

## The Crystal and Molecular Structure of an Orthorhombic Modification of 2,3-Dichloro-1,4-naphthoquinone

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A new modification of 2,3-dichloro-1,4-naphthoquinone was obtained by growing the crystal from the melt. The crystal is orthorhombic, space group  $Pb2_1a$ , with  $a = 16.204$  (12),  $b = 28.686$  (17),  $c = 3.830$  (2) Å,  $Z = 8$ . The structure was solved by the direct method, and refined by full-matrix least squares. Although the molecular geometry is almost the same as that in the triclinic modification, the arrangement of molecules in the orthorhombic form is found to be quite different, being similar to the crystal structure of 2,3-dibromo-1,4-naphthoquinone.

### Introduction

In a recent study of the phosphorescence spectra of 2,3-dichloro-1,4-naphthoquinone, a crystal grown from the melt was found to exhibit spectral features quite different from those of a crystal grown from a toluene solution; the former crystal has an origin peak at  $18\,373\text{ cm}^{-1}$  at 1.7 K, while that of the latter is  $18\,350\text{ cm}^{-1}$  (Narisawa, Sano & I'Haya, 1976). The crystal structure of 2,3-dichloro-1,4-naphthoquinone was previously determined by Métras (1961), who reported the crystal lattice to be triclinic. However, we found that a crystal grown from the melt was orthorhombic, whereas a crystal grown from a toluene solution was triclinic (as reported by Métras). This suggests that the difference in the phosphorescence spectra arises from the difference in crystal structure between the two crystal forms. Thus it is of great interest to determine the crystal structure of the new orthorhombic modification of 2,3-dichloro-1,4-naphthoquinone.

In this paper we report the crystal structure of the orthorhombic modification and discuss the structural differences between the orthorhombic and triclinic crystals.

### Experimental

2,3-Dichloro-1,4-naphthoquinone (Tokyo Kasei Organic Chemicals) was purified by recrystallization, once from ethanol and three times from benzene, and then by zone-refining for 100 passes. A single crystal, 20 mm in diameter, was melt-grown at a pressure of 500 mm Hg of nitrogen in a Bridgman furnace. The crystal is yellow and transparent. A sample,  $0.5 \times 0.5$

$\times 0.5$  mm, was cut from the melt-grown crystal for the structure analysis.

The approximate lattice constants and space group were determined from Weissenberg and precession photographs. The accurate lattice parameters and the intensity data were obtained with a Rigaku four-circle automatic diffractometer, and Mo  $K\alpha$  radiation monochromatized with a graphite plate.

### Crystal data

$C_{10}H_4O_2Cl_2$ , FW 227,  $a = 16.204$  (12),  $b = 28.686$  (17),  $c = 3.830$  (2) Å,  $V = 1780.29$  Å<sup>3</sup>.  $D_c = 1.70$ ,  $D_m = 1.70\text{ g cm}^{-3}$  (by flotation),  $Z = 8$ ;  $\mu = 6.923\text{ cm}^{-1}$  (Mo  $K\alpha$ ). Space group  $Pb2_1a$  (absent spectra:  $0kl$  when  $k$  is odd and  $hk0$  when  $h$  is odd).

1691 reflexions with reliable intensities [ $|F_o| \geq 3\sigma(F_o)$ ] were obtained by measuring all reflexions with  $2\theta \leq 55^\circ$ . Corrections were applied for absorption.

### Determination and refinement of the structure

The correct space group was concluded to be either  $Pbma$  or  $Pb2_1a$  from systematically absent reflexions. However,  $Pbma$  is not probable when we consider the packing of the molecules. Thus, the analysis was first carried out in the space group  $Pb2_1a$ . This space group was verified at a later stage of analysis. *MULTAN* (Germain, Main & Woolfson, 1971) was used to determine the phases of 244 normalized structure factors ( $|E| > 1.5$ ). The correct solution was deduced from the absolute figures of merit,  $\Sigma\alpha, \psi_0$  and the residual index. The positions of 25 atoms among the 28 independent non-hydrogen atoms were revealed from the

*E* map. A Fourier map revealed another three atoms. After the refinement by block-diagonal least squares with isotropic temperature factors, all H atoms were found in the *D* map. The refinement was completed by the *UNICS* (1967) full-matrix least-squares program, with anisotropic temperature factors for non-hydrogen atoms and isotropic for H. The final *R* was 0.053 for all reflexions.\*

The weighting scheme was  $\omega = 1/[\sigma^2(F_o) + (0.08 \times F_o)^2]$ . Atomic scattering factors for C, O and Cl were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965). Atomic coordinates are listed in Table 1.

