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Investigations of the Conformation of Non-Aromatic Ring Compounds. XIII*. The Crystal Structure of Cyclohexane-1,4-dione at −140 °C

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Cyclohexane-1,4-dione is monoclinic with space group $P2_1$ and $Z=2$. The cell dimensions at −140 °C are: $a=6{\cdot}65$, $b=6{\cdot}21$, $c=6{\cdot}87$ Å; $\beta=99°\ 49'$. The structure has been determined with three-dimensional copper reflexion data at −140 °C and refined by the method of least-squares. The molecule is a deformed boat and consists of two planar acetonyl groups making an angle of 38° with each other. The mean values of the C–C distances are 1·536 and 1·515 Å, corresponding to the sp^3–sp^3 and the sp^2–sp^3 bonds respectively. The mean value of the carbonyl bond is 1·210 Å.

Introduction

The present study was undertaken in connection with investigations in this laboratory concerning the stereochemical features of non-aromatic ring compounds (Kwestroo, Meyer & Havinga, 1954; van der Linden, 1958; Altona, Romers & Havinga, 1959; Wessels, 1960; Geise, Romers & Hartman, 1962; Romers & Altona, 1963; van Dort & Havinga, 1963). The molecular structure of cyclohexane-1,4-dione has been under discussion for several years. This compound shows in solution a dipole moment of 1·3 D (Le Fèvre & Le Fèvre, 1935) which has been interpreted in terms of an equilibrium between chair and boat forms (Le Fèvre & Le Fèvre, 1955) as well as a predominant existence of flexible forms (Oosterhoff, 1949; Hazebroek & Oosterhoff, 1951; Allinger & Freiberg, 1961). The similarity of the infrared spectra in the solid state and in solution seems to indicate that the compound has the same conformation in both the solid and the solution. In order to establish this conformation the structure has been determined by means of X-ray diffraction analysis. A preliminary paper about this work (Mossel, Romers & Havinga, 1963) was published at almost the same time as a short communication by Groth & Hassel (1963) on a two-dimensional analysis of the crystal structure of cyclohexane-1,4-dione using room temperature data.

Experimental

Cyclohexane-1,4-dione crystallizes from light petroleum, b.p. 40°–60°, in the form of colourless transparent needles. Its density, determined by means of the flotation method, is 1·28 g.cm^{-3}. The crystals are optically positive ($n_\gamma \gg n_\beta > n_\alpha$) with n_α parallel to [010], n_β approximately parallel to [101] and n_γ approximately parallel to [$\bar{1}$01].

X-ray diffraction data of single crystals were collected with Mo $K\alpha$ radiation at room temperature and with Cu $K\alpha$ radiation both at room temperature and at −140 °C. The symmetry of the crystals is monoclinic and no discontinuous phase transition occurs between 30 °C and −140 °C. The needle direction coincides with the unique axis which was conventionally called the b axis. The unit-cell dimensions (Table 1) at −140 °C were determined with the aid of zero-layer Weissenberg exposures with copper radiation ($\lambda=1{\cdot}5418$ Å) about [010] and [001]. The glancing angles θ of high angle reflexions suitable for measurements were calibrated by means of aluminum powder reflexion lines ($a=4{\cdot}0489$ Å at 20 °C) superposed on the Weissenberg photographs. From the dimensions and the density it can be concluded that the unit cell contains two molecules.

Equi-inclination Weissenberg photographs (unfiltered copper radiation) were made about [010] and [001] for the layers $k, l=0, 1, \ldots, 5$ in both zones at −140 °C. The non-integrated reflexion intensities were estimated visually and reduced to structure factors after multiplication with Lorentz, polarization and spot shape factors. Because the linear absorption coefficient μ is 8 cm^{-1} no absorption correction was applied. The structure factors were put to a common scale by correlation of common reciprocal layer lines belonging to the two zones. The total number of independent reflexions within the copper sphere is

Table 1. *Unit-cell dimensions*

The numbers in the third row refer to values stated by Groth & Hassel

	a	*b*	*c*	*β*	Temperature
M & R	6·73 Å	6·38 Å	6·90 Å	99°	20 °C
M & R	6·65 ± 0·02	6·21 ± 0·01	6·87 ± 0·01	99° 49′ ± 11′	−140 °C
G & H	6·73	6·34	6·96	99°	20 °C

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* Part XII: Mossel, Romers & Havinga (1963).

739, but only 669 reflexions were recorded inclusive of 11 that were too weak to be observable.

Determination of the space group

The rotation diagram about [010] has a mirror plane perpendicular to b^*. Precession photographs of $hk0$ and $0kl$ reciprocal lattice layers (collected with Mo $K\alpha$ radiation), as well as higher layer Weissenberg photographs about [001], show that the reflexions $0k0$ with k odd are absent.

Possible space groups are $P2_1/m$ and $P2_1$. Since the cell contains two molecular units it is necessary for the molecule to possess an inversion centre or a symmetry plane coinciding with a centre or a mirror of the unit cell, as the case may be, if the true space group is $P2_1/m$. Taking into account the length of b (6·2 Å) it is impossible to find a favourable packing of two molecules in the centrosymmetric cell.

The statistical analysis of reflexion data (Howells, Phillips & Rogers, 1950), excluding $h0l$ reflexions, indicates (Fig. 1) that the acentric space group $P2_1$ is the correct one. Since only molecules without inversion centres can occur in acentric space groups (Kitaigorodskii, 1957), it can be concluded that solid cyclohexane-1,4-dione does not possess the chair conformation.

