selben Cu-Lagen und sehr ähnliche Pb-Lagen wie wir gefunden, ferner entspricht sein OH (2) recht gut unserem OH (1). Für den Schwefel hat er denselben y-Parameter und einen ähnlichen x-Parameter wie wir gefunden; sein z_S ist aber von unserem prinzipiell verschieden, ebenso die Lage der Sauerstoffe der Sulfatgruppe im Raum und die zweite Hydroxylgruppe. Araki's Struktur ist jedoch wesentlich schlechter belegt als unsere, wie sich aus der folgenden Gegenüberstellung von R-Werten im Cu-Bereich der Weissenbergkamera ergibt (nicht beobachtete Reflexe für beide Autoren gleich null gesetzt):

	Araki	Bachmann & Zemann
R_{hk0} (ohne $h00$)	$0,22_2$	$0,08_5$
R_{hkl}	$0,28_7$	$0,08_1$

Wir sind der Ansicht, dass daraus klar hervorgeht, dass bei Araki die Übereinstimmung zwischen F_o und F_c nicht genügend gut ist, um leichte Atome neben Blei eindeutig zu lokalisieren. Von der Beweiskraft der beträchtlich besseren Belegung unserer Struktur abgesehen, ist sie auch vom kristallchemischen Gesichtspunkt aus sehr viel befriedigender als diejenige von Araki. Wir müssen folglich die in der vorliegenden Arbeit angegebene Atomanordnung als die richtige ansehen.

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Isomerism of Benzoquinone-Monoximes (Nitrosophenols). X. The Crystal structures of α-2-Bromo- and α-2-Chloro-*p*-Benzoquinone-4-Oxime Acetate*

By E. Fischmann,† C. H. MacGillavry and C. Romers

Laboratory of General and Inorganic Chemistry, Municipal University of Amsterdam, Netherlands;
Organic Chemistry Department, The University of Leiden, Netherlands

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The isomorphous crystal structures of α-2-chloro-*p*-benzoquinone-4-oxime acetate and of the corresponding bromo-compound were determined from projections along [100] and [001] with aid of low temperature data. The unit cell dimensions of the chlorine compound at −140 °C. are

$$a = 7{\cdot}28,\ b = 19{\cdot}04,\ c = 6{\cdot}06\ \text{Å},\ \beta = 96{\cdot}6^\circ,\ Z = 4\ .$$

The space group is $P2_1/a$. The halogen atoms are *syn* with respect to the oxime acetate group.

Introduction

From the products obtained upon benzoylation or acetylation of 2-chloro-*p*-benzoquinone-4-oxime two isomers can be isolated (α and β). The discoverer of the isomeric benzoates (Bridge, 1893) believed the isomers to have different structures, the chlorine atom being *ortho* or *meta* with respect to the acylated oxime group. Kehrmann (1894) put forward strong arguments against this hypothesis and expressed the view that the two forms should be *syn*/*anti* stereoisomeric quinone oxime derivatives:

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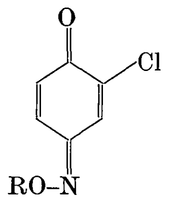
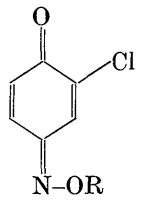
* For the other papers of this serial consult part VIII (Romers & Fischmann, 1960).

† Present address: Philips Research Laboratories, N.V., Philips' Gloeilampenfabriek, Eindhoven, Netherlands.



and



More recently the absorption spectra of the compounds were studied by Ramart-Lucas & Martynoff (1949*a*, *b*) who for the acetates—in accordance with a similar hypothesis for the benzoates—came to the conclusion that the higher melting α-isomer should be the chloro-nitroso-phenol-ester, whereas the β-isomer was considered to be a mixture of chloro-nitroso-phenol-acetate and chloro-benzoquinone-monoxime acetate.

Umans (1959) in an extensive reinvestigation corroborated the viewpoint of Kehrmann and established the *syn*/*anti* stereoisomerism of the benzoates by eliminating other possibilities of isomerism. Umans also prepared the isomeric acetates.

It was deemed important to determine the crystal structures of α-2-chloro-*p*-benzoquinone-monoxime acetate (α-ClBOA) and the corresponding β-form (β-ClBOA) in order to obtain direct evidence on the nature of the stereoisomerism and to establish the configurations of the α and the β-forms. The corresponding bromine compound (α-BrBOA) was also studied. The crystal structure of β-BrBOA was not investigated, since this compound is very unstable and its crystals could not be isolated in pure form. This investigation did not aim at high precision of the measurement of bond lengths and bond angles. For this reason the crystal structures were only studied in projections. In this paper the structures of the α-compounds, are described; in a following paper (Fischmann, MacGillavry & Romers, 1961) the structure of β-ClBOA as well as a discussion of some molecular features of the two forms will be given.

Experimental part

BrBOA and ClBOA were obtained by treatment of 2-bromo- and 2-chloro-*p*-benzoquinone-4-oxime with acetic anhydride. The α- and β-forms were separated (Umans, 1959) by fractional crystallization from ethanol, petroleum ether or a mixture of cyclohexane and a little benzene.