### Results and discussion

The projections of the crystal structure along *a* and *c* are shown in Fig. 1. There are two crystallographically independent molecules in the unit cell (molecules I and II, Fig. 1). The molecules at site I are stacked along *c* to form a molecular column (column I), and those at site II form a separate column (column II), also along *c*. Thus there are two crystallographically different types of molecular column.

All the molecules can be considered to be approximately planar. The equation of the molecular plane, calculated by the least-squares method excluding H atoms, is:  $-0.0724X + 0.4058Y + 0.9111Z = 3.4718$  for molecule I, and  $0.1208X - 0.3891Y + 0.9132Z = -2.8375$  for molecule II, where *X*, *Y* and *Z* are the coordinates (in Å) with respect to the crystal axes *a*, *b* and *c* respectively. These planes make an angle of 47.9° with each other. The deviations of atoms from the least-squares planes are listed in Table 2. O(1), Cl(2), Cl(3) and O(4) deviate slightly from the plane, alternately up and down to avoid steric hindrance.

The bond lengths, bond angles and their standard deviations in each molecule are given in Fig. 2. The bond length of C(2)–C(3) is significantly shorter than other C–C bonds, indicating its double-bond character, while the long bond lengths of C(1)–C(2) and C(3)–C(4) clearly show their single-bond character. No significant difference can be found between the molecular geometry obtained here for the orthorhombic form and that reported by Métras for the triclinic form. The bond lengths and bond angles in the 1,4-naphthoquinone skeleton are also almost the same as those previously reported for 1,4-naphthoquinone (Gaultier & Hauw, 1965), 2,3-difluoro-1,4-naphtho-

quinone (Gaultier, Hauw, Housty & Schvoerer, 1972) and 2,3-dibromo-1,4-naphthoquinone (Breton-Lacombe, 1967).

In the triclinic form also, there are two crystallographically independent molecular sites, each forming separate molecular columns, but the molecular arrangement in each column is significantly different from that in the orthorhombic form. The interatomic distances corresponding to short contacts between columns are listed in Table 3 for both crystal forms. There seems to be no significant difference between the two cases.

Table 1. Fractional atomic coordinates ( $\times 10^4$ )

Molecule I			
	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	3724 (4)	927 (3)	7984 (18)
C(2)	3218 (4)	1409 (3)	6342 (17)
C(3)	3893 (4)	1650 (2)	5744 (15)
C(4)	4742 (4)	1490 (2)	6560 (18)
C(5)	5582 (4)	849 (3)	9072 (21)
C(6)	5647 (5)	398 (4)	10505 (21)
C(7)	4954 (5)	142 (3)	11081 (23)
C(8)	4181 (5)	316 (3)	10313 (20)
C(9)	4102 (4)	754 (2)	8829 (16)
C(10)	4809 (4)	1016 (2)	8191 (16)
O(1)	2653 (3)	708 (2)	8512 (19)
O(4)	5337 (3)	1724 (2)	5945 (18)
Cl(2)	2248 (1)	1593 (1)	5356 (6)
Cl(3)	3841 (1)	2200*	3930 (5)

Molecule II			
C(1)	1605 (4)	3979 (2)	3681 (17)
C(2)	2478 (4)	4150 (2)	3749 (16)
C(3)	3109 (4)	3892 (2)	2572 (15)
C(4)	2983 (4)	3415 (3)	1109 (17)
C(5)	1978 (5)	2788 (3)	-273 (18)
C(6)	1195 (5)	2611 (4)	-411 (29)
C(7)	542 (5)	2881 (3)	768 (22)
C(8)	669 (4)	3323 (3)	2067 (20)
C(9)	1471 (4)	3502 (2)	2220 (16)
C(10)	2126 (4)	3239 (2)	1012 (15)
O(1)	1050 (4)	4210 (2)	4819 (18)
O(4)	3568 (4)	3195 (2)	27 (19)
Cl(2)	2594 (1)	4696 (1)	5364 (5)
Cl(3)	4100 (1)	4087 (1)	2705 (6)

### Hydrogen atomic coordinates ( $\times 10^3$ )

Molecule I				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(5)	597 (6)	102 (4)	879 (30)	5.7 (2.2)
H(6)	618 (5)	32 (3)	1106 (24)	3.7 (1.7)
H(7)	501 (5)	-6 (3)	1224 (23)	2.3 (1.5)
H(8)	375 (5)	12 (3)	1077 (23)	4.1 (1.9)

Molecule II				
H(5)	234 (5)	266 (3)	-66 (18)	1.2 (1.3)
H(6)	114 (6)	227 (4)	-131 (30)	4.9 (4.1)
H(7)	-0 (5)	280 (3)	89 (23)	3.5 (1.5)
H(8)	25 (5)	347 (3)	301 (23)	3.8 (2.1)

