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Isomerism of Benzoquinone Monoximes (Nitrosophenols). XII. The Crystal Structure of β-5-n-Propoxy-*o*-quinone-2-oxime*

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The crystal structure of β-5-n-propoxy-*o*-quinone-2-oxime has been determined by comparison with those of the isomorphous β-5-(2′-bromoethoxy)- and β-5-(2′-chloroethoxy)-*o*-quinone-2-oxime. The unit-cell dimensions of the propoxy compound at −120 °C are $a=10{\cdot}64$, $b=12{\cdot}57$, $c=6{\cdot}63$ Å, $\beta=95°\ 31'$, $Z=4$. The space group is $P2_1/c$. The structure was refined by the method of least-squares with data collected at −120 °C. The mean value of two short distances (1·35 Å) and four long distances (1·45 Å) in the hexagonal ring and the length of the carboxyl bond (1·27 Å) indicate a predominantly oxime-like structure. The intramolecular hydrogen-bonded NOH and CO groups are in the *syn* position. The CH_3–C_2H_4–O-group has the *gauche* conformation. The molecule is planar with the exception of the methyl group which is 1·22 Å outside the plane of the molecule. Exceptionally short intermolecular distances (3·12, 3·25 Å) are found between molecules in adjacent layers in the direction of the c axis.

Introduction

As a part of the investigations on the tautomerism of quinone-oximes (nitrosophenols) in this laboratory Umans (1959) studied the properties of 5-alkoxy-*o*-quinone-2-oximes which occur in two forms. It was concluded by Romers & Umans (1960), in a preliminary account of the crystal structures of some of these oximes, that the stable orange α forms possess the oxime structure. Bartindale, Crowder & Morley (1959) arrived at the same conclusion in their investigation of the crystal structure of α-5-methoxy-*o*-quinone-2-oxime. The first mentioned authors suspected that the green β forms might have a nitrosophenolic character. This hypothesis was mainly supported by the optical properties of the crystals, because the two-dimensional X-ray analysis was not sufficiently accurate to distinguish between the two forms.

Not all β forms are unstable. Umans (1959) proved that the green β form of 5-n-propoxy-*o*-quinone-2-oxime (β-PQO) is stable under normal conditions, while it is difficult to obtain its corresponding orange α form. Since, moreover, β-PQO is isomorphous with β-5-(2′-bromoethoxy) (β-Br EQO) and β-5-(2′-chloroethoxy)-*o*-quinone-2-oxime (β-Cl EQO), the first mentioned compound is ideally suited for a three-dimensional X-ray diffraction analysis.

Morphology and optics

Crystals of β-PQO, melting point 94–95 °C, are lath-shaped prisms with well developed faces (100) and elongated in the direction [001]. They can be cleaved parallel to [010] and [001]. However, persistent twinning with (100) as common twinning plane was found after cleavage parallel to [010].

The crystals have a dark metallic lustre and exhibit a strongly marked pleochroism on inspection in polarized light. When observed through the face (100) with [001] parallel to the direction of the electric vector of polarized light their colour is yellow-green. The colour changes into orange on turning the crystals 90° with respect to the direction of the electric vector. This pleochroism is even more pronounced in the corresponding chloro compound β-Cl EQO which shows a variation between grass-green and garnet-orange. The absorption spectrum of a suspension of β-PQO in Nujol shows maxima at 653 mμ and 323 mμ; its solution in benzene has corresponding maxima at 645 mμ (molecular extinction coefficient $\varepsilon=35$) and at 325 mμ ($\varepsilon=11000$).

The crystals are biaxially negatively birefringent ($n_\alpha \ll n_\beta < n_\gamma$). The obtuse bisectrix interference figure is observable through (100) in convergent polarized light. The angle $2V$ is close to 90° and the difference $(n_\gamma-n_\beta)-(n_\beta-n_\alpha)$ is small. n_β is along [010] and n_α and n_γ are approximately in the respective directions [001] and [100].

Experimental

Crystals of PQO with cross sections of approximately $0{\cdot}3\times0{\cdot}3$ mm were cut in the directions [001] and [010]. The cell dimensions at 20 °C and at −120 °C were obtained from zero-layer Weissenberg photographs about [010] and [001] (copper radiation, $\lambda=1{\cdot}5418$ Å) superposed with aluminum powder lines for calibration purposes. The cell dimensions of β-Br EQO, β-Cl EQO and β-PQO are summarized in Table 1.

Their space groups are $P2_1/c$ and there are four molecules per unit cell. The visually estimated re-

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* See part VIII (Romers & Fischman, 1960) for earlier papers of this series.

Table 1. *Dimensions* (Å) *and densities* (g.cm^{-3}) *of some β-5-alkoxy-o-quinone-2-oximes*

Compound	a	b	c	β	D_m	D_x	Temperature
β-Br EQO	10·86	12·73	6·76	90	1·77	1·75	20 °C
β-Cl EQO	10·70	12·28	6·59	90	1·48	1·54	−120 °C
β-PQO	10·66 ± 0·01	12·67 ± 0·01	6·79 ± 0·02	95° 36′ ± 20′	1·29	1·31	20 °C
β-PQO	10·64 ± 0·01	12·57 ± 0·02	6·63 ± 0·01	96° 31′ ± 30′			−120 °C

flexion intensities were recorded at −120 °C on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. The crystals were dipped into liquid air in order to minimize extinction effects. The first six layers about [001] and the first nine layers about [010] were prepared according to a low temperature technique developed in this laboratory by Altona & Romers (1963). The maximum number of independent reflexions within the copper radiation sphere is 2123. Of these, 1613 reflexions could have been recorded, but only 1332 were observed. The usual Lorentz and polarization factors and film spot corrections were applied. The intensities were not corrected for absorption, because the linear absorption coefficient for copper radiation is only 9·8 cm^{-1}.