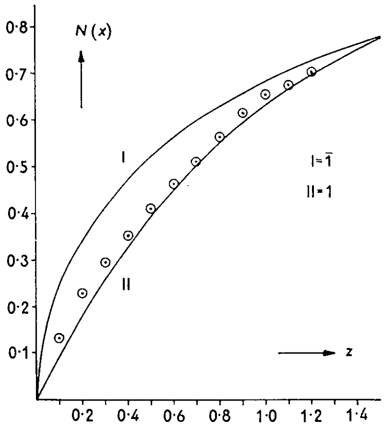

Fig. 1. The intensity distribution of reflexions in cyclohexane-1,4-dione.

The [010] projection

In order to calculate a sharpened Patterson projection $P(uw)$ the Fourier coefficients $F_o^2(h0l)$ were multiplied by $\sin^2\theta \exp(-1{\cdot}40 \sin^2\theta)$. This Patterson projection (Fig. 2(*a*)) reveals that the 'plane' of the molecule is approximately oriented parallel to (010), because it is not composed of continuous ridges, but of scattered peaks in a hexagonal pattern. The projection of such a molecule (Fig. 2(*b*)) should be nearly centrosymmetric, not withstanding its real conformation. The vector diagram of this projected molecule is indicated in Fig. 2(*b*) in an orientation which makes an angle of 42° with the c axis.

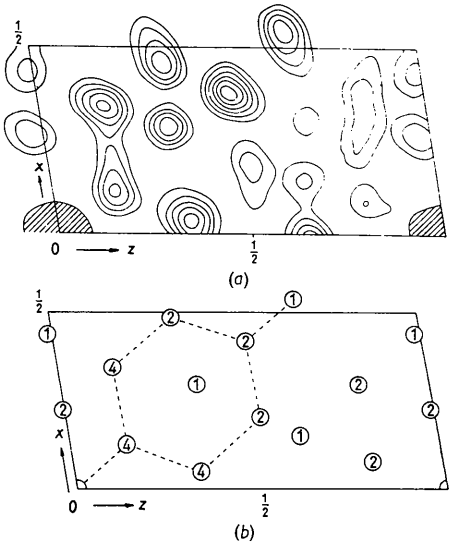

Fig. 2. (*a*) The sharpened Patterson function $P(uw)$. (*b*) The calculated corresponding vector diagram. The peak multiplicities are indicated by numbers in the circles.

The problem remains to find the position of its 'centre' with respect to the origin of the unit cell. The [010] projection has planar group symmetry $p2$. A nearly centric molecule with a pseudo-hexagonal ring of six carbon atoms (Fig. 2(*b*)) gives rise to a strong peak surrounded by six weaker peaks in a hexagonal pattern in Patterson space. There are two candidates at $x=0{\cdot}278$, $z=0{\cdot}333$ and at $x=0{\cdot}375$, $z=0{\cdot}500$, respectively (see Fig. 2(*a*)) which answer to this description. Trials of structure factors $F(h00)$ and $F(00l)$ for $h, l=1, 2, \ldots, 7$ indicated that the latter peak corresponds with the molecular 'centre' at $x=0{\cdot}188$ and $z=0{\cdot}250$. Subsequent calculation of structure factors $F(h0l)$ gave an agreement index $R=27{\cdot}3\%$. After a few cycles of Fourier and difference-Fourier synthesis and structure factor calculations the agreement index decreased to 15·8% after which the two-dimensional refinement was stopped. The final electron density projection $\varrho(yz)$ (Fig. 3) indicates that the boat, but not the chair, conformation fits this projection.

The y-parameters

In order to find the y parameters a sharpened Patterson function $P(uvw)$ was calculated at a grid having spacings 1/40 those of the three cell edges. The sharpening function was the same as the one used for the calculation of $P(uw)$. The key to the solution was the detection of the intramolecular vector O(1)–O(2) (see Fig. 4 for the numbering of the atoms). Its direction was derived from the known x and z parameters and a constructed wire model of the molecule. The peak sought was found in Patterson space at

Table 2. *Calculated and observed structure factors F(hkl) of cyclohexane*-1,4-*dione at* −140 °C