The α-crystals are yellow monoclinic prisms with well developed faces {010} and forms indexed as {110}, {120}, {011}, $\{\bar{1}11\}$, $\{\bar{1}21\}$ and $\{\bar{2}01\}$. The plane $(\bar{2}01)$, making an angle of about 35° with [001] is a perfect cleavage plane. The acute bisectrix interference figure could be observed through a cleavage fragment; the binormals are just outside the field of vision. The crystals are biaxially negatively birefringent ($n_\alpha \ll n_\beta < n_\gamma$) with n_α perpendicular to $(\bar{2}01)$, n_β parallel to [102] and n_γ parallel to [010].

With aid of oscillation and Weissenberg photographs the unit cell dimensions of α-BrBOA were determined at room temperature and those of α-ClBOA at room temperature and at −140 °C. (Table 1). The density of α-ClBOA was measured by the flotation method. There are four molecules per unit cell. Systematic absences of reflexions $0k0$ with k = odd and $h0l$ with h = odd lead to the conclusion that α-BrBOA and α-ClBOA belong to the space group $P2_1/a$ and are isomorphous. This conclusion was confirmed by the ultimate analysis.

The linear absorption coefficients (Cu $K\alpha$ radiation, 1·5418 Å) of the bromine and the chlorine compound are 65 cm.$^{-1}$ and 37 cm.$^{-1}$, respectively. In order to minimize the absorption and to facilitate the absorption correction the crystals were ground to cylinders with diameters of 0·02 cm., resulting in μR values of 0·65 and 0·37, respectively. Equi-inclination Weissenberg photographs (multiple film technique) about [100] (zero and first layer) and about [001] (zero layer) were taken with unfiltered copper radiation at room temperature for the bromine compound and at 20 °C. and at −140 °C. for the chlorine compound. The intensities of the recorded reflexions at −140 °C. were measured visually with a calibrated intensity scale and the usual Lorentz, polarization, absorption and film spot corrections were applied.

The [001] *projection*

Upon visual inspection of $hk0$ reflexions of α-BrBOA the x- and y-parameters of the bromine atom were determined to be $x = 0{\cdot}03$ and $y = 0{\cdot}17$. The assumption that the chlorine atom has the same positional parameters is in agreement with the Patterson map $P(u, v)$ of α-ClBOA. This Patterson function was calculated with Fourier coefficients $F^2\xi^2 \exp(-0{\cdot}17\xi^2)$, $\xi = 2\sin\theta$. It is easily shown that this modified function, first introduced by Schomaker & Shoemaker (see Lipson & Cochran, 1953, p. 173), corresponds essentially to the convolution of the electron density with the negative value of its curvature. By application of the vector-convergence method (Beevers & Robertson, 1950) the positions of the light atoms belonging to the chloro-compound could be detected.

The positions of all atoms, except hydrogen, were introduced into the calculation of structure factors $F(hk0)$. The refinement of the structure based upon

Table 1. *Unit cell dimensions and densities* (g.cm.$^{-3}$)

Compound	a	b	c	β	Z	d_o	d_c	Temp.
α-BrBOA	7·72 Å	19·37 Å	6·06 Å	99·4°	4	—	—	20 °C.
α-ClBOA	7·50	19·20	6·09	96·6	4	1·55	1·55	20
α-ClBOA	7·28	19·04	6·06	96·6	4	—	—	−140

low temperature data proceeded in the conventional way by eight successive cycles of calculations of structure factors, electron density projections (three cycles) and electron density difference maps (five cycles). With an isotropic temperature factor exp $(-1{\cdot}08\sin^2\theta/\lambda^2)$ and without hydrogen contributions (only one of them showed up distinctly on the final difference map), the R factor decreased to 14% (Table 2). The final electron density map $\varrho(x, y)$ (Fig. 1) shows that the molecule is completely free from overlap due to neighbouring molecules. There is, however, partial overlap between the atom pairs C_1 and C_2, C_4 and C_5, N and O_2 and C_7 and C_8, respectively (see Fig. 4 for the numbering of the atoms).

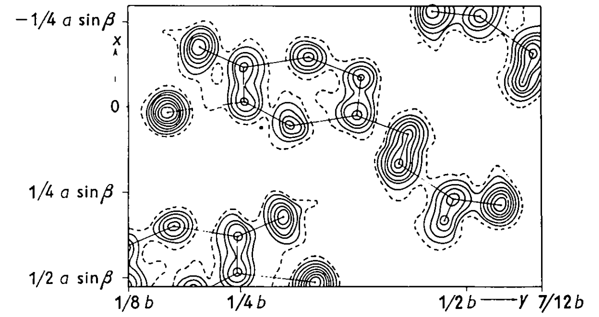


Fig. 1. The projection of the electron density $\varrho(XY)$ of α-2-chlorobenzoquinone-oximeacetate-4 projected along [001]. The contour lines are drawn at 2, 4, 6 ... e.Å^{-2}, those for the chlorine atoms 2, 5, 10, 15 ... e.Å^{-2}. The 2 line is dashed.

