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Isomerism of Benzoquinone-Monoximes (Nitrosophenols). VIII. The Crystal Structure of α-2-Chloro- and α-2-Bromo-5-Methyl-*p*-Benzoquinone-4-Oxime

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The crystals of α-2-chloro- and α-2-bromo-5-methyl-*p*-benzoquinone-4-oxime are isomorphous and monoclinic, space group $P2_1/c$. The dimensions of the unit cell of the chlorine compound are

$$a = 3{\cdot}85,\ b = 13{\cdot}30,\ c = 14{\cdot}15\ \text{Å},\ \beta = 92{\cdot}2°.$$

The crystal structure of the chlorine compound has been determined by normal and generalized electron-density projections along [100]. The molecule has an oxime structure and the oxime group is *syn* with respect to the chlorine atom.

According to Kehrmann & Tichvinsky (1898) 2-chloro-5-methyl-*p*-benzoquinone-4-oxime (Cl*M*BO) and 2-bromo-5-methyl-*p*-benzoquinone-4-oxime (Br*M*BO) can be prepared in two morphologically different forms, yellow crystals (α-form) and white fibres (β-form, more soluble in solvents such as toluene). Although Hodgson & Moore (1926) did not find two forms, investigations by Umans & Talen (Umans, 1959) confirmed the results obtained by Kehrmann and established that the α- and β-forms are not—or at least not easily—interconvertible. The chemical and spectrophotometric investigations gave support to the view that the two forms might be *anti*/*syn* oxime isomers (Kehrmann & Rüst, 1898; Umans, 1959).

The behaviour of Cl*M*BO and Br*M*BO seems to be at variance with theoretical expectations. A consistent picture of the properties of quinone–monoximes had been arrived at by assuming the existence in solution of a dynamic equilibrium between quinone–monoxime and nitrosophenol molecules, interconversions occurring mainly *via* mesomeric ions (cf. Havinga & Schors, 1950, 1951). In the nitrosophenol form rotation of the NO group could be expected to occur at a non-negligible rate at room temperature. Thus in solutions of substituted quinone–monoximes interconversion of *syn*- and *anti*-isomers should take place through the equilibrium with the nitrosophenolic tautomer.

A crystallographic investigation of Cl*M*BO and Br*M*BO was deemed important since the knowledge of the shape of the molecules might prove helpful in the explanation of their rather unexpected behaviour. A preliminary communication (VI) on the structure of the α-compounds and of 3-chloro- and 3-bromo-*p*-benzoquinone-4-oxime (Romers, Brink Shoemaker & Fischmann, 1957) was published earlier. The structures of the β-compounds are discussed in this journal in paper IX of this series (Fischmann, Romers & Umans, 1960). The other reports of this series (not mentioned before) have been published elsewhere (Kraayeveld & Havinga, 1954*a*, *b*; Schors, Kraayeveld & Havinga, 1955; Romers & Umans, 1960).

Experimental part

The crystalline compounds α-Br*M*BO decomposition at 170 °C. and β-Cl*M*BO melting point 187–191 °C., prepared according to the method of Kehrmann, as described by Umans (1959), form monoclinic yellow needles with principal zone [100] and faces {010} and {102}. (102) is a perfect cleavage plane. The crystals are biaxially negatively birefringent ($n_\alpha \ll n_\beta < n_\gamma$) with n_α perpendicular to (102), n_β parallel to [010]

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Table 1. *Dimensions (Ångström units) of the unit cell and densities* (g.cm.$^{-3}$) *of α-2-chloro- and α-2-bromo-5-methyl-p- benzoquinone at room temp.*

Compound	a	b	c	β (degrees)	d_o	d_c	Z
α-Cl*M*BO	3·85	13·30	14·15	92·2	1·58	1·58	4
α-Br*M*BO	3·91	13·6	14·2	90	1·91	1·85	4

and n_γ parallel to $[20\bar{1}]$. The lattice constants (Table 1) were measured from oscillation photographs about [100] and Weissenberg photographs about [100] and [010]. The space group of both compounds is $P2_1/c$. The densities were measured using the flotation method. The cell dimensions suggest that the compounds are isomorphous and the result of this analysis confirms this view.

Only room-temperature exposures with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) were taken. The intensities of the reflexions of Weissenberg equi-inclination photographs were estimated visually using the multiple-film technique. $0kl$ diffraction data of an α-Br*M*BO crystal with a thickness of 0·02 cm. and $0kl$ and $1kl$ diffraction data of an α-Cl*M*BO crystal with a thickness of 0·03 cm. were obtained. The linear absorption coefficients μ of the compounds are 73 and 43 cm.$^{-1}$ respectively. In order to correct for absorption both crystals were treated as cylinders. The usual Lorentz and polarization corrections were made. Spot-shape corrections were applied to the $1kl$ intensity data.

