Crystal and Molecular Structure of *o*-Benzoquinone

By **Alistair L. Macdonald** and **James Trotter**,* Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Crystals of the title compound are orthorhombic with a = 6·3137(7), b = 5·7985(5), c = 6·8865(6) Å, space group $P2_12_12$ and required molecular symmetry C_2. The structure was determined from Cu-K_α diffractometer data by trial-and-error methods, and refined with the addition of Mo-K_α data from reflexions outside the accessible copper sphere. Final R factors are 0·029 for 295 reflexions observed with Cu radiation, and 0·039 for all 465 observed reflexions.

The ring adopts a slight boat conformation with the oxygen atoms displaced by 0·036 Å on either side of the mean ring plane. The molecular motion is that of a rigid body and appropriate corrections have been made to the molecular geometry. Final bond lengths are C=O 1·220, C=C 1·341, and C–C 1·552, 1·469, and 1·454 Å.

THE tetrachloro- and tetrabromo-derivatives of *o*-benzoquinone were synthesized[1] some time before the successful isolation of the parent compound.[2] Earlier workers had inferred its presence in solution but failed to recover it[3] and even doubted its possible existence in the solid state.[4] It was prepared by the silver oxide oxidation of catechol as a red, crystalline solid of uncertain melting point which rapidly decomposed in the atmosphere losing its characteristic red colour and becoming black; a colourless, low-temperature form has also been reported.[5,6] Where it has been used as a reagent, as in addition reactions with dienes,[7-9] it is usually prepared *in situ*.

Perhaps because of this instability neither *o*-benzoquinone nor any of its simple derivatives has been the subject of a structural investigation, although the *para*-isomer has been extensively studied.[10-13] The analysis we describe was undertaken to establish the geometry of the molecule, thus providing a basis of comparison for further studies of some of its derivatives.

EXPERIMENTAL

o-Benzoquinone was prepared according to the method described in ref. 7. A solution of *o*-chloroanil (0·4 g) in ether (5 ml) was added to a solution of catechol (0·18 g) in ether (1 ml) and the mixture maintained at −20 °C for 10 min. The dark-red solid obtained was washed with a little cold ether and recrystallised by vacuum sublimation at 40 °C as thick, bright-red plates with well-developed faces, {001} being particularly prominent. The crystals exhibit sharp extinction under crossed Nicols approximately along their face diagonals, which are close to the a and b axes of the unit-cell. No distinct m.p. was observed since the crystals undergo a phase change between 50 and 60°.

Preliminary cell dimensions and space group information were derived from Weissenberg, precession, and rotation photographs, and more accurate cell parameters were determined from a least-squares treatment of the $\sin^2\theta$ values of 25 planes whose reflexion-angles were measured on the diffractometer with Cu-K_α radiation before data collection.

Crystal Data.—$C_6H_4O_2$, M = 108·1. Orthorhombic, a = 6·3137(7), b = 5·7985(5), c = 6·8865(6) Å, U = 252·11(4) Å^3,

---

[1] T. Zincke, *Ber.*, 1887, **20**, 1776.
[2] R. Willstätter and A. Pfannenstiel, *Ber.*, 1904, **37**, 4744.
[3] O. Hinsberg and A. Himmelschein, *Ber.*, 1896, **29**, 2025.
[4] C. L. Jackson and W. Koch, *Amer. Chem. J.*, 1901, **26**, 10.
[5] R. Willstätter and A. Pfannenstiel, *Ber.*, 1908, **41**, 2508.
[6] W. M. Horspool, *Quart. Rev.*, 1969, **23**, 204.
[7] M. F. Ansell, A. F. Gosden, and R. A. Murray, *J. Chem. Soc.* (*C*), 1971, 1401.
[8] J. A. Barltrop and J. A. D. Jeffreys, *J. Chem. Soc.*, 1954, 154.
[9] F. J. Evans, H. S. Wilgus, and J. W. Gates, *J. Org. Chem.*, 1965, **30**, 1665.
[10] J. M. Robertson, *Proc. Roy. Soc.* ,1935, *A*, **150**, 106.
[11] J. Trotter, *Acta Cryst.*, 1960, **13**, 86.
[12] S. M. Swingle, *J. Amer. Chem. Soc.*, 1954, **76**, 1409.
[13] M. Kimura and S. Shibata, *Bull. Chem. Soc. Japan*, 1954, **27**, 163.