Determination of the structure

Crystals of β-Br EQO were first obtained. Inspection of their optical properties and unit-cell dimensions indicated that the [001] projection was the most favourable for investigation. However, the x and y parameters of the bromine atom were the sole information which could be extracted from the Patterson function $P(uv)$, because the application of minimum functions (Buerger, 1959) failed to reveal the structure. The electron density projection $\varrho(xy)$ based upon the phases of the bromine atom contributions to the structure factors could not be interpreted in terms of a reasonable molecular model. Afterwards we realized that the failure of the vector shift method as well as of the heavy atom technique was due to the poor quality of the diffraction data (absorption errors and twinning) and to the ambiguity of the projection, which shows several possible hexagonal arrays of peaks (Romers & Umans, 1960, Figs. 2 and 3; see also Fig. 4 of this paper).

Meanwhile crystals of β-Cl EQO became available. This compound changes spontaneously at room temperature into the stable orange α form. Moreover, the change is accelerated by X-rays. We only succeeded in collecting $hk0$ and $hk1$ reflexion data at −120 °C. A comparison of the corresponding reflexions $hk0$ of β-Br EQO and β-Cl EQO indicated that their structures are isomorphous. The signs of most structure factors $F(hk0)$ of the chloro compound were determined and its structure was found by calculation of generalized electron density functions $\varrho_0(xy)$, $C_1(xy)$ and $S_1(xy)$ (Romers & Umans, 1960, Figs. 2 and 3). The function $\varrho_0(xy)$ is the ordinary projection of the electron density; the latter two functions are the cosine function C_1 and the sine function S_1 based upon two-dimensional Fourier summations with Fourier coefficients $F(hk1)$ (Cochran & Dyer, 1952; Romers & Fischmann, 1960; Fischmann, MacGillavry & Romers, 1961).

The refinement

The remarkable stability of β-PQO led to the measurement of its unit cell and to the fortuitous discovery that its crystals are isomorphous with the above-mentioned corresponding halogeno compounds. The three-dimensional refinement of the structure of β-PQO by the method of least-squares was based upon

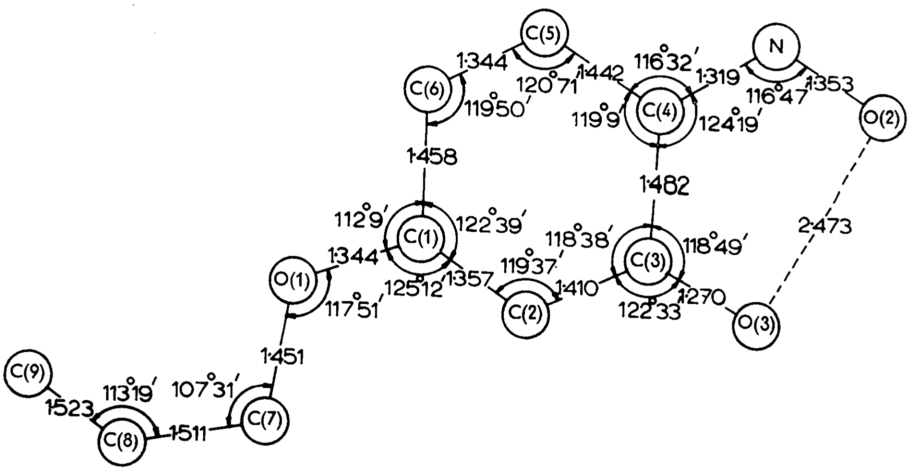


Fig. 1. Intramolecular bond distances (Å) and bond angles in β-PQO.

the positional parameters obtained from the diffraction analysis of the chloro compound. The numbering of the atoms is indicated in Fig. 1. The atomic scattering factors of carbon, nitrogen and oxygen used in the structure factor calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). McWeeny's (1951) form factors for hydrogen were used in the final stages of refinement.

After the first three cycles, in which one overall isotropic temperature factor was applied, the reliability index $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ dropped from 28% to 22%. These calculations were performed on ZEBRA computers at Utrecht and Groningen and a program with diagonal approximation, written by Dr J. C. Schoone, was employed.

The calculations were continued on the Mercury computer at Manchester with least-squares programs written by Mr O. S. Mills (Mills & Rollett, 1961). The following weighting scheme was used: $w = 1/(1+F_o^2/8F_{\mathrm{min}}^2)$, where $|F_{\mathrm{min}}|$ is the observable minimum of $|F_o|$. The next three cycles were carried out with isotropic individual temperature factors. At this stage the reliability index R was 16·7%. A difference map $\varrho_o-\varrho_c$ was calculated. Important positional shifts of the heavy atoms were not found, but the map gave indications of the vibrational movements of the heavy atoms and showed distinctly the positions of the hydrogen atoms.