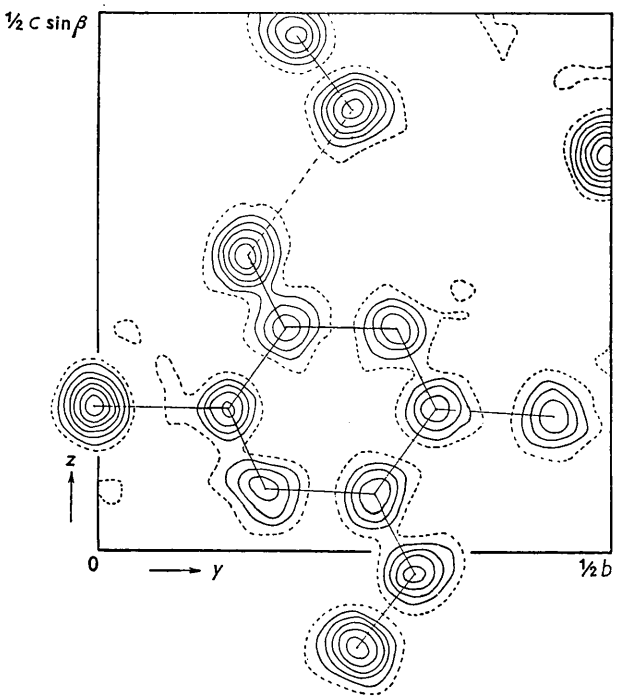

Fig. 1. The projection of the electron density of α-Cl*M*BO along [100]. The contour lines of the chlorine atoms are drawn at intervals of 2, 5, 10, 15, ... e.Å^{-2}, the contour lines of the other atoms are drawn at intervals of 2, 4, 6, ... e.Å^{-2}.

Normal projection along [100]

From the Patterson function $P(vw)$ of α-Br*M*BO the y and z parameters of the bromine atom were determined and by application of the vector-convergence method (Beevers & Robertson, 1950; Buerger, 1959), the details of which are described elsewhere (Fischmann, 1959), the positions of the light atoms were found. The atomic positions were introduced as initial y and z parameters in the refinement of the structure of α-Cl*M*BO. After five successive cycles of calculated structure factors $F(0kl)$ and normal electron-density projections $\varrho(yz)$ (Fig. 1) the reliability index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ decreased to 16% and no more changes of sign were found. Further refinement was attained by successive calculations of difference Fourier maps $\varrho_o(yz) - \varrho_c(yz)$ and structure factors $F(0kl)$. These maps showed that small corrections had to be applied to the positional atomic parameters and that anisotropic thermal motions of the atoms were present. The direction of largest vibration was approximately parallel to [001]. Introduction of the above-mentioned parameter shifts and of a mean temperature factor $\exp[-(1{\cdot}30 + 1{\cdot}55\cos^2\varphi)\sin^2\theta/\lambda^2]$, where φ is the angle between the vector to the reciprocal lattice point $0kl$ and the direction C^*, gave a

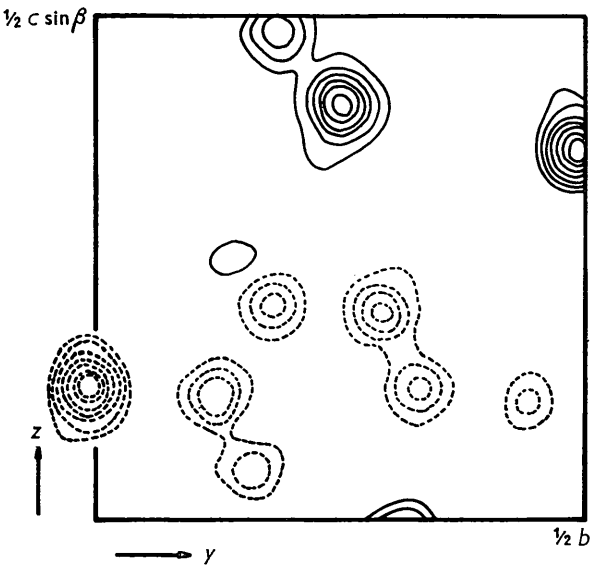

Fig. 2. The imaginary function $S_1(yz)$ of α-Cl*M*BO. The contour lines are drawn to arbitrary scale. The contour lines of the chlorine atoms are drawn at intervals 2·5 times as large as those for the light atoms.