h k l	$\lvert F_c\rvert$	$\lvert F_o\rvert$	h k l	$\lvert F_c\rvert$	$\lvert F_o\rvert$	h k l	$\lvert F_c\rvert$	$\lvert F_o\rvert$	h k l	$\lvert F_c\rvert$	$\lvert F_o\rvert$
+1 +0 +0	11.7	11.5	−5	1.9	2.2	+1	7.0	8.1	−3	5.9	7.3
+2	18.7	18.8	−4	3.3	3.3	+2	6.5	6.4	−2	4.6	5.2
+3	22.7	24.0	−3	2.2	2.4	+3	11.3	10.3	−1	5.1	5.6
+4	7.0	8.8	−2	1.0	.9	+4	2.6	2.4	+0	7.8	8.1
+5	4.2	4.8	−1	1.2	1.8	+5	1.1	1.0	+1	8.1	8.0
+6	.0	.9	+0	.9	1.1	+6	3.2	2.8	+2	6.9	7.2
+7	4.2	4.3	+1	2.3	2.4	−6 +1 +7	1.8	1.5	+3	5.4	5.2
+8	2.3	2.3	+2	.7	.4	−5	1.0	1.2	+4	3.9	3.8
−8 +0 +1	1.5	1.7	+3	2.5	3.5	−4	2.2	2.3	+5	2.1	2.2
−7	3.3	3.2	−6 +0 +8	1.8	2.2	−3	1.0	.7	−6 +2 +6	5.4	5.4
−6	1.7	1.1	−5	5.4	7.3	−2	2.4	2.4	−5	4.2	4.2
−5	6.3	6.5	−4	2.2	2.7	−1	1.9	1.7	−4	3.1	3.1
−	16.5	19.3	−3	.1	.1	+0	2.3	2.4	−3	5.6	5.3
−3	13.6	15.1	−2	9.2	11.5	+1	2.4	2.3	−2	2.1	1.8
−2	6.8	7.1	−1	1.7	2.0	+2	2.9	2.9	−1	8.8	9.2
−1	36.9	31.8	+0	1.6	2.2	+3	1.3	1.2	+0	9.2	9.2
+0	.3	.1	+1	2.2	2.7	+4	2.1	.8	+1	9.5	9.3
+1	7.2	6.6	+2	.7	1.3	−4 +1 +8	6.1	6.1	+2	3.6	3.9
+2	9.8	10.0	+3	2.4	3.3	−3	1.6	1.2	+3	4.3	4.3
+3	8.1	9.1	+1 +1 +0	33.2	23.9	−2	4.6	4.8	+4	3.5	3.4
+4	4.4	5.0	+2	25.4	23.3	−1	8.2	8.5	−5 +2 +7	1.0	1.0
+5	2.4	2.1	+3	10.7	10.9	+0	2.4	2.4	−4	1.6	1.8
+6	2.3	2.5	+4	3.3	3.6	+1	1.8	1.9	−3	4.3	4.0
+7	3.4	3.3	+5	7.9	8.2	+2	1.0	1.0	−2	.9	.4
+8	3.1	3.5	+6	7.2	7.4	+0 +2 +0	40.3	40.1	−1	1.3	1.2
−8 +0 +2	1.6	2.1	+7	3.6	3.3	+1	37.8	33.1	+0	3.0	3.0
−7	1.6	1.2	+8	2.0	1.8	+2	10.4	10.1	+1	2.6	2.7
−6	5.0	5.2	−8 +1 +1	3.2	2.9	+3	15.0	14.9	+2	1.7	1.7
−5	1.1	1.4	−7	4.6	4.0	+4	7.7	8.1	+3	3.4	3.5
−4	1.6	2.1	−6	4.2	4.0	+5	6.5	6.9	−4 +2 +8	1.1	1.3
−3	13.4	14.0	−5	2.4	2.8	+6	5.8	5.9	−3	5.1	5.1
−2	17.1	18.1	−4	5.4	5.5	+7	1.2	1.4	−2	4.4	4.5
−1	10.1	13.5	−3	13.5	14.9	+8	2.4	2.5	−1	2.1	1.9
+0	11.6	12.8	−2	13.0	13.3	−8 +2 +1	3.6	3.5	+0	2.2	2.3
+1	5.2	5.1	−1	8.6	8.7	−7	.9	.6	+1	1.9	1.9
+2	2.2	3.2	+0	20.5	18.6	−6	5.4	4.6	+1 +3 +0	1.8	1.9
+3	11.8	12.5	+1	9.5	9.2	−5	1.7	2.4	+2	12.8	12.5
+4	8.0	8.4	+2	13.1	13.6	−4	7.6	7.3	+3	9.5	9.0
+5	17.2	18.0	+3	4.0	4.0	−3	16.1	16.4	+4	5.2	5.3
+6	3.5	3.5	+4	1.6	2.0	−2	11.6	12.7	+5	4.6	4.0
+7	1.8	2.2	+5	1.8	1.8	−1	18.1	18.9	+6	7.6	7.6
−8 +0 +3	.6	.6	+6	.9	1.1	+0	22.7	20.8	+7	1.1	1.1
−7	9.5	9.0	+7	.5	1.1	+1	10.6	9.6	−7 +3 +1	3.6	3.5
−6	5.4	5.4	+8	1.3	.9	+2	7.1	6.3	−6	3.8	3.6
−5	.3	.1	−8 +1 +2	2.7	2.9	+3	9.0	8.8	−5	2.2	1.9
−4	18.2	19.8	−7	4.0	4.1	+4	.4	.8	−4	3.3	3.4
−3	5.8	7.1	−6	3.3	3.0	+5	.7	1.2	−3	.8	.8