The [100] *projection*

Assuming an approximately planar molecule, it was possible to construct two models of the structure of α-ClBOA with aid of the known projection along [001] and taking into account the packing conditions and the length of the a-axis. One of these models proved to give the required agreement between calculated and observed structure factors $F(0kl)$. In agreement with the crystal optics, the molecule is approximately parallel to the cleavage plane $(\bar{2}01)$.

The refinement of the electron density projection $\varrho(y, z)$ was hindered because only five atoms C_4, C_5, N, O_2 and C_8 were free from overlap (Fig. 2). The overlap of the atoms C_7 and O_3 is caused by a center of symmetry, that of the remaining atoms by the glide plane a, which does not affect the z parameters of atoms C_1 and C_2, and only slightly those of atoms C_3, C_6, O_1 and Cl.

In order to find better y and z parameters of the atoms suffering from overlap, 'mixed' projections (Zachariasen, 1954)

$$\varrho_m(y, z) = \varkappa\varrho(y, z) + \mu C_1(y, z) + \nu S_1(y, z)$$

were calculated in which the coefficients $\varkappa$, μ and ν determine the contributions of the normal projection of the density function ϱ, the cosine function C_1 and the sine function S_1, respectively. The function ϱ is based upon a two-dimensional Fourier summation with Fourier coefficients $F(0kl)$. The cosine function C_1 and the sine function S_1 are similar summations with Fourier coefficients $F(1kl)$ (Cochran & Dyer, 1952; Fridrichsons & Mcl. Mathieson, 1955). Two examples of this procedure are shown in Fig. 3, where the mixed projections are drawn for atoms Cl (full lines) and C_3 (dashed lines) and for atoms O_3 (full lines) and C_7 (dashed lines). The overlap of the first pair is caused by the chlorine atom at height $x = -0{\cdot}016$ and the atom C_3 at height $0{\cdot}500+0{\cdot}045$. Since the cosine modulation is given by $\cos 2\pi x$ it is clear that the function $\varrho + C_1$ suppresses C_3, while the function $\varrho - C_1$ suppresses Cl.

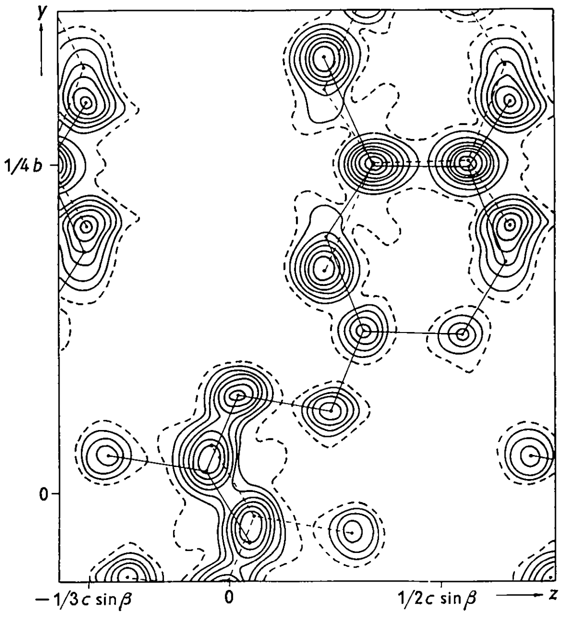


Fig. 2. The projection of the electron density $\varrho(YZ)$ of α-2-chlorobenzoquinone-oximeacetate-4 projected along [100]. The contour lines are drawn at 2, 4, 6 ... e.Å^{-2}, those for the chlorine atoms at 2, 5, 10, 15, ... e.Å^{-2}. The 2 line is dashed.

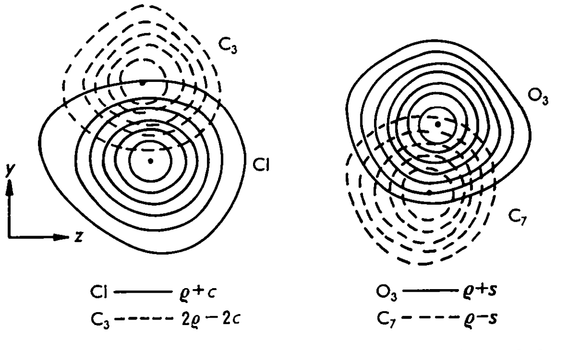


Fig. 3. The mixed projections of atoms C_3, Cl, O_3 and C_7.