$Z = 2$, $D_c = 1{\cdot}424$, $F(000) = 112$. Systematic absences, $h00$ if $h = 2n + 1$, $0k0$ if $k = 2n + 1$; space group $P2_12_12$ (D_2^3, No. 18). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 9·23 cm^{-1}; Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 1·17 cm^{-1}.

The crystals are unstable in air, even in the small volume of air entrapped in a capillary tube (for this reason D_m was not obtained). In order to preserve the crystals during the period of data collection they were coated in the adhesive Araldite used to affix them to the goniometer arcs. The data were collected in two sets. From a crystal of dimensions *ca.* 0·4 × 0·3 × 0·1 mm mounted with *b* parallel to the ϕ axis of a Datex-automated General Electric XRD 6 diffractometer, the intensities of all accessible *hkl* reflexions within the copper sphere ($\theta_{\text{max.}}$ 73°) were measured with Cu-K_α radiation (nickel filter and pulse-height analyser). The scan speed was 1° min^{-1} in 2θ for a θ—2θ scan of range (1·80 + 0·86 tan θ)° in 2θ and the background was measured for 20 s on each side of the scan. The stability of the crystal was monitored by means of a check reflexion measured every 30 reflexions. There was no appreciable drop in the intensity of this standard, all variation being within ±3% of the mean. A reflexion was regarded as 'observed' if $I > 3\sigma(I)$ where $\sigma^2(I) = [S + B + (0{\cdot}03S)^2]$ (S = scan count, B = normalised background count, and $I = S - B$), and on this basis, of the 325 unique reflexions measured, 295 (91%) were significantly above background. Later, Mo-K_α radiation (zirconium filter) and a fresh crystal were used to obtain 354 additional reflexions, θ(Mo) = 26—35°. 170 (48%) of these reflexions were significant. Lorentz and polarisation corrections were applied and the intensities reduced to structure amplitudes. No absorption corrections were made but an empirical correction for extinction was carried out during the refinement process.

Structure Analysis.—There are two molecules in a unit cell having the four-fold space group $P2_12_12$ and each molecule is thus constrained to lie on a two-fold axis. By far the greatest structure factor magnitude is that of the (210) planes and trial calculations indicated that these planes were scattering close to a maximum. In addition, the second order of reflexion from these planes, 420, is also moderately strong and it was initially assumed that all atoms lie on (210). Regular hexagonal geometry and C=O bond lengths of 1·20 Å were assumed and trial *x* and *y* co-ordinates for the four non-hydrogen atoms derived. To position the molecule on the two-fold axis, the strong intensities from (006) and (053) were considered. The spacing of the former set of planes corresponds approximately to that of successive rows of O,O; C,C; *etc.* atoms in the molecule while that of the latter is the diagonal spacing across the ring. With the possible positions thus restricted and from packing considerations trial *z* co-ordinates were found. Structure-factor calculations based on these positions gave an agreement index of 0·26 which fell to 0·124 after four cycles of refinement with isotropic thermal parameters. At this point the hydrogen atom positions were located in a difference electron-density synthesis and were introduced into the refinement. A further four cycles of full-matrix refinement of the positions and anisotropic thermal parameters of the non-hydrogen atoms and the positions and isotropic thermal parameters of the hydrogens led to convergence at R 0·042 for the 295 observed reflexions measured with copper radiation. Two final cycles of refinement with this data set incorporated an empirical extinction correction such that the function minimised was $\Sigma w[F_o - F_c/(1 + gI)]^2$ where g is the extinction parameter and I the uncorrected intensity; R was 0·029.

