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Refinement of the Crystal Structure of *p*-Benzoquinone at −160°C

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Abstract. $C_6H_4O_2$, monoclinic, $P2_1/a$, $a = 6{\cdot}763\ (3)$, $b = 6{\cdot}735\ (3)$, $c = 5{\cdot}711\ (3)$ Å, $\beta = 99{\cdot}55\ (15)$° at −160°C, $Z = 2$, D_c (−160°C) = 1·4 g cm^{-3}, λ(Mo $K\alpha_1$) = 0·70926, λ(Mo $K\alpha_2$) = 0·71354 Å, μ(Mo $K\alpha$) = 1·2 cm^{-1}. The best plane of the molecule makes an angle of 3·2° with the plane (20$\bar{1}$). In contrast to earlier room-temperature X-ray studies it has been found that at −160°C the molecules are not strictly planar, but have a slight chair form with C_{2h} (2/*m*) symmetry.

Introduction. Spectral investigations of *p*-benzoquinone (PBQ) over the last decade have led to conflicting evidence concerning the planarity of the molecule in the solid state. From a proton ENDOR study Lichtenbelt, Fremeyer, Veenvliet & Wiersma (1975) inferred that the molecule is statically distorted into a chair form with C_{2h} (2/*m*) symmetry. Loo & Francis (1976), on the other hand, arrived at a planar structure from phosphorescence spectra of PBQ in chemically mixed crystals with *p*-dichlorobenzene and *p*-dibromobenzene. This conflicting evidence urged an accurate study of the crystal structure of PBQ at low temperature. The structure had been determined by X-ray diffraction at room temperature by different authors, the most recent being that by Trotter (1960). A comparison with the results of earlier X-ray and electron diffraction studies is given by Trotter (1960). In all cases the PBQ molecule was found to be planar within experimental error.

PBQ crystals prepared by Veenvliet & Wiersma (1973) were kindly given to us. The crystals 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 glass capillaries. For the X-ray study we used a slightly yellowish crystal with dimensions 0·6 × 0·3 × 0·3 mm and a mosaic spread smaller than 0·6°. Measurements of cell dimensions and reflexion intensities were made at −160°C on a Nonius CAD-4 automated diffractometer. The crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). The cell dimensions at −160°C differ considerably from Trotter's room-temperature values of $a = 7{\cdot}055\ (4)$, $b = 6{\cdot}795\ (4)$, $c = 5{\cdot}767\ (4)$ Å, $\beta = 101{\cdot}47\ (3)$°. For 1432 independent reflexions with $\sin\theta/\lambda < 0{\cdot}9064$ Å^{-1}, positive intensities were measured with Zr-filtered Mo radiation and the θ–2θ scan technique. Corrections were made for Lorentz and polarization effects and for changes in the intensity of the primary beam. The latter correction, determined from the intensities of two reference reflexions measured at regular intervals, was a maximum of ±3%. Starting from Trotter's coordinates a full-matrix least-squares refinement was carried out. The function minimized, Q, was $\Sigma\, w(F_o - k^{-1}F_c)^2$ with $w = [\sigma_c^2(F_o) + 0{\cdot}0009F_o^2]^{-1}$, σ_c being the standard deviation in F_o based on counting statistics and errors in the filter factor; 218 reflexions with $|F_o| < 3\sigma_c(|F_o|)$ and the very strong reflexion 20$\bar{1}$, which was affected by extinction, were not considered during the refinement. Scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and that of H was from Stewart, Davidson & Simpson (1965). Anisotropic temperature factors were refined for C and O and isotropic temperature factors for H. The positions of the H atoms were constrained at 1·08 Å from their respective C atoms at the bisectors of the CCC angles. For the 1213 reflexions used in the refinement, $R = \Sigma\,|\Delta F|/\Sigma\,|F_o| = 0{\cdot}074$ and $R_w = [\Sigma\, w(\Delta F)^2/\Sigma\, w|F_o|^2]^{1/2} = 0{\cdot}090$; the goodness of fit $G = [\Sigma\, w(\Delta F)^2/(N_o - N_v)]^{1/2} = 4{\cdot}93$. The final atomic coordinates are given in Table 1.*

