value 2·338 g.cm^{-3} (*Handbook of Chemistry and Physics*, 1958).

The thermal expansion of KDP has been studied earlier by De Quervain (1944) and Ubbelohde & Woodward (1947) by the X-ray method at low temperatures. At elevated temperatures the thermal expansion has been studied by macroscopic methods by Mason (1946) and by Haussühl (1964). The mean coefficients obtained by Mason (quoted from Megaw, 1957) are $\alpha_a = 27$ and $\alpha_c = 45$ in units of 10^{-6}°C^{-1}. The values given by Haussühl are $\alpha_a = 26{\cdot}5$ and $\alpha_c = 44{\cdot}4$ in the same units. The mean coefficients obtained in the present study agree well with these values. A detailed discussion regarding the anisotropy in the thermal expansion of KDP and its isomorphs has been given elsewhere (Deshpande & Khan, 1963; Khan, 1966).

References

De Quervain, M. (1944). *Helv. Phys. Acta*, **17**, 509.

Deshpande, V. T. & Khan, A. A. (1963). *Acta Cryst.* **16**, 936.

Deshpande, V. T. & Khan, A. A. (1965*a*). *Acta Cryst.* **18**, 977.

Deshpande, V. T. & Khan, A. A. (1965*b*). *Curr. Sci.* **34**, 633.

Deshpande, V. T. & Khan, A. A. (1966). *Nature, Lond.* **209**, 608.

Deshpande, V. T. & Mudholker, V. M. (1961). *Indian J. Phys.* **35**, 434.

Handbook of Chemistry and Physics (1958), p.632. Cleveland: Chemical Rubber Publishing Co.

Haussühl, S. (1964). *Z. Kristallogr.* **120**, 401.

Khan, A. A. (1966). Ph.D.Thesis, Osmania University.

Klug, H. P. & Alexander, L. E. (1954), p.484. *X-ray Diffraction Procedures*. New York: John Wiley.

Mason, W. P. (1946). *Phys. Rev.* 69, 173.

Megaw, H. (1957). *Ferro-electricity in Crystals*, p.48. London: Methuen.

Sirdeshmukh, D. B. (1963). Ph. D. Thesis, Osmania University.

Ubbelohde, A. R. & Woodward, I. (1947). *Proc. Roy. Soc.* A, **188**, 358.

Acta Cryst. (1967). **22**, 439

Refinement of the crystal structure of anthraquinone.

By Anand Prakash, *Division of the Geological Sciences,* California Institute of Technology, Pasadena, California, U.S.A.*

(*Received* 25 *October* 1966)

The crystal structure of anthraquinone has been refined to an R index of 12·5 % by the full-matrix least squares based on the observed structure factors of Murty. From the refinement it is concluded that there is no formal transfer of one electron from the carbon atom to the oxygen atom in the C=O bond as Murty proposed, although there is no significant change in positional atomic parameters. Principal axes of vibration of thermal ellipsoids for the carbon and oxygen atoms are also calculated.

The structure of anthraquinone was first determined by Sen (1948) and was refined by Murty (1960) by three-dimensional Fourier methods, using form factors obtained by an empirical method (Murty, 1957). However, the final R index remained surprisingly high (19·6 % for the observed reflections). It was therefore thought worthwhile to undertake a further refinement of the structure.

Crystal data

Anthraquinone, $C_{14}H_8O_2$.

$a = 15{\cdot}810 \pm 0{\cdot}015$, $b = 3{\cdot}942 \pm 0{\cdot}005$, $c = 7{\cdot}865 \pm 0{\cdot}010$ Å. $\beta = 102°43' \pm 2'$. Space group $P2_1/a$. $Z = 2$.

The refinement was first carried out by three full-matrix least-squares refinements based on the observed structure factors of Murty and beginning with his final atomic coordinates and isotropic temperature factors. In three cycles,

Table 1. *Atomic parameters and standard deviations*

The parameters of carbon and oxygen are multiplied by 10^4. Temperature factors are of the form $\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Hydrogen parameters are multiplied by 10^3.

