The Isomerism of Benzoquinone–Monoximes (Nitrosophenols). IX. The Fibrous Structures of β-2-Chloro- and β-2-Bromo-5-Methyl-p-Benzoquinone-4-Oxime

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The dimensions of the unit cells of β-2-chloro- and β-2-bromo-5-methyl-p-benzoquinone-4-oxime have been determined from powder and fibre diagrams and are nearly equal ($a = 19\cdot3$, $b = 38\cdot6$, $c = 3\cdot80$ Å, $\gamma = 120°$ and $a = 19\cdot1$, $b = 37\cdot3$, $c = 3\cdot89$ Å, $\gamma = 114\cdot6°$, respectively). The space groups are different ($A2$ and $P2/b$, respectively). The fibres probably consist of helices of molecules linked by hydrogen bonds and have a pseudo-hexagonal character (probably 6_2). There are indications that they form inclusion compounds, e.g. a blue complex with iodine.

Introduction

In the preceding paper (Romers & Fischmann, 1960) the crystal structures of α-2-chloro-5-methyl-p-benzoquinone-4-oxime (α-ClMBO) and of the corresponding isomorphous bromine compound (α-BrMBO) have been discussed. It was shown that the α-isomers have a p-benzoquinone-monoxime structure with the oxime group *syn* with respect to the halogen atom.

A straightforward diffraction analysis of the β-isomers appeared to be impossible, because all attempts to obtain monocrystals yielded tiny fibrous polycrystalline material. Chemical evidence and the knowledge of the crystal structures of the α-forms enabled us to make a hypothesis about the structures of the β-forms that is in accordance with the powder and fibre diagrams.

Experimental part

β-ClMBO and β-BrMBO are obtained simultaneously with the corresponding α-forms as products of the reaction of 2-chloro- and 2-bromo-5-methyl-p-benzoquinone with hydroxylamine (Kehrmann, 1898). Repeated crystallization from solvents such as carbon tetrachloride and benzene yields the purified product in the form of slender white fibres which decompose at 185 °C.

We were not able to effect the conversion of these β-forms into the α-forms.

X-ray exposures (Cu $K\alpha$ radiation) made of oscillating or stationary fibrous material in an ordinary rotation camera gave identical photographs irrespective of the initial orientation of the fibre. Rather sharp reflexions were found on the zero layer $hk0$, but diffuse spots on the first layer $hk1$.

Debye–Scherrer diagrams were made with a Guinier–de Wolff camera (de Wolff, 1948) and were indexed

with use of the $Q = 10^4 \sin^2 \theta$ procedure (de Wolff, 1957). Reflexions $00l$ with $l = 1, 2, \ldots, 5$ fell within the limit of observation with copper radiation, but were not found. Molybdenum radiation was not used, because of the very long exposure time required.

Densities of both compounds were determined using the flotation method.

Table 1. *Calculated and observed $Q = 10^4 \sin^2 \theta$ values of β-2-chloro-5-methyl-p-benzoquinone-4-oxime*

$hk0$	Q_c	Q_o
020, 100, $\bar{1}$20	21·4	21·6
120, $\bar{1}$40, $\bar{2}$20	64·2	64·2
040, 200, $\bar{2}$40	85·6	85·6
140, $\bar{1}$60, 220, $\bar{2}$60, $\bar{3}$20, $\bar{3}$40	149·8	150·0
060, 300, $\bar{3}$60	192·6	192·7
240, $\bar{2}$80, 440	256·8	257·3
160, $\bar{1}$80, 320, $\bar{3}$80, $\bar{4}$20, $\bar{4}$60	278·2	277·5
080, 400, $\bar{4}$80	342·4	342·2
260, $\bar{2}$100, 340, $\bar{3}$100, $\bar{5}$40, $\bar{5}$60	406·6	404·3
180, $\bar{1}$100, 420, $\bar{4}$100, $\bar{5}$20, $\bar{5}$80	449·4	448·0
0100, 500, $\bar{5}$100	535·0	535·1
0120, 600, $\bar{6}$120	770·4	768·1
2100, $\bar{2}$140, 540, $\bar{5}$140, 740, $\bar{7}$100	834·6	833·0
1120, $\bar{1}$140, 620, $\bar{6}$140, 720, $\bar{7}$120	920·2	919·3
0140, 700, $\bar{7}$140	1048·6	1044·1