Combination of the two data sets with refinement of separate scale factors and all other parameters gave a final R of 0·039 for the 465 observed reflexions and led to a reduction in the parameter standard deviations. The final R for all reflexions is 0·062. The weighting scheme used throughout was, $\sqrt{w} = 1{\cdot}0$ for $|F_o| \leqslant F^*$ and $\sqrt{w} = F^*/|F_o|$ for $|F_o| > F^*$, with F^* finally assuming the value 8·0. The final weighted factor, R' ($= \Sigma w\Delta^2/\Sigma w|F_o|^2$) is 0·043 for the observed data and 0·048 for all data. Atomic scattering factors were taken from ref. 14. In the final refinement cycle all parameter shifts were zero and the final positional and vibrational parameters refined with all data are given in Tables 1 and 2. A list of calculated and observed structure factors is contained in Supplementary Publication No. SUP 20627 (9 pp., 1 microfiche).*

TABLE 1

Final fractional co-ordinates (x, y, $z \times 10^4$) with standard deviations in parentheses

	x	y	z
C(1)	4319(2)	3897(3)	5670(2)
C(2)	3746(3)	2918(3)	7556(2)
C(3)	4384(3)	3950(3)	9189(2)
O(1)	3760(2)	3060(2)	4135(2)
H(2)	2880(33)	1546(37)	7566(29)
H(3)	3989(30)	3377(35)	10,410(28)

TABLE 2

Vibrational parameters. Upper values are those derived from the structure analysis while the lower are those calculated for rigid-body motion (in Å^2 × 10^4 with standard deviations in parenthesis)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	392(7)	427(8)	271(6)	4(9)	−16(6)	−17(7)
	397(7)	416(7)	272(7)	4(7)	−9(7)	−7(7)
C(2)	515(9)	483(9)	330(7)	−65(12)	8(8)	37(8)
	511(7)	489(7)	324(7)	−67(7)	13(7)	42(7)
C(3)	504(9)	579(10)	272(7)	−9(12)	22(7)	59(8)
	505(7)	577(7)	270(7)	−10(7)	25(7)	48(7)
O(1)	579(8)	534(7)	310(5)	−75(10)	−38(5)	−59(6)
	581(7)	541(7)	317(7)	−73(7)	−40(7)	−58(7)

	U_{iso}
H(2)	579(57)
H(3)	536(54)

Thermal Motion Analysis.—The effects of thermal vibration on the measured molecular geometry may be eliminated if rigid-body motion is assumed for the molecule.[15a] To test the validity of such an assumption for *o*-benzoquinone a least-squares comparison of the derived anisotropic thermal parameters (Table 2; Figure 1) with those expected for such motion was carried out using a program due to Trueblood.[15b] With the molecular centre of mass as origin the tensors of librational and translational motion with respect to the crystal axes were derived and are given in Table 3. The corresponding calculated U_{ij}

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[14] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[15] (*a*) D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757; (*b*) V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, *B*24, 63.

values are compared with the ' observed ' values in Table 2; the root-mean-square deviation is 0·0006 Å^2, indicating that the rigid-body approximation is valid.

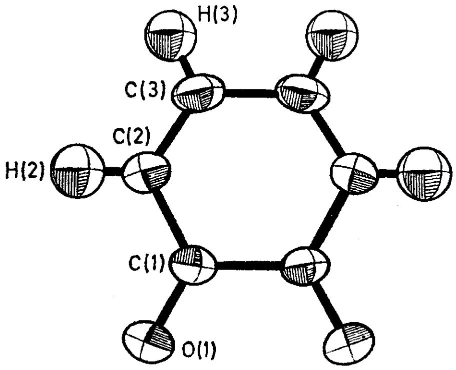

FIGURE 1 Projection of the thermal ellipsoids on the mean molecular plane. The ellipsoids enclose 50% probability

