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A Three-Dimensional Analysis of the Crystal Structure of *p*-Benzoquinone

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A three-dimensional refinement of the crystal structure of *p*-benzoquinone has proceeded by computing observed and calculated differential syntheses, and an initial discrepancy factor of 22·5% has been reduced, after one isotropic and four anisotropic cycles, to 12·4%. The thermal motions of the atoms have been interpreted in terms of the anisotropic translational and rotational oscillations of the molecule, and the final molecular dimensions have been compared with the results of an electron-diffraction investigation of the vapour, with the dimensions of similar molecules, and with theoretical values.

1. Introduction

The crystal structure of *p*-benzoquinone was determined by X-ray diffraction methods in 1935 (Robertson, 1934, 1935); an approximate structure was deduced by trial-and-error methods, and refinement of the atomic positional parameters proceeded by computing successive Fourier projections along the three principal crystallographic axes. In even the best of these projections, that along the *c*-axis, only two of the four carbon and oxygen atoms in the asymmetric unit were separately resolved, and this, together with the fact that the number of reflexions observed in each zone was rather small, suggested that the atomic parameters could be considered as only approximately correct. Robertson points out that, owing to this overlapping of atoms in projection, the measured values of the molecular dimensions are not certain to within a few degrees in valency angle or a few hundredths of an Ångström unit in bond length, but that the distortion of the ring out of the regular hexagon structure which pertains in truly aromatic compounds is quite definite. This distortion can be observed directly, without measurement, on one of the electron-density maps.

The structure of vaporized *p*-benzoquinone has been examined more recently by electron-diffraction techniques (Swingle, 1954), and the molecular dimensions obtained in this investigation are compared in Table 1 with those measured by the X-ray diffraction study of the crystalline material (Fig. 1 shows the labelling of the atoms used throughout this paper). In both investigations the general features of molecular structure observed are similar, the molecule being completely planar, and the bond lengths and valency angles indicating that the six-membered ring deviates significantly from the regular, hexagonal arrangement found in benzene and its derivatives. The two sets of results differ in the lengths assigned to the carbon–oxygen bond (1·14 and 1·23 Å) and in the *A–B–C* valency angle (109 and 116°). In the X-ray investigation, however, the positions of those atoms which were not separately resolved in the Fourier projections were chosen assuming that this valency angle had the tetrahedral value, and if this assumption is incorrect then the measured bond lengths will of course be slightly in error. Another electron-diffraction investigation has also been reported (Kimura & Shibata, 1954), this study yielding molecular dimensions which are almost identical with those given by the X-ray analysis. It was assumed initially, however, that the

Table 1. *Bond lengths* (Å) *and valency angles in p-benzoquinone*

Bond or angle	Robertson (1935)	Swingle (1954)	Kimura & Shibata (1954)	Trotter (1957)
A–B	1·50	1·49	1·52	1·49
A–C′	1·32	1·32	1·31	1·30
B–D	1·14	1·23	1·15	1·19
A–B–C	109°	116°	110°	113°

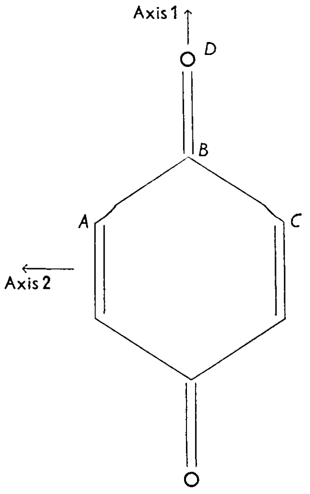

Fig. 1. *p*-Benzoquinone.

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carbon–oxygen distance is 1·14 Å, so that the results (included in Table 1) are strongly dependent on this unjustifiable assumption.

Some further refinement of Robertson's (1935) two-dimensional data has been carried out using $(F_o - F_c)$ syntheses, leading to a significant improvement in the agreement between observed and calculated structure factors (Trotter, 1957); the final molecular dimensions from this investigation are listed in the final column of Table 1. These values agree more closely with Swingle's electron-diffraction results, and indeed, considering the accuracy of each investigation (about ±0·03 Å in bond length and ±3° in valency angle), the two sets of measurements do not differ significantly. However, a new X-ray investigation using three-dimensional methods would be very useful, and would allow the molecular dimensions to be determined with greater precision. The present communication describes such an investigation. A recent analysis of the crystal structure of benzene (Cox, Cruickshank & Smith, 1958) has shown that, in determining accurate bond lengths by the X-ray method, it is important to make an allowance in the refinement process for the effects of anisotropic thermal motions of the atoms, and to correct the measured bond lengths for an apparent shortening due to rotational oscillation of the molecule about axes passing through its centre. In the present analysis of the *p*-benzoquinone structure a complete anisotropic refinement has been carried out, accurate molecular dimensions have been obtained, and the thermal vibrations of the carbon and oxygen atoms have been interpreted in terms of the anisotropic translational and rotational oscillations of the molecule.

2. Crystal data

In attempting to redetermine the lattice constants with more precision than in the previous X-ray investigations, it was found that the usual single-crystal methods using black-reflexion techniques did not give reliable results because of displacement of reflexions from their ideal positions due to distortions in the crystals (see § 3 below), and an effort was made to obtain more accurate results from powder photographs. Excellent powder diagrams were obtained with Cu $K\alpha$, Co $K\alpha$ and Cr $K\alpha$ radiations using a conventional powder camera of diameter 114·6 mm. There was not, however, a sufficient number of well-resolved back-reflexion lines to apply the usual extrapolation methods in which the systematic errors in d values are taken proportional to $\cos^2\theta$ (the Cr $K\alpha$ photographs were considerably weaker than those with the other radiations, so that the number of measurable back-reflexion lines was small even with chromium radiation). The methods were extended to a wider range of θ values by taking the errors proportional to $\frac{1}{2}\,[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$, and the best values of the unit-cell parameters a, b, c and β were obtained by the least-squares method (Cohen, 1935, 1936; Azároff & Buerger, 1958) using the measured θ values of all the diffraction lines which could be unambiguously indexed.