$hk1$	Q_c	Q_o
011	416·4	416·4
111, $\bar{1}$31	448·5	449·4
$\bar{2}$11, $\bar{2}$31	480·6	481·1
131, $\bar{1}$51	512·7	510·2
211, $\bar{2}$51	523·4	523·0
$\bar{3}$31	555·5	555·3
$\bar{3}$11, $\bar{3}$51	576·9	574·5
151, $\bar{1}$71	619·8	614·3
311, $\bar{3}$71	641·1	643·9
$\bar{4}$11, $\bar{4}$71	716·0	715·5
351, $\bar{3}\bar{1}$11, $\bar{5}$11, $\bar{5}$91	897·8	901·2

$hk2$	Q_c	Q_o
042, 202, $\bar{2}$42	1729·8	1733
142, $\bar{1}$62, 222, 262, $\bar{3}$22, $\bar{3}$42	1794·0	1796
062, 302, $\bar{3}$62	1836·8	1840
162, $\bar{1}$82, 322, $\bar{3}$82, $\bar{4}$22, $\bar{4}$62	1922·4	1922
262, $\bar{2}$102, 342, $\bar{3}$102, $\bar{5}$42, $\bar{5}$62	2050·8	2047
182, $\bar{1}$102, 422, $\bar{4}$102, $\bar{5}$22, 582	2093·6	2094

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Table 2. *Calculated and observed Q values of*
β-2-bromo-5-methyl-p-benzoquinone-4-oxime

$hk0$	Q_c	Q_o	hkl	Q_o	Q_o
100	19·8	20·1	500	495·0	494·2
020	20·7	20·9	010	517·6	518·0
$\bar{1}20$	23·6	23·9	5100	590·1	591·0
120	57·4	57·6	001	392·0	391·5
?	?	62·0	111	408·5	409·5
$\bar{2}20$	66·4	66·1	121	415·7	416·1
$\bar{1}40$	68·8	69·2	031	438·8	438·3
200	79·2	79·3	221	458·2	458·2
040	82·8	83·1	231	467·3	466·6
$\bar{2}40$	94·4	94·7	041	475·2	474·4
220	133·7	133·7	131	483·9	485·6
140	136·4	136·5	211	493·3	493·1
$\bar{3}20$	148·2	148·3	151	499·6	498·8
$\bar{1}60$	155·4	156·0	?	?	512·9
$\bar{3}40$	159·6	157·7	221	525·8	525·9
$\bar{2}60$	164·1	164·8	321	540·3	539·4
300	178·2	178·1	161, $\bar{3}11$	549·1	548·5
240	229·6	229·6	$\bar{2}61$	557·0	555·9
320	249·6	249·6	231	568·7	567·2
$\bar{4}40$	264·4	264·4	$\bar{2}51$	573·4	572·2
$\bar{2}80$	275·2	276·1	151	584·0	583·2
$\bar{1}80$	283·4	284·2	$\bar{3}61$	605·3	604·7
$\bar{4}60$	300·3	300·6			
400	316·8	316·6			
080	331·2	332·1			
340	362·4	362·4			
260	366·9	367·0			
$\bar{4}80$	377·6	378·3			
420	405·1	404·3			
540	408·8	408·8			
$\bar{5}60, 2100$	427·8	428·0			
$\bar{3}100$	442·3	443·7			
$\bar{1}100$	452·9	453·8			
$\bar{5}80$	488·2	488·2			

In Tables 1 and 2 are listed the observed and calculated Q values of both $β$-compounds.

Unit-cell dimensions and space groups

The fibre periods c of $β$-BrMBO and $β$-ClMBO are 3·9 and 3·8 Å, respectively. The zero layer $hk0$ of the chlorine compound fibre photograph was indexed on a hexagonal lattice with $a = 19·3$ Å. However, the powder lines of the Guinier photographs could be interpreted only in terms of an orthorhombic body-centered lattice with

$$a = 19·3, \quad b = 33·4, \quad c = 3·80 \text{ Å}$$

and 12 molecules in the unit cell.

