14	0.7	0.7	117
3	2	-13	1.3	1.4	215
3	2	-12	2.8	2.8	258
3	2	-11	2.1	2.0	37
3	2	-10	3.3	2.7	178
3	2	-9	3.8	3.2	43
3	2	-8	2.3	2.2	318
3	2	-7	9.0	7.6	146
3	2	-6	8.2	7.3	9
3	2	-5	4.0	3.4	243
3	2	-4	5.3	3.8	4
3	2	-3	8.0	7.1	287
3	2	-2	8.6	8.3	354
3	2	-1	2.1	1.0	90
3	2	0	2.5	1.5	262
3	2	1	8.0	6.0	110
3	2	2	6.7	6.1	120
3	2	3	12.5	11.1	15
3	2	4	9.5	7.6	42
3	2	5	5.1	4.9	37
3	2	6	7.7	7.4	258
3	2	7	10.3	9.1	59
3	2	8	4.3	4.0	179
3	2	9	4.1	4.1	40
3	2	10	6.3	6.5	177
3	2	12	2.1	2.6	281
4	2	-11	1.5	1.7	183
4	2	-11	2.1	2.0	353
4	2	-10	1.6	1.1	86
4	2	-9	3.9	3.7	270
4	2	-8	1.7	1.7	28
4	2	-7	6.1	5.5	200
4	2	-6	2.9	2.3	64
4	2	-5	3.1	3.0	70
4	2	-4	4.0	2.7	231
4	2	-3	3.8	2.9	54
4	2	-2	2.7	2.3	88
4	2	-1	9.6	9.2	292
4	2	0	3.9	3.5	143
4	2	1	11.0	9.7	109
4	2	2	6.4	5.5	80
4	2	3	3.1	2.1	194
4	2	4	5.3	5.0	14
4	2	5	2.1	1.8	333
4	2	6	3.2	3.2	115
4	2	7	2.9	2.7	31
4	2	8	5.8	5.6	339
4	2	10	3.4	3.8	253
4	2	11	1.4	1.1	336
4	2	12	1.1	1.4	300
5	2	-8	2.5	2.3	243
5	2	-7	2.5	2.4	75
5	2	-6	4.9	4.9	328
5	2	-5	3.0	3.5	323
5	2	-4	7.2	7.3	222
5	2	-3	4.9	4.7	69
5	2	-2	4.9	5.5	124
5	2	-1	3.9	3.8	327
5	2	0	4.4	4.4	264
5	2	1	4.4	4.4	58
5	2	2	5.0	4.9	231
5	2	3	5.3	5.1	157
5	2	4	6.3	5.9	323
5	2	5	4.9	5.0	186
5	2	6	1.9	1.7	11
5	2	7	2.6	2.4	303
6	2	-9	1.2	1.2	31
6	2	-8	0.7	1.1	214
6	2	-7	2.2	2.5	11
6	2	-6	1.6	1.5	278
6	2	-5	3.1	2.6	166
6	2	-3	1.7	1.6	60
6	2	-2	2.8	4.7	203
6	2	-1	3.4	3.3	203
6	2	0	3.1	3.3	247
6	2	1	5.8	6.6	214
6	2	2	1.6	1.1	280
6	2	3	2.1	2.5	104
6	2	4	1.7	2.0	158
6	2	5	1.6	1.3	42
6	2	6	3.4	3.2	283
7	2	-7	1.2	1.2	104
7	2	-6	1.0	0.9	96
7	2	-5	0.5	0.4	153