Table 2. *Calculated and observed structure factors*

$F(0kl)$ (one asymmetric unit) and $F(1kl)$ (two asymmetric units)

h k l	F_c	F_o	h k l	F_c	F_o	h k l	F_c	F_o	h k l	F_c	F_o	h k l	F_c	F_o	h k l	F_c	F_o
0 0 2	-0.6	0.5	0 613	-5.0	6.2	015 4	-3.0	3.0	1 3 $\bar{4}$	-17.3	18.0	1 6$\bar{14}$	5.3	6.0	110$\bar{11}$	3.1	2.4
0 0 4	-13.9	12.7	0 614	3.2	3.0	015 5	-4.2	4.1	1 3 $\bar{5}$	-4.9	6.4	1 615	-6.8	3.4	11012	4.5	4.2
0 0 6	-4.4	4.6	0 615	-2.2	1.8	015 6	-4.2	4.3	1 3 5	20.2	17.4	1 6$\bar{16}$	-3.6	6.6	110$\bar{12}$	6.1	8.6
0 0 8	9.7	10.6	0 616	3.4	3.2	015 7	4.3	4.3	1 3 6	-2.8	1.8	1 7 0	6.5	6.6	110$\bar{13}$	-1.3	2.0
0 012	-12.3	11.7	0 7 1	13.0	13.9	016 0	6.4	5.0	1 3 $\bar{6}$	-10.2	11.8	1 7 1	17.6	19.8	11014	-4.3	2.2
0 014	4.3	4.7	0 7 2	-4.2	4.7	016 4	-5.1	5.4	1 3 $\bar{7}$	-5.6	5.4	1 7 $\bar{1}$	-12.0	12.6	110$\bar{14}$	3.0	4.2
0 016	4.4	4.3	0 7 3	-5.0	5.2	016 5	-1.9	1.9	1 3 7	5.0	7.4	1 7 2	-7.2	10.2	111 $\bar{1}$	-10.2	13.2
0 018	1.8	1.0	0 7 5	-6.2	6.0	016 6	0.8	0.8	1 3 8	10.3	8.6	1 7 $\bar{3}$	4.2	4.8	111 $\bar{2}$	-3.5	3.4
0 1 1	6.5	5.4	0 7 7	6.9	6.9	017 1	1.2	1.1	1 3 $\bar{8}$	-1.8	2.8	1 7 3	16.4	17.8	111 $\bar{3}$	8.3	6.4
0 1 2	-10.9	9.1	0 7 8	5.8	5.6	1 0 0	3.3	1.4	1 3 9	5.4	6.8	1 7 $\bar{5}$	14.2	16.4	111 3	4.9	5.0
0 1 3	-7.7	5.8	0 710	2.6	2.8	1 0 2	102	116	1 3 $\bar{9}$	-15.3	15.4	1 7 6	2.5	2.2	111 5	-6.2	5.0
0 1 4	4.1	4.5	0 711	-5.0	4.8	1 0 $\bar{2}$	-22.6	22.4	1 310	-4.1	2.0	1 7 $\bar{6}$	-17.4	18.6	111 $\bar{5}$	1.0	1.6
0 1 5	-8.1	7.0	0 713	-4.8	4.6	1 0 4	-5.1	4.8	1 3$\bar{10}$	6.7	8.4	1 7 7	-13.3	12.4	111 6	-6.9	7.0
0 1 6	-1.2	2.2	0 715	5.5	4.8	1 0 6	-11.4	6.6	1 311	14.5	9.0	1 7 $\bar{7}$	-6.6	10.0	111 7	-5.0	2.8
0 1 7	7.1	6.9	0 8 0	7.4	8.1	1 0 $\bar{6}$	12.8	12.6	1 3$\bar{11}$	3.9	4.8	1 7 8	-4.8	4.8	111 $\bar{8}$	-3.7	4.8
0 1 8	-3.6	3.8	0 8 1	-2.4	2.0	1 0 8	-8.9	8.2	1 3$\bar{12}$	4.6	5.6	1 7 $\bar{8}$	-7.2	9.4	111 9	-5.9	4.6
0 110	-1.5	1.8	0 8 3	4.4	4.4	1 0 $\bar{8}$	-3.9	4.4	1 3$\bar{13}$	3.1	2.0	1 7 9	6.0	2.8	111 $\bar{9}$	-7.3	9.4
0 111	-5.0	5.3	0 8 4	-9.8	9.4	1 010	13.1	8.4	1 3$\bar{16}$	1.1	2.6	1 7 $\bar{9}$	-7.7	8.8	11110	5.7	5.8
0 112	2.3	3.4	0 8 5	-8.1	9.1	1 01$\bar{0}$	-20.2	19.2	1 3$\bar{17}$	-8.5	11.4	1 7$\bar{10}$	3.8	2.8	111$\bar{10}$	2.7	2.4
0 113	-2.5	2.9	0 8 6	-4.0	4.1	1 01$\bar{2}$	4.2	4.8	1 4 0	1.4	1.4	1 711	4.6	2.4	11111	4.9	3.0
