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The Crystal and Molecular Structure of 1-Cyclohexenyl-1-cyclobutenedione

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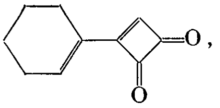
The crystal structure of 1-cyclohexenyl-1-cyclobutenedione,

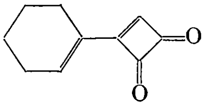


has been determined by the application of the symbolic addition phase determination procedure. The space group is $P2_1/c$ and the cell dimensions are: $a = 11{\cdot}27$, $b = 9{\cdot}30$, $c = 8{\cdot}15$ Å, and $\beta = 96°\,13'$ with $Z = 4$.

Except for two carbon atoms in the cyclohexene ring and the hydrogen atoms, the other ten atoms of the molecules are essentially coplanar. The molecules lie in the ($\bar{2}02$) planes and are packed parallel to each other. One C = O distance is 0·056 Å shorter than the other. The difference in length is probably accounted for by the fact that one C = O bond is part of a conjugated system of single and double bonds.

Introduction

A series of interesting derivatives of cyclobutene have been prepared in recent years (see *e.g.* Smutny, Caserio & Roberts, 1960; Sharts & Roberts, 1961). One of these is cyclohexenylcyclobutenedione,



The X-ray analysis of this material was undertaken to study the effect of the extended conjugated system and the configuration of the cyclobutenedione group. In some previous analyses, for example, four-membered rings were found to be planar as in tetraphenylcyclobutane (Dunitz, 1949), and non-planar, as in C_4F_8 (Lemaire & Livingston, 1952) and C_4Cl_8 (Owen & Hoard, 1951).

After completing this structure determination, we learned of an independent structure study of this compound by Schoomer (1960). His analysis is not yet complete; however, it is evident that the configuration of the molecule and the placement in the unit cell are in agreement in both analyses. We wish to thank Dr R. Marsh of the California Institute of Technology for making Dr Schoomer's results available to us. He has also kindly made available to us, prior to publication, the manuscript on a companion compound, phenylcyclobutenedione (Wong, Marsh & Schomaker, 1964).

Experimental

The material crystallizes in slightly elongated prisms, yellow in color, and sensitive to light, gradually decomposing when exposed to light for a short period of time. Preliminary precession photographs indicated the crystal to be monoclinic, in space group $P2_1/c$. Further precession photographs taken with the crystal mounted on the b axis were used to obtain the unit cell parameters:

$$a = 11{\cdot}27 \pm 0{\cdot}03,\ b = 9{\cdot}30 \pm 0{\cdot}02,\ c = 8{\cdot}15 \pm 0{\cdot}02 \text{ Å},$$
$$\beta = 96°\,13' \pm 10',\ Z = 4\,.$$

The density computed on the basis of four molecules in the unit cell is 1·267 g.cm^{-3}. The density measured by flotation in a solution of silver nitrate is 1·257 g.cm^{-3}.

Intensity data were collected with the Weissenberg equi-inclination method along the b axis. If the crystals were protected from light, they were fairly stable in the X-ray beam. To test for decomposition, a zero layer photograph was taken at the end of the experiment and was found to agree with the original one. There were 1169 independent reflections of which 910 were assigned intensities greater than zero. The intensities were estimated visually with the use of a calibrated film strip. The readings were processed on the IBM 7090 computer (Norment, 1963) to correct for spot size, Lorentz and polarization factors, and to place the data on an absolute scale. The output of the program is in the form of structure factor magnitudes, $|F|$, and normalized structure factor magnitudes, $|E|$, where

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2/\varepsilon \sum_{j=1}^{N} f_{j\mathbf{h}}^2\,. \qquad (1)$$

The $F_{\mathbf{h}}^2$ values in equation (1) are those from which the effects of thermal motion have been removed.

For space group $P2_1/c$, $\varepsilon=1$ except for the $h0l$ and $0k0$ reflections where $\varepsilon=2$, f_j is the atomic scattering factor for the jth atom, and N is the number of atoms in the unit cell.

The distribution of the normalized structure factors $|E|$ is listed in Table 1.