−2	19.9	21.4	−5	4.1	4.0	+6	2.8	2.9	−2	10.6	10.1
−1	10.4	10.4	−4	10.3	10.5	+7	2.3	2.3	−1	6.2	6.7
+0	4.1	4.9	−3	3.8	4.4	−8 +2 +2	2.7	2.8	+0	3.6	4.3
+1	14.1	13.6	−2	11.0	11.3	−7	3.7	3.5	+1	9.6	9.5
+2	17.0	17.5	−1	28.5	32.0	−6	2.6	2.2	+2	10.6	10.7
+3	.7	.4	+0	9.2	9.3	−5	1.5	1.3	+3	5.5	5.7
+4	16.3	18.8	+1	5.7	5.2	−4	7.4	8.4	+4	5.0	4.8
+5	1.5	1.7	+2	2.1	2.3	−3	9.6	10.8	+5	.5	.7
+6	1.5	1.5	+3	3.8	4.2	−2	2.9	2.9	+6	.7	.8
+7	8.9	10.3	+4	5.5	5.6	−1	2.7	3.4	+7	2.3	2.7
−8 +0 +4	4.0	4.2	+5	4.6	5.7	+0	9.8	10.5	−7 +3 +2	1.7	1.4
−7	.4	.1	+6	6.9	7.2	+1	2.6	2.5	−6	.3	.1
−6	2.8	2.7	+7	4.5	5.2	+2	10.4	10.2	−5	7.9	7.1
−5	11.4	11.2	−8 +1 +3	4.4	4.9	+3	2.7	2.8	−4	4.1	4.2
−4	4.5	4.9	−7	2.4	2.3	+4	15.3	13.8	−3	3.8	3.6
−3	6.2	7.7	−6	4.6	4.5	+5	12.0	12.3	−2	11.4	12.1
−2	.4	.7	−5	19.2	18.2	+6	4.1	4.0	−1	6.9	7.5
−1	1.1	2.0	−4	11.6	11.8	+7	4.6	4.8	+0	8.1	8.7
+0	3.2	4.0	−3	9.9	10.5	−8 +2 +3	5.5	5.2	+1	4.7	4.9
+1	1.2	2.2	−2	23.6	25.7	−7	5.5	5.2	+2	6.2	6.0
+2	1.0	1.0	−1	10.4	12.4	−6	2.0	1.8	+3	7.5	7.4
+3	4.9	6.1	+0	13.9	15.3	−5	1.7	1.8	+4	4.8	4.9
+4	3.4	3.5	+1	7.9	7.7	−4	10.4	10.7	+5	5.0	5.0
+5	5.5	5.9	+2	14.2	14.4	−3	13.8	14.8	+6	1.6	1.8
+6	2.2	2.1	+3	2.2	2.4	−2	4.7	5.4	+7	3.7	3.9
−6 +0 +5	4.0	3.6	+4	4.4	4.5	−1	14.1	14.9	−7 +3 +3	1.5	1.3
−5	.1	.1	+5	8.6	8.5	+0	2.5	2.7	−6	7.8	7.6
−4	3.7	5.1	+6	5.4	6.3	+1	15.9	15.1	−5	4.9	5.0
−3	2.9	4.4	+7	2.4	2.7	+2	3.8	3.9	−4	14.2	13.7
−2	3.1	4.1	−8 +1 +4	2.4	2.3	+3	11.7	10.7	−3	7.8	8.2
−1	1.7	1.8	−7	2.2	2.2	+4	10.3	10.6	−2	8.4	8.0
+0	1.6	2.2	−6	8.8	8.3	+5	4.9	5.3	−1	14.1	14.5
+1	14.9	17.7	−5	6.2	6.2	+6	3.3	3.2	+0	7.5	7.4
+2	.9	.8	−4	2.2	2.7	+7	4.9	5.0	+1	10.7	9.4
+3	6.1	5.5	−3	3.0	3.9	−7 +2 +4	3.2	3.3	+2	2.5	2.4
+4	7.2	6.4	−2	2.6	2.7	−6	1.6	1.8	+3	5.0	5.0
+5	5.1	4.9	−1	2.8	3.2	−5	8.2	8.7	+4	4.8	4.6
−8 +0 +6	.8	2.0	+0	2.9	3.2	−4	10.7	11.1	+5	.7	.7
−7	6.9	6.9	+1	3.7	3.9	−3	3.8	4.0	+6	4.1	4.5
−6	1.5	1.3	+2	3.1	3.4	−2	4.4	4.9	−7 +3 +4	3.5	3.3
−5	1.3	.7	+3	4.6	4.6	−1	.8	.9	−6	1.5	1.5
−4	2.7	2.4	+4	2.8	2.8	+0	1.8	2.1	−5	8.2	7.7
−3	8.0	8.0	+5	1.3	1.2	+1	2.8	2.5	−4	.5	.1
−2	2.2	2.4	+6	2.2	2.1	+2	3.2	3.3	−3	6.5	6.4
−1	3.4	4.0	−7 +1 +5	2.0	1.9	+3	2.2	2.4	−2	6.1	6.0
+0	19.7	17.9	−6	1.3	1.1	+4	7.0	7.0	−1	1.8	1.9
+1	1.2	1.1	−5	1.9	1.9	+5	2.9	2.8	+0	2.1	2.2
+2	5.0	5.3	−4	.6	1.0	+6	1.3	1.0	+1	4.9	4.4
+3	4.7	4.9	−3	.9	1.0	−7 +2 +5	.2	.6	+2	1.7	1.9
+4	2.1	2.4	−2	5.5	6.4	−6	2.1	1.9	+3	5.6	5.4
+5	2.9	3.1	−1	6.5	6.6	−5	2.5	2.2	+4	1.8	2.0
−6 +0 +7	1.1	1.5	+0	16.4	15.5	−4	.8	.9	+5	2.3	2.3