In order to carry out this procedure the structure

Table 2. *Structure factors $F(0kl)$, $F(hk0)$ and $F(1kl)$ (one asymmetric unit) of α-2-chloro-p-benzoquinone-4-oxime acetate at* −140 °C.

h	*k*	*l*	F_c	F_o
0	0	0	102	—
	2		$\overline{5{\cdot}9}$	4·2
	4		5·1	6·0
	6		6·8	8·7
	8		$\overline{10{\cdot}2}$	11·6
	10		$\overline{6{\cdot}0}$	5·6
	12		4·7	6·8
	14		$\overline{10{\cdot}0}$	9·0
	16		2·7	3·6
	20		$\overline{5{\cdot}0}$	5·9
	22		$\overline{8{\cdot}5}$	9·0
	24		7·1	7·2
	26		$\overline{2{\cdot}0}$	2·6
0	0	1	$\overline{2{\cdot}7}$	2·8
	1		$\overline{14{\cdot}3}$	15·5
	2		23·7	24·0
	3		$\overline{3{\cdot}2}$	3·2
	4		2·6	3·4
	5		9·4	9·7
	6		4·0	5·0
	8		$\overline{10{\cdot}7}$	10·9
	9		3·5	3·7
	11		13·2	13·3
	12		1·8	2·6
	13		$\overline{3{\cdot}4}$	4·1
	14		3·6	3·9
	15		4·8	5·4
	16		$\overline{4{\cdot}2}$	4·9
	17		1·0	1·2
	19		$\overline{6{\cdot}2}$	7·0
	20		$\overline{2{\cdot}9}$	3·4
	22		2·0	1·3
	23		1·5	1·8
	24		$\overline{1{\cdot}5}$	1·5
0	0	2	$\overline{12{\cdot}0}$	11·9
	1		$\overline{12{\cdot}1}$	11·9
	2		14·5	13·1
	3		3·9	3·0
	4		5·7	4·5
	5		5·5	4·2
	6		$\overline{14{\cdot}2}$	13·5
	7		$\overline{6{\cdot}4}$	6·3
	8		10·1	9·2
	9		9·0	8·9
	10		2·0	1·4
	11		1·7	2·1
	12		$\overline{3{\cdot}9}$	3·8
	14		3·6	3·4
	18		$\overline{5{\cdot}8}$	5·6
	19		$\overline{1{\cdot}4}$	1·4
	20		1·3	1·5
	22		1·8	1·4
	23		2·1	1·4
	26		3·7	4·8
0	0	3	12·9	14·2
	1		16·0	15·4
	2		3·8	4·4
	3		2·3	2·5
	4		5·8	5·6
	5		$\overline{2{\cdot}6}$	2·8
	6		$\overline{3{\cdot}8}$	4·0
	7		8·4	7·4
	9		2·1	1·8
	11		$\overline{3{\cdot}3}$	3·4
	12		$\overline{3{\cdot}1}$	3·1
	13		4·9	5·2
	14		0·6	1·4
	15		$\overline{4{\cdot}4}$	4·1
	17		$\overline{1{\cdot}9}$	1·4
0	18	3	$\overline{4{\cdot}7}$	4·8
	19		4·9	4·5
	21		2·2	1·6
	22		$\overline{1{\cdot}6}$	2·5
	25		3·3	2·5
0	0	4	10·9	10·6
	1		3·4	3·3
	2		5·1	4·5
	4		$\overline{3{\cdot}4}$	3·8
	5		$\overline{1{\cdot}3}$	1·8
	6		2·6	2·6
	7		17·9	15·3
	8		$\overline{6{\cdot}4}$	6·2
	9		$\overline{2{\cdot}1}$	2·0
	10		$\overline{3{\cdot}5}$	3·2
	11		2·6	3·0
	12		3·7	4·0
	13		2·8	3·6
	15		3·4	2·9
	17		$\overline{4{\cdot}0}$	4·0
	18		3·1	3·6
	19		0·6	1·4
	20		$\overline{3{\cdot}8}$	3·9
0	0	5	4·8	3·9
	1		$\overline{3{\cdot}9}$	3·9
	2		$\overline{3{\cdot}0}$	2·1
	4		$\overline{1{\cdot}8}$	2·7
	5		6·7	5·6
	6		1·2	1·5
	7		$\overline{7{\cdot}8}$	7·0
	8		$\overline{5{\cdot}8}$	6·2
	9		9·9	8·5
	10		$\overline{1{\cdot}8}$	1·7
	11		5·7	6·1
	12		6·1	5·5
	15		$\overline{2{\cdot}2}$	1·7
	17		2·8	2·4
	18		1·9	2·5
0	1	6	$\overline{5{\cdot}7}$	6·0
	2		$\overline{1{\cdot}5}$	1·7
	5		1·8	1·6
	6		$\overline{3{\cdot}1}$	2·5
	7		$\overline{1{\cdot}2}$	1·1
	8		1·1	1·1
	9		1·8	2·1
	10		2·4	1·7
	11		4·3	3·7
	12		$\overline{2{\cdot}2}$	1·8
	13		$\overline{2{\cdot}7}$	2·0
	15		1·4	1·6
0	0	7	$\overline{5{\cdot}6}$	5·1
	1		2·7	2·9
	2		3·2	3·6
	4		0·4	0·6
	6		$\overline{5{\cdot}8}$	5·4
	7		4·8	4·5
	8		4·2	3·8
0	0	8	$\overline{2{\cdot}2}$	2·5
	1		2·3	2·0
	7		3·3	3·4
	8		$\overline{3{\cdot}6}$	3·9
	9		2·3	1·5
1	1	0	$\overline{6{\cdot}2}$	5·6
	2		$\overline{4{\cdot}8}$	4·3
	3		$\overline{2{\cdot}4}$	1·7
	4		$\overline{5{\cdot}7}$	5·6