The following two cycles (Nos. 7 and 8) were calculated with anisotropic temperature factors. In view of the small positional shifts after the eighth cycle ($<0{\cdot}0013$ Å) the refinement could be considered completed. However, the reliability index was still rather high (14·8%) and a careful survey of all structure factors revealed the poor quality of some non-zero Weissenberg photographs. Moreover, it had been discovered that the formerly measured length of the c axis (Romers & Umans, 1961) was 0·18 Å too long.

New diffraction data were collected at −120 °C for the faulty levels, resulting in a reliability index of 11·84%. Hydrogen atoms were placed at the positions indicated by the difference Fourier map, but their contributions to the structure factors reduced R only to 11·65%. The hydrogen atoms contribute mainly to the very strong reflexions 002 and 102 which define the plane of the molecule and the reflexion 100. But these three reflexions suffer seriously from extinction, which explains the negligible influence of the hydrogen atoms on the reliability index.

Two more cycles of least-squares (Nos. 9 and 10) were calculated with the hydrogen contributions added to the structure factors. They were kept in fixed positions and their scattering factors (McWeeny, 1951) were multiplied with a constant overall isotropic temperature factor $B=2{\cdot}22$ Å^{-2}. The last cycle but one gave three shifts: $\Delta x(\mathrm{C}(1))=-0{\cdot}016$, $\Delta y(\mathrm{C}(2))=0{\cdot}011$ and $\Delta z(\mathrm{C}(9))=-0{\cdot}015$ Å; all other positional shifts were much smaller. The last cycle gave only minor shifts (average value 0·0016 Å) with the exception of $\Delta x(\mathrm{C}(1)) = +0{\cdot}0057$ and $\Delta z(\mathrm{C}(9)) = +0{\cdot}0092$ Å. In view of these oscillations it might have been better to continue the refining process with another cycle with reduced shifts for the atoms C(1) and C(9), but this intention was prevented by lack of computing facilities. However, the reliability

Table 2. *Final positional parameters in fractions of cell edges*

	x	y	z
C(1)	0·2845	0·0241	0·3010
C(2)	0·3864	0·9640	0·2672
C(3)	0·5026	0·0140	0·2431
C(4)	0·5101	0·1315	0·2575
C(5)	0·3988	0·1909	0·2952
C(6)	0·2900	0·1398	0·3170
C(7)	0·1486	0·8723	0·3023
C(8)	0·0139	0·8497	0·3431
C(9)	0·9167	0·9034	0·1928
N	0·6133	0·1873	0·2383
O(1)	0·1686	0·9861	0·3233
O(2)	0·7185	0·1318	0·2061
O(3)	0·6012	0·9622	0·2109
H(1)	0·929	0·872	0·062
H(2)	0·815	0·887	0·200
H(3)	0·928	0·976	0·153
H(4)	0·997	0·890	0·456
H(5)	0·005	0·230	0·357
H(6)	0·200	0·842	0·423
H(7)	0·155	0·848	0·154
H(8)	0·392	0·888	0·267
H(9)	0·405	0·270	0·316
H(10)	0·198	0·163	0·333
H(11)	0·694	0·065	0·267

Table 3. *Vibrational parameters*

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	0·00446	0·00054	0·00239	0·00276	0·00026	0·01228
C(2)	0·00440	0·00085	0·00098	0·00268	0·00173	0·01230
C(3)	0·00465	0·00060	−0·00006	0·00307	−0·00067	0·01086
C(4)	0·00448	−0·00084	−0·00108	0·00285	0·00109	0·01265
C(5)	0·00610	0·00059	0·00286	0·00231	−0·00011	0·01586
C(6)	0·00536	0·00086	0·00438	0·00262	−0·00068	0·01832
C(7)	0·00461	−0·00089	0·00259	0·00256	−0·00076	0·01926
C(8)	0·00467	−0·00156	0·00754	0·00459	0·00011	0·02303
C(9)	0·00413	−0·00014	0·00021	0·00542	−0·00253	0·03209
N	0·00487	−0·00042	0·00138	0·00322	−0·00036	0·01722
O(1)	0·00369	0·00057	0·00424	0·00271	−0·00053	0·02019
O(2)	0·00439	−0·00145	0·00286	0·00349	−0·00023	0·02501
O(3)	0·00397	0·00014	0·00288	0·00308	−0·00091	0·01649

Table 4. *Observed and calculated structure factors of β-PQO*

Table 4 (*cont.*)

hkl	Fo	Fc
• 6	12	
-4	80	46
-3	-27	-22
-2	-60	-31
-1	0	4
0	57	59
1	26	30
2	0	-5
3	-29	-31
• 6	13	
-3	20	24
-2	-20	-23
-1	0	4
0	67	74
1	-32	-29
2	-75	-100
3	8	18
• 6	14	
-2	-67	-65
-1	0	13
0	122	131
1	-58	-46
• 7	0	
-6	299	276
-4	-168	-161
-2	-136	-128
0	257	251
2	-126	-110
4	0	-15
• 7	1	
-7	95	77
-6	69	61
-5	-153	-169
-4	-111	-94
-3	128	138
-2	58	51
-1	105	93
0	90	70
1	-229	-265
2	-99	-86
3	142	148
4	0	21
5	0	-11
6	0	13
• 7	2	
-7	38	44
-6	53	52
-5	-34	-42
-4	0	-5
-3	32	38
-2	-29	-19
-1	0	9
0	0	-6
1	-71	-59
2	44	38
3	23	28
• 7	3	
-7	67	74
-6	28	26
-5	-59	-52
-4	-47	-46
-3	-28	-4
-2	0	9
-1	40	37
0	116	108
1	0	-10
2	-124	-136
3	0	-14
4	63	60
5	24	25
6	-19	-13
• 7	4	
-7	-75	-62
-6	0	-0
-5	95	84
-4	0	-10
-3	-111	-113
-2	55	69
-1	101	86
0	-126	-111
1	0	11
2	81	72
3	-81	-79
4	0	-4
5	90	86
• 7	5	
-5	-19	-32
-4	117	112
-3	0	10
-2	-135	-138
-1	77	60
0	70	55
1	-83	-62
2	36	44
3	44	41
4	-83	-81
5	-26	-25
6	38	75