For the monoclinic system the $\sin^2\theta$ equation, expressed in terms of the reciprocal cell dimensions, is

$$\sin^2\theta = A_0h^2 + B_0k^2 + C_0l^2 + D_0hl$$

where

$$A_0 = \tfrac{1}{4}\lambda^2a^{*2},\quad B_0 = \tfrac{1}{4}\lambda^2b^{*2},$$
$$C_0 = \tfrac{1}{4}\lambda^2c^{*2},\quad D_0 = \tfrac{1}{4}\lambda^2 . 2a^*c^* . \cos\beta^* .$$

Taking the systematic errors in the d values proportional to $\frac{1}{2}\,[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$, it can be shown that the errors in $\sin^2\theta$ are proportional to this expression multiplied by $\sin^2\theta$. Letting δ be 10 times this latter expression (the factor 10 being introduced to make the δ values more nearly equal to the other terms involved, thus facilitating computation), taking D as the proportionality constant, and allowing for random observational errors, we write for each diffraction line,

$$A_0h_i^2 + B_0k_i^2 + C_0l_i^2 + D_0hl + D\delta_i - \sin^2\theta_i = \varepsilon_i\ .$$

Equating to zero the first derivatives of $\Sigma\varepsilon_i^2$ with respect to A_0, B_0, C_0, D_0 and D, five simultaneous equations (the normal equations) are obtained, and these may be solved for the five unknowns, and the unit-cell parameters then calculated from A_0, B_0, C_0 and D_0. Hess (1951) has shown that a different weighting of the individual measurements in the least-squares analysis gives more correct results, and this method too was applied. The best values of the lattice constants obtained lead to the following crystal data (the standard deviations, σ, of the unit-cell parameters being determined from the least-squares formulae). The density was measured by flotation in aqueous potassium iodide solution. As the crystals slowly dissolved in this flotation medium, a solution of approximately the correct density was prepared with one crystal, and a fresh crystal was introduced just before the final adjustment was made. The mean of several determinations was 1·320 g.cm.$^{-3}$, close to the value quoted by Robertson (1·318 g.cm.$^{-3}$).

p-Benzoquinone, $C_6H_4O_2$; molecular weight = 108·1; melting point = 115·7 °C.

Monoclinic prismatic,

a = 7·055 Å	$\sigma(a)$ = 0·004 Å
b = 6·795	$\sigma(b)$ = 0·004
c = 5·767	$\sigma(c)$ = 0·004
β = 101° 28′	$\sigma(\beta)$ = 1·6′

Volume of the unit cell = 270·97 Å^3.

Density, calculated (with two molecules per unit cell) = 1·325 g.cm.$^{-3}$, measured = 1·320 g.cm.$^{-3}$.

Absorption coefficient for X-rays, λ = 1·542 Å, μ = 9·81 cm.$^{-1}$.

Total number of electrons per unit cell = $F(000)$ = 112.

Absent spectra: $h0l$ when h is odd; $0k0$ when k is odd.

Space group is C_{2h}^5–$P2_1/a$.

Molecular symmetry-centre.

3. Intensity measurements

Single-crystals of *p*-benzoquinone suitable for recording the intensity data were obtained from the walls and neck of a bottle which had been unopened for a few months. The crystals, which had been deposited by sublimation, were stout prisms elongated along the *b*-axis. They were very volatile and tended to twist or bend very readily, so that great care was necessary in mounting a specimen for recording the X-ray data. To preserve the crystals during the X-ray exposures they were sealed in thin-walled Lindemann-glass capillaries. A number of crystals were mounted and examined by taking a few setting photographs before one sufficiently free from strain to give suitable X-ray photographic records was obtained.

The intensities of the hkl reflexions were recorded on moving-film exposures for a crystal rotating about the *b*-axis, using Cu $K\alpha$ radiation. Layers with $k = 0 \rightarrow 6$ were recorded, the equi-inclination method being used for the non-equatorial levels. The multiple-film technique (Robertson, 1943) was used to correlate strong and weak reflexions, and the range of intensities measured was about 20,000 to 1, the estimates being made visually. To correlate the various layers, $hk0$ and $0kl$ precession films were taken using Mo $K\alpha$ radiation, with multiple exposures for intensity correlation. The crystal which was used for all these photographs had a uniform cross-section, and no absorption corrections were applied.

Of 619 reflexions within the Cu $K\alpha$ sphere, 58 have $k = 7$ or 8, and these have not been recorded on the Weissenberg films, since they lie outside the observable range for a crystal rotating about the *b*-axis in the conventional Weissenberg goniometer. Their intensities are likely to be small (no reflexions with $k = 7$ or 8 were visible on the precession films) and any effect of their omission on the process of refinement will be apparent in greater series-termination corrections for the y-coordinates than for the x- and z-parameters. Of the remaining 561 reflexions, 337 have been observed.

The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, Lorentz and polarization factors being applied, together with the rotation factors appropriate to equi-inclination Weissenberg photographs (Tunell, 1939). The scale of the observed structure factors was adjusted at each stage of the refinement so that $\Sigma|F_o| = \Sigma|F_c|$; the values of the measured structure amplitudes, on a scale derived by comparison with the final set of F_c, are listed in Table 2. An estimate of the accuracy of these F_o values can be made by comparing the two independent values for those reflexions measured by Robertson (1935) and in the present investigation. After adjusting the scale of Robertson's amplitudes by comparison with the present values, the discrepancy between the two sets of measurements, expressed as

$$\frac{\Sigma\big||F_{\text{Present}}| - |F_{\text{Robertson}} \times 1{\cdot}07|\big|}{\Sigma|F_{\text{Present}}|} \times 100\%$$

was 9·5%, 1·9% of this value being due to $20\bar{1}$, which is apparently reduced by extinction in Robertson's measurement. The accuracy of the F_o measured in the present investigation is probably then about 7–8%; these values of F_o have been used throughout this analysis.

4. Refinement of positional and thermal parameters

The positional and temperature parameters of the carbon and oxygen atoms determined by Trotter (1957) were taken as a starting point for the three-dimensional refinement; structure factors were calculated for all the observed reflexions, no contribution being included from the hydrogen atoms at this stage. McWeeny's (1951) scattering factor was used for the carbon atoms, corrected for thermal vibration as usual by the factor $\exp\left[-B\,(\sin^2\theta/\lambda^2)\right]$, with $B = 4{\cdot}9$ Å^2 for atoms A and C, and $3{\cdot}5$ Å^2 for atom B. For the oxygen atom (D) McWeeny's curve, $(f^{\text{II}} + 2f^{\perp})/3$, was used with $B = 6{\cdot}0$ Å^2. The value of R, the usual discrepancy factor, was 22·5%.

Refinement then proceeded by computing observed and calculated differential syntheses, a new set of atomic coordinates being obtained from the corrections of the F_o synthesis, combined with the back-shift (series-termination) corrections from the F_c synthesis. The values of the isotropic temperature factors were altered to minimize the differences between the observed and calculated peak densities. Recalculation of the structure factors revealed that R had been reduced, but only to 21·0%.

A second set of observed and calculated differential syntheses was computed, and further small changes made in the positional parameters. The values of the six second derivatives ($\partial^2\varrho/\partial x^2$, $\partial^2\varrho/\partial x\partial y$ etc.) of the observed and calculated electron densities at the atomic positions indicated that the thermal motions of the carbon and oxygen atoms were strongly anisotropic, and further refinement required that allowance be made for this effect. For each carbon and oxygen atom the isotropic temperature factor was therefore replaced by the term

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

depending on six parameters, b_{ij}, which are different for each atom, and are related to the components of the mean-square vibration tensor (Cruickshank, 1956*a*). The criterion for determining the six b_{ij}'s for an atom is to require that the six second derivatives of the observed and calculated electron densities be equal at the atomic position (Cochran, 1951). In the structure

