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Isomerism of Benzoquinone-Monoximes (Nitrosophenols). XI. The Crystal Structure of β-2-Chloro-*p*-Benzoquinone-4-Oxime Acetate

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The crystal structure of β-2-chloro-*p*-benzoquinone-4-oxime acetate has been determined by means of two projections along [100] and [101] using low-temperature data. The space group is $P2_1/n$ and the unit-cell dimensions are

$$a = 7{\cdot}14,\ b = 19{\cdot}88,\ c = 6{\cdot}80\ \text{Å},\ \beta = 113^\circ\ \text{at}\ -140\ ^\circ\text{C}.$$

The chlorine atom is *anti* with respect to the oxime acetate group.

Experimental part

The crystals of β-2-chloro-*p*-benzoquinone-4-oxime acetate (β-ClBOA), m.p. 138 °C., can be separated by means of repeated crystallization from the corresponding α-form (Umans, 1959). They are small yellow monoclinic platelets with a well developed principal zone which we chose as the *c*-axis. The crystals exhibit well developed faces {010} and smaller faces {100}. There is cleavage along the latter faces.

Optical examination indicates that the crystals are biaxially negatively birefringent ($n_\alpha \ll n_\beta < n_\gamma$), with n_α nearly perpendicular to (100), n_β approximately parallel to [001] and n_γ parallel to [010]. The crystals are strongly pleochroic. If polarized light is travelling along [010] and the electric vector is along [001] the crystal appears dark yellow; the colour is light yellow if the electric vector is perpendicular to (100). A section of the crystal cut parallel to (100) with polarized light travelling perpendicular to this plane shows a slightly darker yellow colour if the electric vector is parallel to [010] than if it is parallel to [001]. This indicates that the molecules are found in planes parallel to (100) and that the conjugated-bond system probably makes an angle of about 45° with the *b*-axis. This conclusion was ultimately confirmed by the X-ray analysis.

In Table 1 are summarized the dimensions of the monoclinic unit cell at 20 °C. and at −140 °C. The cell edges were measured with aid of oscillation and Weissenberg photographs about [100], [001] and [101]. Systematic absences of reflexions $0k0$ with k = odd and $h0l$ with $h+l$ = odd indicate the space group $P2_1/n$.

The intensities of $hk0$ reflexions were recorded at 20 °C. and those of $0kl$ and $hk\bar{h}$ reflexions at 20 °C. and at −140 °C., respectively, with zero-layer Weissenberg photographs, using the multiple-film technique. Very small crystals were used and no absorption corrections were applied. The intensities were corrected in the usual way for Lorentz and polarization effects. Comparison of the unit-cell volumes of α- and β-ClBOA leads to the conclusion that the number of molecules of β-ClBOA per unit cell is four. β-ClBOA is too unstable for an easy determination of its density to be possible.

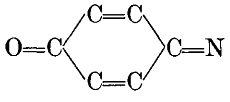
The Patterson functions $P(u, v)$ and $P(v, w)$

Intensities $hk0$ were collected at 20 °C., and $0kl$ at −140 °C. From these, Patterson functions were calculated with Fourier coefficients $F^2\xi^2 \exp(-0{\cdot}17\xi^2)$, where $\xi = 2 \sin \theta$.

With the aid of the information acquired from optical study of the crystal (vide supra) it was possible to find solutions of these Patterson maps. Strong peaks are expected:

(*a*) between the centres of the ring systems across the symmetry centre,

(*b*) between the chlorine atoms.



