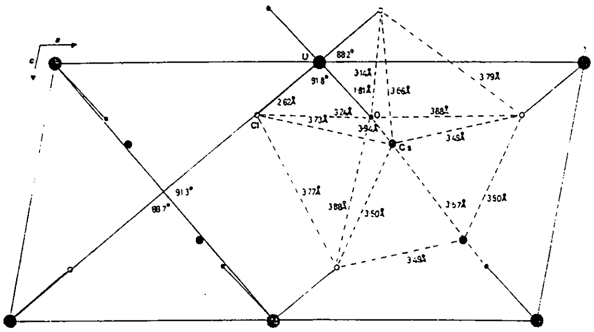

Fig. 2. Interatomic distances and angles.

correction to y_{Cl} of less than one-third its standard deviation. No further refinement was attempted, as the purpose of the investigation had already been achieved.

Atom coordinates, together with their standard deviations, are listed in Table 1. Interatomic distances and angles are shown in Fig. 2. Observed and calculated structure factors are listed in Table 2.

Discussion

Uranium(VI) is six-coordinate in this compound, *i.e.* discrete $[UO_2Cl_4]^{2-}$ ions exist, and no atoms are shared by coordination polyhedra, as occurs with $CsUO_2OCl$. The O–U–O group is linear by symmetry, with the four chlorine atoms in the perpendicular plane. The four U–Cl bonds are necessarily equal, but the chlorine atoms are not at the corners of a square, the angle subtended at the uranium by the mirror related chlorines being 95°. In view of the uncertainty in the chlorine *y* parameter it is doubtful whether this distortion is real.

Eight chlorine and three oxygen atoms at distances between 3·49 and 3·94 Å give the cæsium ion eleven neighbours. The chlorine atoms are arranged approximately at the corners of a cube with the cæsium at the centre (*i.e.* as in cæsium chloride), this cube being somewhat distorted by the three oxygen approaches.

We wish to thank Dr D. van der Helm and Dr A. L. Patterson for making various computer programs available to us, to thank Professor D. R. Llewellyn for his interest in this work, and to acknowledge financial assistance from the Research Committee of the University of New Zealand.

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Isomerism of Benzoquinone Monoximes (Nitrosophenols).
XIII. The Crystal Structure of *p*-Methoxyindophenol *N*-Oxide*

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(*Received* 14 *May* 1965)

The crystals of *p*-methoxyindophenol *N*-oxide are orthorhombic with space group *Pbca* and $Z=8$. The unit-cell dimensions at −180 °C are $a=23{\cdot}91$, $b=12{\cdot}15$, $c=7{\cdot}403$ Å. After several unsuccessful attempts with direct methods the structure was solved from a three-dimensional Patterson analysis with Mo $K\alpha$ data collected at −180 °C.

The anisylic part of the molecule shows the normal distribution of bond distances and bond angles. The benzene ring of this part is tilted, however, by an angle of 64° out of the planar system of the benzoquinone *N*-oxide moiety of the molecule. The distribution of bond angles and bond distances in the latter part is similar to those found in *p*-benzoquinone itself and in *p*-benzoquinone-4-oximes. The bond distances are compared with the results obtained from bond order calculations.

Introduction

The present investigation originated from a spectroscopic study of molecules, free radicals and ions belonging to a class of indophenol dyes. This research was carried out in 1953 by Dr R. Vroom in the department of theoretical organic chemistry, University of Leiden. The compounds studied by Vroom (1966) have the composition

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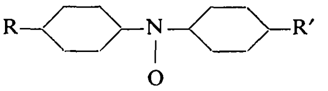
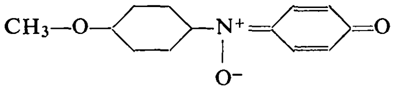
* Part XII: Romers, 1964.