	5		16·3	14·6
	6		$\overline{8{\cdot}8}$	8·4
	7		9·2	9·1
1	8	0	8·4	8·6
	9		$\overline{9{\cdot}8}$	9·5
	10		1·4	1·8
	11		4·5	5·0
	13		3·1	3·6
	14		2·1	0·9
	15		$\overline{10{\cdot}2}$	11·4
	16		$\overline{11{\cdot}2}$	12·0
	17		$\overline{3\ 8}$	2·9
	18		$\overline{1{\cdot}6}$	2·0
	19		4·1	5·6
	20		$\overline{2{\cdot}9}$	3·5
	21		$\overline{4{\cdot}5}$	5·5
	22		$\overline{2{\cdot}1}$	2·6
	23		6·2	6·3
	24		1·2	0·9
	27		$\overline{3{\cdot}0}$	2·3
2	0	0	10·9	10·9
	1		$\overline{7{\cdot}5}$	7·8
	2		20·3	22·8
	3		13·9	13·0
	4		$\overline{14{\cdot}7}$	14·8
	5		1·3	2·1
	6		3·5	3·3
	7		2·7	3·9
	8		1·8	0·7
	9		$\overline{7{\cdot}4}$	6·2
	10		$\overline{3{\cdot}5}$	6·2
	11		$\overline{8{\cdot}0}$	6·7
	12		8·9	8·5
	13		$\overline{4{\cdot}8}$	4·5
	14		$\overline{6{\cdot}3}$	5·6
	15		1·9	2·8
	16		5·3	5·4
	18		8·0	9·0
	19		2·9	2·8
	20		$\overline{1{\cdot}6}$	2·0
	21		$\overline{1{\cdot}1}$	1·1
	22		$\overline{3{\cdot}0}$	3·7
	23		2·3	1·3
	26		$\overline{2{\cdot}5}$	2·0
3	3	0	$\overline{9{\cdot}2}$	10·8
	4		$\overline{9{\cdot}0}$	8·1
	5		$\overline{3{\cdot}3}$	2·8
	6		$\overline{7{\cdot}8}$	7·6
	7		2·6	2·1
	9		$\overline{15{\cdot}6}$	15·1
	10		0·1	1·2
	11		9·1	9·9
	12		2·5	2·3
	13		12·9	12·1
	14		6·5	5·7
	15		$\overline{7{\cdot}6}$	6·8
	16		$\overline{1{\cdot}6}$	1·8
	17		7·4	6·8
	18		3·3	2·8
	19		0·7	1·3
	20		3·8	4·8
	21		$\overline{5{\cdot}5}$	6·2
	23		5·2	5·0
4	0	0	7·8	8·4
	1		7·5	8·3
	2		$\overline{1{\cdot}7}$	1·5
	3		$\overline{4{\cdot}9}$	5·2
	4		$\overline{2{\cdot}2}$	2·2
	5		$\overline{5{\cdot}8}$	6·4
	6		10·7	12·7
	7		10·8	10·8
	8		0·8	1·2
4	9	0	$\overline{4{\cdot}1}$	4·6
	10		$\overline{2{\cdot}2}$	3·2
	11		2·4	1·9
	12		3·1	4·0
	14		$\overline{5{\cdot}6}$	5·4
	16		$\overline{2{\cdot}1}$	2·4
	18		4·1	5·0
	19		2·2	2·7
	20		$\overline{2{\cdot}2}$	2·4
	21		2·1	1·7
	24		4·2	4·3
5	1	0	7·0	8·7
	2		4·5	3·9
	3		$\overline{5{\cdot}5}$	5·8
	4		2·8	1·8
	5		7·8	7·8
	6		3·0	1·6
	8		1·9	1·9
	9		$\overline{6{\cdot}5}$	7·2
	11		1·4	2·3
	14		2·0	3·2
	15		$\overline{5{\cdot}4}$	7·0
	16		$\overline{1{\cdot}6}$	1·3
	17		3·0	3·0
	18		$\overline{3{\cdot}8}$	3·9
	19		3·7	3·0
	21		$\overline{2{\cdot}9}$	3·9
	22		$\overline{5{\cdot}7}$	4·1
6	0	0	8·7	8·2
	1		6·8	7·1
	2		$\overline{8{\cdot}5}$	7·4
	3		1·2	1·4
	4		$\overline{3{\cdot}0}$	2·8
	5		$\overline{2{\cdot}0}$	2·4
	6		4·9	5·1
	7		6·5	6·2
	8		$\overline{5{\cdot}1}$	5·1
	10		$\overline{0{\cdot}6}$	1·4
	11		$\overline{2{\cdot}2}$	2·4
	12		6·9	6·2
	13		3·9	4·2
	14		$\overline{1{\cdot}9}$	2·9
	15		$\overline{3{\cdot}1}$	3·8
	16		$\overline{1{\cdot}9}$	1·7
7	3	0	5·1	4·5
	4		$\overline{2{\cdot}4}$	2·8
	5		1·1	1·0
	6		$\overline{2{\cdot}2}$	1·4
	8		6·6	5·7
	9		$\overline{3{\cdot}8}$	4·2
	10		$\overline{4{\cdot}1}$	3·4
	11		2·0	2·0
	14		6·0	6·0
	15		$\overline{1{\cdot}5}$	1·6
8	0	0	4·2	3·3
	1		2·6	2·5
	2		$\overline{1{\cdot}3}$	2·3
	3		1·2	1·3
	5		$\overline{6{\cdot}6}$	5·6
	6		4·2	3·6
	8		2·6	2·3
	9		$\overline{2{\cdot}2}$	1·8
	10		$\overline{5{\cdot}7}$	4·0
	11		$\overline{1{\cdot}0}$	1·6
	12		5·5	4·8
9	1	0	5·4	3·1
	2		3·0	2·3
	3		$\overline{1{\cdot}9}$	1·6
	4		$\overline{3{\cdot}8}$	3·3