Let the ring centre be located at x, y, z in crystal space, and the chlorine atom of the same molecule at x', y', z', with x approximately equal to x', since the

Table 1. *Unit-cell dimensions of* β-ClBOA

a	b	c	β	d_c	Z	Temp.
7·18 ± 0·05 Å	19·95 ± 0·05 Å	6·80 ± 0·05 Å	113°	1·478	4	20 °C.
7·14	19·88	6·80	113	—	4	−140

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molecule is approximately parallel to the (100) plane. In vector space there are two corresponding vectors, due to the centre of symmetry, with their end points at $2x, 2y, 2z$ and $2x', 2y', 2z'$, respectively, and separated by a distance 6·4 Å. Their approximate relative weights are $6\times6\times6+2\times6\times7=400$, and $17\times17=289$, respectively. The first peak could be identified unambiguously in both projections, at A (Fig. 1(*a*)) and B (Fig. 1(*b*)) respectively. The position of the centre of the ring is thereby fixed. The Cl–Cl peak should be found in the *a*-axis projection (Fig. 1(*b*)) at the practically unforeshortened distance 6·4 Å from B. Assignment of this maximum is facilitated by location of the other Harker Cl–Cl-vectors, namely $\frac{1}{2}, \frac{1}{2}-2y', \frac{1}{2}$ and $\frac{1}{2}-2x', \frac{1}{2}, \frac{1}{2}-2z'$, due to the glide plane and the screw axis, respectively. Both these Harker vectors have double weight compared with the one at $2x', 2y', 2z'$. The former is identified as projected at E and F. The $2y'$ value now being known, the peak $2x', 2y', 2z'$ should be on the lower dotted line in Fig. 1, with an u-coordinate approximately equal to that of A, and at the expected distance 6·4 Å from B. It is clear that the peak projects in the region of C and D respectively. The corresponding third Harker peak $\frac{1}{2}-2x', \frac{1}{2}, \frac{1}{2}-2z'$ falls in both projections in a wide maximum and so does not permit any further precision in the position of Cl.

A more exact location of the Cl–Cl peak D in $P(v, w)$ was found by shifting a model of the molecule (without the acetate group), with Cl on the line C–D, and keeping the line connecting the chlorine atom and the centre of the ring directed at peak B. In this way point D was determined and several peaks of $P(v, w)$ were identified. The solution was confirmed by the calculation of $\varrho(x, y)$ (not shown in this paper). The refinement of that projection was, however, abandoned, since there is too much overlap.

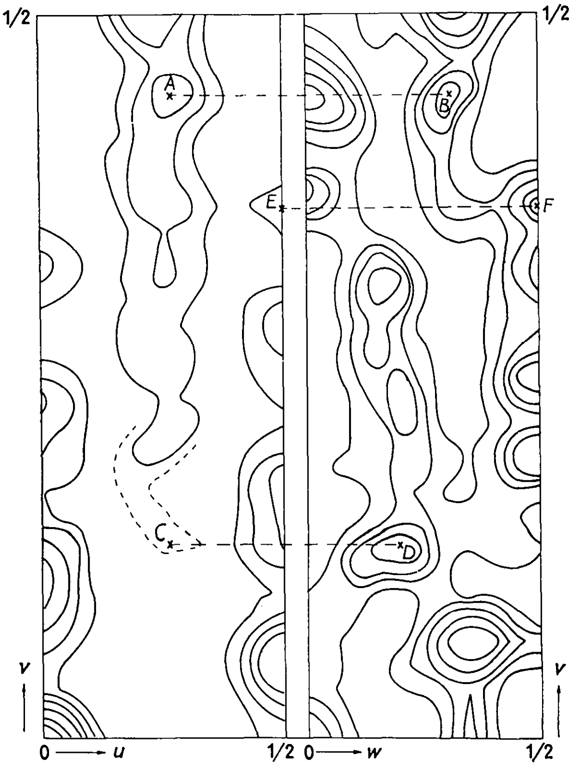

Fig. 1. The Patterson projections $P(u, v)$ and $P(v, w)$ of β-ClBOA.

The [100] *projection*

Structure factors were calculated for the known part of the molecule, that is, all atoms except the acetate group. The first Fourier map showed clearly the atoms belonging to this group, thus giving further support to the assumption that the structure model was correct.