R and R′ being H, O, OH, NO_2 or OCH_3. They show very strong absorption bands in the visible region of the spectrum which can be attributed to $\pi-\pi^*$ transitions. Their position in the spectrum depends on the type of substituent R, the degree of protonation and the angles which the benzene rings make with the planar C–NO–C system. Hanson (1953) determined the crystal structure of the free radical di-*p*-methoxyphenyl nitric oxide and found that the benzene rings make angles of 33° with the planar C–NO–C group according to the molecular symmetry C_2. From spectroscopic evidence Vroom predicted that in the molecule *p*-methoxyindophenol *N*-oxide (PMI) of molecular formula



the benzoquinone ring should be coplanar with the C–NO–C group and that the angle between the two rings should be about 60°. The main purpose of this investigation was to verify this prediction and to determine the value of this angle.

The diffraction analysis of PMI proved to be a far more difficult task than could be foreseen during the initial phase of the research. In addition to vector analysis, trial-and-error procedures and direct methods were employed during the work, which was discontinued several times. Finally the improvement of Weissenberg diffraction technique at low temperatures in this laboratory (Altona, 1964) enabled us to collect complete molybdenum diffraction data at −180 °C. The resolution had increased considerably and led to a successful analysis of the Patterson function. We will confine ourselves to those points of the research which are relevant to the vector analysis and discuss briefly why our attempts to apply direct methods failed.

Experimental

PMI, $C_{13}H_{11}NO_3$, was prepared by the method of Kehrmann & Decker (1921). Aqueous solutions of PMI show a strong absorption band at 370 mμ with an extinction coefficient $\varepsilon=43{,}000$. The crystals, belonging to the orthorhombic dipyramidal class, are orange-red needles melting at 126 °C. They occur in forms {010} and {110} and are elongated along [001]. Systematic extinctions $0kl$ for $k=$odd, $h0l$ for $l=$odd and $hk0$ for $h=$odd uniquely determine the space group *Pbca*. Unit-cell dimensions at 20 °C, −120 °C and at −180 °C are listed in Table 1. It follows from the observed density of 1·36 g.cm^{-3} that the cell contains 8 molecules. On inspection in polarized light the needles exhibit weak pleochroism. When observed in the direction [100] with [001] parallel to the electric vector of polarized light the colour is red. The colour changes into orange on turning the crystal 90° with respect to the electric vector. If the crystal is observed in the same way through the face (010), the colour is slightly darker red if the electric vector makes an angles of 45° with [001] than when the electric vector and [001] are parallel or perpendicular to each other.

Several diffraction photographs were made at room temperature and at −120 °C (Cu $K\alpha$ radiation). Finally non-integrated equi-inclination Weissenberg photographs were made at −180 °C about [001] for the layers $l=0, 1, \ldots 10$ with filtered Mo $K\alpha$ radiation, about [010] for the layer $k=0$ with Mo $K\alpha$ radiation, and for the layers $k=1, 2, \ldots 9$ with Cu $K\alpha$ radiation. Altogether 3145 reflexion intensities recorded at −180 °C were visually estimated and reduced to structure factors in the usual way. Lorentz, polarization and spot-shape factors, but no absorption correction, were applied. Only 2863 structure factors were ultimately used during the refinement of the structure (see below). This last number compares favourably with the number of about 1200 structure factors recorded with copper radiation at −120 °C.

Table 1. *Unit-cell dimensions* (Å) *of* PMI *at room temperature*, −120 °C *and* −180 °C.

a	*b*	*c*	T (°C)
24·0	12·53	7·49	20
23·9	12·45	7·45	−120
23·91 ± 0·01	12·15 ± 0·01	7·403 ± 0·005	−180

Difficulties were met in putting on a common scale the structure factors of *b*- and *c*-axis photographs according to the method of Rollett & Sparks (1960) adapted by Rutten (Geise, 1964). Owing to splitting of the crystal used at low temperature exposures, several reflexions with small ξ-values on the upper level *c*-axis photographs were discarded, with the result that the corresponding reciprocal lines start at *h* values of 8 or higher and run to about 40 or 50 .On the other hand, the same reciprocal rows recorded on *b*-axis films start at *h* values of 1 or 2 and stop at values between 10 and 25. The overlap range of common reflexions is too small to guarantee a proper scaling of both zones. When this effect was recognized the *b*-axis reflexions were also discarded in the refining process and scaling factors for the different reciprocal levels $l=0, 1 \ldots 10$ were calculated after each cycle of least squares.