Table 2 (*cont.*)

h	*k*	*l*	F_c	F_o
9	5	0	1·6	2·3
	6		2·7	1·8
	7		1·7	1·2
	8		2·5	1·9
	9		$\overline{5\cdot0}$	3·2
	10		$\overline{7\cdot4}$	5·1
	11		3·4	2·3
1	1	1	3·7	3·0
	2		$\overline{3\cdot5}$	3·5
	3		$\overline{6\cdot9}$	8·9
	4		$\overline{16\cdot1}$	15·5
	5		$\overline{8\cdot4}$	8·5
	6		$\overline{1\cdot8}$	1·8
	7		5·7	5·8
	8		13·9	13·3
	9		$\overline{2\cdot2}$	3·0
	10		$\overline{4\cdot8}$	5·6
	11		$\overline{1\cdot6}$	2·0
	12		1·7	2·5
	13		$\overline{1\cdot0}$	0·7
	14		6·4	9·1
	15		$\overline{4\cdot1}$	3·8
	16		$\overline{10\cdot7}$	11·5
	17		8·5	8·3
	18		$\overline{6\cdot8}$	7·4
	20		1·7	1·8
	22		$\overline{6\cdot9}$	7·6
	23		0·9	1·6
	24		3·5	2·6
1	1	$\bar{1}$	2·1	2·6
	2		$\overline{5\cdot6}$	5·1
	3		$\overline{3\cdot8}$	2·6
	4		11·4	9·6
	5		5·2	4·8
	6		12·2	9·8
	7		7·5	6·5
	8		$\overline{6\cdot2}$	5·4
	9		7·0	5·8
	10		15·0	13·0
	11		$\overline{1\cdot6}$	2·0
	12		1·0	1·0
	13		$\overline{3\cdot2}$	3·8
	14		$\overline{14\cdot6}$	13·6
	15		$\overline{4\cdot1}$	4·1
	16		6·9	7·4
	18		$\overline{6\cdot3}$	7·0
	20		$\overline{6\cdot7}$	7·6
	21		$\overline{1\cdot9}$	2·5
	22		4·5	5·6
	24		$\overline{3\cdot8}$	4·0
1	1	2	$\overline{1\cdot6}$	1·8
	2		3·2	3·9
	3		9·8	10·7
	4		$\overline{1\cdot5}$	2·0
	6		5·1	5·1
	7		$\overline{11\cdot9}$	12·3
	8		3·4	4·5
1	9	2	5·0	5·9
	10		8·1	8·2
	11		$\overline{7\cdot0}$	7·2
	12		1·4	2·3
	13		$\overline{6\cdot9}$	7·9
	14		$\overline{3\cdot8}$	4·1
	15		11·1	11·8
	16		$\overline{3\cdot0}$	3·2
	17		$\overline{6\cdot3}$	7·3
	18		$\overline{4\cdot1}$	4·1
	19		$\overline{0\cdot7}$	1·4
	21		6·7	8·0
	22		$\overline{1\cdot8}$	2·0
	23		$\overline{3\cdot6}$	4·2
1	1	$\bar{2}$	$\overline{7\cdot0}$	9·5
	3		6·6	5·7
	4		4·1	4·8
	5		$\overline{5\cdot8}$	5·2
	6		6·1	5·5
	7		1·7	1·2
	9		5·5	5·3
	10		5·5	5·5
	11		$\overline{1\cdot5}$	2·2
	12		1·3	1·0
	13		$\overline{0\cdot8}$	0·7
	14		$\overline{5\cdot4}$	4·2
	15		6·7	6·7
	16		$\overline{2\cdot1}$	1·1
	17		2·8	2·5
	18		$\overline{2\cdot7}$	3·0
	19		$\overline{2\cdot1}$	2·5
	20		$\overline{3\cdot4}$	3·8
	21		5·2	6·1
	22		2·3	2·8
	23		$\overline{3\cdot1}$	2·8
1	1	3	1·3	2·0
	2		$\overline{5\cdot0}$	5·5
	3		4·9	5·7
	4		6·8	6·8
	5		1·7	1·8
	7		$\overline{3\cdot8}$	4·7
	8		$\overline{1\cdot6}$	2·9
	9		2·5	4·1
	10		5·7	6·1
	11		$\overline{4\cdot5}$	5·4
	13		$\overline{5\cdot9}$	5·8
	14		$\overline{7\cdot2}$	7·1
	17		$\overline{4\cdot6}$	5·7
	20		$\overline{4\cdot4}$	5·6
	21		3·1	3·0
	22		4·8	4·6
1	1	$\bar{3}$	$\overline{4\cdot8}$	5·6
	2		$\overline{2\cdot3}$	3·4
	3		4·8	5·5