H	K	L	F(OBS)	F(CAL)	α
7	2	-4	1.0	1.3	346
7	2	-3	0.9	0.8	263
7	2	-2	1.6	2.1	278
7	2	-1	1.7	2.0	250
7	2	4	3.1	2.4	45
7	2	5	1.6	2.0	294
8	2	-2	0.6	0.7	196
8	2	-1	0.9	0.2	27
8	2	0	1.2	1.5	28
3	3	0	6.4	6.4	235
3	3	1	1.7	0.8	23
3	3	2	7.2	7.3	302
3	3	3	11.4	10.1	95
3	3	4	3.5	3.2	35
3	3	5	8.5	7.4	142
3	3	6	7.2	6.2	58
3	3	7	1.8	1.8	348
3	3	8	2.1	1.5	270
3	3	9	1.5	1.1	255
3	3	10	1.6	1.0	191
3	3	11	1.6	1.6	30
4	3	-12	0.8	0.9	117
4	3	-8	2.0	1.7	152
4	3	-7	1.7	1.5	25
4	3	-6	3.5	3.2	31
4	3	-5	5.8	5.6	175
4	3	-4	3.9	3.3	293
4	3	-3	6.0	5.6	128
4	3	-2	7.7	7.3	268
4	3	-1	4.4	3.9	52
4	3	0	3.1	2.7	149
4	3	1	5.0	5.0	75
4	3	2	5.8	5.7	347
4	3	3	10.2	9.9	184
4	3	4	6.8	7.0	67
4	3	5	2.3	1.2	212
4	3	6	3.9	3.6	84
4	3	7	3.8	3.1	315
4	3	8	1.6	1.8	130
4	3	10	2.2	2.3	12
4	3	11	1.5	1.9	351
5	3	-9	1.1	1.4	118
5	3	-8	2.1	2.2	122
5	3	-7	2.1	1.9	51
5	3	-6	2.8	2.9	276
5	3	-5	2.4	2.9	260
5	3	-4	2.1	2.1	157
5	3	-3	4.3	4.2	18
5	3	-2	3.4	2.7	274
5	3	-1	2.0	2.0	49
5	3	0	1.7	1.8	13
5	3	1	2.1	1.6	240
5	3	2	0.7	1.2	162
5	3	3	2.8	2.7	197
5	3	4	1.7	1.5	340
6	3	-6	1.5	1.2	260
6	3	-5	2.2	1.3	58
6	3	-4	2.9	2.6	30
6	3	-3	3.1	2.7	332
6	3	-2	1.8	1.3	346
6	3	0	2.1	2.3	296
6	3	1	2.1	1.7	237
6	3	2	1.8	1.9	276
6	3	3	1.0	1.0	217
6	3	4	1.3	1.4	333
6	3	5	2.0	1.4	250
7	3	-1	1.1	1.5	32
7	3	0	2.1	2.2	254
7	3	1	1.7	1.9	295
7	3	2	1.7	2.0	233
4	4	0	2.1	2.2	71
4	4	1	2.6	2.8	344
4	4	2	3.8	3.6	185
4	4	3	1.5	1.4	243
4	4	4	3.1	3.2	101
4	4	5	1.7	1.7	205
4	4	7	1.0	1.0	151
4	4	8	2.6	2.7	63
4	4	9	1.2	1.4	143
5	4	-7	1.4	0.9	201
5	4	-6	1.9	2.4	187
5	4	-5	2.3	2.2	120
5	4	-4	1.7	1.6	18
5	4	-3	3.4	3.9	350
5	4	-2	1.6	2.2	158
5	4	-1	1.1	0.7	188
5	4	0	1.5	1.0	354
5	4	1	0.9	1.0	32
5	4	2	1.3	1.3	148
5	4	3	2.3	2.2	18
5	4	4	1.7	1.7	301
5	4	5	1.6	1.6	130
5	4	6	1.4	0.9	122
6	4	-4	1.1	1.0	6
6	4	-3	2.0	1.8	239
6	4	-2	3.0	2.7	70
6	4	-1	1.6	1.7	101
6	4	0	1.0	1.0	354
6	4	1	2.1	2.1	6
6	4	3	0.8	1.1	336
6	4	4	2.1	2.1	351
5	5	0	2.3	1.9	41
5	5	1	1.5	1.6	155
5	5	2	3.1	3.1	85
5	5	3	1.3	1.7	256