hkl	Fo	Fc
• 7	0	
-7	-15	-32
-6	91	114
-5	36	26
-4	0	-25
-3	0	-7
-2	-112	-129
-1	-27	-17
0	122	121
1	28	22
2	0	7
3	-22	-10
4	-67	-75
5	0	6
6	36	56
• 7	7	
-5	-107	-107
-4	63	54
-3	93	98
-2	-83	-94
-1	27	23
0	47	55
1	-115	-103
2	60	64
3	43	49
4	-138	-132
5	0	17
• 7	8	
-5	15	26
-4	67	52
-3	22	29
-2	-109	-144
-1	-63	-66
0	102	114
1	0	29
2	24	24
3	0	-8
4	-135	-112
• 7	9	
-5	-51	-50
-4	0	4
-3	41	39
-2	-29	-36
-1	0	-12
0	95	78
1	-24	-28
2	-44	-55
3	19	29
• 7	10	
-2	63	82
-1	0	-17
0	-122	-107
1	0	14
2	44	57
3	-22	-28
• 7	11	
-3	0	-17
-2	-19	-34
-1	0	16
0	44	46
1	0	-16
2	-18	-26
3	28	31
• 7	12	
-4	80	43
-3	52	42
-2	0	16
-1	0	-18
0	-119	-85
1	0	-10
2	95	96
3	12	20
• 7	13	
1	-38	-31
• 8	0	
-6	-313	-294
-4	432	505
-2	-443	-508
0	224	220
2	45	53
4	-84	-94
• 8	1	
-5	-39	-37
-4	-44	-49
-3	-67	-62
-2	0	7
-1	170	183
0	97	88
1	-178	-166
2	-107	-97
3	27	30
4	0	37
5	38	35
• 13	2	
-3	148	130
-2	0	-15
-1	-127	-138
0	0	-1
1	60	57

hkl	Fo	Fc
• 9	1	
-5	35	31
-4	0	-2
-3	-108	-86
-2	-111	-95
-1	104	99
0	170	180
1	-40	-41
2	-144	-135
3	-39	-41
4	37	33
5	51	52
• 9	2	
-5	-60	-60
-4	-90	-77
-3	141	161
-2	184	194
-1	-186	-203
0	-203	-211
1	149	137
2	120	103
3	-24	-33
• 9	3	
-5	72	69
-4	44	28
-3	-110	-110
-2	-100	-100
-1	67	48
0	151	145
1	55	46
2	-99	-94
3	-29	-32
4	24	19
• 9	4	
-5	84	89
-4	0	-23
-3	-173	-201
-2	58	69
-1	222	244
0	-88	-77
1	-146	-149
2	27	27
3	29	34
• 9	5	
-5	60	57
-4	0	10
-3	-37	-42
-2	0	6
-1	-40	-40
0	-43	-47
1	127	116
2	0	27
3	-94	-90
4	0	26
5	26	28
• 9	6	
-5	24	28
-4	-91	-85
-3	-99	-105
-2	154	165
-1	151	150
0	-187	-217
1	-102	-90
2	163	169
3	0	2
4	-75	-74
• 9	7	
-4	-47	-40
-3	0	-22
-2	0	16
-1	0	6
0	0	15
1	32	27
2	-34	-42
3	-45	-52
4	36	48
• 9	8	
-2	49	62
-1	0	-32
0	-111	-102
1	-40	-29
2	79	75
3	40	53
• 9	9	
-2	-32	-51
-1	24	21
0	83	68
1	28	22
2	-47	-43
3	-34	-38
• 9	10	
0	-24	-17
1	0	-18
2	0	-15
3	8	19
• 9	11	
-2	-80	-74
-1	0	-6
0	67	50
1	51	39

hkl	Fo	Fc
• 8	2	
-7	-89	-80
-6	-111	-114
-5	110	132
-4	153	152
-3	-109	-120
-2	-106	-89
-1	63	63
0	0	-14
1	0	-5
2	43	39
3	0	-1
4	0	-1
• 8	3	
-6	32	40
-5	83	74
-4	-51	-53
-3	-117	-115
-2	0	6
-1	90	60
0	80	79
1	40	46
2	-62	-79
3	-58	-61
4	0	20
• 8	4	
-7	87	85
-6	-53	-55
-5	-127	-144
-4	63	50
-3	137	142
-2	0	-12
-1	-91	-87
0	0	-15
1	43	41
2	0	-7
3	-24	-26
• 8	5	
-3	-72	-70
-2	38	31
-1	77	78
0	-131	-131
1	0	5
2	130	137
3	-44	-53
4	-58	-48
5	58	53
• 8	6	
-6	-95	-120
-5	-87	-90
-4	194	226
-3	94	85
-2	-190	-244
-1	0	-17
0	107	94
1	-51	-38
• 8	7	
-3	-42	-46
-2	55	65
-1	123	113
0	-107	-117
1	-111	-97
2	97	110
3	0	16
4	-32	-41
• 8	8	
-4	119	96
-3	65	71
-2	-51	-75
-1	-95	-87
0	0	-15
1	0	26
2	73	72
3	27	28
• 8	9	
-4	-63	-45
-3	-58	-60
-2	20	28
-1	87	82
0	0	2
1	-87	-68
2	0	1
3	15	28
• 8	10	
-4	-40	-21
-3	19	32
-2	44	55
-1	-24	-26
0	-29	-29
1	0	3
2	-20	-28
• 8	11	
2	22	18
• 8	12	
0	-119	-72
1	-91	-82
• 13	1	
-1	-58	-47
0	0	1
1	42	31