Table 2 (*cont*).

h k l	|Fc|	|Fo|	h k l	|Fc|	|Fo|	h k l	|Fc|	|Fo|	h k l	|Fc|	|Fo|
−7 +3 +5	1.6	1.3	+2	6.8	7.2	−1	2.7	3.4	−3	5.5	5.2
−6	.3	.1	+3	5.1	5.1	+0	2.8	3.2	−2	.9	1.2
−5	2.5	2.4	+4	11.4	11.1	+1	6.6	6.4	−1	5.6	5.9
−4	2.1	2.5	+5	3.9	4.4	+2	1.1	1.0	+0	7.5	8.1
−3	5.3	5.5	+6	5.6	6.4	+3	2.9	2.9	+1	5.2	5.7
−2	3.9	4.5	−7 +4 +3	.4	.6	+4	6.4	6.7	+2	1.7	2.0
−1	10.4	10.5	−6	3.2	3.1	+5	2.9	3.1	+3	3.3	3.3
+0	6.6	7.1	−5	3.7	3.5	+6	1.7	1.8	+4	1.8	2.1
+1	5.8	6.2	−4	2.4	2.1	−6 +5 +2	1.2	1.0	+5	4.3	4.3
+2	8.6	7.8	−3	7.7	7.6	−5	5.4	5.2	−5 +6 +2	1.3	1.4
+3	3.4	3.1	−2	7.8	8.0	−4	4.0	3.4	−4	3.2	3.2
+4	3.9	3.9	−1	5.7	6.2	−3	3.0	2.7	−3	2.9	2.8
+5	1.2	1.2	+0	1.2	1.2	−2	5.4	5.4	−2	2.3	2.9
−6 +3 +6	6.3	6.0	+1	6.6	6.4	−1	7.1	7.5	−1	5.9	6.6
−5	3.4	3.0	+2	8.0	8.0	+0	3.7	3.9	+0	.7	.1
−4	3.8	3.5	+3	7.7	7.7	+1	4.1	3.8	+1	5.6	6.5
−3	2.7	2.4	+4	4.4	4.5	+2	4.9	4.9	+2	.6	.1
−2	7.5	6.9	+5	6.7	7.4	+3	4.4	4.1	+3	4.8	5.4
−1	3.5	3.1	+6	3.5	3.9	+4	1.5	1.7	+4	3.6	4.0
+0	6.2	6.0	−6 +4 +4	2.1	2.4	+5	.4	.6	−5 +6 +3	3.3	3.5
+1	3.3	2.9	−5	2.4	2.5	+6	3.4	3.2	−4	4.7	4.6
+2	3.3	3.0	−4	9.4	9.0	−6 +5 +3	4.8	4.9	−3	.7	.1
+3	7.3	7.0	−3	1.3	1.3	−5	6.9	6.6	−2	4.5	5.4
+4	1.2	1.3	−2	5.5	5.6	−4	4.9	4.9	−1	2.2	2.5
−5 +3 +7	1.7	1.7	−1	6.1	6.1	−3	6.8	6.2	+0	1.3	1.7
−4	2.3	2.5	+0	3.0	3.1	−2	5.3	5.1	+1	1.9	2.4
−3	1.9	1.8	+1	3.8	4.1	−1	6.6	6.1	+2	5.5	6.2
−2	2.1	1.8	+2	5.1	5.0	+0	4.6	4.6	+3	.6	.1
−1	4.3	4.2	+3	2.4	2.2	+1	4.6	4.8	+4	6.2	7.5
+0	1.2	1.0	+4	4.9	4.9	+2	4.8	4.8	−4 +6 +4	4.1	4.1
+1	.3	.3	+5	1.8	1.7	+3	3.1	3.4	−3	2.4	2.7
+2	4.0	3.9	−6 +4 +5	2.8	2.5	+4	1.0	1.1	−2	.4	.1
−3 +3 +8	3.1	3.0	−5	1.6	1.5	+5	3.9	4.4	−1	6.3	6.2
−2	3.9	4.0	−4	4.1	4.1	−6 +5 +4	2.7	2.5	+0	1.0	1.5
−1	3.9	4.3	−3	4.6	4.3	−5	4.3	4.4	+1	3.9	3.9
+0	3.0	2.9	−2	4.2	4.6	−4	3.6	4.0	+2	1.1	1.3
+0 +4 +0	13.1	13.8	−1	.8	.9	−3	3.0	3.0	+3	3.1	2.8
+1	18.4	17.0	+0	6.5	6.6	−2	5.4	5.4	−3 +6 +5	1.0	1.0
+2	7.5	7.3	+1	1.4	1.7	−1	2.3	2.4	−2	1.0	1.2
+3	6.9	7.0	+2	5.2	5.2	+0	5.9	5.3	−1	3.7	3.5
+4	7.6	8.0	+3	3.3	3.3	+1	3.7	3.8	+0	2.3	2.6
+5	4.0	3.6	+4	2.1	1.9	+2	.8	.8	+1	3.3	2.9
+6	2.9	3.3	−5 +4 +6	2.2	2.0	+3	3.6	3.9	+1 +7 +0	2.2	2.5
+7	3.0	3.4	−4	4.8	4.6	+4	1.2	1.3	+2	2.7	3.0
−7 +4 +1	2.4	2.8	−3	2.7	2.2	−5 +5 +5	2.6	2.8	+3	.9	.8
−6	2.2	2.2	−2	3.4	3.1	−4	3.7	4.0	+4	1.8	1.8
−5	3.5	3.0	−1	4.7	4.4	−3	3.2	2.8	−4 +7 +1	1.7	1.7
−4	4.8	4.6	+0	5.3	4.9	−2	2.1	1.8	−3	1.7	1.9
−3	8.6	7.7	+1	7.5	6.9	−1	6.4	5.7	−2	1.0	1.3
−2	7.5	7.1	+2	.9	.7	+0	4.3	4.2	−1	3.2	3.5
−1	4.8	4.2	+3	3.0	3.3	+1	4.7	4.2	+0	3.0	3.6
+0	15.1	13.6	−4 +4 +7	2.9	2.5	+2	4.1	4.2	+1	3.0	3.3
+1	2.7	2.9	−3	2.5	2.7	+3	3.8	3.1	+2	1.6	1.1
+2	4.8	5.3	−2	1.1	.8	−4 +5 +6	1.5	1.5	+3	2.0	2.1
+3	8.3	7.7	−1	.7	.6	−3	4.2	4.9	−2 +7 +2	3.9	3.9
+4	3.6	4.0	+0	3.8	4.1	−2	1.1	1.2	−1	1.1	1.1
+5	4.4	4.6	+1	.8	.7	−1	4.5	4.9	+0	3.3	3.4
+6	1.9	2.0	+1 +5 +0	5.0	4.8	+0	4.8	5.1	+1	2.6	2.8
+7	2.5	2.5	+2	.9	.9	+1	3.3	3.6	+2	.5	1.0
−7 +4 +2	2.3	2.4	+3	4.9	5.4	+2	2.5	2.8	+3	.5	.7
−6	3.3	3.3	+4	3.6	3.6	+0 +6 +0	11.7	13.7	−3 +7 +3	2.7	2.9
−5	1.6	1.4	+5	.7	.7	+1	4.6	5.1	−2	4.0	4.5
−4	4.7	4.8	+6	2.8	3.1	+2	7.1	8.4	−1	2.4	2.5
−3	1.3	1.7	−6 +5 +1	3.9	4.4	+3	5.1	5.6	+0	5.1	6.0
−2	6.2	6.0	−5	1.0	1.0	+4	2.7	3.5	+1	1.5	1.9
−1	5.2	5.6	−4	4.7	4.2	+5	2.3	2.5	+2	2.0	2.5
+0	4.9	5.5	−3	3.6	3.5	−5 +6 +1	2.5	2.8	−2 +7 +4	2.0	2.0
+1	5.0	5.0	−2	1.5	1.9	−4	2.2	2.4	−1	.5	.6
									+0	4.0	4.0