The general positions in a body-centered orthorhombic cell are at least 8-fold. Twelve molecules can be placed in this cell with the aid of either one 8-fold and one 4-fold or three 4-fold positions.* The special

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* Occupancy of 2-fold positions is impossible since the symmetry $2/m$ would be required for the molecule.

4-fold position should be on a symmetry plane, since the shape of the molecules does not permit any other choice. Because of the very short c-axis this symmetry plane should be a mirror perpendicular to c, leading to the space group $I2mm$. The combination of one 8-fold and one 4-fold position leads to a structure in which the molecules are separated by distances of 1·9 Å from each other. The occupancy of three 4-fold positions would require the intensity distribution of $hk2$ reflexions to be the same as those for $hk0$ reflexions. This is not observed. We conclude that an orthorhombic space group is incompatible with the shape and the number of molecules Z.

A body-centered orthorhombic lattice can be transformed into a base-centered monoclinic cell in three different ways. The choice is obvious since the powder lines of the $β$-bromine compound Guinier photograph can be indexed unequivocally on a primitive monoclinic lattice with a short orthogonal c-axis (Table 3). The chloro- and bromo-compounds are not isomorphous, although the cell dimensions are nearly the same. The systematic absences of reflexions ($hk0$ with $k = $ odd for $β$-BrMBO and hkl with $k+l = $ odd for $β$-ClMBO) indicate the space groups Pb or $P2/b$ for the bromine compound, but the space groups $A2$, Am or $A2/m$ for the chlorine compound. However, the latter two space groups can be excluded on the same grounds as the orthorhombic space groups.

Hydrogen-bonding in $β$-ClMBO

The infrared absorption spectra of solutions of $β$-ClMBO in tetrachloroethene exhibit an absorption band at 3570 cm.$^{-1}$ which is attributed to a free OH stretching frequency. No infrared absorption spectrum of the $α$-chloro-isomer could be recorded since suitable polar solvents, transparent in the infrared range, were not available. Infrared spectra (KBr discs) of $α$- and $β$-ClMBO are essentially similar. The OH stretching frequency is shifted towards 3170 cm.$^{-1}$ which is characteristic in the presence of the OH group involved in hydrogen bonding.

Inspection of the hydrogen bonding in crystals of 3-chloro-p-benzoquinone-4-oxime (Romers, Brink Shoemaker & Fischmann, 1957), $α$-2-chloro-5-methyl-p-benzoquinone-4-oxime (the preceding paper), $α$-methoxy-o-benzoquinone-2-oxime (Bartindale, Crowder & Morley, 1959) and $α$-5-(2'-chloroethoxy)-o-benzoquinone-2-oxime (Romers & Umans, 1960) shows that hydrogen bridges link oxime and carbonyl groups of successive molecules in a head-tail coupling. Assuming the presence in the $β$-isomers of head-tail

Table 3. *Cell dimensions (Ångström units), densities (g.cm.$^{-3}$) and space groups*
of β-2-chloro- and β-2-bromo-5-methyl-p-benzoquinone-4-oxime

Compound	a	b	c	$γ$ (degrees)	$γ$ (Å^3)	d_o	d_c	Z	Space group
$β$-ClMBO	19·3	38·6	3·80	120	2453	1·40	1·39	12	$A2$
$β$-BrMBO	19·1	37·3	3·89	114·6	2519	1·69	1·76	12	$P2/b$ (or Pb)

chains parallel to the fibre-axis the puzzling problem of reconciling the observed very short fibre period with a period of 15 Å found in α-ClMBO arises.