\* This coordinate was fixed to determine the origin.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32387 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

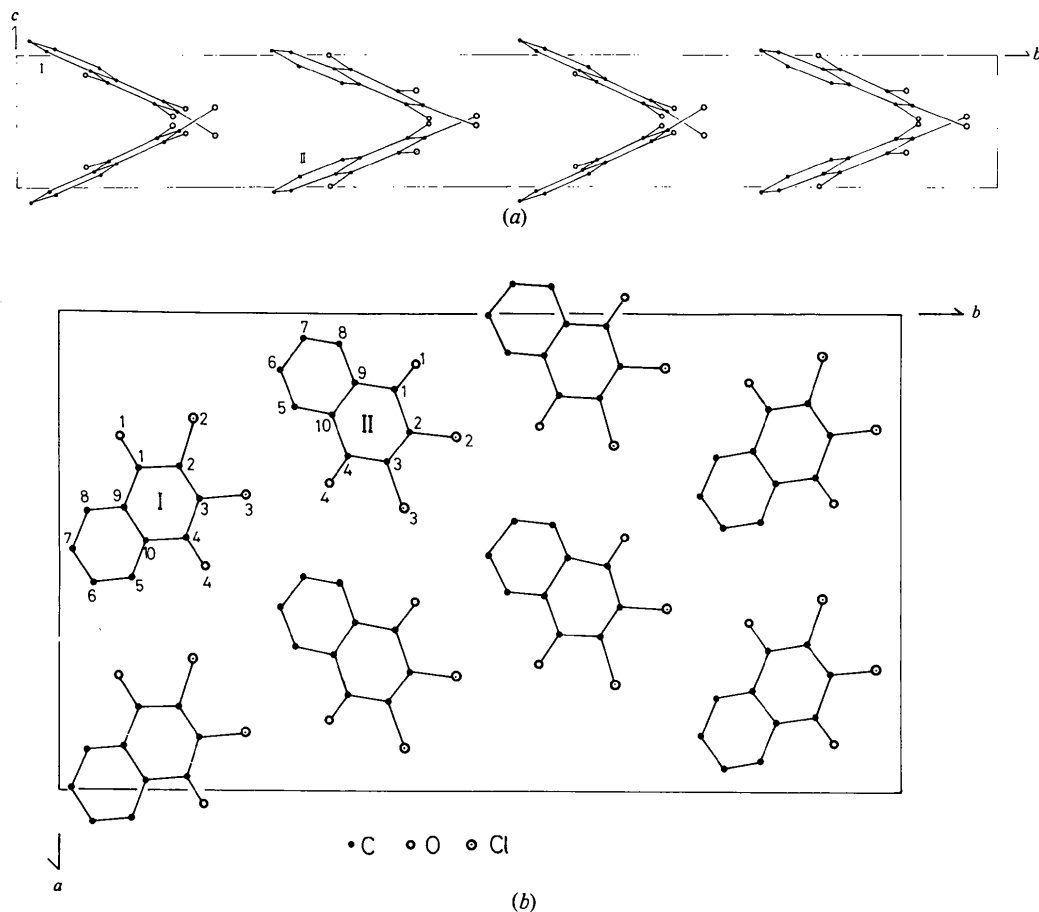


Fig. 1. Projections of the crystal structure of the orthorhombic form (a) along *a* and (b) along *c*.

Table 2. Atomic deviations ( $\text{\AA}$ ) from the least-squares planes of the molecules

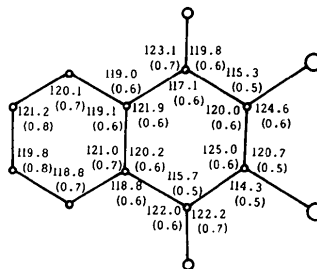
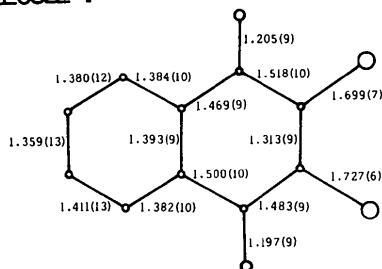
	Molecule I	Molecule II
C(1)	-0.004	-0.002
C(2)	0.004	0.001
C(3)	-0.004	0.001
C(4)	-0.004	-0.003
C(5)	0.027	0.017
C(6)	-0.006	0.013
C(7)	-0.022	-0.004
C(8)	0.005	-0.018
C(9)	0.005	-0.007
C(10)	0.005	-0.008
O(1)	0.011	0.029
O(4)	-0.016	-0.021
Cl(2)	-0.013	-0.021
Cl(3)	0.010	0.024