$x=0{\cdot}536$, $y=0{\cdot}169$ and $z=-0{\cdot}097$. Nearly all remaining peaks were easily identified and y parameters were attributed to the eight heavy atoms. The y parameters of O(2) were arbitrarily chosen zero and kept zero during the refinement of the structure. At this stage the calculation of all structure factors resulted in an R index of 22·1%.

The refinement

Refinement of the structure started with calculation of three successive cycles of structure factors and electron density sections parallel to (001) with the same grid as indicated for the calculation of $P(uvw)$. This resulted in an R index of 15·1%. Further refinement was attained by the method of least-squares with a program devised by Mills & Rollett (1961) on the Mercury computer of the University of Oxford. The weight factor used was

$$w=1/\{1+[(|F_o|-b)/a]^2\} \text{ with } a=b=5{\cdot}0\ .$$

The scattering curves of carbon and oxygen used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). The scattering curve of hydrogen employed was the one proposed by McWeeny (1951). After two cycles with isotropic temperature factors the agreement index became 13·2%.

Next, the hydrogen atoms were placed at calculated positions assuming tetrahedral bond angles for the carbon atoms C(2), C(3), C(5) and C(6) and C–H distances of 1·08 Å. The hydrogen atoms were kept in fixed positions throughout the refinement with an isotropic temperature factor $B=2{\cdot}0$ Å^2. After two more cycles and adding the hydrogen contributions to the structure factors, R dropped to 9·8%.

At this stage a three-dimensional difference Fourier synthesis indicated a fairly marked anisotropy of the

Table 3. *Positional parameters (fractions of cell edges) and thermal parameters* (Å^2)

Standard deviations of the parameters (Å and Å^2 respectively) are given in brackets.
The isotropic temperaturefactor B of hydrogen atoms is 2·0 Å^2

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0·4273	0·1745	0·4466	0·0216	0·0163	0·0210	−0·0049	−0·0001	0·0048
	(0·006)	(0·008)	(0·006)	(0·003)	(0·003)	(0·003)	(0·006)	(0·006)	(0·004)
C(2)	0·5168	0·1740	0·2564	0·0193	0·0245	0·0201	−0·0049	−0·0022	0·0137
	(0·006)	(0·009)	(0·006)	(0·003)	(0·003)	(0·003)	(0·007)	(0·006)	(0·004)
C(3)	0·3559	0·2226	0·0724	0·0228	0·0276	0·0203	−0·0070	0·0012	0·0116
	(0·006)	(0·008)	(0·006)	(0·003)	(0·004)	(0·003)	(0·006)	(0·006)	(0·005)
C(4)	0·1732	0·0773	0·0601	0·0213	0·0276	0·0211	−0·0016	−0·0031	0·0065
	(0·006)	(0·009)	(0·007)	(0·003)	(0·004)	(0·003)	(0·006)	(0·006)	(0·005)
C(5)	0·1003	0·0298	0·2541	0·0163	0·0340	0·0224	−0·0018	0·0016	0·0100
	(0·006)	(0·008)	(0·007)	(0·003)	(0·004)	(0·003)	(0·006)	(0·006)	(0·005)
C(6)	0·1979	0·1773	0·4228	0·0226	0·0321	0·0202	0·0050	−0·0026	0·0197
	(0·006)	(0·010)	(0·006)	(0·003)	(0·004)	(0·003)	(0·007)	(0·007)	(0·005)
O(1)	0·5384	0·1720	0·6062	0·0253	0·0247	0·0219	−0·0048	−0·0028	−0·0016
	(0·005)	(0·007)	(0·004)	(0·002)	(0·002)	(0·002)	(0·005)	(0·005)	(0·003)
O(2)	0·0898	0·0000	−0·0941	0·0301	0·0445	0·0226	−0·0192	−0·0148	0·0066
	(0·005)	(0·007)	(0·005)	(0·003)	(0·003)	(0·002)	(0·005)	(0·005)	(0·004)
H(1)	0·641	0·2877	0·268	—	—	—	—	—	—
H(2)	0·586	0·0134	0·237	—	—	—	—	—	—
H(3)	0·307	0·387	0·079	—	—	—	—	—	—
H(4)	0·421	0·205	−0·061	—	—	—	—	—	—
H(5)	0·139	−0·139	0·298	—	—	—	—	—	—
H(6)	−0·062	0·036	0·237	—	—	—	—	—	—
H(7)	0·144	0·337	0·389	—	—	—	—	—	—
H(8)	0·149	0·127	0·558	—	—	—	—	—	—