The approximate values of bond angles in the above-mentioned bridges are:
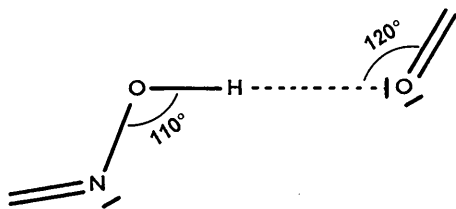
These angles indicate *four* possible preferential orientations of hydrogen bonds in p-benzoquinone-monoxime, shown by arrows in Fig. 1(a), but only *two* in β-ClMBO if it is assumed that the oxime group is *anti* with respect to the chlorine atom (Fig. 1(b)). The *Stuart* model of β-ClMBO molecules in
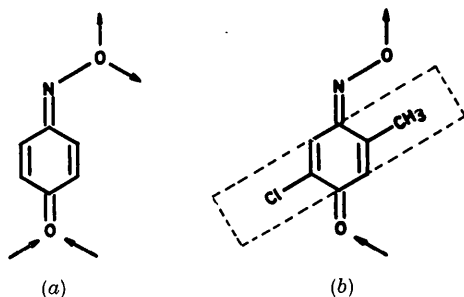
Fig. 1. Preferential orientations of hydrogen bonds in p-benzoquinone-monoxime (a) and in β-ClMBO (b).
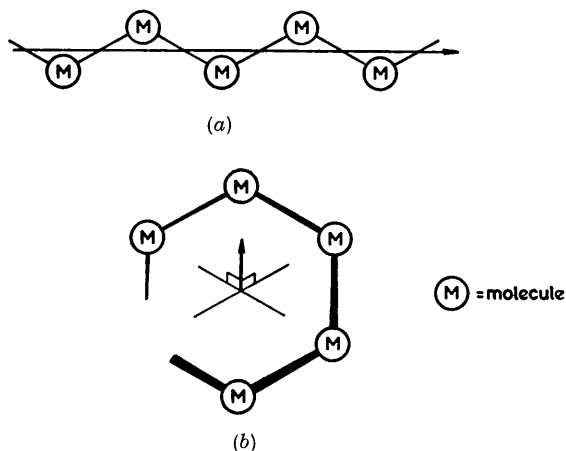

Fig. 2. Two ways of chain formation in fibres of β-ClMBO: a zig-zag chain (a) and a (pseudo-)hexagonal helix (b).

anti-configuration suggests two possible arrangements of hydrogen bridges:

1. A zig-zag chain of molecules with a period of about 15 Å (Fig. 2(a)) which cannot be reconciled with the shortness of the fibre period.
2. A (pseudo-) hexagonal ring or helix of molecules (Fig. 2(b)) which is consistent with the short fibre period.

The two-dimensional model

A model of six molecules in a hexagonal ring arrangement with hydrogen bonds (2·7 Å) was constructed. It was possible to place such a model on a two-dimensional hexagonal lattice with plane group $p6$ and a period of 19·3 Å (Fig. 3). The intensities of the first 10 $hk0$ reflexions (hexagonal indices) were calculated on the basis of this model and compared
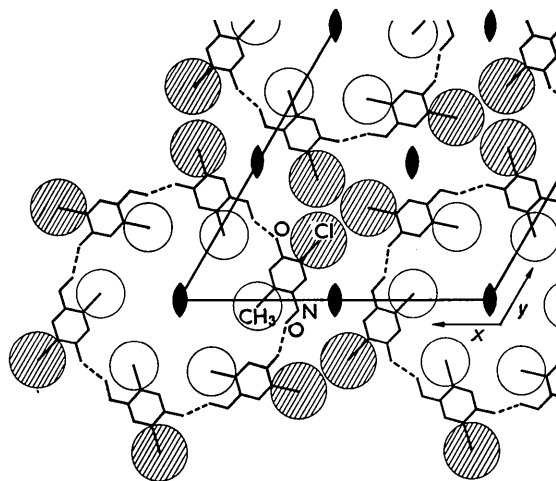

Fig. 3. The two-dimensional model of β-ClMBO. The large shaded circles are the chlorine atoms, the open circles are the methyl groups. The dashed lines indicate the hydrogen bonds.

with the visually estimated intensities of the corresponding powder lines (Table 4). Only multiplicity corrections were applied in this calculations. There is good agreement for the first five reflexions. No attempts were made to obtain a better agreement since there are too many parameters (at least 26) and not enough experimental data (only 15 hexagonally indexed prism reflexions).