Table 1. *Distribution of the normalized structure factor magnitudes*

	Experimental	Theoretical
$\|E\| > 3$	0·26%	0·3%
$\|E\| > 2$	3·6	5·0
$\|E\| > 1$	29·7	32·0

The theoretical values were computed for a centrosymmetrical crystal with atoms in random positions. Statistical averages for the normalized structure factors are given in Table 2. The experimental values imply that the crystal is centrosymmetric.

Table 2. *Statistical averages for normalized structure factors* $|E|$

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle\|E\|\rangle$	0·781	0·798	0·886
$\langle\|E^2-1\|\rangle$	0·941	0·968	0·736
$\langle\|E^2\|\rangle$	1·018	1·000	1·000

Phase determination

The phases were determined by means of the symbolic addition procedure (Karle & Karle, 1963). To initiate this procedure, three linearly independent reflections were chosen to specify the origin (Hauptman & Karle, 1953). The signs of four other reflections were specified symbolically by a letter. The symbols for these four reflections were specified one at a time as the need arose in the course of the phase determination. The seven reflections forming the basic starting set are given in Table 3. These reflections were chosen on the basis of the large number of interactions obtained from application of the Σ_2 formula and on their relatively high $|E|$ values. The Σ_2 formula is

$$sE_{\mathbf{h}} \sim s\sum_{\mathbf{k}} E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}} \qquad (2)$$

where s means 'sign of'.

Table 3. *Basic starting set for applying the* Σ_2 *formula*

hkl	$\|E\|$	Sign
743	2·94	+
732	2·97	+
$\bar{5}04$	2·61	+
$\bar{4}04$	2·91	*a*
$\bar{2}02$	2·53	*b*
741	2·97	*c*
$\bar{2}34$	2·22	*d*

The probability that a phase determined by Σ_2 is positive is given by (Hauptman & Karle, 1953; Woolfson, 1954)

$$P_+(E_{\mathbf{h}}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{|E_{\mathbf{h}}|\sum_{\mathbf{k}} E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}}{\sqrt{N}}\,. \qquad (3)$$

Hence, the virtue of using reflections with large E magnitudes is apparent. Only those reflections with $|E|>1·5$ were considered. As many terms in Σ_2 as possible were used to determine each phase. In the initial stages a phase was often accepted on the basis of only one or two contributions to Σ_2. However, the probabilities as indicated by equation (3) were always very high, and as the phase determination progressed the phases found in the early stages could be confirmed by additional contributors to Σ_2.

Three particularly strong two-dimensional reflections were used in the basic starting set for applying the Σ_2 formula, the $\bar{4}04$ ($|E|=2·9$), the $\bar{2}02$ ($|E|=2·5$) and $\bar{5}04$ ($|E|=2·6$). Generally, it is advantageous to avoid using two-dimensional data in the initial set of phases, since they seem to be involved in more exceptions to the Σ_2 formula than three-dimensional data. The reason for using them here was the overwhelming number of Σ_2 interactions in which they were involved, probably because the nearly planar molecules lie in the ($\bar{2}02$) planes. These two-dimensional reflections were used primarily in combinations with three-dimensional reflections.

Phases for 132 reflections were determined with Σ_2 as functions of the symbols a, b, c and d. At this point, it was feasible to determine the value (+ or −) of the unknown symbols by the use of other independent phase determining formulae. An application of the Σ_1 relationship for space group $P2_1/c$ (Hauptman & Karle, 1953),

$$sE_{2h,0,2l} \sim s\sum_{k}(-1)^{k+l}(E^2_{hkl}-1)\,, \qquad (4)$$

to the $\bar{4}04$ and the 10,0,6 reflections is shown in Table 4. Note that both positive and negative signs are determined by this Σ_1 relationship directly from the magnitudes of the normalized structure factors and that no previous knowledge of any phases is needed.