Hydrogen atoms are assigned arbitrarily an isotropic B value of 3·5 Å^2. Standard deviations (in final significant figure) are given in parenthesis.

	x	y	z	B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}
C(1)	1314 (5)	4166 (25)	3985 (10)	50 (4)	640 (69)	162 (14)	30 (26)	−2 (11)	−26 (48)
C(2)	0507 (5)	2707 (25)	3406 (9)	46 (3)	765 (74)	138 (12)	41 (30)	25 (10)	−16 (53)
C(3)	0277 (4)	1390 (19)	1742 (9)	32 (3)	433 (59)	167 (13)	22 (19)	30 (9)	0 (43)
C(4)	0850 (4)	1547 (19)	0616 (9)	26 (2)	488 (59)	166 (11)	33 (19)	41 (8)	32 (42)
C(5)	1662 (5)	2960 (23)	1215 (10)	33 (3)	648 (69)	219 (15)	−19 (24)	53 (10)	46 (54)
C(6)	1894 (5)	4274 (24)	2894 (11)	43 (4)	618 (68)	211 (16)	16 (25)	−32 (11)	−109 (52)
C(7)	0605 (4)	0137 (23)	−1157 (9)	33 (3)	660 (69)	152 (12)	41 (22)	51 (9)	49 (46)
O(8)	1109 (4)	0229 (21)	−2119 (8)	44 (3)	1503 (79)	171 (10)	−111 (24)	81 (8)	−190 (17)
H(1)	145 (5)	514 (22)	519 (11)						
H(2)	007 (5)	245 (23)	416 (11)						
H(5)	207 (5)	323 (23)	036 (10)						
H(6)	246 (5)	565 (22)	337 (11)						

---

* Contribution no. 1420.

the R index went down from 22·3 to 17·2 %. The temperature factors of carbon and oxygen atoms were then allowed to become anisotropic, and hydrogen atoms were introduced in their fixed positions, derived from chemical considerations. The quantity minimized was $\Sigma w(|F_o|^2-1/k^2|F_c|^2)^2$, where $w=(1+\sin^2\theta/0{\cdot}98)(5^2+F_o{}^2)^{-2}$. The reflections 200, 201, 210, 011, and 111 were given zero weight, as they were presumed to be affected by extinction. After two anisotropic cycles, refinement of carbon and oxygen was stopped. Two cycles of refinement for hydrogen atomic positions were then carried out, using the weighting scheme $w=(5^2+F_o{}^2)^{-2}$, and omitting reflections having $\sin^2\theta/\lambda^2>0{\cdot}25$. The magnitude of the shifts in the final refinement cycles was less than 10 % of their e.s.d.'s for the heavy atoms and about 50 % of their e.s.d.'s for the hydrogen atoms. Form factors for O, C, and H were taken from *International Tables for X-ray Crystallography* (1962). Because minimum estimates for unobserved reflections were not available, these reflections were not included in the refinement or in the R index. The final R value is 12·5 % and the scale factor k to be applied to the observed structure factors of Murty is 0·775.

After the refinement, a difference map in the plane of the molecule was computed, with hydrogen atoms omitted in the structure-factor calculation. It is shown in Fig. 1. The final set of parameters along with their standard deviations is listed in Table 1. Interatomic distances and angles are listed in Table 2. Principal axes of vibration of thermal ellipsoids for the carbon and oxygen atoms calculated by the method given by Waser (1955) are listed in Table 3.

Table 2. *Interatomic distances and angles*

Standard deviation in interatomic distances involving only heavy atoms is $\simeq 0{\cdot}011$ Å and in those involving hydrogen atoms is $\simeq 0{\cdot}08$ Å.

Distances*	
C(1)–C(2)	1·381 Å
C(6)–C(5)	1·390
C(2)–C(3)	1·380
C(5)–C(4)	1·383
C(4)–C(7)	1·472
C(3)–C(7′)	1·495
C(1)–C(6)	1·388
C(3)–C(4)	1·401
C(7)–O(8)	1·213
C(1)–H(1)	1·00
C(2)–H(2)	1·01
C(5)–H(5)	1·03
C(6)–H(6)	1·04

Angles*	
C(2) –C(1)–C(6)	119·8°
C(1) –C(6)–C(5)	120·2
C(1) –C(2)–C(3)	120·0
C(6) –C(5)–C(4)	120·3
C(2) –C(3)–C(4)	120·7
C(3) –C(4)–C(5)	118·9
C(3) –C(4)–C(7)	120·7
C(4) –C(3)–C(7′)	120·8
C(4) –C(7)–C(3′)	118·4
C(4) –C(7)–O(8)	120·5
C(3′)–C(7)–O(8)	121·0

* Uncorrected for thermal vibrations.