The overlap of the neighbouring molecules in each column is shown in Fig. 3, together with that in the triclinic form. First, it should be noted that the relative orientations of the neighbouring molecules are completely different in the two crystal forms. A molecule of

2,3-dichloro-1,4-naphthoquinone has a dipole moment along its long molecular axis. In the triclinic form, the neighbouring molecules are arranged so as to have a centre of symmetry between them. Thus their dipole moments are cancelled out. On the other hand, in the orthorhombic form, all molecules in a molecular column have their dipole moment in the same direction. Consequently, each column has a dipole moment, and such dipole moments of molecular columns are not wholly cancelled out in the crystal. This means that a crystal of the orthorhombic form must have a permanent polarization. A similar structural aspect can be found in the crystal structure of 2,3-dibromo-1,4-naphthoquinone (Breton-Lacombe, 1967).

The overlap of neighbouring molecules in column I is appreciably different from that in column II of the orthorhombic form, while it is almost the same in the two types of column of the triclinic form. The mean separation of the molecular planes is  $3.490 \text{ \AA}$  in column I and  $3.498 \text{ \AA}$  in column II of the orthorhombic form, and  $3.70 \text{ \AA}$  in the triclinic form. The crystal densities are respectively  $1.70$  and  $1.58 \text{ g cm}^{-3}$  for the orthorhombic and triclinic forms.

## MOLECULE I



## MOLECULE II

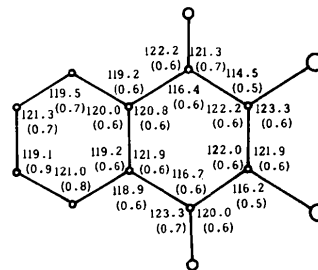
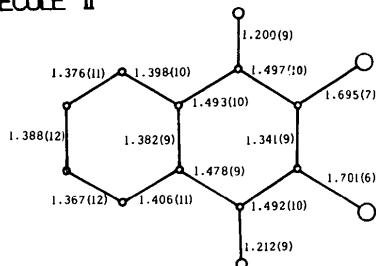


Fig. 2. Bond lengths (Å), bond angles (°) and their standard deviations in molecules I and II.

Table 3. Short contacts between columns (Å)

## Orthorhombic

O(4)I...C(2)I(i)	3.160
O(1)I...C(2)II(ii)	3.168
C(3)I...O(4)II	3.253
C(3)II...O(1)II(i)	3.318
O(4)II...C(7)II(iii)	3.337
O(4)I...C(6)II(i)	3.367
C(7)I...O(1)II(iv)	3.440

## Triclinic

C(2)I...O(1)I'(v)	3.15
C(2)I...O(4)I'(vi)	3.29
C(2)I...O(1)I'(v)	3.32
C(6)II...O(4)II'(v)	3.37
C(3)I...O(1)II(vi)	3.38
O(4)II...C(7)I(vii)	3.39
C(7)II...O(4)I	3.44
O(4)II...C(2)II(vi)	3.46

## Symmetry code

None  $x, y, z$ (i)  $0.5 + x, y, 1 - z$ (ii)  $0.5 - x, -0.5 + y, z$ (iii)  $0.5 + x, y, -z$ (iv)  $0.5 - x, -0.5 + y, -1 + z$ (v)  $x, 1 + y, 1 + z$ (vi)  $x, 1 + y, z$ (vii)  $1 + x, 1 + y, z$ 

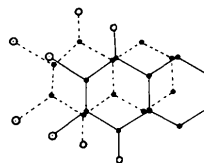
The structural difference between the two crystal forms of 2,3-dichloro-1,4-naphthoquinone, which was revealed by the present study, seems to be responsible for the difference in the phosphorescence spectra for the two crystal forms. Possibly, differences will also be found in other physical properties. The relation between the physical properties and the crystal structures of the two crystal forms will be reported elsewhere.

The computer used was a HITAC 8700/8800 at the Computer Center, University of Tokyo, with the UNICS (1967) system of programs.

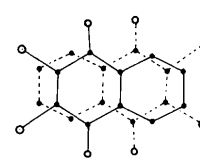
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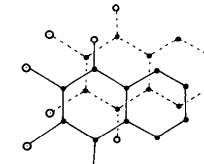
## MOLECULE I



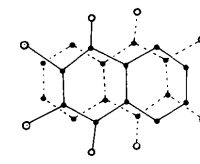
## MOLECULE I



## MOLECULE II



## MOLECULE II



(a)

(b)

Fig. 3. The overlap between the neighbouring molecules in the columns of the (a) orthorhombic, and (b) triclinic forms.

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