hkl	Fo	Fc
• 9	12	
0	119	110
• 10	0	
-2	-136	-142
0	306	332
2	-327	-356
4	248	251
• 10	1	
-5	70	61
-4	0	-2
-3	-40	-42
-2	0	4
-1	0	6
0	-19	-28
1	19	19
2	104	86
3	-31	-28
4	-120	-111
• 10	2	
-4	-19	-27
-3	-36	-22
-2	29	28
-1	84	85
0	80	57
1	-136	-133
2	-138	-137
3	126	117
4	111	122
• 10	3	
-5	24	30
-4	28	33
-3	27	31
-2	-31	-36
-1	-170	-174
0	0	7
1	217	228
2	45	48
3	-135	-134
4	-83	-72
5	11	37
• 10	4	
-4	40	28
-3	27	33
-2	0	2
-1	-91	-94
0	0	8
1	150	155
2	-50	-54
3	-123	-133
4	53	56
• 10	5	
-4	80	61
-3	70	65
-2	-38	-45
-1	-123	-121
0	0	-5
1	105	100
2	0	3
3	0	-12
4	22	22
• 10	6	
-2	-53	-64
-1	-49	-37
0	107	105
1	115	89
2	-116	-110
3	-94	-37
• 10	7	
-5	40	33
0	-40	-44
1	0	4
2	56	51
• 10	8	
-4	-87	-64
-3	36	35
-2	59	75
-1	0	-1
0	-24	-24
1	-55	-43
2	-27	-30
3	43	44
• 10	9	
0	-32	-38
1	0	10
2	57	57
• 11	0	
2	74	80
4	-124	-131
• 11	1	
-5	-42	-44
-4	0	5
-3	67	72
-2	0	-13
-1	-59	-53
0	40	43
1	0	10
2	-55	-48
3	0	5
4	51	45

hkl	Fo	Fc
• 11	2	
-5	63	62
-4	-46	-50
-3	-70	-72
-2	36	39
-1	18	20
0	0	12
1	30	30
2	-20	-17
3	-64	-59
• 11	3	
-5	-9	-12
-4	28	22
-3	26	39
-2	0	-7
-1	-40	-41
0	0	1
1	-47	-46
2	0	4
3	136	140
• 11	4	
-5	-30	-27
-4	-47	-35
-3	0	-13
-2	68	75
-1	38	36
0	-53	-51
1	-24	-23
2	0	9
3	27	31
• 11	5	
-5	-51	-51
-4	0	7
-3	75	80
-2	24	21
-1	-57	-50
0	-56	-54
1	0	-13
2	32	33
3	79	70
• 11	6	
-1	-26	-17
0	0	-12
1	0	3
2	73	72
3	15	17
• 11	7	
-4	-36	-27
-3	75	71
-2	31	53
-1	-63	-53
0	0	-24
1	16	13
2	-20	-23
• 11	8	
0	47	40
1	-44	-32
2	-33	-30
• 11	9	
-2	44	54
-1	-47	-34
0	-41	-40
1	57	45
• 12	0	
-4	-45	-31
-2	0	-30
0	51	55
2	-32	-30
• 12	1	
-4	-41	-34
-3	0	-17
-2	24	13
-1	40	40
0	0	5
1	-42	-39
• 12	2	
-1	-90	-97
0	63	67
1	90	100
2	-40	-44
• 12	3	
-4	-24	-17
-3	-40	-37
-2	0	15
-1	45	42
0	0	-6
1	-40	-41
• 12	4	
-4	-32	-28
-3	-103	-94
-2	0	0
-1	40	32
0	29	33
1	0	25
2	-30	-33
• 12	5	
1	-71	-66

index was reduced only from 11·65% to 11·60%, indicating that convergence had been attained. The final calculated structure factors from cycle 10 are listed in Table 4.

The parameters and the accuracy

The final positional parameters in fractions of the cell edges are listed in Table 2. The mean positional standard deviation (0·0035 Å) obtained from inverted matrix diagonal elements in cycle 10 is surprisingly low. Its value is an underestimate since the absolute weights were unknown during the refinement and the adopted weight scheme may have obscured the influence of very weak and very strong reflexions. Therefore, the mean positional standard deviation was estimated by the method of Cruickshank (1960). The standard deviation found in this way (0·0055 Å) is, according to Cruickshank, perhaps 20% too high, but it seems safe to accept this value. The standard deviations in the cell edges are approximately 0·002 Å per measured length of 1·5 Å. It follows that the mean standard deviations in the interatomic bond lengths are $(2\times0{\cdot}0055^2+0{\cdot}002^2)^{\frac{1}{2}}=0{\cdot}008$ Å, giving a 1% significance level of 0·024 Å.