Table 2. *Measured and calculated structure factors*

hkl	F_o	F_c
001	28·3	+30·5
002	33·4	−34·7
003	13·5	−14·8
004	1·2	+1·7
005	2·1	−3·2
006	2·5	−4·3
007	<0·8	+0·7
$20\bar{7}$	1·0	−1·7
$20\bar{6}$	1·2	−2·0
$20\bar{5}$	<1·3	−0·5
$20\bar{4}$	6·2	−7·2
$20\bar{3}$	19·1	−16·9
$20\bar{2}$	13·8	+11·9
$20\bar{1}$	69·1	+68·0
200	30·8	+29·5
201	30·9	−30·3
202	16·9	−17·4
203	1·7	+2·9
204	2·0	−3·0
205	4·6	−6·6
206	<1·0	+0·4
$40\bar{7}$	<0·8	−0·8
$40\bar{6}$	<1·2	−0·8
$40\bar{5}$	3·2	−2·8
$40\bar{4}$	6·1	−5·0
$40\bar{3}$	4·4	+3·0
$40\bar{2}$	21·1	+20·5
$40\bar{1}$	15·2	+12·7
400	11·9	−11·2
401	9·7	−10·1
402	<1·2	+0·8
403	1·4	−2·0
404	4·1	−5·8
405	<1·0	−0·2
$60\bar{6}$	<0·9	−0·9
$60\bar{5}$	<1·1	−1·2
$60\bar{4}$	<1·3	+0·8
$60\bar{3}$	6·1	+5·1
$60\bar{2}$	5·9	+4·2
$60\bar{1}$	2·8	−2·1
600	3·9	−3·8
601	<1·3	−0·8
602	<1·3	−1·0
603	2·0	−2·9
604	<0·8	−0·4
$80\bar{4}$	0·6	+1·1
$80\bar{3}$	0·8	+1·2
$80\bar{2}$	<1·0	−0·3
$80\bar{1}$	0·9	−1·1
800	0·7	−0·6
801	<0·9	−0·5
802	<0·6	−0·9
011	20·0	−20·1
012	2·2	+1·6
013	11·4	+12·3
014	0·8	+1·8
015	<0·8	−1·0
016	<0·7	+0·7
017	<0·4	−0·1
$11\bar{7}$	0·4	−0·6
$11\bar{6}$	0·6	−0·9
$11\bar{5}$	<0·7	−0·6
$11\bar{4}$	2·3	−3·6
$11\bar{3}$	3·7	−4·6
$11\bar{2}$	0·5	+0·6
$11\bar{1}$	20·4	+18·8
110	23·1	+22·5
111	<0·4	+1·9
112	5·9	−5·8
113	4·5	−6·2
114	<0·7	−1·4
115	<0·8	−1·0
116	0·8	−1·0
117	<0·4	+0·8
$21\bar{7}$	<0·5	−0·4
$21\bar{6}$	<0·7	0
$21\bar{5}$	0·6	−0·8
$21\bar{4}$	2·9	−4·7
$21\bar{3}$	0·9	−1·3
$21\bar{2}$	11·1	+10·0
$21\bar{1}$	0·7	0
210	18·1	−16·4
211	1·0	−0·1
212	14·9	+14·2
213	1·9	+3·1
214	0·8	−1·9
215	0·8	+1·2
216	<0·6	+0·4
$31\bar{7}$	<0·5	−0·5
$31\bar{6}$	<0·7	−0·2
$31\bar{5}$	<0·8	−1·3
$31\bar{4}$	2·1	−2·5
$31\bar{3}$	0·9	−0·5
$31\bar{2}$	11·0	+7·0
$31\bar{1}$	13·6	+11·0
310	1·3	+2·1
311	3·6	−3·9
312	3·6	−5·3
313	<0·7	−1·5
314	<0·8	−0·7
315	1·0	−1·1
316	<0·4	+0·7
$41\bar{7}$	<0·4	−0·2
$41\bar{6}$	<0·6	−0·3
$41\bar{5}$	<0·8	−0·9
$41\bar{4}$	<0·8	−0·4
$41\bar{3}$	1·5	+2·2
$41\bar{2}$	0·7	−0·1
$41\bar{1}$	4·4	−5·8
410	<0·6	−0·9
411	4·7	+7·0
412	2·0	+2·8
413	<0·8	−0·9
414	0·7	+1·1
415	<0·6	+0·7
$51\bar{6}$	<0·6	−0·3
$51\bar{5}$	0·7	−1·0
$51\bar{4}$	0·7	−0·5
$51\bar{3}$	2·0	+2·2
$51\bar{2}$	4·5	+4·1
$51\bar{1}$	0·8	+1·0
510	2·2	−2·0
511	2·2	−2·5
512	<0·8	−0·7
513	<0·8	−0·4
514	0·8	−1·0
515	<0·4	+0·4
$61\bar{6}$	<0·4	−0·1
$61\bar{5}$	<0·6	0
$61\bar{4}$	<0·7	+0·2
$61\bar{3}$	<0·8	−0·2
$61\bar{2}$	0·9	−1·2
$61\bar{1}$	<0·8	−0·5
610	1·2	+1·7
611	1·1	+1·4
612	<0·8	+0·3
613	0·6	+0·8
614	<0·4	+0·4
$71\bar{5}$	<0·5	−0·2