0 114	8.8	10.3	0 8 7	-4.4	4.6	1 014	-14.3	8.4	1 4 1	-15.9	14.6	1 7$\bar{11}$	-6.4	8.0	111$\bar{12}$	3.4	4.8
0 115	5.3	4.8	0 8 8	4.8	4.7	1 01$\bar{4}$	3.9	4.4	1 4 $\bar{1}$	-3.2	3.4	1 713	-4.9	2.4	11113	-5.2	3.8
0 118	1.0	1.4	0 8 9	3.2	3.9	1 016	6.7	3.6	1 4 2	12.8	13.6	1 7$\bar{13}$	8.7	12.8	111$\bar{13}$	3.6	5.8
0 2 0	-11.8	9.0	0 810	-3.0	3.1	1 01$\bar{6}$	-5.5	6.8	1 4 $\bar{2}$	-19.8	29.2	1 7$\bar{14}$	-1.7	1.6	112 1	-4.7	3.4
0 2 1	-6.8	5.5	0 816	1.8	1.0	1 1 1	-2.3	2.2	1 4 3	1.9	3.0	1 715	-5.8	3.0	112 $\bar{1}$	4.9	5.0
0 2 2	-5.0	5.2	0 9 1	5.4	6.1	1 1 $\bar{1}$	-32.5	20.0	1 4 $\bar{3}$	-15.7	5.4	1 7$\bar{15}$	-2.6	2.4	112 2	9.0	9.8
0 2 3	5.0	5.1	0 9 2	5.7	4.9	1 1 2	-27.1	27.4	1 4 4	18.6	18.6	1 7$\bar{16}$	-2.4	4.0	112 $\bar{2}$	-6.7	6.4
0 2 4	-18.1	15.1	0 9 3	-8.6	7.8	1 1 $\bar{2}$	-8.6	7.8	1 4 $\bar{4}$	16.1	16.8	1 8 0	-13.1	13.2	112 3	4.9	6.0
0 2 5	-9.7	9.2	0 9 4	-4.0	4.0	1 1 3	24.1	30.8	1 4 5	-0.9	2.4	1 8 1	2.9	3.4	112 4	8.2	7.4
0 2 6	5.9	6.3	0 9 5	-8.0	7.6	1 1 $\bar{3}$	1.1	4.2	1 4 6	-16.0	14.6	1 8 $\bar{1}$	-5.9	6.2	112 5	2.7	2.0
0 2 7	-2.5	3.2	0 9 7	11.7	10.6	1 1 4	-8.7	6.2	1 4 $\bar{6}$	-1.2	4.2	1 8 2	11.8	12.6	112 $\bar{5}$	5.5	4.8
0 2 8	12.8	11.2	0 9 8	-6.5	6.1	1 1 $\bar{4}$	2.9	5.2	1 4 7	1.9	2.6	1 8 $\bar{2}$	-12.1	17.8	112 6	-7.4	6.0
0 210	-4.4	4.7	0 9 9	6.5	6.8	1 1 5	23.6	21.6	1 4 $\bar{7}$	-4.0	5.0	1 8 3	-5.5	3.4	112 $\bar{6}$	3.1	4.4
0 212	-4.2	3.4	0 911	-4.8	4.1	1 1 6	4.4	1.8	1 4 8	-12.4	9.6	1 8 $\bar{3}$	12.2	15.0	112 7	-3.3	3.2
0 215	-1.6	1.2	0 912	-1.8	1.7	1 1 $\bar{6}$	6.0	9.4	1 4 $\bar{8}$	-3.3	4.4	1 8 4	9.6	12.8	112 8	-3.9	1.8
0 216	5.3	5.0	0 915	3.3	2.8	1 1 7	-21.4	22.4	1 4 9	-2.5	3.6	1 8 $\bar{4}$	2.8	5.0	112 $\bar{8}$	-5.2	6.8
0 3 1	11.6	9.9	010 0	1.8	1.8	1 1 $\bar{7}$	-10.3	12.0	1 4$\bar{12}$	4.7	5.0	1 8 5	5.5	4.2	112 9	-4.0	2.2
0 3 2	-6.9	7.8	010 1	1.6	1.8	1 1 8	-2.2	3.2	1 4$\bar{13}$	-2.9	4.0	1 8 $\bar{5}$	8.3	11.0	112 $\bar{9}$	5.6	7.6
0 3 3	-8.0	8.2	010 2	-1.9	1.3	1 1 $\bar{8}$	-13.5	13.4	1 4$\bar{16}$	-7.9	11.2	1 8 6	-16.8	16.2	11210	2.0	2.0
0 3 4	-7.2	7.3	010 4	-3.1	3.3	1 110	-6.0	3.8	1 4$\bar{17}$	-1.2	1.6	1 8 $\bar{6}$	11.8	14.4	112$\bar{10}$	-2.0	2.6
0 3 6	10.0	11.5	010 5	3.5	3.6	1 111	6.3	6.8	1 5 0	-17.9	15.4	1 8 7	-11.8	12.6	112$\bar{12}$	3.6	4.8
0 3 7	7.8	8.7	010 6	5.6	5.5	1 11$\bar{1}$	2.5	2.0	1 5 1	-11.8	15.0	1 8 $\bar{7}$	-3.5	4.2	113 0	-6.4	7.2