The three-dimensional models

In the space group $A2$ two-fold axes and two-fold screw axes alternate in one direction. In order to get

Table 4. *Observed and calculated intensities of prism reflexions (hexagonally indexed) of β-ClMBO*

	100	110	200	210	300	220	310	400	320	500
Estimated	w	s	m	vs	w	m	w	w	w	m
Calculated	183	3500	1150	9400	310	225	2060	1000	1150	860

an idea of the three-dimensional structure, models with the following symmetry were considered:

1. Substitution of a diad 2 by 6.
2. Substitution of a screw 2_1 by 6_1 (see Fig. $4(a)$).
3. Substitution of a diad 2 by 6_2 (see Fig. $4(b)$).
4. Substitution of a screw 2_1 by 6_3 (see Fig. $4(c)$).

It is also possible to construct models with a trigonal character. These can, however, be deduced from the above-mentioned hexagonal models and therefore were not considered further. Since almost all known fibre structures exhibit a helical arrangement of (molecular) chains in the fibre direction a ring structure is highly improbable. Since the reflexions 001, 003 and 005 are forbidden by the centering A and the
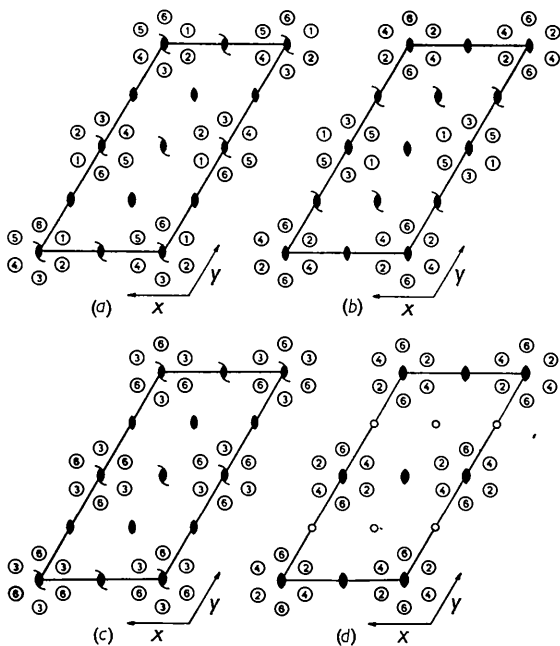

Fig. 4. Possible ways of placing (pseudo-)hexagonal helices in the unit cells with symmetry $A2$ (Figs. (a), (b), (c), respectively) and $P2/b$ (Fig. (d)).

reflexions 002 and 004 are also unobserved, it is impossible to decide whether the helices are really hexagonal, nor can a distinction be made between 6_1, 6_2 or 6_3. The remarkable similarity of cell dimensions, but difference in space group of β-ClMBO and β-BrMBO, suggests a structural relationship between both kinds of fibres. The similarity is conceivable if one assumes for the bromocompound a two-string helical structure deviating slightly or not at all from the centro-symmetric space group $P2/b$ (Fig. $4(d)$), which corresponds to the two-string helical arrangement (Fig. $4(b)$) of the chloro-compound. Fig. $4(d)$ is derivable from Fig. $4(b)$ by replacing the screw axes by centres of symmetry.

Concluding remarks

It is also possible to construct a helical structure with molecules in syn-configuration. However, as was shown by Kehrmann (1898) and Umans (1959) the α- and β-form of ClMBO are formed simultaneously and have so far resisted attempts at interconversion. For this reason dimorphism must be excluded. Since it has been shown that the α-form is in syn-configuration, chemical evidence (Umans, 1959) leads to the conclusion that the β-form is in anti-configuration.

The measured densities of the β-compounds are much smaller than those of the corresponding α-isomers. The large channels within the helices with a diameter of about 6 Å may account for these lower densities. Inclusion of solvent molecules like CCl_4, CH_3OH, benzene and dioxane which can be packed in the channels are probably responsible for the deviation from the theoretical value of the chlorine content found after recrystallization from these solvents. After sublimation the chlorine content approaches the theoretical value.