$71\bar{4}$	<0·6	+0·6
$71\bar{3}$	1·0	+1·4
$71\bar{2}$	<0·7	+0·4
$71\bar{1}$	0·8	−0·8
710	0·7	−0·9
711	<0·7	−0·2
712	<0·6	−0·2
713	<0·4	−0·5
$81\bar{4}$	<0·4	−0·1
$81\bar{3}$	<0·5	−0·2
$81\bar{2}$	<0·6	−0·2
$81\bar{1}$	<0·6	+0·2
810	<0·6	+0·4
811	<0·5	+0·4
812	<0·3	+0·5
020	22·2	−20·1
021	12·1	−12·6
022	<0·5	+1·3
023	2·0	+3·0
024	5·4	+5·3
025	4·9	+4·9
026	<0·8	−0·1
027	1·1	−1·9
$12\bar{7}$	<0·5	+0·4
$12\bar{6}$	2·0	−2·4
$12\bar{5}$	3·3	−3·3
$12\bar{4}$	2·3	+2·7
$12\bar{3}$	6·1	+6·0
$12\bar{2}$	6·0	−7·1
$12\bar{1}$	11·5	−12·5
120	12·1	+12·0
121	9·9	+10·3
122	8·0	−8·5
123	4·3	−5·2
124	6·3	+5·4
125	4·3	+4·7
126	0·7	−0·6
$22\bar{7}$	<0·5	−0·3
$22\bar{6}$	2·0	+2·5
$22\bar{5}$	3·5	+4·0
$22\bar{4}$	1·7	+2·2
$22\bar{3}$	0·7	+0·2
$22\bar{2}$	6·3	−6·8
$22\bar{1}$	13·5	−12·9
220	10·3	−10·2
221	0·9	+0·5
222	1·5	+2·6
223	4·5	+5·1
224	6·9	+6·4
225	<0·8	+0·7
226	2·5	−2·6
$32\bar{7}$	0·5	−0·9
$32\bar{6}$	1·1	−1·3
$32\bar{5}$	<0·8	+0·7
$32\bar{4}$	2·4	+2·1
$32\bar{3}$	1·7	−2·1
$32\bar{2}$	6·8	−5·3
$32\bar{1}$	4·1	+4·6
320	6·4	+5·8
321	6·3	−5·5
322	4·0	−4·5
323	5·6	+5·0
324	5·1	+5·5
325	0·8	−0·5
326	2·0	−2·6
$42\bar{7}$	<0·4	+0·8
$42\bar{6}$	1·9	+1·9
$42\bar{5}$	1·1	+1·2
$42\bar{4}$	1·0	−0·4
$42\bar{3}$	3·4	−2·6
$42\bar{2}$	4·3	−4·1
$42\bar{1}$	3·8	−4·2
420	1·9	−1·0
421	<0·7	+1·2
422	4·3	+3·7
423	5·3	+5·3
424	<0·8	+1·0
425	2·5	−2·4
$52\bar{6}$	<0·6	+0·1
$52\bar{5}$	<0·8	+0·6
$52\bar{4}$	<0·8	−0·3
$52\bar{3}$	1·2	−1·3
$52\bar{2}$	<0·8	+0·7
$52\bar{1}$	1·3	+1·4
520	2·0	−1·9
521	1·4	−1·8
522	2·7	+2·7
523	3·4	+3·8
524	<0·7	0
525	<0·4	−2·0
$62\bar{6}$	<0·5	+0·5
$62\bar{5}$	<0·7	−0·2
$62\bar{4}$	0·8	−0·8
$62\bar{3}$	0·8	−1·0
$62\bar{2}$	1·0	−1·3
$62\bar{1}$	1·4	−1·0
620	<0·8	+0·3
621	2·3	+2·1
622	3·3	+2·9
623	<0·7	+0·5
624	1·2	−1·5
$72\bar{5}$	<0·5	0
$72\bar{4}$	<0·7	−0·2
$72\bar{3}$	<0·8	0
$72\bar{2}$	<0·8	+0·1
$72\bar{1}$	<0·8	−0·5
720	<0·8	−0·4
721	0·9	+1·0
722	1·6	+1·6
723	<0·4	+0·2
$82\bar{4}$	<0·4	−0·2
$82\bar{3}$	<0·6	−0·3
$82\bar{2}$	<0·6	−0·4
$82\bar{1}$	<0·6	+0·2
820	0·7	+0·8
821	1·2	+1·1
031	8·1	+8·0
032	3·9	−2·8
033	6·7	−5·7
034	<1·0	−0·6
035	1·6	+1·9
036	<0·8	+0·5
$13\bar{7}$	<0·4	−2·1
$13\bar{6}$	<1·0	+0·1
$13\bar{5}$	9·2	+8·2
$13\bar{4}$	11·2	+10·5
$13\bar{3}$	4·9	−4·4
$13\bar{2}$	18·5	−16·8
$13\bar{1}$	1·3	−1·0
130	<0·5	+0·3
131	21·6	−21·1
132	9·3	−9·0
133	15·1	+14·4
134	15·7	+13·1
135	<1·0	+0·5
136	3·8	−3·6
$23\bar{7}$	<0·4	−0·3
$23\bar{6}$	<0·9	−0·9
$23\bar{5}$	<1·1	+0·4
$23\bar{4}$	3·2	+2·9
$23\bar{3}$	2·4	+1·8
$23\bar{2}$	4·6	−4·2