The probability formula for Σ_1,

$$P_+(E_{2h,0,2l}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh\frac{|E_{2h,0,2l}|\sum_{k}(-1)^{k+l}(E^2_{hkl}-1)}{2\sqrt{N}}\,, \qquad (5)$$

indicated a probability of 0·97 that the phase of the $\bar{4}04$ reflection is positive and a probability of 0·95 that the phase of the 10,0,6 reflection is negative. The symbolic phases of the $\bar{4}04$ and 10,0,6 reflections are a (originally assigned) and $-a$ (from Σ_2), respectively. From these indications, the symbol a could be assumed to be most probably positive. Similar application of the Σ_1 formula to the $\bar{2}02$ and 12,0,4 reflections gave a probability of 0·77 and 0·82 respec-

Table 4. *Application of the Σ_1 relationship,*
$sE_{2h,02,2l} \sim s \sum_k (-1)^{k+l}(E^2_{hkl}-1)$

$2h,0,2l$	hkl	$(-1)^{k+l}(E^2{}_{hkl}-1)$
404 ($\lvert E\rvert=2{\cdot}91$)	$\bar{2}02$	+5·38
	$\bar{2}12$	+0·37
	$\bar{2}22$	+0·24
	$\bar{2}32$	+0·56
	$\bar{2}42$	−0·73
	$\bar{2}52$	+0·89
	$\bar{2}62$	+1·61
		+8·32
10,0,6 ($\lvert E\rvert=2{\cdot}02$)	513	−0·20
	523	+0·71
	533	−0·95
	545	−7·63
	553	−1·00
	563	−0·49
	573	−0·60
		−10·16

tively, that the symbol *b* is negative. There were no simple relationships from which *c* and *d* could be evaluated. Hence, without using more complex phase determining formulae, such as equation (3·1·2) of Karle & Hauptman (1959), to determine the signs represented by *c* and *d*, four possibilities remained. Of the four possible combinations, where *abcd* are $+-++$, $+-+-$, $+---$ and $+--+$, the first combination proved to be the correct one. It was also the combination which had the fewest inconsistencies in the Σ_2 relationships.

Structure

A preliminary *E* map (a three-dimensional density map with *E* values rather than *F* values for the Fourier coefficients) was computed with the use of only the 132 phases obtained from the phase determining procedure. This map, based on eleven phases per atom, showed clearly the positions of the twelve heavy atoms in the asymmetric unit. The final three-dimensional *F* map containing all the experimental reflections is illustrated in Fig. 1. The drawing is a composite of sections through maximum density projected onto a ($\bar{4}04$) plane, since the molecule is seen most clearly in that direction.

The coordinates of the atoms as read from the initial *E* map were subjected to a least-squares refinement by the ORFLS program (Busing, Martin & Levy, 1962) which has been adapted in our Laboratory to the IBM 7030 (STRETCH). Two cycles with isotropic and two cycles with anisotropic temperature factors and unit weights for all reflections were performed. In the course of this refinement,

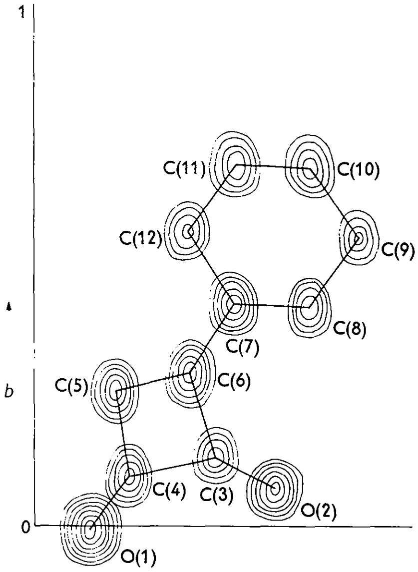


Fig. 1. A composite of sections through maximum density projected onto a ($\bar{4}04$) plane. The contours are equally spaced at 1 e.Å^{-3} and begin with the 2 e.Å^{-3} contour.

Table 5. *Fractional coordinates for cyclohexenylcyclobutenedione*

The thermal parameters are of the form $T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.
Each thermal parameter is multiplied by 10^4