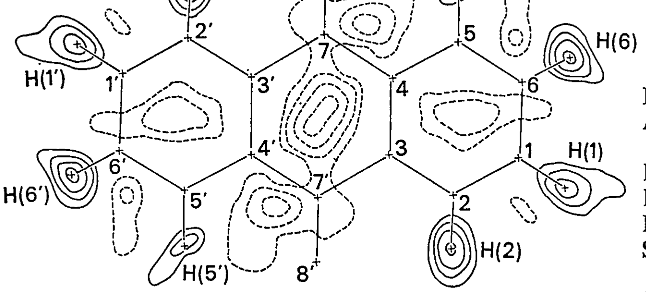

Fig. 1. Difference synthesis in the plane of the molecule. Contours are drawn at intervals of 0·1 e.Å^{-3}, starting from ±0·2 e.Å^{-3}.

Table 3. *Temperature ellipsoids*

The lengths of the principal axes are given in B units and their direction cosines are referred to the crystallographic cell axes.

	Axis	Length	cos A	cos B	cos C
C(1)	1	5·73	−0·871	−0·238	0·610
	2	3·88	−0·178	0·968	0·210
	3	3·36	0·457	−0·076	0·764
C(2)	1	5·17	−0·605	−0·792	0·208
	2	4·05	−0·792	0·609	0·213
	3	3·23	0·078	0·037	0·954
C(3)	1	3·96	−0·182	−0·038	0·999
	2	3·17	−0·850	−0·495	0·015
	3	2·53	−0·493	0·868	0·052
C(4)	1	3·98	0·118	0·243	0·913
	2	3·13	−0·371	−0·888	0·345
	3	2·18	−0·921	0·389	0·217
C(5)	1	5·22	0·023	0·223	0·945
	2	4·05	0·273	−0·939	0·143
	3	2·85	−0·961	−0·261	0·293
C(6)	1	7·02	−0·677	−0·220	0·834
	2	3·75	−0·359	0·932	0·026
	3	3·00	0·642	0·289	0·551
C(7)	1	4·45	0·352	0·822	0·360
	2	3·49	0·186	−0·531	0·765
	3	2·63	−0·917	0·207	0·534
O(8)	1	9·86	0·211	−0·951	0·174
	2	4·42	0·597	0·309	0·590
	3	2·78	−0·774	−0·021	0·788

The molecular plane calculated by the method given by Schomaker, Waser, Marsh & Bergman (1959) is $0{\cdot}3004x-0{\cdot}8910y+0{\cdot}2657z=0$, where x, y, z are the coordinates expressed in Å and are referred to the unit-cell axes. The maximum deviation of the individual atom from the mean molecular plane is 0·011 Å.

Positional atomic parameters do not differ significantly from those of Murty. However, it is clear from the state of refinement and from the difference map (Fig. 1) that there is no indication of the formal transfer of one electron from carbon to oxygen atom in the C=O bond, as proposed by Murty (1960) on the basis of electron counts. The conclusion is in agreement with structural studies of anthraquinone derivatives (Bailey, 1958; Prakash, 1965) and of benzoquinone (Trotter, 1961), where no indication of electron transfer was found.

The calculations were carried out with the CRYRM (IBM 7094) program. I am grateful to Professor Barclay Kamb and Dr R. E. Marsh for their valuable suggestions. The work was supported by the National Science Foundation.

References

Bailey, M. (1958). *Acta Cryst.* **11**, 103.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Murty, B. V. R. (1957). *Acta Cryst.* **10**, 146.

Murty, B. V. R. (1960). *Z. Kristallogr.* **113**, 445.

Prakash, A. (1965). *Z. Kristallogr.* **122**, 272.

Schomaker, V., Waser, J., Marsh, R. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Sen, S. N. (1948). Thesis, Calcutta University.

Trotter, J. (1961). *Acta Cryst.* **14**, 553.

Waser, J. (1955). *Acta Cryst.* **8**, 731.