Table 2 (*cont.*)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
$23\bar{1}$	0·7	−0·5	045	<0·9	+0·5	$74\bar{4}$	<0·6	−0·1	$65\bar{4}$	<0·7	−0·6
230	6·7	+6·6	046	1·3	−1·2	$74\bar{3}$	<0·7	+0·2	$65\bar{3}$	<0·9	−0·1
231	2·4	−1·8	$14\bar{6}$	<0·7	+0·3	$74\bar{2}$	<0·8	+0·4	$65\bar{2}$	1·1	+1·1
232	7·1	−6·2	$14\bar{5}$	2·0	+2·3	$74\bar{1}$	<0·8	+0·2	$65\bar{1}$	1·1	+0·9
233	<1·0	−1·0	$14\bar{4}$	<1·0	+1·0	740	<0·8	−0·4	650	<1·0	−0·5
234	2·7	+2·5	$14\bar{3}$	1·5	−1·9	741	1·0	−1·0	651	1·1	−1·1
235	<1·0	+0·7	$14\bar{2}$	2·2	+1·9	742	<0·4	−0·6	652	<0·7	−0·1
236	<0·7	−0·5	$14\bar{1}$	2·8	+3·1	$84\bar{2}$	<0·3	−0·2	$75\bar{3}$	<0·5	+0·8
$33\bar{6}$	3·3	+3·5	140	2·2	−2·7	$84\bar{1}$	<0·4	0	$75\bar{2}$	<0·7	+0·5
$33\bar{5}$	5·0	+5·1	141	2·0	−2·6				$75\bar{1}$	<0·7	−0·1
$33\bar{4}$	<1·0	−0·6	142	2·6	+3·2	051	5·8	+7·2	750	<0·7	−0·8
$33\bar{3}$	8·2	−7·1	143	1·0	−0·5	052	2·0	+2·5	751	<0·3	−0·7
$33\bar{2}$	2·4	−2·3	144	4·7	−4·1	053	3·2	−3·1			
$33\bar{1}$	0·8	−0·3	145	<0·9	−1·1	054	2·0	−2·3	060	9·7	+9·6
330	14·1	−12·3	146	0·9	+1·1	055	<1·0	+0·5	061	2·1	+4·0
331	7·8	−7·4	$24\bar{6}$	<0·8	+0·3	056	<0·5	+0·4	062	2·6	−3·4
332	11·2	+11·0	$24\bar{5}$	1·8	+2·0	$15\bar{6}$	<0·6	−0·6	063	2·9	−3·3
333	12·4	+12·9	$24\bar{4}$	1·5	+1·5	$15\bar{5}$	1·8	−2·0	064	<0·9	−1·1
334	<1·0	+1·0	$24\bar{3}$	1·5	−1·4	$15\bar{4}$	3·1	−3·5	065	0·7	−1·1
335	4·8	−4·1	$24\bar{2}$	2·2	−2·0	$15\bar{3}$	<1·1	−1·0	$16\bar{5}$	0·8	−0·9
$43\bar{6}$	<0·8	+0·1	$24\bar{1}$	0·9	+0·4	$15\bar{2}$	3·6	+3·6	$16\bar{4}$	<0·9	+0·8
$43\bar{5}$	1·1	+1·0	240	1·8	−1·8	$15\bar{1}$	2·9	+4·1	$16\bar{3}$	<1·0	+0·9
$43\bar{4}$	1·1	+0·7	241	2·0	−2·4	150	3·4	+4·2	$16\bar{2}$	2·5	−2·9
$43\bar{3}$	1·1	−1·2	242	2·4	+1·9	151	5·6	+4·9	$16\bar{1}$	2·0	−3·3
$43\bar{2}$	<0·9	−0·3	243	3·4	+3·6	152	<0·9	−0·4	160	2·0	+3·1
$43\bar{1}$	3·0	+2·7	244	<1·0	+0·8	153	4·7	−5·0	161	2·2	+3·6
430	1·0	−0·5	245	1·6	−1·4	154	3·1	−3·0	162	<0·9	−1·1
431	3·8	−3·6	246	<0·3	−1·0	155	<0·9	−0·7	163	<1·0	−1·2
432	1·2	−1·1	$34\bar{6}$	0·8	+0·8	$25\bar{6}$	<0·6	−0·2	164	<0·9	+1·4
433	1·2	+1·8	$34\bar{5}$	<0·9	+0·8	$25\bar{5}$	1·0	+1·1	165	<0·5	+0·9
434	<1·0	+0·7	$34\bar{4}$	<1·0	−0·4	$25\bar{4}$	1·8	+1·7	$26\bar{5}$	<0·8	−0·9
435	<0·7	−0·5	$34\bar{3}$	<0·9	+0·2	$25\bar{3}$	1·3	−1·4	$26\bar{4}$	1·9	−2·1
$53\bar{6}$	1·2	+1·8	$34\bar{2}$	1·3	+1·1	$25\bar{2}$	4·2	−4·7	$26\bar{3}$	2·0	−2·3
$53\bar{5}$	<0·9	+0·3	$34\bar{1}$	1·1	−0·6	$25\bar{1}$	<0·8	−0·4	$26\bar{2}$	2·1	+2·5
$53\bar{4}$	2·1	−2·0	340	1·0	−1·0	250	6·7	+6·1	$26\bar{1}$	7·4	+7·5
$53\bar{3}$	1·9	−1·6	341	1·9	+2·2	251	3·5	+2·9	260	3·6	+4·1
$53\bar{2}$	1·2	−1·0	342	0·9	−0·3	252	3·6	−3·1	261	2·5	−2·8
$53\bar{1}$	4·7	−4·4	343	5·0	−4·2	253	3·6	−2·9	262	2·0	−3·5
530	3·6	−3·1	344	1·1	−1·6	254	1·1	+0·7	263	<0·9	−1·1
531	4·4	+5·0	345	1·3	+1·2	255	<0·8	+0·7	264	<0·8	−1·1
532	9·5	+7·7	$44\bar{6}$	<0·6	+0·9	$35\bar{6}$	<0·5	−0·9	$36\bar{5}$	<0·7	+0·4
533	1·0	+1·4	$44\bar{5}$	<0·8	+0·7	$35\bar{5}$	1·2	−1·6	$36\bar{4}$	<0·9	+0·4
534	2·9	−2·9	$44\bar{4}$	<1·0	−0·6	$35\bar{4}$	<1·1	−1·0	$36\bar{3}$	1·5	−1·5
$63\bar{5}$	<0·8	+0·2	$44\bar{3}$	1·4	−1·0	$35\bar{3}$	1·3	+1·4	$36\bar{2}$	2·2	−2·1
$63\bar{4}$	<0·9	−0·2	$44\bar{2}$	<0·9	+0·2	$35\bar{2}$	3·3	+2·9	$36\bar{1}$	1·1	+1·6
$63\bar{3}$	<1·0	−0·1	$44\bar{1}$	<0·9	−0·7	$35\bar{1}$	3·5	+3·4	360	2·8	+2·7
$63\bar{2}$	<1·1	+0·7	440	1·6	−1·5	350	3·4	+3·4	361	<1·0	−0·6
$63\bar{1}$	<1·1	0	441	1·0	+0·9	351	<1·0	−0·2	362	<1·0	−1·1
630	1·4	−1·3	442	2·4	+2·7	352	4·5	−4·2	363	0·9	+1·3
631	<1·0	−0·7	443	<1·0	+1·0	353	3·6	−3·0	364	<0·7	+1·1
632	<0·9	+0·7	444	1·5	−1·1	354	<0·9	−0·6	$46\bar{4}$	<0·8	−1·0
623	<0·8	+0·5	445	<0·4	−1·0	355	<0·4	−0·2	$46\bar{3}$	0·9	+1·0
$73\bar{5}$	<0·5	−0·4	$54\bar{5}$	<0·8	0	$45\bar{5}$	<0·8	+0·6	$46\bar{2}$	4·1	+3·7
$73\bar{4}$	<0·8	−0·6	$54\bar{4}$	<0·9	−0·2	$45\bar{4}$	1·0	−0·6	$46\bar{1}$	2·6	+2·7
$73\bar{3}$	<0·9	−0·6	$54\bar{3}$	<1·0	0	$45\bar{3}$	2·0	−2·0	460	1·1	−1·2
$73\bar{2}$	1·1	−1·3	$54\bar{2}$	<1·0	+0·3	$45\bar{2}$	<1·1	−0·3	461	2·2	−2·4
$73\bar{1}$	0·9	−0·9	$54\bar{1}$	<1·0	+0·4	$45\bar{1}$	3·6	+3·2	462	<0·9	−1·0
730	1·7	+1·6	540	<1·0	+0·7	450	2·0	+2·0	463	<0·8	−0·9
731	3·2	+3·0	541	1·0	−0·6	451	1·9	−1·7	$56\bar{4}$	<0·6	−0·5
732	<0·8	+0·9	542	2·9	−2·5	452	2·2	−2·3	$56\bar{3}$	<0·8	−0·8
$83\bar{3}$	<0·6	+0·2	543	0·8	−1·2	453	<1·0	+0·2	$56\bar{2}$	<0·9	+0·5
$83\bar{2}$	<0·7	0	544	0·7	+0·7	454	<0·7	+0·6	$56\bar{1}$	0·9	+1·2
$83\bar{1}$	0·7	−0·3	$64\bar{5}$	<0·6	−0·1	$55\bar{5}$	<0·7	−0·5	560	<0·9	−0·1
830	<0·7	−0·3	$64\bar{4}$	<0·8	−0·3	$55\bar{4}$	<0·9	+0·2	561	<0·8	−0·6
831	<0·4	+0·2	$64\bar{3}$	<0·9	0	$55\bar{3}$	1·1	+1·3	562	0·9	+0·6
			$64\bar{2}$	<0·9	−0·2	$55\bar{2}$	2·4	+2·0	$66\bar{3}$	<0·5	+1·3
040	1·5	+0·4	$64\bar{1}$	<1·0	−0·7	$55\bar{1}$	1·6	+1·6	$66\bar{2}$	0·9	+1·2
041	2·4	−2·5	640	<0·9	+0·2	550	<1·1	−0·3	$66\bar{1}$	<0·7	−0·2
042	2·5	−2·3	641	1·1	+1·3	551	2·0	−2·2	660	0·9	−1·1
043	2·9	+2·2	642	<0·8	+0·8	552	2·2	−1·8	661	<0·6	−0·8
044	2·6	+3·3	643	0·7	−0·6	553	<0·8	−0·5			