* indicates those F(obs) which appear to have been affected by extinction or underestimation.
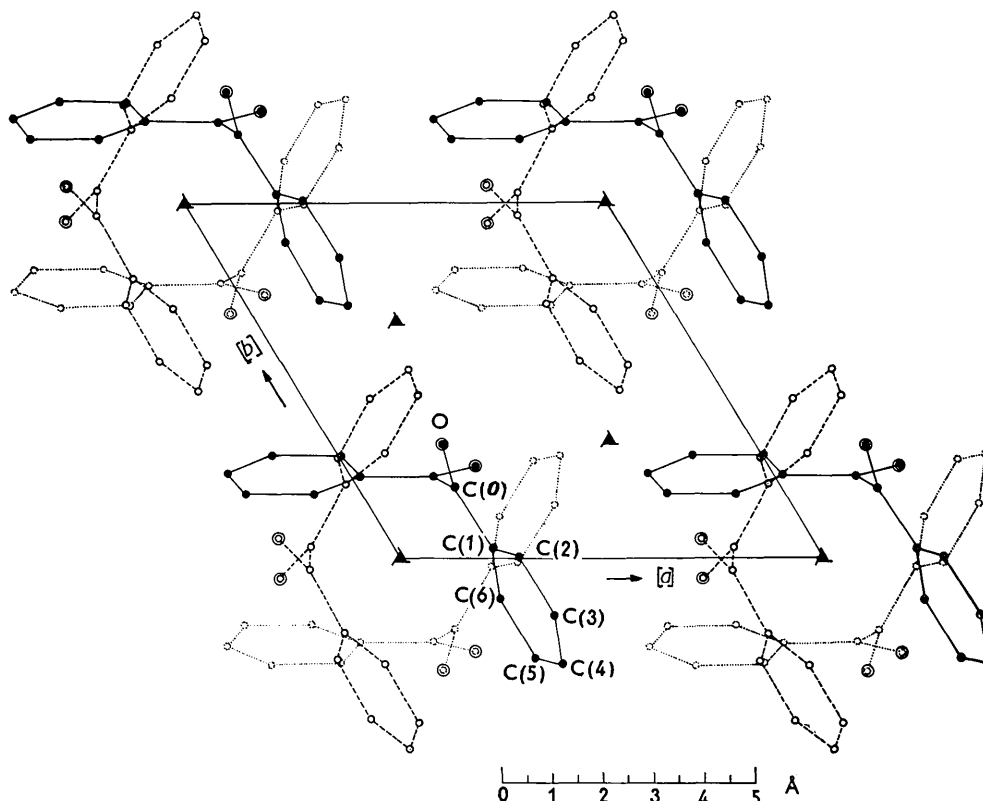
Fig. 3. Projection of molecules on (0001), showing packing between the groups arranged around the 3_1 axis. Molecules drawn with full lines have their mid points at $z=0$; those with broken lines at $z=\frac{1}{3}$, and those with dotted lines at $z=\frac{2}{3}$.

Table 3. *Bond lengths and inter-bond angles*

(Uncorrected for thermal vibrations)

		Standard deviation, σ
C(O)–C(O')	1·523 Å	0·007 Å
C(O)–O	1·210	0·007
C(O)–C(1)	1·482	0·007
C(1)–C(2)	1·382	0·007
C(2)–C(3)	1·389	0·010
C(3)–C(4)	1·389	0·010
C(4)–C(5)	1·400	0·010
C(5)–C(6)	1·386	0·008
C(6)–C(1)	1·398	0·007
C–H (assumed)	1·08	
C(1)–C(O)–C(O')	119·3°	0·4°
O–C(O)–C(O')	118·1	0·4
O–C(O)–C(1)	122·4	0·4
C(O)–C(1)–C(2)	118·9	0·4
C(O)–C(1)–C(6)	119·4	0·4
C(2)–C(1)–C(6)	121·6	0·4
C(1)–C(2)–C(3)	120·3	0·5
C(2)–C(3)–C(4)	118·4	0·6
C(3)–C(4)–C(5)	121·4	0·6
C(4)–C(5)–C(6)	119·9	0·6
C(5)–C(6)–C(1)	118·3	0·5

and these four atoms are $+0\cdot0059$, $-0\cdot0191$, $+0\cdot0075$ and $+0\cdot0055$ Å out of this plane respectively. The normals to these two planes intersect at an angle of

$6° 51'$. The normals to the two benzene rings are inclined at $76° 18'$, and the normals to the two planes containing C(1), C(O), O, C(O') and C(1'), C(O'), O', C(O) make an angle of $68° 24'$. The dimensions of the molecule correspond well to those in similar structures which have previously been published, the mean C–C bond in the benzene ring being 1·391 Å, and the C–O bond of 1·210 Å agrees with the value of 1·222 Å found in p-benzoquinone (Trotter, 1960).