0 3 8	0.7	1.1	010 7	4.7	4.8	1 11$\bar{2}$	-19.0	21.0	1 5 $\bar{1}$	-19.9	25.4	1 8 8	-13.0	10.8	113 $\bar{1}$	-4.1	5.2
0 3 9	7.4	7.3	010 8	4.1	5.0	1 11$\bar{3}$	13.2	16.4	1 5 2	-4.4	5.2	1 8 $\bar{8}$	-11.3	12.8	113 3	6.4	6.6
0 311	-6.4	5.6	01012	-3.8	3.9	1 114	6.2	4.6	1 5 $\bar{2}$	-3.0	1.8	1 8 9	-4.0	2.0	113 $\bar{3}$	5.2	6.0
0 312	-2.9	2.8	01014	1.8	1.4	1 11$\bar{4}$	-1.3	2.0	1 5 3	11.1	12.6	1 810	4.8	2.8	113 5	3.7	1.8
0 314	-2.0	1.9	011 1	4.9	5.8	1 115	-8.0	4.8	1 5 4	8.5	9.8	1 811	3.9	2.6	113 $\bar{5}$	6.7	8.2
0 315	2.9	1.7	011 2	1.9	1.9	1 11$\bar{5}$	-3.9	5.2	1 5 $\bar{4}$	14.8	18.4	1 8$\bar{12}$	7.6	9.8	113 7	-3.8	2.4
0 4 0	11.2	11.2	011 3	-6.7	7.1	1 116	8.9	5.0	1 5 5	-6.5	8.2	1 8$\bar{13}$	-1.4	6.0	113 $\bar{7}$	-3.5	5.4
0 4 1	6.2	6.5	011 4	1.7	2.0	1 11$\bar{7}$	-4.0	3.2	1 5 $\bar{5}$	7.5	9.0	1 814	-3.0	2.0	113 8	-5.5	4.2
0 4 2	6.8	6.3	011 6	-2.7	2.8	1 2 0	-23.3	21.2	1 5 6	10.8	10.6	1 8$\bar{14}$	1.0	1.6	113 $\bar{9}$	4.8	2.4
0 4 3	2.0	2.6	011 8	4.7	5.7	1 2 1	26.5	31.0	1 5 $\bar{6}$	1.6	2.2	1 8$\bar{15}$	-3.4	5.4	113 9	-3.0	2.6
0 4 4	-12.6	13.5	011 9	2.5	2.6	1 2 $\bar{1}$	-9.3	12.0	1 5 7	-11.9	11.8	1 9 0	-7.5	8.0	113$\bar{10}$	-2.4	3.0
0 4 5	3.9	3.3	01110	2.7	3.0	1 2 2	-20.4	22.8	1 5 $\bar{7}$	-1.3	1.2	1 9 1	2.0	1.8	11311	3.0	1.8
0 4 7	0.8	1.5	01111	-5.2	6.1	1 2 $\bar{2}$	-20.6	22.0	1 5 8	-7.1	6.8	1 9 $\bar{1}$	-11.9	12.8	113$\bar{11}$	1.3	1.8
0 4 9	2.7	3.5	01112	-1.1	1.7	1 2 3	-4.3	4.4	1 5 $\bar{8}$	5.0	5.2	1 9 $\bar{2}$	9.2	11.4	114 0	-7.0	7.6
0 411	2.5	2.4	01113	-1.3	1.1	1 2 $\bar{3}$	18.6	15.4	1 5 9	-9.7	11.8	1 9 3	9.4	10.0	114 1	-4.9	6.0
0 412	-2.4	2.0	012 0	7.2	7.4	1 2 4	3.9	4.8	1 5$\bar{11}$	6.0	2.8	1 9 $\bar{3}$	-11.2	12.2	114 $\bar{1}$	4.2	6.0
0 414	1.1	1.3	012 1	1.2	1.1	1 2 $\bar{4}$	15.5	15.6	1 5$\bar{11}$	7.6	8.8	1 9 4	8.0	6.0	114 2	4.9	6.8
0 5 1	-0.5	1.2	012 2	2.5	2.0	1 2 5	4.6	7.6	1 5$\bar{12}$	4.7	5.2	1 9 $\bar{4}$	2.4	2.6	114 $\bar{2}$	4.1	4.6
0 5 2	6.9	5.7	012 4	-6.0	5.5	1 2 6	-22.6	22.6	1 5$\bar{13}$	7.0	7.8	1 9 5	-9.9	9.4	114 3	-2.5	2.6
0 5 3	-9.0	7.9	012 5	-2.0	1.9	1 2 $\bar{6}$	21.2	18.8	1 5$\bar{14}$	-5.2	5.8	1 9 $\bar{5}$	16.0	17.0	114 $\bar{3}$	3.3	3.6
0 5 4	4.6	5.0	012 7	-3.4	3.2	1 2 7	-9.6	9.8	1 5$\bar{15}$	-1.5	1.6	1 9 6	-1.8	1.8	114 4	-2.1	1.4