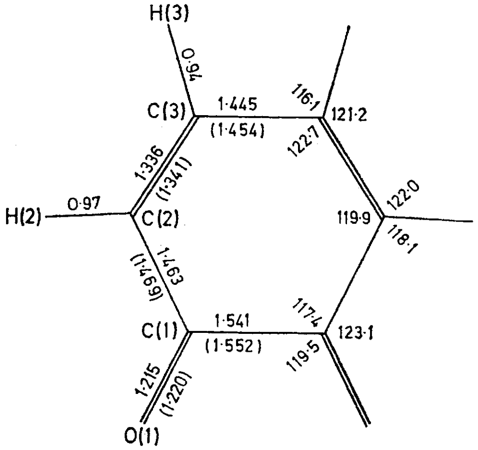

FIGURE 2 Bond lengths and angles. Standard deviations are 0·002 Å and 0·1° except for C(1)–C(1^{I}) 0·003, C(3)–C(3^{I}) 0·004, C–H 0·02 Å, and C–C–H, 1·0°. Values in parentheses are corrected for thermal motion. The corresponding corrected angles do not differ from those shown

The principal axes of translational motion are almost coincident with those of the molecule. That of smallest amplitude (0·158 Å) is along the direction of the two fold axis and the others (0·202 and 0·180 Å) lie within 6° of the molecular plane and the plane normal respectively. The largest librational amplitude (5·8°) occurs around the two-fold axis, but the axes of smaller amplitude deviate from the molecular axes by 20°. However, as the motion in these directions is fairly isotropic (root-mean-square components of 3·3 and 3·9°), the principal axes are probably not significantly displaced from the molecular axes. The components of the correlation tensor S are negligible. Corrections to the molecular geometry are included in Figure 2.

TABLE 3

Components of molecular translational ($T_{ij} \times 10^4$ Å^2) and librational (R_{ij} in deg.^{2}) tensors referred to the crystal axes, with standard deviations in parentheses

	11	22	33	12	13	23
T	341(6)	391(4)	251(3)	34(5)	0(7)	0(7)
R	13·6(5)	12·4(6)	33·9(1·4)	1·9(5)	0(2·3)	0·(23)

Principal axes of T (Å) and R (deg.) and their direction cosines

T	0·202	0·4535	0·8913	0·0
	0·180	0·8913	−0·4535	0·0
	0·158	0·0	0·0	−1·0
R	5·8	0·0	0·0	−1·0
	3·9	0·8088	0·5881	0·0
	3·3	0·5879	−0·8089	0·0

DISCUSSION

The final electron-density distribution in the mean ring plane, with all atoms including hydrogen clearly resolved, and the crystal structure as viewed along the b axis are shown in Figures 3 and 4; the latter also shows the atom numbering used in the analysis.

The molecules lie on the two-fold axes parallel to c and the tilt of the molecular plane to (010) is 56° 41′. In projection along c the molecules are seen to adopt a ' staggered herringbone ' type of packing, *i.e.* layers of molecules at 0, b, $2b$, *etc.*, are interspaced by screw-related layers at $x/2$ ($b/2$, $3b/2$, *etc.*). In the corresponding ' end-on ' view of the *para*-isomer the molecules are arranged in parallel rows.[10]

Small, but significant, deviations from planarity are observed in the molecule. The equation of the best, least-squares plane through the ring atoms (X, Y in Å) is $0{\cdot}8357X - 0{\cdot}5492Y = 1{\cdot}0461$ and χ^2 ($= \Sigma\Delta^2/\sigma^2$) is 109·9. The displacements of the atoms from this plane are: C(1) −0·0082(15), C(2) 0·0013(19), C(3) 0·0091(18), and O(1) −0·0364(13) Å, with the symmetry-related atoms displaced in the opposite directions. The ring has,