analyses of anthracene (Cruickshank, 1956*d*, 1957*a*), naphthalene (Cruickshank, 1957*b*) and benzene (Cox, Cruickshank & Smith, 1958), the b_{ij}'s were refined by solving on an electronic computer sets of sixth-order linear equations which relate the differences in the second derivatives to the changes in the b_{ij}'s (Cruickshank, 1956*a*), but the necessary programmes for these computations were not readily available to us. In the first anisotropic cycle therefore, the b_{ij}'s were adjusted by trial (starting with values corresponding to isotropic motion as a first approximation) to make the observed and calculated curvatures equal, and in subsequent cycles more accurate corrections could be estimated from the changes in the second derivatives produced by the trial changes in b_{ij}.

This procedure is not strictly accurate for the oxygen atom, for which the electron-density distribution is not spherically-symmetrical for the atom at rest, apart from any thermal anisotropy (McWeeny, 1951). At the beginning of the anisotropic refinement, the ratios of observed to calculated values of $\partial^2\varrho/\partial y^2$ and $\partial^2\varrho/\partial z^2$ were approximately unity for all the atoms. For $\partial^2\varrho/\partial x^2$, however, the ratios were 0·89 for the carbon atoms and 0·77 for the oxygen atom. From the values of $f^{\parallel}$ and $f^{\perp}$ for oxygen we calculated that the ratio of minimum to maximum curvature, apart from thermal anisotropy, is about 0·87, and (since $0·89 \times 0·87 = 0·77$) it appears that the lower value of the ratio of observed to calculated values of $\partial^2\varrho/\partial x^2$ for oxygen in comparison with the carbon atoms is due to this real asymmetry of the oxygen atom. We did not, however, make any allowance for the difference between $f^{\parallel}$ and $f^{\perp}$, but simply used the spherically-symmetrical scattering factor, and included all the anisotropy in the temperature parameters. In interpreting the thermal vibrations of the atoms, it must be remembered then that we have overestimated the thermal anisotropy of the oxygen atom.

Hydrogen atoms were included in the structure-factor calculations at the stage of the first anisotropic cycle, coordinates (Table 3) being obtained by assuming that they lie on the diagonals of the ring with C–H distances of 1·08 Å. McWeeny's (1951) scattering factor curve for hydrogen was used, with an isotropic temperature factor ($B = 5·5$ Å^2). Refinement proceeded

Table 3. *Assumed hydrogen fractional coordinates*

Atom	x	y	z
H_A	+0·1868	−0·0459	+0·4094
H_C	−0·0812	+0·3270	−0·1929

Table 4. *Variation of R during the refinement*

	R (%)
Initial coordinates	22·5
Isotropic cycle	21·0
1st anisotropic cycle	17·0
2nd anisotropic cycle	15·7
3rd anisotropic cycle	13·0
4th anisotropic cycle	12·4

Table 5. *Observed and calculated peak heights and curvatures in the 4th anisotropic cycle*

	ϱ		ϱ_{xx}		ϱ_{xy}		ϱ_{xz}		ϱ_{yy}		ϱ_{yz}		ϱ_{zz}	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	6·53	6·47	−42·80	−42·90	−0·21	−0·45	1·30	2·64	−39·77	−41·64	1·17	0·82	−53·80	−53·53
B	6·86	6·73	−45·36	−44·58	−1·58	−1·17	3·78	4·87	−48·03	−48·77	−2·47	−2·17	−54·14	−52·92
C	6·30	6·12	−40·47	−39·09	−0·69	−0·81	5·13	6·05	−44·30	−43·93	0·09	−0·62	−46·22	−44·41
D	7·50	7·44	−37·57	−37·65	−4·92	−3·81	−1·18	0·63	−49·54	−49·26	−8·94	−7·61	−51·62	−50·33

Table 6. *Observed and calculated U_{ij}*

(Values in 10^{-2} Å^2)

	U_{11}		U_{12}		U_{13}		U_{22}		U_{23}		U_{33}	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	6·36	6·20	−1·38	−1·20	0·80	0·99	5·34	5·03	1·47	1·24	8·76	8·77
B	4·76	5·52	−0·55	−0·85	0·90	0·98	4·84	5·71	1·04	1·26	7·74	7·75
C	5·87	6·20	−0·77	−0·50	1·11	1·00	5·32	5·03	1·64	1·25	8·53	8·54
D	6·44	5·52	−0·71	−0·85	1·14	0·98	8·07	7·85	1·29	1·31	12·82	12·84

by computing successive observed and calculated differential syntheses, and adjusting the positional and temperature parameters of the carbon and oxygen atoms at each stage. The variation of the discrepancy factor, R, during the refinement process is shown in Table 4, the final value being 12·4%. The values of the observed and calculated peak electron-densities and curvatures in the differential syntheses of the fourth anisotropic cycle are listed in Table 5 (where $\varrho_{xx}=\partial^2\varrho/\partial x^2$, $\varrho_{xy}=\partial^2\varrho/\partial x\partial y$ etc.). The values of b_{ij} were of course adjusted slightly to minimize the differences between observed and calculated values before the final structure factors were computed. The mean coordinate shift in the final cycle was 0·0026 Å, and the maximum shift 0·0036 Å; the mean series-termination correction was 0·014 Å, and maximum 0·017 Å, the corrections in the y-coordinates being of the same order of magnitude as those in the x- and z-coordinates, so that the effect of omitting planes with $k=7$ and 8 is negligible.

The final measured and calculated structure factors are listed in Table 2.

We did not compute any three-dimensional (F_o-F_c) syntheses, but a final $hk0$ difference map revealed only one significant feature—a trough of 0·4 e.Å^{-2} at the centre of the six-membered ring.

5. Description of the anisotropic thermal motion

The final set of anisotropic thermal parameters b_{ij} for the carbon and oxygen atoms were taken as those determined after the fourth anisotropic cycle. The b_{ij}'s for each atom were then transformed to symmetric tensors **U**, such that

$$\overline{u^2}=\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}l_il_j$$

is the value of the mean-square oscillation in Å^2 in a direction $\mathbf{l}=(l_1, l_2, l_3)$ (Cruickshank, 1956*a*). These tensors were referred, not to the crystallographic axes, but to the natural molecular axes: axis 1 passing through the centre of the molecule and through atom B, axis 2 through the mid-point of AC', and axis 3 normal to the mean molecular plane. The transformation of the b_{ij}'s to the U_{ij}'s was carried out in two stages: the b_{ij}'s were first transformed to **U** tensors referred to crystal axes a', b and c, where a' is perpendicular to b and c (Rollett & Davies, 1955), and ordinary orthonormal tensor transformations were then used for the change to the molecular axes. The values of the six independent U_{ij}'s for each carbon and oxygen atom are listed in Table 6 in the columns headed 'Obs.'. The terms U_{11}, U_{22} and U_{33} give directly the values of u^2 parallel to the molecular axes.

The anisotropic thermal motion may be analysed in terms of the rigid-body vibrations of the molecule (Cruickshank, 1956*b*). The vibrations can be expressed in terms of the symmetric tensors **T**, giving the anisotropic translational vibrations of the mass centre, and $\boldsymbol{\omega}$, the anisotropic angular oscillations about axes through the centre. The **T** and $\boldsymbol{\omega}$ tensors for *p*-benzoquinone, determined by least squares from the four **U** tensors, are given in Table 7. The r.m.s. amplitudes of translational oscillation in the directions of the molecular axes, obtained from the square roots of the diagonal elements of **T** are 0·24, 0·22 and 0·24 Å respectively. The corresponding r.m.s. amplitudes of angular oscillation obtained from $\boldsymbol{\omega}$ are 7·3°, 5·8° and 3·7°. As pointed out in § 4, these values are a slight overestimate of the thermal vibration.