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·0675	−0·0116	0·3421	88	53	213	−20	5	−29
O(2)	0·3042	0·0711	0·5912	117	66	257	−12	−58	−3
C(3)	0·2245	0·1365	0·5083	54	111	119	−2	2	18
C(4)	0·1129	0·0959	0·3896	53	44	130	−27	6	−25
C(5)	0·0949	0·2537	0·3720	44	90	120	−19	−15	−19
C(6)	0·1968	0·2901	0·4764	48	21	110	18	6	−1
C(7)	0·2511	0·4245	0·5275	55	49	128	−2	16	3
C(8)	0·3515	0·4166	0·6347	52	120	128	15	−10	4
C(9)	0·4162	0·5498	0·6972	67	101	241	7	−4	26
C(10)	0·3762	0·6867	0·5988	100	151	230	13	30	7
C(11)	0·2394	0·6920	0·5689	83	113	220	23	−2	44
C(12)	0·1928	0·5627	0·4663	99	58	191	20	13	9
Standard error									
C	0·0008	0·0014	0·0012	8	26	17	11	10	15
O	0·0007	0·0009	0·0010	8	18	16	8	9	11

the R index decreased from 26·4% to 15·0%.* The refined atomic coordinates and temperature factors are listed in Table 5.

Except for C(10) and C(11) in the cyclohexene ring, and the hydrogen atoms, the remaining atoms in the molecule lie essentially in a plane. The equation for the least-squares plane through the cyclobutenedione group is

$$-7{\cdot}1640x+0{\cdot}0133y+6{\cdot}8142z=1{\cdot}8500 \qquad (6)$$

and for all the heavy atoms except C(10) and C(11), the equation is

$$-7{\cdot}1196x+0{\cdot}1138y+6{\cdot}8361z=1{\cdot}8781\,. \qquad (7)$$

Table 6 lists the deviations of the individual atoms from the least-squares planes. In the cyclobutenedione group, the r.m.s. deviation from coplanarity is 0·0063 Å. If four of the atoms from the cyclohexene ring are also included, the r.m.s. deviation from coplanarity is 0·0124 Å. C(10) of the cyclohexene ring is 0·38 Å below and C(11) is 0·38 Å above the plane through the molecule.

The bond distances and angles are illustrated in Fig. 2 and listed in Table 7. The single and double carbon bonds have values consistent with a conjugated system. The double bonds in the two rings are arranged *trans* to each other. The bond connecting the two rings with a value of 1·43 Å is considerably shorter than an ordinary single bond. The two bonds adjacent to the double bond in the cyclobutene ring with values of 1·48 Å are also shorter than ordinary single bonds, though not as short as C(6)–C(7). The values for the bond lengths in the cyclobutene ring, which must be highly strained, are quite normal in contrast to the values of 1·56–1·60 Å for C–C bonds found in cyclobutane and various derivatives of cyclobutane (Dunitz & Schomaker, 1952; Lemaire & Livingston, 1952; Owen & Hoard, 1951). The dimensions of the cyclobutenedione group in the cyclohexyl compound are similar to those found in the phenyl compound (Wong, Marsh & Schomaker, 1964).

Table 6. *Distances of atoms from least-squares planes*

Cyclobutenedione group, equation (6)		All atoms except C(10) and C(11) equation (7)	
Atom	Δ	Atom	Δ
O(1)	−0·0026 Å	O(1)	−0·0214 Å
O(2)	0·0002	O(2)	0·0057
C(3)	0·0071	C(3)	0·0138
C(4)	−0·0034	C(4)	−0·0084
C(5)	0·0084	C(5)	0·0181
C(6)	−0·0097	C(6)	0·0105
		C(7)	−0·0115
		C(8)	0·0056
		C(9)	−0·0133
		C(12)	0·0009

Table 7. *Bond lengths and angles in cyclohexenylcyclobutenedione*

The standard deviations range from 0·012 to 0·018 Å for the bond lengths and 0·8° to 1·2° for the angles

Bond		Angle	
O(1)–C(4)	1·170 Å	O(1)–C(4)–C(3)	141·8°
		O(1)–C(4)–C(5)	133·1
O(2)–C(3)	1·226	O(2)–C(3)–C(4)	136·1
		O(2)–C(3)–C(6)	134·8
C(3)–C(4)	1·547	C(6)–C(3)–C(4)	89·0
C(4)–C(5)	1·486	C(3)–C(4)–C(5)	85·0
C(5)–C(6)	1·395	C(4)–C(5)–C(6)	94·9
C(6)–C(3)	1·480	C(5)–C(6)–C(3)	91·0
C(6)–C(7)	1·433	C(3)–C(6)–C(7)	135·7
		C(5)–C(6)–C(7)	133·3
		C(6)–C(7)–C(8)	116·1
		C(6)–C(7)–C(12)	119·4
C(7)–C(8)	1·354	C(12)–C(7)–C(8)	124·4
C(8)–C(9)	1·499	C(7)–C(8)–C(9)	121·1
C(9)–C(10)	1·546	C(8)–C(9)–C(10)	113·6
C(10)–C(11)	1·536	C(9)–C(10)–C(11)	109·9
C(11)–C(12)	1·525	C(10)–C(11)–C(12)	110·0
C(12)–C(7)	1·504	C(11)–C(12)–C(7)	112·3