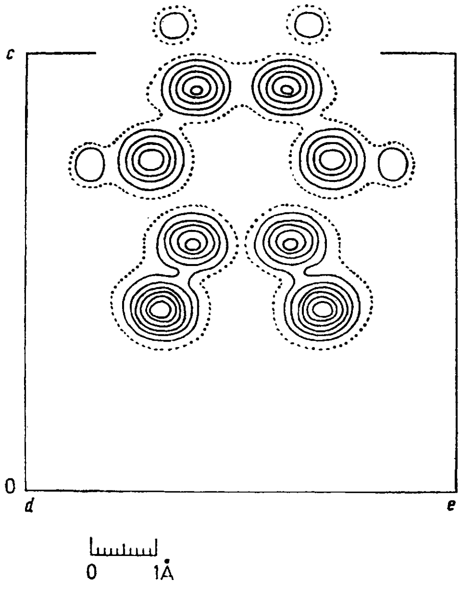

FIGURE 3 A section of the final electron-density distribution through the mean plane of the molecule. The vertical lines at d and e are the intersections of the mean plane with successive (010) planes. Contours are at intervals of 2 eÅ^{-3}, starting from 2 eÅ^{-3} except for the hydrogen atoms which are represented by the one-electron contour. The zero contour is shown as a broken line

therefore, adopted a slight twisted-boat conformation. Presumably the deviations of the oxygen atoms from the ring plane arise as a result of steric repulsion, since the O(1) · · · H(2) and O(1) · · · O(1^{I}) distances [2·58(2) and 2·757(3) Å] are both less than the sum of the appropriate van der Waals radii and, in addition, O(1) is involved in several short intermolecular contacts. The small displacements of C(1) and C(3) may then be explained as being due to a slight buckling of the ring as a result of these interactions. C(1) is displaced in the same direction as O(1) while C(3) is displaced in the opposite direction. In benzocyclobutenedione,[16] cyclohexenylbutenedione,[17] and phenylcyclobutenedione,[18] where the geometry is such as to allow the oxygen atoms to be more than 3·0 Å apart, planarity of the cyclobutenedione system is observed. In contrast the oxygen atoms are significantly displaced from the ring plane in catechol.[19] However, alloxan[20] and the nitranilate anion[21] have also been found to be planar.

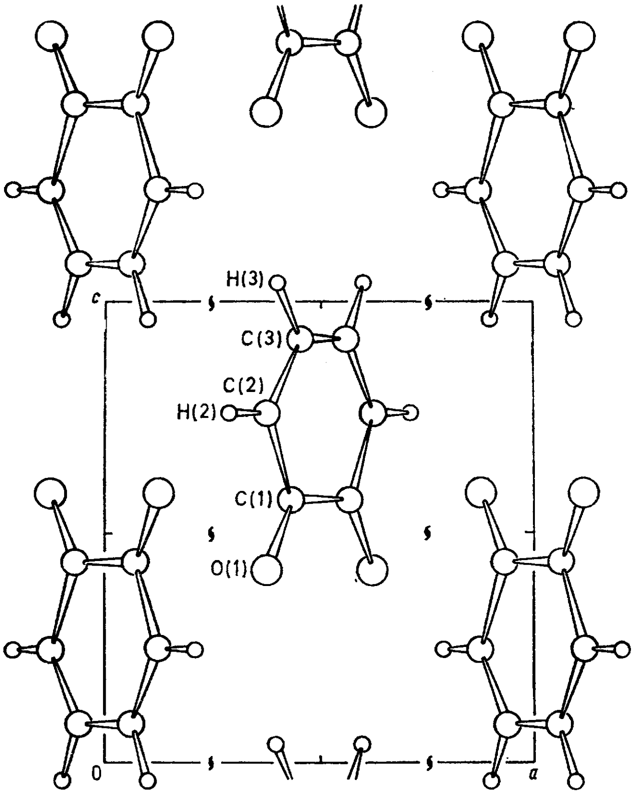

FIGURE 4 Projection of the structure along the *b* axis (*b* into the paper) with atom numbering as used in the analysis