Table 7. *Values of T_{ij}* (in 10^{-2} Å^2) *and ω_{ij} (in degrees^2)*

$$\mathbf{T}=\begin{pmatrix}5·52 & -0·85 & 0·98\\ & 4·85 & 1·24\\ & & 5·68\end{pmatrix}\qquad \boldsymbol{\omega}=\begin{pmatrix}52·52 & -2·29 & -0·34\\ & 33·76 & -0·30\\ & & 14·01\end{pmatrix}$$

Conversely, given the **T** and $\boldsymbol{\omega}$ tensors, the **U** tensors for each atom may be calculated. The resulting values of U_{ij} are listed in Table 6 in the columns headed 'Calc.'. The r.m.s. difference between the $U_{ij}^{\text{obs.}}$ and the $U_{ij}^{\text{calc.}}$ is 0·0036 Å^2. This corresponds to an estimated standard deviation for $U_{ij}^{\text{obs.}}$ of $0·0036\times(24/12)^{\frac{1}{2}}=0·0051$ Å^2, allowing for the fact that 12 parameters have been determined from $24U_{ij}^{\text{obs.}}$. The resulting e.s.d.'s of the elements of **T** and $\boldsymbol{\omega}$, given by least-squares formulae using the e.s.d. of $U_{ij}^{\text{obs.}}$, are shown in Table 8 in positions corresponding to those of the elements in Table 7.

Table 8. *Values of $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$*

$$\sigma(\mathbf{T})=\begin{pmatrix}0·26 & 0·25 & 0·33\\ & 0·34 & 0·34\\ & & 0·75\end{pmatrix}\qquad \sigma(\boldsymbol{\omega})=\begin{pmatrix}16·22 & 7·18 & 8·53\\ & 4·79 & 3·06\\ & & 2·94\end{pmatrix}$$

Within experimental error the principal axes of **T** and $\boldsymbol{\omega}$ coincide with the molecular axes. The r.m.s. amplitudes of translational vibration along the three molecular axes do not differ significantly, but there are significant differences in the angular oscillations about the three axes. The largest angular oscillation is that about axis 1, and the smallest that about the

Table 9. *Coordinates of the carbon and oxygen atoms*

Atom	x	y	z	X'	Y	Z'	Standard deviations (Å)			
							$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	r.m.s. σ
A	0·1069	−0·0272	0·2334	+0·7388	−0·1850	+1·1961	0·0054	0·0064	0·0053	0·0057
B	0·0638	0·1703	0·1341	+0·4414	+1·1571	+0·6841	0·0051	0·0053	0·0053	0·0052
C	−0·0459	0·1848	−0·1095	−0·3173	+1·2559	−0·5671	0·0057	0·0058	0·0062	0·0059
D	0·1182	0·3168	0·2502	+0·8175	+2·1523	+1·2769	0·0062	0·0052	0·0055	0·0056

plane normal. The large values of the e.s.d.'s of the ω_{ij} are a consequence of the small distances of the atoms from the molecular axes, especially axis 1.

6. Coordinates, molecular dimensions and orientation

The final coordinates of the carbon and oxygen atoms obtained from the differential syntheses of the fourth anisotropic cycle are listed in Table 9; x, y, z are fractional coordinates referred to the crystal axes, and X', Y, Z' are coordinates in Å units referred to the orthogonal axes a', b, c. The bond lengths and valency angles in the *p*-benzoquinone molecule, calculated from these coordinates, are given in Table 10, together with the values obtained by Robertson (1935) and Trotter (1957)—both these latter sets being given to 0·001 Å in bond length and 1′ in valency angle for comparison purposes, although their accuracy is of course not as good as this. The new bond lengths and valency angles show some quite large differences from those of Robertson (1935); the mean coordinate difference is 0·09 Å and the maximum 0·12 Å, the largest change in a bond length being 0·08 Å in the carbon-oxygen bond. The differences between the new values and those of Trotter (1957) are smaller, but still fairly large; the mean coordinate difference is 0·05 Å, the maximum 0·07 Å, and the largest change in a bond length about 0·03 Å. There are no significant differences between the new values for chemically equivalent bond lengths and valency angles, and the mean values are given in the second column of Table 11.

Table 10. *Bond lengths and valency angles*

Bond or angle	Robertson (1935)	Trotter (1957)	Present analysis
A–B	1·499 Å	1·499 Å	1·467 Å
B–C	1·498	1·481	1·467
A–C′	1·320	1·303	1·312
B–D	1·140	1·189	1·218
A–B–C	109° 35′	113° 26′	117° 40′
C′–A–B	125 13	124 15	120 58
B–C–A′	125 11	122 10	121 22
A–B–D	125 13	124 21	121 00
C–B–D	125 09	121 49	121 20

Slight corrections are necessary to allow for the angular oscillations, which cause the atoms to appear to close to the centre of the molecule (Cruickshank, 1956*c*). The radial error in the position of an atom is given by

$$\frac{1}{2r}\left(\frac{s^2}{1+s^2/q^2}+\frac{t^2}{1+t^2/q^2}\right)$$

where s^2 and t^2 are the two mean-square amplitudes of vibration of the atom in the angular oscillations, q^2 is the Gaussian peak-width parameter for an atomic peak without the angular oscillations, and r is the distance from the centre. Using the magnitudes of the angular oscillations obtained in § 5 from the analysis of the anisotropic thermal motion, and an approximate value of q^2, the increases in the radial distances of the atoms are: atoms A and C, 0·0108 Å; atom B, 0·0090 Å; and atom D, 0·0130 Å. The effect of these corrections is to increase the lengths of the carbon–carbon bonds by about 0·010 Å and of the carbon–oxygen bond by about 0·004 Å, but to leave the angles virtually unaltered. The corrected mean bond lengths and valency angles are shown in the third column of Table 11, and also in Fig. 2. Since we have overestimated the thermal anisotropy of the oxygen atom, the corrections applied are possibly a little too large.

Table 11. *Mean bond lengths and valency angles*

Bond or angle	Mean without rotational correction	Mean with rotational correction	E.s.d.
A–B (C–C)	1·467 Å	1·477 Å	0·006 Å
A–C′ (C=C)	1·312	1·322	0·008
B–D (C=O)	1·218	1·222	0·008
A–B–C (C–C–C)	117° 40′	117° 48′	37′
C′–A–B (C=C–C)	121 10	121 06	27
A–B–D (C–C=O)	121 10	121 06	27

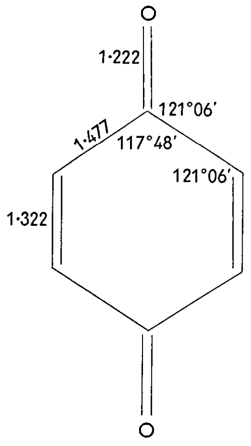


Fig. 2. Final bond lengths and valency angles.