The nearest intermolecular distances are between the oxygen atom and its three nearest-neighbour contacts, *viz.* C(6) of the molecule at $(-y, x-y, \frac{1}{3}+z)$, 3·310 Å, C(3) of the molecule at $(1-x, 1+y-x, \frac{1}{3}-z)$, 3·323 Å, and C(4) of the molecule at $(x, 1+y, z)$, 3·416 Å. There are also a number of C–C contacts from 3·58 Å upwards.

Analysis of thermal vibrations

The large thermal motion of the atoms in benzil crystals at room temperature has already been indicated qualitatively by observation of the diffuse scattering (Lonsdale & Smith, 1941). An approximate quantitative treatment can be obtained from the present structure determination, but a full examina-

tion of the problem must await the further investigation of the structure at lower temperatures. The magnitudes and orientations of the thermal ellipsoid for each atom, derived from the B_{ij} values quoted in Table 1, are given in Table 4, where l, m and n are the direction cosines relative to the standard orthogonal axes a^*, b and c.

Table 4. *Orientation and magnitudes of the thermal ellipsoids*

The direction cosines, l, m and n give the orientation relative to the orthogonal axes a^*, b and c

	B	l	m	n
C(O)	4·10	0·5456	−0·8358	−0·0621
	7·23	0·0366	−0·0503	0·9981
	5·53	0·8373	0·5468	−0·0032
C(1)	3·90	−0·8041	0·5569	0·2083
	6·74	0·1928	−0·0871	0·9774
	4·72	0·5624	0·8260	−0·0373
C(2)	4·65	0·7339	−0·6548	0·1805
	7·30	−0·2604	−0·5166	−0·8157
	7·26	0·6202	0·5378	−0·5711
C(3)	4·78	0·4598	−0·8678	0·1885
	11·13	−0·4518	−0·4114	−0·7916
	7·63	0·7645	0·2789	−0·5812
C(4)	4·88	−0·0943	−0·9699	0·2246
	12·58	0·5487	0·1376	0·8246
	6·86	0·8307	−0·2010	−0·5192
C(5)	4·11	0·0826	−0·9567	−0·2791
	12·48	0·4558	−0·2128	0·8643
	6·59	0·8862	0·1986	−0·4185
C(6)	4·37	−0·6050	0·6343	0·4813
	8·07	0·4251	−0·2538	0·8688
	5·14	0·6732	0·7303	−0·1161
O	4·03	−0·0221	−0·9531	−0·3018
	10·97	−0·7056	−0·1990	0·6801
	7·45	−0·7083	0·2279	−0·6681

From these figures, it is evident that for the seven carbon atoms in the half-molecule, the largest vibrations are almost parallel to c. Since the benzene ring lies very nearly in the plane (20$\bar{1}$) which is inclined by 17° to (100), it appears that the major vibrations of these seven carbon atoms are almost in the plane of the benzene ring. This does not, however, apply to the oxygen atom, the vibrations of which are more complex and preclude the treatment of even half the molecule as a rigid body.

These atomic vibrations were resolved into their translation and rotation components by a least-squares method described by Cruickshank (1956), which has been written as a computer program by Bujosa & Cruickshank (1961). This treatment is strictly valid only when the whole molecule may be regarded as a rigid body, or when the internal vibrations are small enough to be neglected in comparison with the vibrations of the whole molecule. In the case of benzil, the vibrations of the oxygen atom contradict the rigid-body approximation, and if half of the molecule (the asymmetric unit) is considered as vibrating about the mid-point of the central C(O)–C(O') bond, this would involve bending this bond unless the twofold axis of symmetry is retained at all stages of the vibrations. A true centre of inertia of the whole molecule lies on one side of the central bond and not at the mid-point.