	4		$\overline{9\cdot0}$	8·7
	5		3·6	2·7
	6		$\overline{2\cdot9}$	3·7
1	7	$\bar{3}$	$\overline{3\cdot6}$	2·0
	8		11·9	9·9
	9		6·7	6·6
	10		$\overline{8\cdot1}$	6·8
	12		0	0·8
	13		$\overline{2\cdot6}$	2·5
	14		7·3	7·2
	15		8·0	7·2
	16		$\overline{8\cdot8}$	8·1
	17		$\overline{3\cdot8}$	2·6
	18		$\overline{2\cdot4}$	2·5
	19		1·8	0·6
	20		1·1	1·4
	21		3·7	4·7
	22		$\overline{5\cdot0}$	6·5
1	2	4	$\overline{9\cdot1}$	9·9
	3		$\overline{5\cdot5}$	6·1
	4		$\overline{2\cdot5}$	2·6
	5		1·2	1·0
	6		1·6	0·7
	7		6·9	7·4
	8		$\overline{2\cdot3}$	2·4
	9		$\overline{10\cdot2}$	11·3
	10		1·2	2·2
	11		2·2	2·2
	13		2·5	2·7
	14		$\overline{3\cdot9}$	3·3
	15		$\overline{10\cdot6}$	11·3
	16		3·2	2·6
	17		3·4	2·7
1	18	4	$\overline{4\cdot9}$	5·4
	19		0·9	1·0
	20		$\overline{2\cdot6}$	2·8
1	2	$\bar{4}$	5·4	5·8
	3		$\overline{6\cdot0}$	6·0
	4		$\overline{5\cdot2}$	6·0
	5		8·1	7·4
	6		$\overline{2\cdot3}$	2·3
	7		7·2	8·6
	8		2·1	2·4
	10		5·9	4·2
	11		2·9	2·5
	12		2·4	2·6
	13		2·1	0·8
	15		$\overline{6\cdot6}$	5·8
	16		$\overline{5\cdot0}$	4·8
	17		1·5	1·2
	18		$\overline{1\cdot2}$	1·0
	19		0·8	2·0
	20		2·2	2·4
1	1	5	3·0	3·4
	2		3·5	3·4
	3		$\overline{5\cdot2}$	6·1
	4		$\overline{7\cdot4}$	7·7
	5		$\overline{1\cdot1}$	1·1
	6		$\overline{2\cdot1}$	3·4
	8		3·6	4·0
1	9	5	$\overline{2\cdot0}$	3·2
	10		3·8	4·3
	11		$\overline{1\cdot9}$	1·1
	12		3·1	2·6
	14		3·0	2·8
	15		$\overline{2\cdot3}$	2·6
	16		$\overline{5\cdot4}$	5·4
	17		2·5	2·8
	18		$\overline{0\cdot7}$	1·0
1	1	$\bar{5}$	$\overline{2\cdot4}$	2·8
	2		$\overline{4\cdot9}$	3·6
	3		$\overline{5\cdot8}$	4·6
	4		5·2	4·7
	5		1·1	1·6
	6		3·9	5·3
	7		11·0	11·8
	9		$\overline{2\cdot6}$	2·5
	10		2·8	1·9
	11		4·4	3·8
	13		3·2	2·6
	14		$\overline{1\cdot5}$	1·0
	15		$\overline{6\cdot6}$	7·3
	16		3·8	3·8
	17		5·4	4·7
	18		$\overline{1\cdot7}$	1·6
1	3	6	6·3	4·5
	4		$\overline{3\cdot4}$	4·2
	6		$\overline{1\cdot9}$	1·0
	7		$\overline{5\cdot5}$	8·0
	8		8·1	7·8
	9		$\overline{0\cdot4}$	1·0
	10		$\overline{3\cdot1}$	3·2
	11		$\overline{3\cdot4}$	2·6
	12		1·1	1·2
	13		$\overline{2\cdot4}$	1·9
	14		5·5	5·4
	15		3·1	2·8
1	1	$\bar{6}$	$\overline{4\cdot7}$	4·1
	2		$\overline{3\cdot1}$	2·6
	3		2·3	1·7
	4		4·3	4·0
	7		$\overline{1\cdot5}$	0·7
	8		$\overline{3\cdot4}$	2·8
	9		6·4	5·3
	10		2·3	1·8
	14		$\overline{3\cdot4}$	3·5
1	5	7	$\overline{1\cdot9}$	2·6
	7		$\overline{2\cdot2}$	2·1
	8		$\overline{3\cdot9}$	3·4
1	1	$\bar{7}$	$\overline{2\cdot9}$	2·2
	3		4·7	3·9
	4		$\overline{3\cdot9}$	3·0
	5		1·2	1·8
	6		0·4	1·0
	7		$\overline{2\cdot3}$	1·8
	9		3·5	2·7