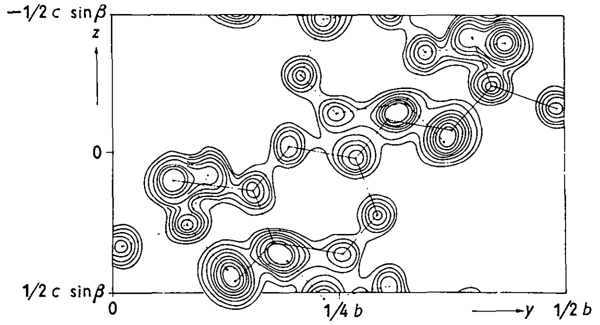

Fig. 2. The electron density of β-ClBOA projected along [100]. The contour lines are at arbitrary scale. Those of the chlorine atoms have been drawn at intervals twice as large as for the other atoms.

The projection was then refined by calculation of electron density projections $\varrho(y, z)$ (Fig. 2) and difference maps $\varrho_o-\varrho_c$, using −140 °C. data. An isotropic temperature factor $\exp(-2{\cdot}76 \sin^2\theta/\lambda^2)$ was used in the calculation of the structure factors $F(0kl)$ (Table 2) and the disagreement factor R decreased to 12·2%. No hydrogen contributions were included in these calculations.

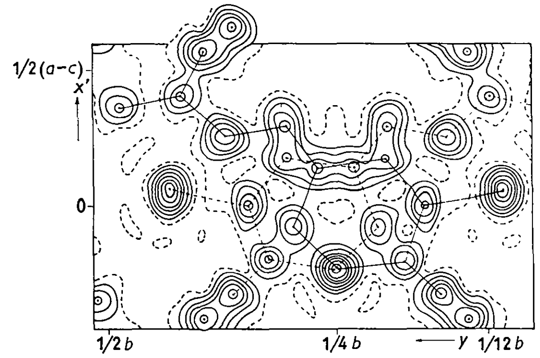

Fig. 3. The projection of the electron density $\varrho(X'Y)$ of β-2-chlorobenzoquinone-oximeacetate-4 projected along [101]. The contourlines are drawn at 2, 4, 6, ... e.Å^{-2}, those for the chlorine atoms at 2, 5, 10, 15, ... e.Å^{-2}. The 2 line is dashed.

Table 2. *Structure factors* $F(0kl)$ *and* $F(hk\bar{h})$ *(one symmetric unit) of β-2-chloro-p-benzoquinone-4-oxime acetate at* −140 °C.

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

The [101] *projection*

With aid of a model it was discovered that the projection along [101] should allow recognition of the molecules without too much overlap. The structure factors $F(hk\bar{h})$ were calculated. After refinement with aid of electron-density maps (Fig. 3) and difference maps the disagreement factor R (using −140 °C. data) of the structure factors $F(hk\bar{h})$ (Table 2) decreased to 11·7%. No hydrogen contributions were included and a temperature factor $\exp(-1{\cdot}65\sin^2\theta/\lambda^2)$ was applied.

Accuracy

The final structural parameters are given in Table 3. For the numbering of atoms consult Fig. 4.

Applying the same reasoning as was used in the previous article (Fischmann, MacGillavry & Romers, 1961) we arrived at errors of 0·07 Å in the C–C bonds, and at somewhat smaller errors in the remaining bonds. Calculation of standard positional errors of carbon with the method of Cruickshank (1949) results in $\sigma(x')=0{\cdot}019$ Å, $\sigma(y)=0{\cdot}020$ Å ([101] projection) and $\sigma(x)=0{\cdot}015$ Å and $\sigma(y)=0{\cdot}016$ Å ([100] projection).

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

	X	*Y*	*Z*
Cl	0·148	0·066	0·100
O_1	0·136	0·135	0·475
O_2	0·158	0·374	$0{\cdot}\overline{089}$
O_3	0·146	0·396	$0{\cdot}\overline{421}$
N	0·164	0·306	$0{\cdot}\overline{136}$
C_1	0·128	0·175	0·339
C_2	0·138	0·153	0·138
C_3	0·156	0·194	$0{\cdot}\overline{008}$
C_4	0·135	0·269	0·017
C_5	0·133	0·296	0·214
C_6	0·113	0·251	0·358
C_7	0·157	0·416	$0{\cdot}\overline{246}$
C_8	0·190	0·490	$0{\cdot}\overline{172}$

These numbers lead to standard errors of 0·03 Å or less in the C–C bonds. However, since there is much overlap in both projections, this result is an underestimation.