The single bonds in the cyclohexene ring are somewhat shorter adjacent to the double bond. The angles near the double bond are greater than 120° and progressively decrease to tetrahedral values at C(10) and C(11).

There is a considerable difference in the two C=O bond lengths, 1·170 and 1·226 Å. It is suggested that C(4)=O(1) is a quinone type bond and that C(3)=O(2) is a ketone type bond. *Tables of Interatomic Distances* (1958) lists the values of 1·15 ± 0·02 (av.) and 1·23 ± 0·01 (av.), respectively, for the values of C=O

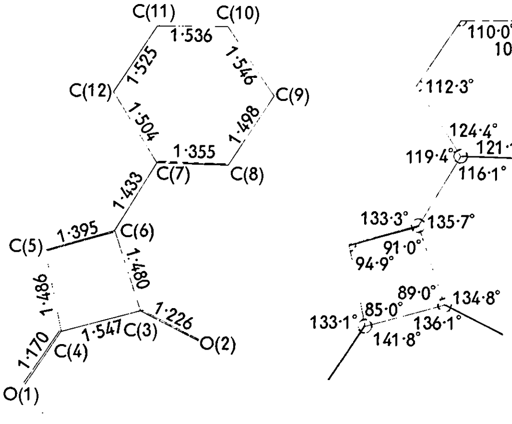


Fig. 2. The bond lengths and angles in cyclohexenylcyclobutenedione. The standard deviations range from 0·012 to 0·018 Å for the bond lengths and 0·8° to 1·2° for the angles.

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* A microfilm containing a list of the computed and observed structure factors has been deposited with the Library of Congress, Washington, D.C., U.S.A. The reel number is 8481.

bonds in various quinones and ketones. The C(4) = O(1) appears to be part of the conjugated system of bonds which traverses both rings.

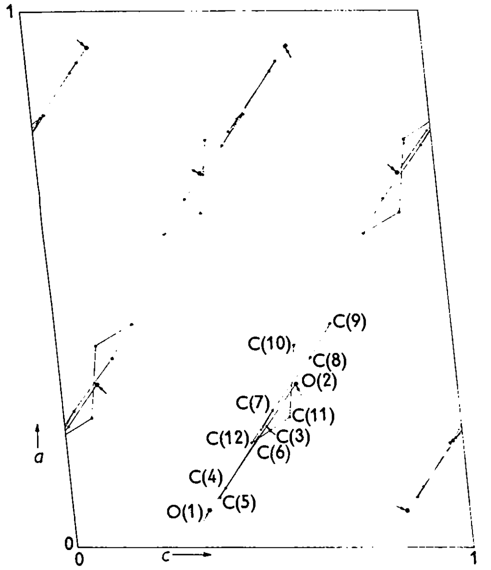

Fig. 3. Projection along the *b* axis of the contents of the unit cell. The small arrows identify the oxygen atoms in each molecule.

Fig. 3 shows a projection along the *b* axis of the contents of the unit cell. The interesting feature is that the nearly planar molecules pack in planes parallel to each other. A similar parallel packing had been observed for *p*-benzoquinone (Robertson, 1935) and phenylcyclobutenedione (Wong, Marsh & Schomaker, 1964). There are many intermolecular distances in the range 3·49–3·57 Å. Two shorter distances occur between molecules which are related by a screw axis. One is 3·43 Å between O(2) and C(9'). The other is 3·23 Å between O(1) and C(5''). It is interesting to note that the C(4) = O(1) bond is directed toward the H atom on C(5''). Similar C–H · · · O distances have been found, *e.g.* in 4,4'-dinitrobiphenyl (Boonstra, 1963).

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