The final vibrational parameters, defining a temperature factor

$$\exp\left(-b_{11}h^2-b_{12}hk-b_{13}hl-b_{22}k^2-b_{23}kl-b_{33}l^2\right),$$

are listed in Table 3. It has been shown (Altona, Knobler & Romers, 1963) that the absolute values of the b parameters are doubtful in the case of visual estimation of photographically recorded intensities. The question arises whether the data are sufficiently accurate to allow for anisotropic refinement. Since no program was immediately available to determine the principal axes of the ellipsoid of vibration of all atoms, we confined ourselves to calculate the *mean* principal vibration directions of the eight atoms C(1) · · · C(6), N and O(3), belonging to the planar part of the molecule (see next section). A similar procedure has been applied by Stam & MacGillavry (1963) according to a method proposed by Waser (1955) and improved by Busing & Levy (1958).

The largest vibration with mean square displacement $\langle u_1^2\rangle=0{\cdot}0344$ Å^2, or $B_1=2{\cdot}72$ Å^2, makes an angle of 23° with the normal to the above-mentioned plane of the molecule. The second largest vibration with $\langle u_2^2\rangle=0{\cdot}0253$ Å^2, or $B_2=1{\cdot}99$ Å^2, makes an angle of 44° with the normal and of 49° with the positive a axis. The smallest vibration $\langle u_3^2\rangle=0{\cdot}0214$ Å^2, or $B_3=1{\cdot}69$ Å^2 makes an angle of 81° with the normal and of $-57°$ with the positive a axis. These numbers roughly agree with the indications of the difference Fourier synthesis made during an earlier stage of the refinement. Judging from the rather small B values found in this determination we estimate that a correction of at most 0·005 Å owing to the rotational oscillations of the molecules should be added to the distances involving the tail atoms C(7), C(8) and C(9). These corrections are at most 0·003 Å for all distances involving the remaining atoms of the molecule. In view of the uncertainties of the absolute values of the *b* parameters and of the lack of computational facilities these corrections have been omitted.

Discussion of the structure

The distances and bond angles between the atoms in the structure were calculated on the X1 computer of the University of Leiden with the aid of a program written by Geise, Jonkers & Romers (1963). The intramolecular bond distances and bond angles are indicated in Fig. 1. The ring atoms C(1) $\cdots$ C(6) and the atoms N and O(3) define a plane

$$0{\cdot}1598X-0{\cdot}0726Y+Z-2{\cdot}4213=0$$

with respect to an orthogonal coordinate system XYZ, where X and Y have the directions [100] and [010] respectively, and Z is perpendicular to (001). The deviations of atoms C(1) $\cdots$ C(6) and atoms N and O(3) from this plane (Table 5) are within the standard deviations of the coordinates. The atoms O(1) and O(2) are possibly and C(7) and C(8) are significantly outside of this plane, C(9) being at a large distance (1·20 Å).

Table 5. *Distances from the molecular plane*

C(1)	−0·0058 Å	C(8)	−0·0337 Å
C(2)	+0·0012	C(9)	−1·2048
C(3)	−0·0030	N	−0·0025
C(4)	−0·0023	O(1)	−0·0227
C(5)	−0·0004	O(2)	+0·0168
C(6)	+0·0036	O(3)	+0·0019
C(7)	−0·0894		

The NO(H) group is *syn* with respect to the CO(H) group and the intramolecular distance O(2)–O(3) (2·473 Å) is comparable to the intramolecular hydrogen bonds found in salicylic acid (2·590 Å, Cochran, 1953), maleic acid (2·46 Å, Shahat, 1952), and cytosine-5-acetic acid (2·506 Å, Marsh, Bierstedt & Eichhorn, 1962). A Fourier synthesis was calculated (Fig. 2) in the plane of the molecule. This calculation was performed on the computer Pascal, Philips Laboratories, Eindhoven with a program devised by Dr P. Braun. The Fourier map clearly shows the hydrogen atoms bound to the carbon atoms C(2), C(5) and C(6). A fourth hydrogen atom is found half way between the oxygen atoms O(2) and O(3). Its peak value (1·5 e.Å^{-3}) is, however, lower than those of the other hydrogen atoms.

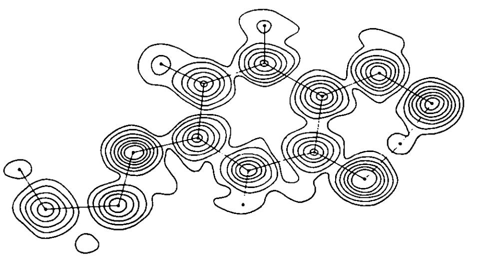


Fig. 2. Electron density map of β-PQO calculated in the plane of the molecule. The contour lines are drawn at 1, 2, 4, 6 ... e.Å^{-3}.

The bond distances C(1)–C(2) (1·357 Å) and C(5)–C(6) (1·344 Å) in *ortho* positions are significantly shorter than the four other bond distances in the ring. The C(3)–O(3) bond (1·270 Å) and the C(4)–N bond (1·319 Å) have a pronounced double-bond character. The distribution of longer and shorter bond distances in the ring as well as the short C(3)–O(3) and C(4)–N bonds clearly indicate a predominantly oxime-like structure. The molecular structure might be described in terms of resonance between the structures (*a*), (*b*), (*c*) ... (*h*) of Fig. 3.