0 5 5	-5.7	6.0	012 8	2.7	3.4	1 2 $\bar{7}$	7.6	11.4	1 6 0	-17.0	14.6	1 9 $\bar{6}$	10.1	13.4	114 $\bar{4}$	-7.0	7.2
0 5 6	-6.7	6.5	01210	-1.9	1.9	1 2 8	3.8	4.0	1 6 1	-8.9	10.6	1 9 7	-8.8	9.0	114 5	-2.7	2.0
0 5 7	2.7	2.3	01211	-1.7	1.7	1 2 $\bar{8}$	-14.3	14.0	1 6 $\bar{1}$	-1.8	6.6	1 9 $\bar{7}$	8.7	12.8	114 $\bar{5}$	-5.3	6.8
0 5 9	2.2	2.2	01212	-1.8	1.6	1 210	15.2	8.4	1 6 2	21.1	23.8	1 9 9	14.5	11.4	114 6	-2.9	2.0
0 510	-2.3	2.7	013 1	3.1	3.9	1 21$\bar{0}$	-1.9	1.8	1 6 $\bar{2}$	-3.1	4.0	1 9 $\bar{9}$	-8.0	10.2	114 $\bar{6}$	-2.0	2.0
0 511	-4.6	4.8	013 2	4.5	4.3	1 21$\bar{1}$	-2.8	3.4	1 6 3	19.1	19.4	1 910	-9.1	7.2	115 0	-1.6	2.2
0 514	-1.7	1.8	013 5	-2.1	2.9	1 21$\bar{2}$	9.2	10.2	1 6 $\bar{3}$	3.7	3.4	1 911	8.1	6.4	115 $\bar{1}$	-4.8	5.8
0 515	2.9	1.6	013 6	-4.3	4.7	1 21$\bar{3}$	-3.1	2.0	1 6 4	12.5	16.0	1 9$\bar{11}$	1.7	1.8	115 $\bar{2}$	4.7	5.6
0 516	1.9	1.4	013 7	4.9	5.1	1 21$\bar{3}$	3.2	4.0	1 6 $\bar{4}$	2.3	2.0	1 9$\bar{14}$	-2.2	3.2	115 3	4.5	5.2
0 6 0	15.2	14.9	014 0	3.0	3.1	1 21$\bar{4}$	5.7	7.2	1 6 5	7.5	9.6	110 0	-8.4	10.4	115 4	4.5	4.0
0 6 1	11.3	12.4	014 1	2.8	2.9	1 21$\bar{5}$	-0.8	1.4	1 6 $\bar{5}$	9.7	12.8	110 1	-5.1	5.4	115 $\bar{5}$	-2.8	1.8
0 6 2	-5.0	4.5	014 2	-3.0	3.1	1 21$\bar{6}$	-2.3	2.2	1 6 7	-3.8	3.4	110 $\bar{2}$	-6.7	10.8	115 $\bar{5}$	7.2	8.2
0 6 3	3.6	3.4	014 3	2.2	2.2	1 21$\bar{7}$	1.0	1.8	1 6 $\bar{7}$	2.9	1.8	110 4	5.3	4.8	115 6	-3.4	2.4
0 6 4	-1.9	2.0	014 4	-2.2	2.7	1 3 0	12.6	11.8	1 6 8	-13.4	14.2	110 $\bar{4}$	18.6	19.2	115 7	-6.9	5.8
0 6 5	-2.1	1.9	014 5	-2.2	1.6	1 3 1	6.2	7.2	1 6 $\bar{8}$	-4.5	2.8	110 5	-14.2	15.0	115 $\bar{8}$	-4.4	3.2
0 6 6	4.9	5.6	014 8	3.1	3.0	1 3 $\bar{1}$	-17.6	23.2	1 6 9	11.5	9.4	110 6	-2.9	2.4	116 0	-1.6	3.0
0 6 7	-4.3	4.1	014 9	3.3	3.4	1 3 2	2.1	2.8	1 6$\bar{10}$	-12.0	12.6	110 $\bar{6}$	2.6	2.8	116 1	-3.5	3.6
0 6 8	8.1	7.6	01410	-1.7	1.3	1 3 $\bar{2}$	22.5	25.4	1 6$\bar{11}$	5.5	6.4	110 7	7.7	8.0	116 $\bar{1}$	-0.3	1.2
0 6 9	2.6	1.9	015 1	2.9	3.6	1 3 3	22.3	24.4	1 6$\bar{12}$	9.1	10.8	110 $\bar{8}$	-5.8	7.4	116 2	6.3	5.8
0 610	-3.1	2.7	015 2	3.3	3.9	1 3 $\bar{3}$	6.0	9.2	1 6$\bar{13}$	4.5	6.0	11010	8.1	7.0	116 $\bar{2}$	-5.3	6.0
0 612	-7.6	7.5	015 3	-3.4	3.5	1 3 4	-4.8	5.8	1 614	-9.9	5.4	110$\bar{10}$	-5.7	5.2	116 3	5.2	6.4
															116 4	2.3	2.0
															116 $\bar{4}$	2.3	2.6
															116 5	-2.7	3.2