Discussion of the structure and comparison with α-ClBOA

A part of the crystal structure of β-ClBOA is shown in Fig. 4. In accordance with the optical examination, the molecules are found in planes approximately parallel to (100). There is one exceptionally short intermolecular distance (3·33 Å) between two chlorine atoms. There are a few other short distances (< 3·8 Å) between the light atoms of different molecules in directions approximately perpendicular to (100). The shortest intermolecular distances, however, are found in planes approximately parallel to (100), e.g. the distances (not shown in Fig. 4) between N and C_6 (3·40 Å) and between O_1 and C_3 (3·41 Å). All other intermolecular distances in planes parallel to (100) are larger than 4·0 Å. This distribution of intermolecular distances might explain the cleavage along (100).

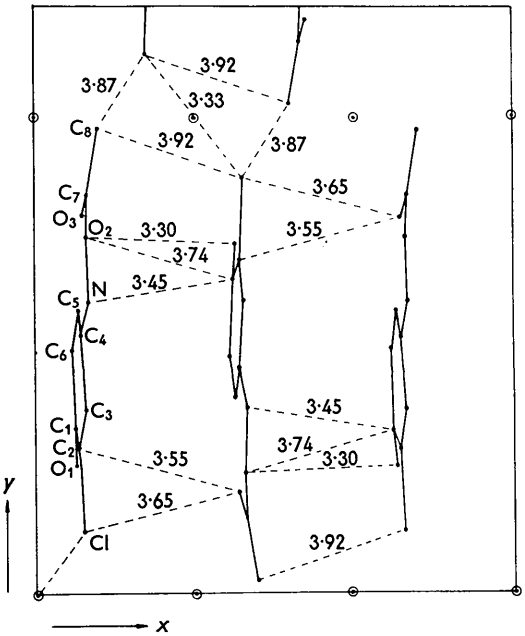

Fig. 4. The crystal structure of β-ClBOA viewed along [001]. The dashed lines indicate intermolecular distances.

As can be seen clearly in Fig. 2 and Fig. 3 the chlorine atom is *anti* with respect to the oxime acetate group. It was shown in the previous paper (Fischmann *et al.*, 1961) that the chlorine atom and the oxime acetate group are in *syn* configuration in α-ClBOA. This result confirms Kehrmann's postulate of *syn*- and *anti*-molecules (1894).

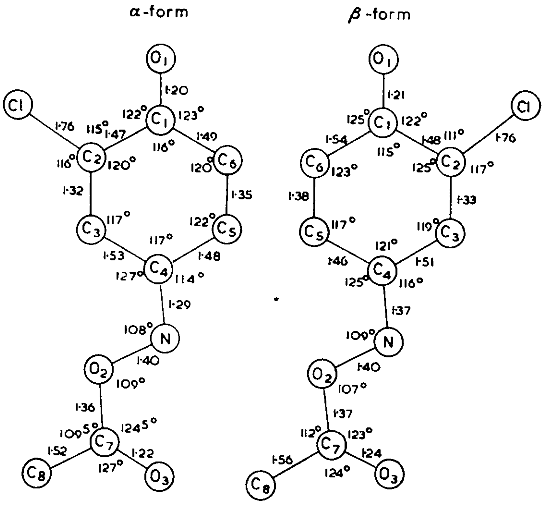

Fig. 5. Bond distances and bond angles of α- and β-ClBOA.