Bond lengths, before and after correction for thermal motion, and valency angles are shown in Figure 2. The C(1)–C(1^{I}) bond (1·552 Å) is yet another example of an abnormally long bond between (approximately) trigonally hybridised carbon atoms. It is similar in length to the bonds between the diketonic groups mentioned earlier and to that in oxalic acid[22] and its derivatives, and is much longer than the 1·48—1·51 Å normally accepted for C(sp^2)–C(sp^2) bonds. The lengthening cannot simply be a result of steric interaction, since it is found equally in planar and non-planar molecules.[23]

TABLE 4

Bond lengths between trigonally hybridised carbon atoms

Molecule	C–C	C=C
trans-Hexa-1,3,5-triene [a]	1·458(2)	1·337(2) [term.]
cis-Hexa-1,3,5-triene [b]	1·462(2)	1·336(3) [term.]
Cyclohexa-1,3-diene [c]	1·465(2)	1·348(1)
Butadiene [d]	1·463(3)	1·341(2)
Ethylene [e]		1·337(2)
Mean	1·462(2)	1·340(2)
o-Benzoquinone [f]	1·469(2) 1·454(4)	1·341(2)

[a] Ref. 24. [b] Ref. 25. [c] Ref. 26. [d] Ref. 27. [e] Ref. 28. [f] This work.

Otherwise the molecular dimensions are normal. Table 4 lists some bond lengths[24-28] between trigonally hybridised carbon atoms as determined by electron diffraction with those of *o*-benzoquinone for comparison. C(1)–C(2) is longer by 0·015 Å than C(3)–C(3^{I}) and the difference can be attributed to a greater electron localisation in the C=O bond than in C=C as a result of the electronegativity of the oxygen. A similar difference was noted in a comparison of the single-bond lengths in acrolein and butadiene.[27] The C=O bond length (1·220 Å) is the same as that found in *p*-benzoquinone[11] and is a normal ketone length.

TABLE 5

(*a*) Intramolecular, non-bonded distances (Å) *

O(1) · · · O(1^{I})	2·693(3) [2·757] †	H(2) · · · H(3)	2·33(3)
		H(3) · · · H(3^{I})	2·27(4)
O(1) · · · H(2)	2·58(2)		

(*b*) Intermolecular contacts <3·4 Å

O(1) · · · H(2^{II})	2·56(2)	C(1) · · · H(2^{II})	3·04(2)
O(1) · · · H(3^{III})	2·58(2)	C(3) · · · H(2^{VII})	3·05(2)
O(1) · · · H(2^{VI})	2·86(2)	C(3) · · · H(2^{VIII})	3·15(2)
O(1) · · · C(1^{IV})	3·028(2)	C(8) · · · H(3^{VIII})	3·22(2)
O(1) · · · C(1^{V})	3·102(2)	C(3) · · · H(3^{VII})	3·35(2)

† Corrected for thermal motion.

* Here and elsewhere, Roman numerals denote the following equivalent positions:

I $1 - x, 1 - y, z$
II $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
III $x, y, -1 + z$
IV $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
V $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$
VI $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
VII $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$
VIII $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$

---

[16] F. H. Allen and J. Trotter, *J. Chem. Soc.* (*B*), 1970, 916.

[17] I. L. Karle, K. Britts, and S. Brenner, *Acta Cryst.*, 1964, **17**, 1506.

[18] C.-H. Wong, R. E. Marsh, and V. Schomaker, *Acta Cryst.*, 1964, **17**, 131.

[19] C. J. Brown, *Acta Cryst.*, 1966, **21**, 170.

[20] W. Bolton, *Acta Cryst.*, 1964, **17**. 147.

[21] G. B. Jensen and E. K. Anderson, *Acta Cryst.*, 1964, **17**, 243.