final reliability index $R = 10{\cdot}4\%$. The structure factors $F(0kl)$ and $F(1kl)$ (see next section) are listed in Table 2. The final positional parameters are found in Table 3.

Generalized projection along [100]

The cleavage plane, the optical indicatrix, and the very strong reflexions 102 and 204 showed that the

molecules are packed in the planes (102). Approximate x parameters of all atoms were obtained (Fischmann, 1959), enabling us to determine the signs of most structure factors $F(1kl)$. An isotropic temperature factor $\exp[-2{\cdot}36\sin^2\theta/\lambda^2]$ was applied. After five successive calculations of structure factors, generalized projections (modulus functions) $\varrho_1(yz)$, its imaginary part $S_1(yz)$ (Fig. 2) and its real part $C_1(yz)$ (Cochran & Dyer, 1952; Fridrichsons & Mathieson, 1955) the reliability index decreased to 18·7% and no more changes of sign occurred.

The accuracy of the analysis

The standard deviations $\sigma(y)=0{\cdot}02$ Å and $\sigma(z)=0{\cdot}02$ Å of the carbon atoms, as determined in the normal projection [100], were calculated in the usual way (Cruickshank, 1949). The standard deviations of the nitrogen, oxygen and chlorine atoms are, of course, smaller, but in the following considerations they are treated as equal to those of the carbon atoms. The errors in the x parameters were estimated by comparing the values $x_c=(2\pi)^{-1}\cos^{-1}(C_1/\varrho_1)$ and $x_s=(2\pi)^{-1}\sin^{-1}(S_1/\varrho_1)$ (Table 4).

Table 3. *The atomic parameters of* α-Cl*M*BO *expressed in fractions of cell edges*

	x	y	z
C_1	0·622	0·1824	0·2062
C_2	0·764	0·1224	0·1284
C_3	0·878	0·1630	0·0520
C_4	0·990	0·2694	0·0508
C_5	0·850	0·3301	0·1291
C_6	0·703	0·2890	0·2040
C_7	0·918	0·4432	0·1220
N	0·121	0·3120	−0·0194
O_1	0·496	0·1429	0·2739
O_2	0·200	0·2516	−0·0893
Cl	0·646	−0·0063	0·1301

The variation of errors $a\Delta x$ suggests that the 'standard' deviation $\sigma(x)$ is probably less than 0·06 Å for the carbon atoms and presumably smaller for the other atoms. In its most unfavourable position a bond between two atoms of the same molecule (Fig. 3) makes an angle of 24° with the plane of projection. This yields an upper limit of standard deviation in bond lengths $(0{\cdot}06^2\sin^2 24° + 0{\cdot}02^2\times 2\cos^2 24°)^{\frac{1}{2}} = 0{\cdot}036$ Å. The errors in the cell constants are about 0·5% and do not affect appreciably the above-mentioned standard deviation of bond length. According to the conventional criteria (Cruickshank & Robertson, 1953) deviations in bond length larger than 0·10 Å have to be considered as significant in this analysis.