factors $F(0kl)$ and $F(1kl)$ were calculated simultaneously. With an isotropic temperature factor $\exp(-0{\cdot}80 \sin^2\theta/\lambda^2)$ the final R factor was 14·7% for the structure factors $F(1kl)$ (see Table 2). Finally the structure factors $F(0kl)$ were refined by calculation of difference maps $\varrho_o(y,z)-\varrho_c(y,z)$. Although there were some indications of hydrogen peaks, no hydrogen contributions were included in the structure factor calculations. With the anisotropic temperature factor $\exp[-(1{\cdot}065+0{\cdot}435\sin^2\varphi)\sin^2\theta/\lambda^2]$ where φ is the angle between the vector to the reciprocal point $0kl$ and the direction b^*, the reliability index R decreased to 11·2% (Table 2).

The accuracy

The accuracy of this analysis was estimated in three ways:

(1) By comparison of y-parameters belonging to atoms free from overlap in both projections. This leads

to errors of 0·01 Å for chlorine and of 0·03 Å for the light atoms. Assuming the errors in the x and z parameters to be the same, the positional errors for chlorine and the light atoms are 0·017 Å and 0·052 Å, respectively. This leads to errors in C–C bonds of 0·07 Å.

(2) By comparison of 'chemically' equivalent bonds in the molecule, the mean error in C–C bonds is 0·04 Å. The comparison with the accurately determined bond lengths in *p*-benzoquinone (Trotter, 1960) leads to errors of 0·05 Å.

(3) By calculation of standard positional errors with the method of Cruickshank (1949). Standard errors

$$\sigma(x)=0{\cdot}03,\quad \sigma(y)=0{\cdot}022,\quad \sigma(z)=0{\cdot}020\ \text{Å}$$

were found for the carbon atoms. The standard error in C–C bond lengths should be smaller than 0·045 Å. Since there is much overlap the third method leads to an underestimation of the errors.

Discussion of the crystal structure

The positional parameters of the molecule α-ClBOA are summarized in Table 3. Both projections, see Figs. 1 and 2, show clearly that the chlorine atom is *syn* with respect to the oxime acetate group in α-ClBOA. In Fig. 4 a part of the crystal structure is viewed along [001]. The molecular distances and the intermolecular distances smaller than 3·65 Å are indicated in the figure. A discussion of the bond distances and a survey of bond angles of α-ClBOA is found in the next paper.

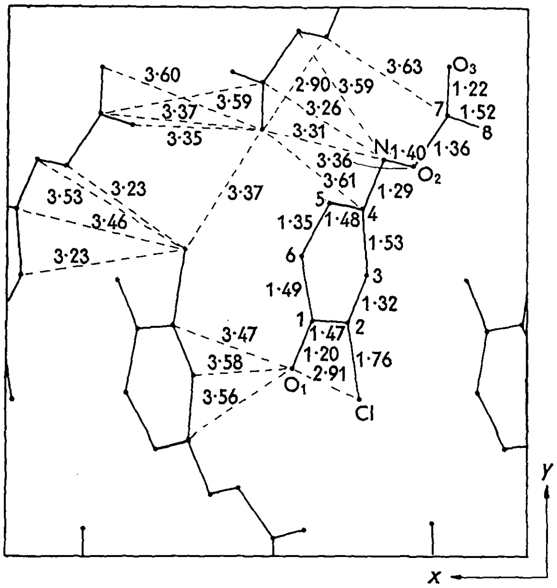


Fig. 4. The crystal structure of α-ClBOA, viewed along [001]. The dashed lines indicate intermolecular distances.

The molecules form a layer structure approximately parallel to the plane ($\bar{2}01$). Nearly all short intermolecular distances are crowded in the planes ($\bar{2}01$). Only a few short distances are found between molecules belonging to different layers. The shortest distance of this group is 3·70 Å. These structural features explain the easy cleavage in the plane ($\bar{2}01$) and are in complete agreement with the crystal optics.

Table 3. *Structural parameters of* α-ClBOA *in fractions of the cell edges at* −140 °C.

	X	*Y*	*Z*
Cl	$0{\cdot}\overline{016}$	0·168	0·226
O_1	0·175	0·204	0·659
O_2	$0{\cdot}\overline{170}$	0·425	0·020
O_3	$0{\cdot}\overline{272}$	0·537	0·047
N	$0{\cdot}\overline{085}$	0·438	0·236
C_1	0·119	0·256	0·562
C_2	0·019	0·253	0·338
C_3	$0{\cdot}\overline{045}$	0·306	0·212
C_4	$0{\cdot}\overline{022}$	0·379	0·317
C_5	0·072	0·384	0·547
C_6	0·152	0·328	0·655
C_7	$0{\cdot}\overline{267}$	0·483	$0{\cdot}\overline{057}$
C_8	$0{\cdot}\overline{356}$	0·469	$0{\cdot}\overline{292}$

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