When these structures are given weights as indicated in Fig. 3 and when bond orders p and distances R_1 and R_2 are used as stated in Table 6 the bond lengths calculated from

$$R=R_1-(R_1-R_2)\times 1{\cdot}333p/(0{\cdot}333p+1)$$

(Cruickshank & Sparks, 1960; Cruickshank, 1962) are as shown in Table 6. The standard deviation between the calculated and observed values is 0·015 Å.

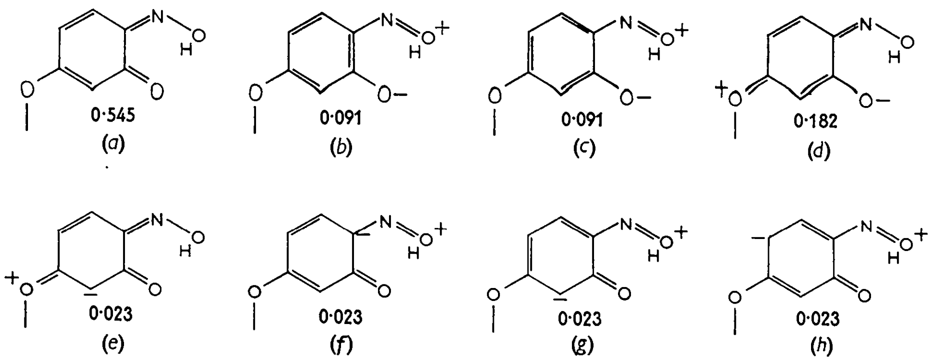


Fig. 3. Canonical 'structures' of β-PQO.

Table 6. *Calculated and observed bond distances* (Å) *in* β-PQO

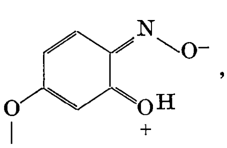
Bond	p	R(calc.)	R(obs.)	ΔR
C(1) – C(2)	0·682	1·373	1·357	0·016
C(2) – C(3)	0·272	1·430	1·410	0·020
C(3) – C(4)	0·091	1·461	1·482	0·021
C(4) – C(5)	0·136	1·453	1·458	0·005
C(5) – C(6)	0·863	1·352	1·344	0·008
C(1) – C(6)	0·114	1·457	1·458	0·001
C(1) – O(1)	0·205	1·325	1·344	0·019
C(3) – O(3)	0·635	1·264	1·270	0·006
C(4) – N	0·750	1·304	1·319	0·015

R_1(C – C) = 1·477 (sp^2–sp^2 hybridization)
R_1(C – O) = 1·36 (phenolic)
R_1(C – N) = 1·36 (average value of nitro compounds)
R_2(C = C) = 1·337 (ethylene)
R_2(C = O) = 1·222 (*p*-benzoquinone)*
R_2(C = N) = 1·28 (average value of oximes)†

* Trotter (1960).
† Quoted by Romers & Fischmann (1960).

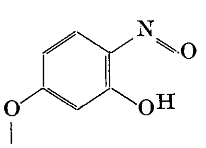
The problem remains how to reconcile the apparent oxime character of the molecule with its absorption spectrum, which suggests a nitroso structure. The absorption band in visible light with λ(max) = 653 mμ is a 'forbidden' *n*–π* transition (Orgel, 1953; Keussler & Lüttke, 1959; Mijs, 1959) with a very low extinction coefficient (ε = 35). The pleochroism of β-PQO (see *Morphology and optics* above) closely resembles the example of pleochroism occurring in crystals of *m*-nitronitrosobenzene given by Nakamoto & Suzuki (1952). According to these authors the *n*–π* absorption is perpendicular to the plane of the molecule. It can be seen from Fig. 5 that this direction is approximately parallel to the *c* axis of the crystals of β-PQO, explaining the observed green colour when the electric vector of the polarized light is parallel to [001].

We suggest the following explanation of the observed optical properties. The shortness of the O(2)–O(3) distance indicates a very strong hydrogen bond with internal proton dissociation (Ubbelohde & Gallagher, 1955) between oxime-like and nitrosophenolic structures. Thus, the counterparts of the structures (*a*), (*b*), *etc.* are the nitrosophenolic structures:



(*a*′)

,



(*b*′)

etc.

This explanation implies a disordering of the bridge hydrogen atom H(11) in the crystal structure. The low peak value of the electron density of this atom (Fig. 2), midway between oxygen atoms O(2) and O(3) is in accordance with this assumption. A similar disordering of hydrogen atoms in the crystal structure of cytosine-5-acetic acid was reported by Marsh *et al.* (1962).

The conformation of the propoxy group deserves special attention. The angle δ between the plane C(9)C(8)C(7) and the plane C(8)C(7)O(1) is 47°, *i.e.* the conformation is *gauche*. It is not yet known why the molecule prefers the *gauche* instead of the planar *trans* conformation and it is interesting to note that the corresponding α forms of Br EQO and Cl EQO also have the *gauche* conformation in their halogenoethoxy groups (Romers & Umans, 1960). The molecule β-PQO might attain complete planarity if the conformation of its tail were *trans* (δ = 180°) or eclipsed (δ = 0°). The first possibility, with even lower potential energy than the ideal gauche conformation (δ = 60°), is apparently ruled out, because the long, protuding tail prevents a tight packing. The sterically unfavorable eclipsed form is also ruled out. It is, however, surprising that the actual conformation (δ = 47°) deviates significantly from the pure *gauche* form.