Discussion of the structure

The distribution of long and short bond distances (mean values 1·47 Å and 1·31 Å respectively) in the six-membered ring (Fig. 3) permits the conclusion that the molecule has a *p*-benzoquinone-4-oxime structure. The bond lengths of C_1–O_1 (1·21 Å) and C_4–N (1·28 Å) are significantly shorter than those for single bonds of C–O (1·45 Å) and C–N (1·43 Å) and this, again excludes the presence of a nitrosophenol structure. The NOH group is *syn* with respect to the chlorine atom. There are no significant differences between the bond lengths, C–N and N–O, and the bond angle, CNO, in α-Cl*M*BO and those in other known oxime structures (Table 5).

Hydrogen bonds (2·69 Å) which connect the carbonyl group of one molecule with the oxime group of the next molecule act as links in infinite chains. The symmetry elements which evolve this kind of hydrogen-bonded chain are in the case of the crystals of α-Cl*M*BO and 3-chloro-*p*-benzoquinone-4-oxime a glide plane and in the case of the structures of

Table 4. *The x parameters of the carbon atoms determined in two ways*

	Relative peak heights in							
	C_1	S_1	ϱ_1	x_c	x_s	$\bar{x}$	Δx	$a.\Delta x$
C_1	−180	−175	251	0·605	0·640	0·622	0·018	0·07 Å
C_2	0	−225	225	0·750	0·778	0·764	0·014	0·05
C_3	165	−158	228	0·879	0·878	0·878	0·001	0·00
C_4	242	30	244	1·000	0·980	0·990	0·010	0·04
C_5	122	−173	212	0·840	0·860	0·850	0·010	0·04
C_6	− 72	−220	232	0·698	0·708	0·703	0·005	0·02
C_7	185	− 83	203	0·895	0·941	0·918	0·023	0·09
	Mean peak height		228				Mean error	0·04

Table 5. C–N *and* NO *bond distances in some oxime compounds*

	C–N	N–O	C–N–O	Reference
α-Cl*M*BO	1·28	1·32	114°	This paper
3-Chloro-*p*-benzoquinone-4-oxime	1·25	1·39	114	Romers, Brink Shoemaker & Fischmann, 1957
syn-*p*-Chloro-benzaldoxime	1·31	1·36	112·5	Jerslev, 1950
Dimethylglyoxime	1·27	1·38	114	Meritt & Lanterman, 1952
Acetoxime	1·29	1·36	111	Bierlein & Lingafelter, 1951
5-Methoxy-*o*-quinone-2-oxime	1·22	1·36	117	Bartindale, Crowder & Morley, 1959

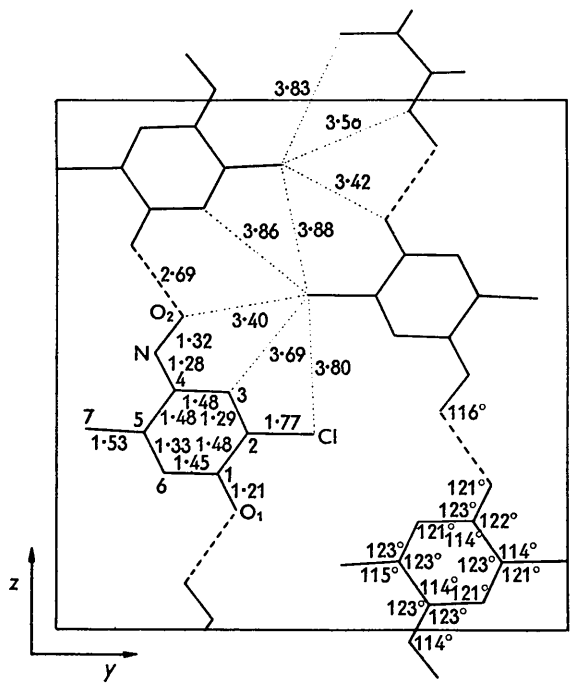

Fig. 3. Bond angles, bond distances and intermolecular distances in crystals of α-2-chloro-5-methyl-*p*-benzoquinone-4-oxime. The molecules are viewed along [100].

α-5-(2′-chloroethoxy)-*o*-quinone-2-oxime (Romers & Umans, 1960) and α-5-methoxy-*o*-quinone-2-oxime, a two-fold screw axis.

The Van der Waals contacts between the molecules packed on top of each other (not shown in Fig. 3) are larger than 3·3 Å. All other intramolecular distances indicated in Fig. 3 are larger than 3·4 Å.

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