The vector analysis

The most striking features of the intensity distribution are very strong reflexions $0k0$ for $k=4n$ (Table 2) and the close resemblance of reflexions h, k, l to reflexions $h, k+4, l$. Notwithstanding several exceptions this relationship holds for the groups:

eee when $k=0$ (mod 4)
oee when $k=0$ (mod 4), $e=$even
eeo when $k=2$ (mod 4), $o=$odd
oeo when $k=2$ (mod 4)

and to a less degree unconditionally for the other four groups. The reflexions that do not obey this rule, *i.e.* *eee* and *oee* when $k=2$ (mod 4) and *eeo* and *oeo* when $k=0$ (mod 4) are rather weak. It is evident that the molecules are packed in layers at $y=\pm\frac{1}{8}$ and $y=\pm\frac{3}{8}$. The exceptions to the distribution rules, however, warn us that the molecules cannot be completely planar. It is also clear that such intensity distribution, or more correctly such distribution of atomic positions in the unit cell, prevents a proper determination of scale and overall temperature factor by Wilson's (1949) method.

An unsharpened Patterson synthesis $P(uvw)$ based upon the −180 °C data was calculated for the sections $v=0$, $v=\frac{1}{2}$, and $w=0$ on a grid $u=1/180$, $v=1/90$ and $w=1/60$. The orientation of the molecule is readily derived from the section $v=0$ (Fig. 1) and is in accordance with the observed pleochroism. The peak A at $u=0{\cdot}225$, $w=0{\cdot}22$, due to the interaction N–O(3), is single (apart from the doubling of all peaks in this section caused by the mirror plane). A few additional sections $v=0$, $1/90, \ldots 10/90$ were calculated through this peak and the true vector end was located at $v=0{\cdot}02$ outside the mirror plane, indicating that the molecule is slightly tilted with respect to the plane (010). This peak, the key to the ultimate solution, was lost in the background of the earlier computed vector maps that were based upon the 20 °C or −120 °C data. Moreover these older Patterson functions were rather blurred and did not allow us to find the accurate orientation of the molecule.

A minimum function (Fig. 2) constructed by shifting two sections $P(u0w)$ over the vector A revealed the position of the molecule with respect to the a-glide perpendicular to [001]. If we define the position of the 'centre' of the benzoquinone moiety

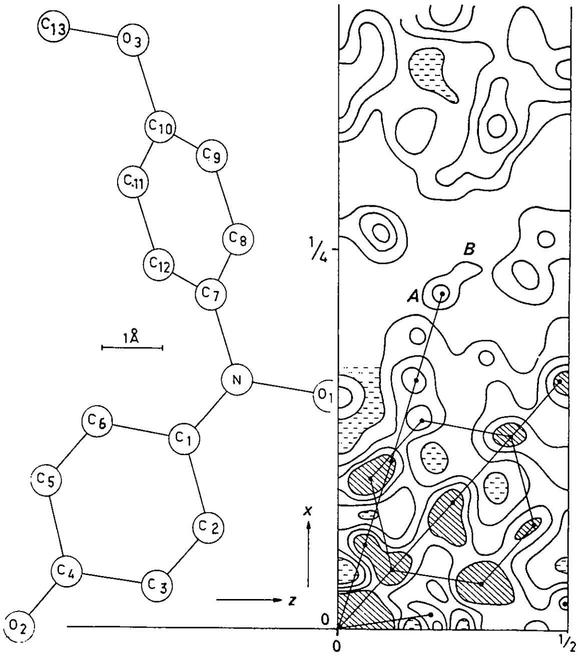


Fig. 1. The Patterson section $P(u0w)$ and the molecular orientation of *p*-methoxyindophenol *N*-oxide.