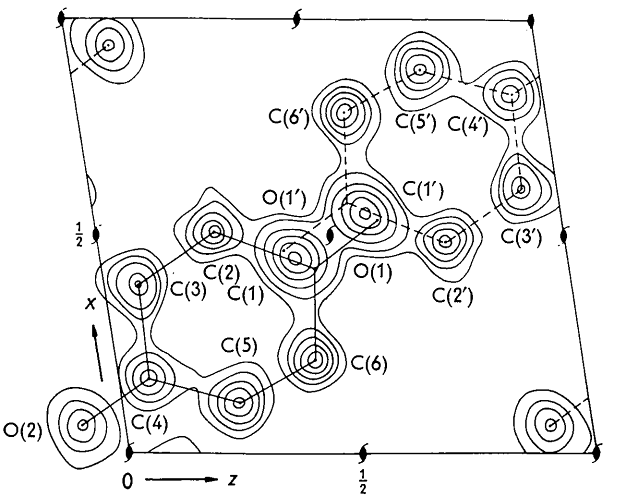

Fig. 3. The electron density projection $\varrho(xz)$. The contour lines are at arbitrary scale, those of O(2), C(1), C(1′), O(1) are drawn at intervals twice as large as those of the other atoms.

thermal motions of the heavy atoms with directions of maximum vibration approximately parallel to the b axis. After another four cycles of least-squares calculations with individual anisotropic temperature parameters, R decreased to 8·07% and no more significant shifts were indicated.

In Table 2 are listed the observed and calculated values of structure factors based upon the final least-squares cycle. In Table 3 are listed the positional parameters, in fractions of cell edges. The numbers in brackets refer to the standard deviations in Å. The thermal parameters U_{11}, U_{12} *etc.* defined by the equation

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}\right.$$
$$\left.+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right]$$

are also listed in Table 3. The numbers in brackets indicate the standard deviations of these parameters.

Discussion of the structure and packing

The bond distances and bond angles, uncorrected for thermal motions are shown in Fig. 4. Since most intramolecular bonds are approximately parallel to (010), the contribution of the standard deviations $\sigma(y)$ to the errors in the bond distances can be neglected.

The mean standard deviation of x and z parameters of the heavy atoms is 0·0059 Å and the error in cell

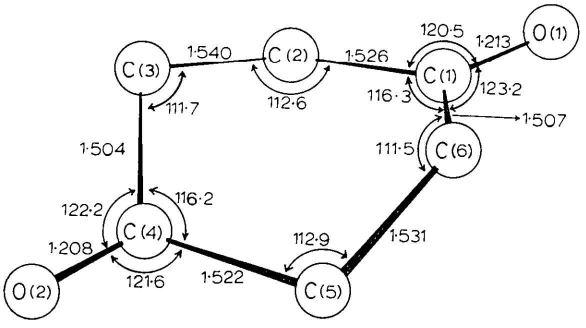

Fig. 4. A perspective drawing of cyclohexane-1,4-dione with bond distances (Å) and bond angles (°).