However, in the absence of facilities for a more detailed and rigorous treatment, the rigid-body approximation was tried. The program computes the magnitudes and directions of the principal moments of inertia about the centre of inertia or other specified point (in this case the mid-point of C(O)–C(O')), and transforms the atomic coordinates and thermal parameters to these inertial axes. The translational and rotational components are then solved and a calculated set of temperature factors obtained for each atom. Then the observed values of B along the direction from the atom to the fixed point are worked out and compared with the calculated values. Table 5

Table 5. *Observed and calculated B(radial)*

	B(obs)	B(calc)		B(obs)	B(calc)
C(O)	7·00	7·06	C(4)	5·18	5·31
C(1)	5·32	5·86	C(5)	4·97	4·62
C(2)	6·03	6·54	C(6)	5·07	4·47
C(3)	5·74	6·13	O	6·60	5·83

shows the measure of agreement between the radial B values resulting from this approximate treatment. This test is insensitive to the non-rigid-body vibrations of the oxygen atom which may well be in a plane at right angles to the radial direction.

The program also calculates the corrections to be applied to the atomic coordinates to allow for the angular oscillations; these are applied to the existing coordinates and the result is given in Table 6. The largest corrections are in the y coordinates, that for oxygen being 0·0144 Å. These all result in increases

Table 6. *Corrected atomic coordinates*

	x/a	y/b	z/c
C(O)	0·2272	0·1930	0·0529
C(1)	0·2315	0·0222	0·0769
C(2)	0·2849	0·0029	0·1701
C(3)	0·2870	−0·1568	0·1955
C(4)	0·2341	−0·2954	0·1250
C(5)	0·1793	−0·2766	0·0306
C(6)	0·1779	−0·1168	0·0056
O	0·2594	0·3121	0·1134

Table 7. *Corrected bond lengths*

C(O)–C(O')	1·533 Å	C(3)–C(4)	1·400 Å
C(O)–O	1·219	C(4)–C(5)	1·407
C(O)–C(1)	1·486	C(5)–C(6)	1·388
C(1)–C(2)	1·389	C(6)–C(1)	1·410
C(2)–C(3)	1·391		

in the bond lengths, the maximum change being 0·012 Å, and the mean 0·007 Å. The revised values of the bond lengths are given in Table 7. The mean C–C distance in the benzene ring is thus 1·398 Å, compared with 1·391 Å for the uncorrected coordinates.

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The Conformation of Non-Aromatic Ring Compounds. XIV.*
The Crystal Structure of *trans*-2,3-Dichloro-1,4-dithiane at −180 °C

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The structure of *trans*-2,3-dichloro-1,4-dithiane has been determined from projections along [100], [010], and [$\bar{1}$ 01] by means of data obtained at about −180 °C with molybdenum radiation. The space group is *Pn* with

$$a = 7·174, \ b = 7·511, \ c = 6·726 \text{ Å}, \ \beta = 93·93°, \text{ and } Z = 2.$$

The dithiane ring has the chair form with the chlorine atoms in axial positions. A comparison is made with similarly substituted 1,4-dioxanes.

Introduction

The present study is an extension of the studies made in this laboratory on substituted cyclohexanes (Kwestroo, Meijer & Havinga, 1954; Wessels, 1960; van Dort, 1963), dioxanes (Altona & Romers, 1963*a*, *b*; Altona, Knobler & Romers, 1963*a*, *b*) and dithianes (Kalff & Havinga, 1962).

We have been able to synthesize some 2,3-disubstituted (dichloro-, chlorobromo-, and dibromo-) and one 2,5-disubstituted (dibromo-)1,4-dithiane (Kalff, 1964). Since the unit cell of the dichloro compound contains only two molecules and its absorption coefficient is the lowest, this compound was chosen for structure determination.

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* Part XIII: Mossel & Romers (1964).

Experimental

trans-2,3-Dichloro-1,4-dithiane was prepared by addition of chlorine to 1,4-dithiene in chloroform (Kalff, 1964). The compound crystallizes from hexane in small needles, elongated along the *a* axis and twinned on the plane (001). A specimen used for collecting 0*kl* data was obtained by cutting a twinned crystal. Crystals of a different habit were obtained by slowly evaporating a solution in chloroform. The crystals from the latter solvent appeared in the form of plates with (010) as main face and again twinned according to (001). These crystals were used for collecting *h0l* and *hkh* data. All specimens were sealed in dry Lindemann capillaries.

Unit-cell dimensions (Table 1) were measured from zero level Weissenberg photographs about [100] and