Table 2. *A few of the strongest unitary structure factors*

h	k	l	U	h	k	l	U	h	k	l	U	h	k	l	U
0	4	0	0·56	2	0	0	0·07	30	0	0	0·41	17	2	5	0·32
0	8	0	0·54	2	4	0	0·45	6	4	6	0·58	21	2	5	0·32
0	10	0	0·33	2	8	0	0·43	6	8	6	0·34	6	6	7	0·35
0	12	0	0·54	2	12	0	0·30	3	4	3	0·20	24	0	6	0·37
0	14	0	0·37	2	16	0	0·38	0	2	1	0·41	18	4	2	0·33
0	16	0	0·43	2	20	0	0·29	18	6	1	0·34	9	2	1	0·14
0	20	0	0·37	2	24	0	0·24	9	2	5	0·33	12	0	8	0·25
0	24	0	0·24	12	0	0	0·33	15	2	5	0·38	0	0	16	0·57

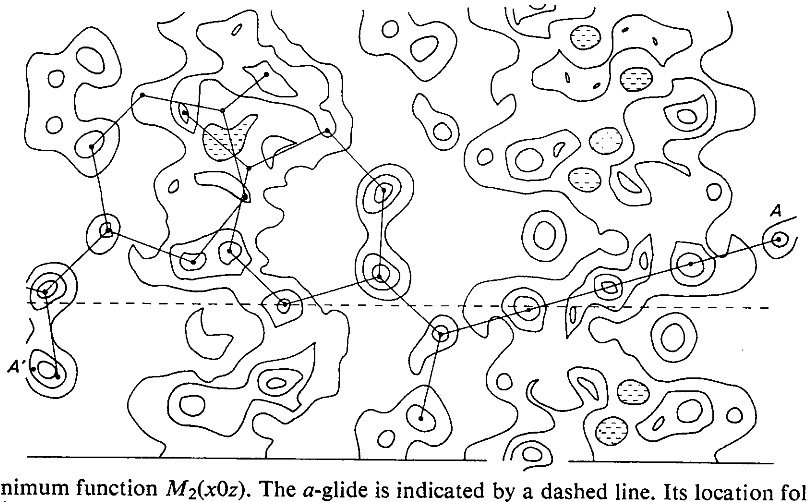
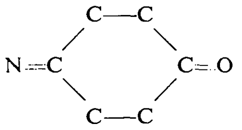


Fig. 2. A part of the minimum function $M_2(x0z)$. The a-glide is indicated by a dashed line. Its location follows from the position of the molecules A and A'. Only one atom A' belonging to the latter molecule is shown.



by x, $y=0{\cdot}125$, $z=0{\cdot}069$ and bear in mind that this part is perpendicular to screw axes running parallel to [010], we can expect in the Harker section $v=\frac{1}{2}$ a 'centre–centre' interaction at $-2x, \frac{1}{2}, \frac{1}{2}-2z$, surrounded by a hexagonal array of peaks. This Harker section contains indeed a hexagonal pattern of peaks (Fig. 3) and the sought peak C is located at $u=0{\cdot}426$, $w=0{\cdot}362$, giving the value $x=0{\cdot}287$.

The tilt of the anisylic ring was determined by inspection of the section $w=0$, that only shows one strong peak $u=0{\cdot}09$, $v=0{\cdot}10$ at a distance 2·42 Å from the origin and outside the heavily populated lines $u00$, $u\frac{1}{4}0$ and $u\frac{1}{2}0$. This vector was interpreted as a fourfold interaction of N–C(8), C(7)–C(9), C(12)–C(10) and C(11)–O(3) resulting in a tilt of about 60°.

A trace of the interaction N–C(13) can be seen at position B in Fig. 1. However, this methyl group was located more accurately from packing considerations in a three-dimensional wire model of the structure.