Upon examination of molecular models it was expected that iodine molecules would fit into the channel and that an inclusion complex comparable to the well-known blue iodine amylose compound (Rundle & Baldwin, 1943; Rundle & Edwards, 1943) might be formed between the β-form of the 2-halogeno-5-methyl-quinone-4-oxime and iodine (Fischmann, 1959). Upon mixing methanolic solutions of the β-isomers and iodine and drying, an intensively blue-coloured product resulted. The α-isomers did not exhibit this phenomenon.

This formation of clathrate compounds by the β-isomers may be considered as an independent indication in favour of the assumption of the helical structure. The question of the stability of syn- and anti-forms of quinone monoximes as a more general phenomenon and the reason for it in the case of the 2-halogeno-5-methyl-quinone-4-oximes is being studied in this laboratory.

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The Crystal Structure of Cesium Triborate, Cs₂O . 3 B₂O₃

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Crystalline cesium triborate, $Cs_2O.3B_2O_3$, has been prepared and the structure determined. The crystals belong to the space group $P2_12_12_1$, with unit-cell dimensions

$$a = 6 \cdot 18, \quad b = 8 \cdot 48, \quad c = 9 \cdot 17 \text{ Å}.$$

A complete set of atomic parameters has been determined from electron-density projections along the two shortest axes. The structure has one out of every three boron atoms four-fold coordinated by oxygen, the other two being three-fold coordinated. The basic unit of the structure is a six-membered ring, interlinked with identical rings to a continuous three-dimensional network. The structure is related to the structure of some other crystalline and vitreous alkali borates. It is shown that the fraction of boron atoms in four-fold coordination in the known alkali borate structures is a simple function of the alkali content up to the diborate composition.

Introduction

Glasses can be prepared in a wide composition range of the binary systems of boron oxide with any one of the alkali metal oxides. Moreover a considerable number of crystalline compounds can be obtained in these systems. A total of between 30 and 40 anhydrous alkali borates are reported in the literature, and more are certain to exist. Very little has previously been known about the crystal structures of the anhydrous alkali borates; only two borates of the metaborate composition have been investigated (Zachariasen, 1937; Fang, 1938). The author has recently determined the crystal structures of potassium pentaborate and rubidium pentaborate (Krogh-Moe, 1959a). In the present work the crystal structure of cesium triborate will be reported. These new structure investigations indicate some basic principles in the crystal chemistry of the alkali borates. The results are also of interest in discussing the structure of the alkali borate glasses.

Experimental

Cesium triborate was prepared by crystallization from a melt (or glass) below 800 °C. The melt was obtained by fusing together the stoichiometric amounts of cesium carbonate and boric acid, raising the temperature to about 1000 °C. for a short time to drive off water and carbon dioxide.

Phase relationships, unit-cell data and the approximate cesium-atom position have previously been reported for this compound (Krogh-Moe, 1958a, b). The crystals are orthorhombic, space group $P2_12_12_1$, with axial lengths:

$$a = 6 \cdot 18, \quad b = 8 \cdot 48, \quad c = 9 \cdot 17 \text{ Å}.$$

2 formula units $Cs_2O.3 B_2O_3$ in the cell correspond to a calculated density of 3·39 g.cm.⁻³.

Mo $K\alpha$ radiation and the multiple-film technique were used to take integrated, equatorial Weissenberg $0kl$ and $h0l$ photographs. The crystals used for the exposures had quadratic crossections perpendicular to the axis of rotation, with side lengths about 0·008 cm. No corrections for absorption were made. (The linear absorption coefficient of cesium triborate for Mo $K\alpha$-radiation is $\mu = 81\cdot4$ cm.⁻¹). The relative intensities were estimated visually by comparison with a standard scale, and the usual corrections for the Lorentz and polarization factors were made.

Structure analysis

According to an earlier study by the author, the cesium atoms occupy a general four-fold position in the structure (Krogh-Moe, 1959b). Three cesium parameters therefore have to be determined. Using the signs calculated from the approximate cesium posi-