The bond angles and bond distances of α-ClBOA and β-ClBOA are shown in Fig. 5. Although no statistical significance can be given (Cruickshank & Robertson, 1953) to the distribution of long and short bonds in the ring system, it is clearly in agreement with a quinonoid ring structure in both cases. This is also shown in Table 4 in which a comparison is made between the carbonyl bond, double bonds (mean values) and single bonds (mean values) of *p*-benzoquinone (Trotter, 1960), α-2-chloro-5-methyl-*p*-benzoquinone-4-oxime (Romers & Fischmann, 1960) and α- and β-ClBOA.

Table 4. *Comparison between carbonyl bond, double and single bonds*

	p-Benzoquinone	α-2-Chloro-5-methyl-*p*-benzoquinone-4-oxime	α-ClBOA	β-ClBOA
C=O	1·222 Å	1·21 Å	1·22 Å	1·21 Å
C–C	1·477	1·48	1·49	1·50
C=C	1·322	1·31	1·33	1·36

The molecules are not quite planar. In the α molecule, the atoms O_1, C_1, C_2, C_3, C_6 and Cl form an approximately planar group, within the limits of accuracy. (For the numbering of atoms, see Fig. 5.)

The atoms C_4, C_5, C_6, N and O_2 are again coplanar; this plane makes an angle of 6° with the first. Finally, the planar acetyl group, i.e. the atoms C_7, C_8, O_2, O_3 and N, is rotated 7° upward about the bond N–O_2.

The deviations from planarity are less systematic in the case of β-ClBOA, as can be seen from the x-parameters in Table 3. The acetyl group $O_2C_7C_8O_3$ is rotated around the bond O_2–C_7 out of the 'plane' of the rest of the molecule, so that the distance between the non-bonded atoms O_3 and N is slightly increased.

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Reduction of U_3O_8 to U_3O_{8-x} in Mode of Crystallographic Out-of-Step

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When a single crystal of orthorhombic U_3O_8 is heated *in vacuo*, its electron diffraction patterns exhibit an interesting sequence of changes. First, some of the diffraction spots suffer a splitting, and then the splitting becomes pronounced with the elevation of temperature. The reduction of U_3O_8 to U_3O_{8-x} underlying these pattern changes seems to proceed, until the lower composition limit of U_3O_8 phase in the UO_2–U_3O_8 phase diagram is reached. An interpretation for these anomalous diffraction patterns is carried out on the basis of diffraction theory of out-of-step structure. The physical quantities involved in the interference function, made up for the present purpose, are determined by comparing implications of the resulting interference function with the patterns actually obtained. By this, the mode of out-of-step in this problem is revealed, together with its physical meaning. It is concluded that a particular manner of valency conversions of uranium ions takes place in the reduction of U_3O_8 to U_3O_{8-x}, and that slight positional changes accompanying the valency conversions are responsible for the pattern changes.

In the course of the study of calcination of precipitated ammonium diuranate ($(NH_4)_2U_2O_7.xH_2O$) to U_3O_8, an extremely unusual crystal growth has been encountered (Doi *et al.*, 1960). Under particular conditions of the precipitation and the subsequent calcination, the resulting U_3O_8 particles take a characteristic shape, so thin as to be semitransparent to electron beams, and have, moreover, an almost single-crystalline atomic arrangement. Such a situation will be favourable in utilizing the present-day electron optical techniques. For example, crystallographic aspects in a variety of chemical changes of U_3O_8 will be successfully investigated, since changes in morphology and atomic arrangement can be observed both *in situ* in an advanced electron microscope. As the first step, the study of U_3O_8 heated *in vacuo* is dealt with in the following.

Experimental

U_3O_8 was prepared by calcination at 600 to 700 °C. of ammonium diuranate precipitated under a particular condition (Doi *et al.*, 1960). The powder was mounted on a carbon-backed collodion film. The U_3O_8 particles meeting the purpose were chosen by observing on the fluorescent screen their electron microscopic images along with their selected area electron diffraction patterns. The heating of the specimen was carried out *in situ* in the apparatus by intensifying the electron beam impinging on it. Although the exact temperature of the specimen at varied stages was unknown, the