The standard deviations of the coordinates of the carbon and oxygen atoms, estimated using $|F_o - F_c|$ as an estimate of $\sigma(F)$ (Cruickshank, 1949), are included in Table 9. The corresponding e.s.d.'s of the mean bond lengths and valency angles are given in the final column of Table 11.

The best plane through the carbon and oxygen atoms, derived by the least-squares method is

$$0{\cdot}85224X' - 0{\cdot}01527Y - 0{\cdot}52292Z' = 0\ .$$

The direction cosines of the molecular axes referred to the orthogonal axes are

axis 1:	+0·3120	+0·8178	+0·4835
axis 2:	+0·4207	−0·5740	+0·7025
axis 3:	+0·8522	−0·0153	−0·5229

The corresponding direction angles are

axis 1:	71° 49′	35° 08′	61° 05′
axis 2:	65° 07′	125° 02′	45° 22′
axis 3:	31° 33′	90° 53′	121° 32′

These values differ by at most 1·9° from those given by Robertson (1935) and by a maximum of 1·0° from those given by Trotter (1957).

The deviations of the atoms from the mean plane are

A	+0·0070	*C*	+0·0070
B	+0·0008	*D*	−0·0039

These deviations are not significant for, on two degrees of freedom (Weatherburn, 1947),

$$\chi^2 = \Sigma\Delta^2/\sigma^2 = 113{\cdot}85 \times 10^{-6}/(0{\cdot}0056)^2 = 3{\cdot}63\ .$$

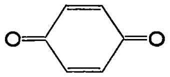
7. Discussion

The *p*-benzoquinone molecule is completely planar within the limits of experimental error, the maximum deviation from the mean plane being only 0·007 Å. The molecular dimensions measured by the present investigation are in very good agreement with those of the more reliable of the electron-diffraction investigations (Swingle, 1954), the values being

C−C	= 1·49 Å from E.D.	1·477 Å from X-ray
C=C	= 1·32	1·322
C=O	= 1·23	1·222
C−C−C	= 116°	117° 48′

Indeed the agreement is so good that it would appear that the electron-diffraction investigator was unduly pessimistic about the accuracy of his results.

The measured length of the C–C bond (1·477 Å) is very close to the value in butadiene (1·483 Å). The C=C bond (1·322 Å), however, is 0·015 Å less than the corresponding bond length in butadiene (1·337 Å) and 0·017 Å less than the bond length in ethylene (1·339 Å), and since these differences are about double the estimated standard deviation they are possibly significant, and indeed almost in the region of 'highly significant'. Simple molecular orbital calculations give values of 1·46 Å and 1·35 Å for the two bonds (Goodwin & Vand (1955) have suggested that a reliable C–C bond order–bond length curve can be obtained by assuming that the C–C distance in *p*-benzoquinone is 1·485 Å—which is close to the measured value). There is no doubt that the C=C double bond is very significantly shorter than 1·35 Å. More up-to-date molecular orbital methods would suggest a C=C length only a little greater than the value in ethylene, but as pointed out above the measured distance is possibly shorter than even this. It would appear that the two adjacent C=O bonds produce a definite localization of the π-electrons in the C=C bond, and a consequent shortening below the distance in ethylene. If this is the case then there is no resonance with any excited structures, and the ground state of the molecule is represented accurately by the *p*-quinone structure:



The C–C distance of 1·477 Å would then represent the single-bond distance for carbon atoms in these particular states of hybridization (approximately sp^2-sp^2). This is in excellent agreement with the length deduced for this type of bond (1·479 Å) by Dewar & Schmeising (1959), on the assumption that there is no π-electron delocalization in conjugated and hyperconjugated systems.

The C=O distance is similar to the length found in ketones.

The valency angles deviate slightly but significantly from 120°, but the differences are much smaller than those suggested by the previous analyses.

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. The shortest oxygen–oxygen distance is 3·64 Å, the shortest oxygen–carbon separations are 3·34 Å, 3·39 Å and 3·45 Å, and the shortest carbon–carbon distance is 3·47 Å.

The author is indebted to Prof. J. M. Robertson for first suggesting this problem, and to Dr F. R. Ahmed for assistance with the computation of structure factors and differential syntheses.

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The Crystal Structure of 1,5-Dinitronaphthalene

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Crystals of 1,5-dinitronaphthalene are monoclinic, space group $P2_1/a$, with two molecules in the unit cell. The structure has been determined from projections along the three principal crystallographic axes, and details of the molecular geometry and dimensions have been obtained. The nitrogen atom and all the carbon atoms lie on one plane, but the planes of the nitro groups are rotated about the C–N bonds 49° out of the aromatic plane.

Introduction

The author has recently investigated the crystal and molecular structures of aromatic nitro compounds in which the steric effects of groups *ortho* to the nitro groups prevent the attainment of completely coplanar configurations, and reduce the resonance interaction between the nitro groups and the aromatic π-electrons (Trotter, 1958, 1959*a*, *b*, *c*, *d*). In all the molecules studied so far, the nitro groups have been hindered by two ortho groups, and are rotated about the C–N bonds approximately 65° out of the aromatic planes. The structure of 1,5-dinitronaphthalene, in which there is overcrowding effectively only on one side of the nitro group, has now been determined. The structure of this molecule has been investigated previously by Sevastyanov, Zhdanov & Umansky (1947, 1948), but these authors, from one projection only, made the unlikely deduction that the molecule is completely planar.

Experimental

Crystals of 1,5-dinitronaphthalene are off-white in colour, and consist of prisms elongated along the *c*-axis. Sevastyanov, Zhdanov & Umansky (1947, 1948) quote a value of 1·62 g.cm.$^{-3}$ for the measured density, but in redetermining the density it was found that the crystals floated in carbon tetrachloride, so that the true value must be less than 1·595 g.cm.$^{-3}$. An accurate value was determined by flotation in a mixture of chloroform and carbon tetrachloride, and also in aqueous potassium iodide solution; the mean of several determinations was 1·578 g.cm.$^{-3}$.

The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *c*-axis, an *hk*0 Weissenberg film, and 0*kl* and *h*0*l* precession films. The values of the unit-cell parameters differ slightly, but significantly, from those given in the previous investigation.

Crystal data

1,5-Dinitronaphthalene, $C_{10}H_6N_2O_4$; $M = 218{\cdot}2$; m.p. 217 °C.

Monoclinic,

$a = 7{\cdot}76 \pm 0{\cdot}02,\ b = 16{\cdot}32 \pm 0{\cdot}04,\ c = 3{\cdot}70 \pm 0{\cdot}01$ Å, $\beta = 101°\,48' \pm 10'$.

Volume of the unit cell = 458·7 Å^3.

Density, calculated (with $Z = 2$) = 1·579 g.cm.$^{-3}$, measured = 1·578 g.cm.$^{-3}$.

Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 12{\cdot}3$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}52$ cm.$^{-1}$.

Total number of electrons per unit cell = $F(000) = 224$.

Absent spectra: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group is $P2_1/a$–C_{2h}^5.

Molecular symmetry-centre.

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