Table 1. *Fractional coordinates* (×10⁴)

Standard deviations in units of the last decimal place are given in parentheses.

	x	*y*	*z*
O(1)	1166 (2)	3186 (2)	2573 (2)
C(1)	634 (2)	1712 (2)	1384 (2)
C(2)	−454 (2)	1899 (2)	−1072 (2)
C(3)	1061 (2)	−292 (2)	2359 (2)
H(2)	−760	3356	−1835
H(3)	1875	−466	4141

Calculations were performed with the set of programs in the XRAY system (1975).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33184 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The two molecules in the unit cell lie at the inversion centers (0,0,0) and $(\frac{1}{2},\frac{1}{2},0)$. The structure consists of layers parallel to $(20\bar{1})$, as can be seen from Fig. 1. The best plane through the C and O atoms of the molecule, defined by $0{\cdot}9384X - 0{\cdot}0071Y - 0{\cdot}3454Z = 0$ (X,Y,Z orthonormal axes parallel to **a**, **b** and **c***), makes an angle of only 3·2° with $(20\bar{1})$. Between the layers there are no distances shorter than the sum of the relevant van der Waals radii. Comparison of the present low-temperature cell dimensions with Trotter's room-temperature values shows that the decrease in temperature reduces the distance between the layers by as much as 4·4%, whereas within the layers the contraction is small (0·0 and 0·9% along [102] and **b** respectively).

From Fig. 2 we see that, in contrast to the earlier room-temperature studies, the molecule shows significant deviations from planarity ($\chi^2 = 131$ for seven degrees of freedom for the best plane B of the C and O atoms). O, C(1), C(2) and C(3) lie in a plane which makes an angle of 0·3° with the best plane B ($\chi^2 = 0{\cdot}03$ for three degrees of freedom). The molecule has a slight chair shape with symmetry C_{2h} ($2/m$) in agreement with the proton ENDOR study of Lichtenbelt *et al.* The present low-temperature values for the bond lengths and angles are not significantly different from the room temperature values corrected for libration given by Trotter (1960).

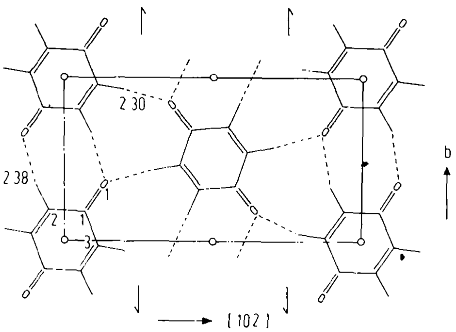
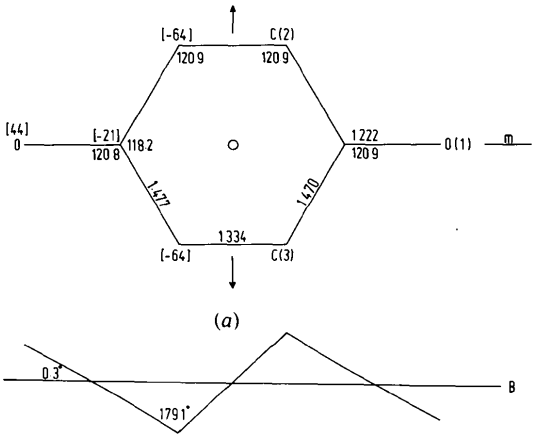


Fig. 1. The structure around the $(20\bar{1})$ plane with the numbering scheme and those intermolecular distances shorter than the sum of the relevant van der Waals radii [$r(C) = 1{\cdot}7$, $r(O) = 1{\cdot}4$, $r(H) = 1{\cdot}1$ Å; Pauling, 1960].



(*a*)

(*b*)

Fig. 2. Structure of the molecule. (*a*) Bond lengths (Å) and angles (°), with deviations from the best plane B ($\times 10^{-4}$ Å) in square brackets, and the molecular symmetry. Standard deviations in bond lengths and angles are 0·003 Å and 0·1° respectively; no libration corrections were applied. (*b*) Projection along C(2)—C(3); the distances from the best plane B are exaggerated by a factor of 10.

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