[22] R. G. Delaplane and J. A. Ibers, *Acta Cryst.*, 1969, *B*, **25**, 2423.

[23] J. H. Robertson, *Acta Cryst.*, 1965, **18**, 410.

[24] M. Traetteberg, *Acta Chem. Scand.*, 1968, **22**, 628.

[25] M. Traetteberg, *Acta Chem. Scand.*, 1968, **22**, 2294.

[26] M. Traetteberg, *Acta Chem. Scand.*, 1968, **22**, 2305.

[27] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, 1968, **1**, 463.

[28] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, 1965, **42**, 2683.

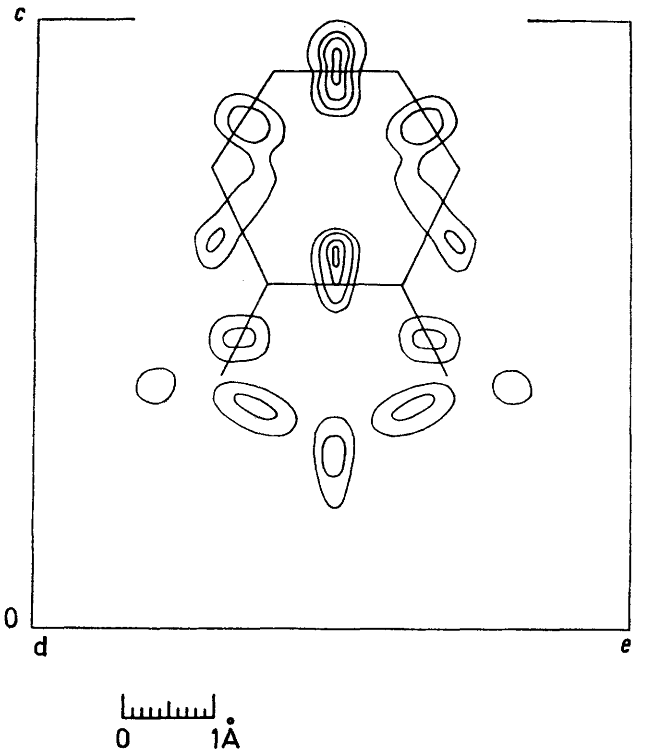

FIGURE 5 A section of the final electron-density difference synthesis through the mean molecular plane. Contours are at intervals of 0·05 $e\text{Å}^{-3}$ starting from 0·05 $e\text{Å}^{-3}$

As expected, the mean value of the angles in the ring is 120° but the angles at C(1) and C(3) are significantly different from this value. The angles found are the same as in butadiene [C=C–C 123·3(5)°] and in acrolein [C–C=O 124·0(7)°].[27]

Some intramolecular distances and the shortest intermolecular contacts are listed in Table 5. As already discussed the short contacts involving O(1) are responsible for the non-planarity of the molecule.

Residual Electron Density.—A final electron-density difference synthesis was calculated with the contributions from all atoms subtracted out and all positive peaks in the resulting map $>0·05$ $e\text{Å}^{-3}$ are shown in Figure 5. The estimated standard deviation in the electron density [29] is 0·04 $e\text{Å}^{-3}$. It is plausible to attribute the residual peaks to bonding electrons and to the density associated with the lone-pair electrons of the sp^3 hybridised oxygen atoms. Such features, which demonstrate the inadequacy of the spherical-atom approximation, have become more prominent with the increased precision of *X*-ray measurements and reflect the need for aspherical form factors in accurate analyses. Where such have been used the observed effects are much reduced.[30]

We thank Dr. L. Weiler for assistance in preparation of the crystals, the University of British Columbia Computing Centre for assistance, and the National Research Council of Canada for financial support.

[2/2234 *Received, 25th September*, 1972]

---

[29] D. W. J. Cruickshank, *Acta Cryst.*, 1949, **2**, 154.
[30] H. H. Cady and A. C. Larson, *Acta Cryst.*, 1965, **18**, 485.