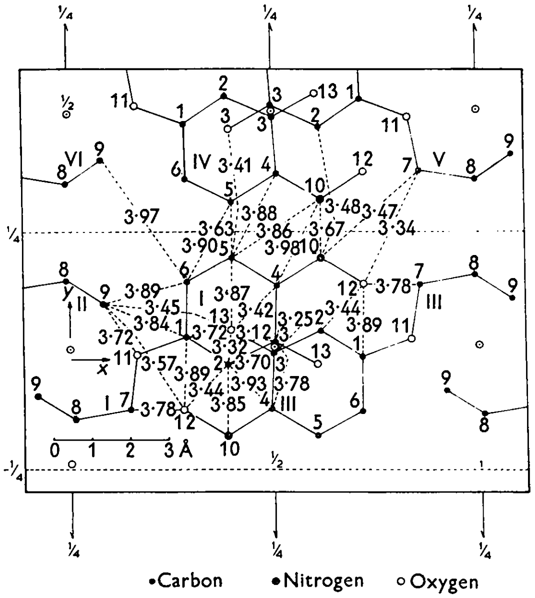


Fig. 4. Part of the crystal structure of β-PQO viewed along the *c* axis.

The intermolecular distances smaller than 4 Å, shown in Fig. 4, and smaller than 3·75 Å, shown in Fig. 5, are between the reference molecule I at x, y, z and the molecules

II at $\bar{x}, \bar{y}, \bar{z}$,
III at $1-x, \bar{y}, \bar{z}$,
IV at $x, \frac{1}{2}-y, \frac{1}{2}+z$,
V at $1-x, \frac{1}{2}+y, \frac{1}{2}-z$,
VI at $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$,
VII at $1-x, \bar{y}, 1-z$.

The screw axis operation has been omitted in Fig. 5 for the sake of clarity. A few rather short distances are found between molecules I and III (Fig. 5). The shortest distance, O(3)–C(3), is 3·12 Å. Similar and

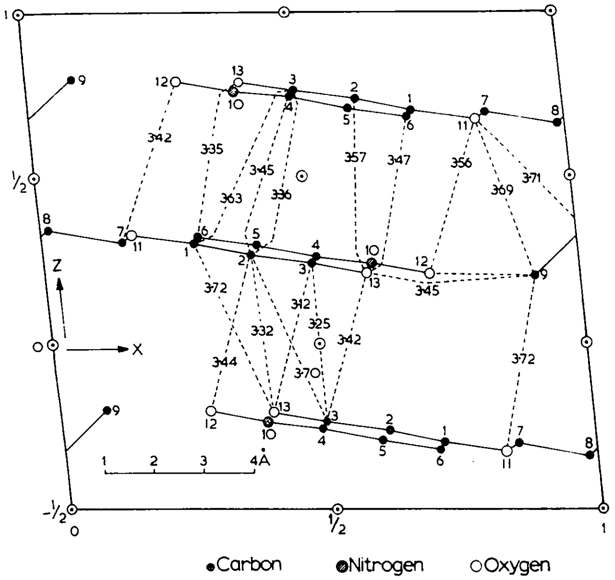


Fig. 5. Part of the crystal structure of β-PQO viewed along the *b* axis. The screw axis operation has been omitted.

even shorter distances between oxygen and carbon atoms have been found in the crystal structures of chloranil (Chu, Jeffrey & Sakurai, 1962) and of parabanic acid (Davies & Blum, 1955). The packing in these last-mentioned structures is of a herring-bone type; β-PQO packs more or less in the form of a layer structure. Consequently there are also rather short intermolecular C · · · C distances (3·25, 3·36 Å).

The glide planes (010) at $y = \pm\frac{1}{4}$ (Fig. 4) and the planes (001) at $z \simeq 0$ and $z \simeq \frac{1}{2}$ (Fig. 5) have cleavage character, because they are only penetrated by intermolecular distances. The layer character also facilitates the twinning found after cutting the crystals parallel to [010], because only a few intermolecular contacts approximately parallel to [100] are involved in the reorientation of the layers with a change of angle β into 180°–β. Finally the layer-type structure is in accordance with the observed orientation of the optical indicatrix, since n_γ is parallel to the longest direction of the molecule and n_α is approximately perpendicular to the plane of the molecule.

The author wishes to thank Prof. Dr E. Havinga for his continuous interest in this investigation. The structure determination dealt with in this paper originated from the synthetic and analytical research of Dr A. J. H. Umans, who provided the crystals and cooperated during the first stages of the diffraction analysis. The discussion with Dr P. Hartman on the optical properties of β-PQO is highly appreciated.

The lack of computational facilities in all but the final stage of this research made it necessary to resort to different computers. The author wishes to express his gratitude to Dr J. C. Schoone and Dr D. Smits for calculations carried out on the ZEBRA computers of the Universities of Utrecht and Groningen respectively. He is also indebted to Mr O. S. Mills who gave valuable advice on the least-squares calculations carried out on the Mercury computer of the University of Manchester. Finally he is grateful to Dr P. Braun and to the N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands for the use of the Pascal computer.

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