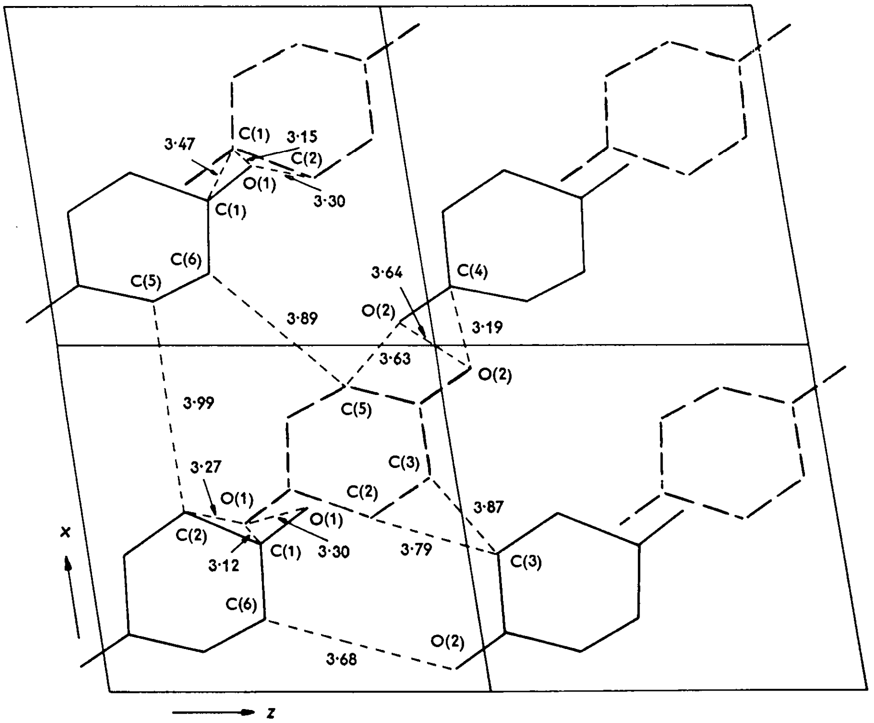

Fig. 5. The molecular packing viewed down the b axis. The molecules at x, y, z are indicated by full lines, the molecules at $\bar{x}, \frac{1}{2}+y, \bar{z}$ by broken lines. Some intermolecular distances smaller than 4 Å are indicated by dashed lines.

edges is 0·0032 Å per length of 1·50 Å. It follows that the mean standard deviation of intramolecular bonds is $\sqrt{(2\times 0\cdot0059^2+0\cdot0032^2)}=0\cdot009$ Å, giving a 1% significance level of 0·027 Å. The standard deviation in bond angles is 0·77° giving a 1% significance level of 2·5°.

The intramolecular bond distances seem to be quite normal. The bonds C(2)–C(3) and C(5)–C(6) (average value 1·536 Å) do not deviate significantly from the accepted value (1·526 Å) for the sp^3–sp^3 bonds (Lide, 1962). The bonds C(1)–C(2), C(3)–C(4), C(4)–C(5) and C(1)–C(6) (mean value 1·515 Å) are somewhat smaller and do not deviate significantly from the accepted value (1·505 Å) for the sp^3–sp^2 bonds. Their difference (0·022 Å) from the mean value of the bonds C(2)–C(3) and C(5)–C(6) is in the range of possible significance. The two carbonyl bonds with a mean value of 1·21 Å closely resemble the carbonyl bonds of *p*-benzoquinone with lengths of 1·222 Å (Trotter, 1960).

The molecule has a boat-shaped conformation with C(6) as prow, C(3) as stern and both carbonyl groups as oars. It can be described more adequately as being composed of two planar acetonyl groups C(2)–C(1)–O(1)–C(6) and C(5)–C(4)–O(2)–C(3) twisted with respect to one another. The equations of these planes were calculated with respect to an orthogonal coordinate system XYZ with directions a, b and c^* according to the method of Schomaker, Waser, Marsh & Bergman (1959). These equations are respectively

$$0\cdot0120X+0\cdot9999Y+0\cdot0068Z-1\cdot1314=0 \quad \text{(I)}$$

and

$$0\cdot5910X+0\cdot7932Y+0\cdot1469Z-0\cdot3220=0\,. \quad \text{(II)}$$

The distances of the atoms C(2), C(1), O(1), C(6) and the atoms C(5)–C(4)–O(2)–C(3), respectively, from plane (I) and plane (II) are less than 0·0014 Å. The angle between planes (I) and (II) is 38·3°. The dihedral angle between the planes C(2)–C(3)–C(4) and C(1)–C(2)–C(3) is 52·8° and the dihedral angle between the planes C(4)–C(5)–C(6) and C(1)–C(6)–C(5) is 53·4°. The angle between the carbonyl CO vectors is 154·8°. If the molecule should maintain the same conformation in the solution, the angle of 155° would account for the measured electric dipole moment of 1·3 D.

The mean value of bond angles C(1)–C(2)–C(3), C(2)–C(3)–C(4), C(4)–C(5)–C(6) and C(5)–C(6)–C(1) is 112·2°. The difference (2·7°) from the pure tetrahedral value (109·5°) is significant and indicates a flattening of the six-membered ring system. The same flattening is also found in dihalogeno-substituted dioxan compounds (Romers & Altona, 1963; Altona & Romers, 1963) and in dioxan and cyclohexane (Davis & Hassel, 1963).

The crystals are composed of layers of molecules parallel to (10$\bar{1}$). The 'plane' of the molecule is approximately perpendicular to the b axis which explains why the smallest index of refraction is found in the direction [010]. The packing is shown in Fig. 5, in which most intermolecular distances smaller than 4·0 Å are indicated by dashed lines. The cleavage character of (10$\bar{1}$) is explained by the few small intermolecular contacts between molecules in subsequent layers. Most van der Waals contacts occur between molecules of the type x, y, z (full lines) and the type $\bar{x}, \frac{1}{2}+y, \bar{z}$ (broken lines) in the same layer. The shortest intermolecular distances are C(1)–O(1′) (3·12 Å), O(1)–C(1′) (3·15 Å) and C(1)–C(1′) (3·20 Å). Several short intermolecular C–O distances have been reported in recent years (Sime & Abrahams, 1960; Chu, Jeffrey & Sakurai, 1962; Romers & Altona, 1963; Altona & Romers, 1963). Those found in this structure account for the fibrous character of the needle-like crystals grown in the **b** direction.

All calculations with exception of the least-squares refinement were performed on the X1 computer of the University of Leiden. We used structure factors and Fourier synthesis programs written in machine code by Mrs E. W. M. Rutten-Keulemans (Rutten, 1963). The reflexion intensities were reduced to structure factors by means of a program written in ALGOL 60 by Mr H. J. V. H. Geise. The program used for calculating the bond distances and bond angles was devised by M. H. L. Jonkers and C. Altona.

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