The failure of the application of direct methods

Our lack of success in the analysis of the −120 °C data by direct methods according to procedures described by Hauptmann & Karle (1954) and Woolfson (1961) can be attributed to three causes. In the first place, we encountered difficulties (as happened with the −180 °C data) in correlating the different reciprocal layers and in finding the proper absolute scale and overall temperature factor. These difficulties gave rise to serious errors in the calculated unitary and normalized structure factors. In the second place, the amount of information, *i.e.* the number of reflexions, was too limited. This limitation compelled us to relate the sought signs of structure factors with a too small group of continually used strong structure factors. For example the relation $s(h+2, k+4, l)=s(hkl)\,s(240)$ does not hold for several structure factors. Applying this relation to the row $h21$ would give $s(h+2, 2, 1)=-s(h21)$ if $s(240)=+$ and $s(h+2, 2, 1)=s(h21)$ if $s(240)=-$. Such distribution of signs would imply an impossible concentration of atoms along the lines $x=\frac{1}{4}$, $y=\frac{1}{8}$, z or $x\simeq 0$, $y=\frac{1}{8}$, z.

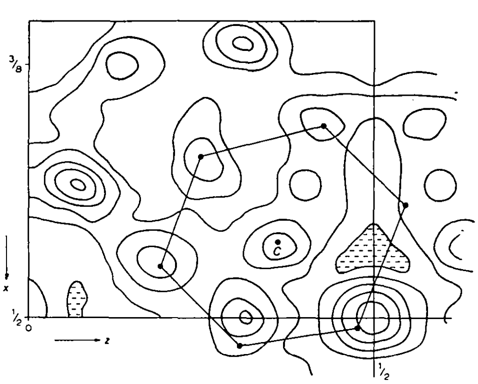


Fig. 3. A part of the Harker section $P(u\frac{1}{2}w)$.

The third source of error is inherent in the structure. A careful survey of the −180 °C data made it clear that direct methods yield the correct signs or at least a number of correct sign combinations for reflexions *eee* and *oee* when $k=0$ (mod 4) and for reflexions *eeo* and *oeo* when $k=2$ (mod 4), if the reflexions 240, 280 *etc.* are discarded. The results are less reliable for the other four groups and no signs could be found for the first four groups *eee* and *oee* when $k=2$ (mod 4) and *eeo* and *oeo* when $k=0$ (mod 4). A calculated electron density map based upon these signs gives a planar structure without atoms C(8), C(9), C(11), C(12) and C(13); the missing atoms have to be found by other methods.

The refinement

Structure factors were calculated for the model derived from the vector analysis. The reliability index, defined in the usual way, amounted to 53%. The atomic scattering factors of carbon, nitrogen and oxygen used in this work are those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), McWeeny's (1951) form factors of hydrogen being used during the final stages of refinement. A subsequent Fourier synthesis gave more accurate positional parameters for all 17 heavy atoms and resulted in an R value of 33·5%. Further refinement was attained by the method of least squares and a survey of the applied procedures is given in Table 3. The weight factor used was $w=(a+F_{\text{lim}})/(a+F_o+bF_o^2)$ with $F_{\text{lim}}=11$, $a=3{\cdot}5$ and $b=0{\cdot}1$.

Little progress was made during cycles 5, 6 and 7. At this stage a careful survey was made of all calculated structure factors, and corrections were applied for erroneously indexed reflexions and a few mistakes in intensity estimations. The agreement between observed and calculated structure factors was unsatisfactory for the upper levels $l=8$, 9 and 10. Considerable time was spent in attempts to recorrelate and rescale common structure factors obtained from c-axis and b-axis exposures.

Finally the b-axis reflexions were eliminated and the scaling factors of each level $l=0, 1\ldots 10$ were determined in a version of the structure-factor least-squares program that contains the n scale factors coupled with the overall temperature factor in an $(n+1)\times(n+1)$ block matrix.

The last four cycles were calculated with anisotropic temperature factors of the form

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right].$$

After cycle 13, with $R=12{\cdot}0\%$, the greatest shifts were about one third of the standard deviations and no further refinement was attained*.

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* Tables of structure factors are available on request at the authors' address in Leiden, The Netherlands.

The positional parameters and their standard deviations are given in Table 4 and the vibrational parameters are listed in Table 5. The rather high value of the final R index can be attributed to the splitting of the crystal at low temperature. None the less the standard deviations are low as a consequence of the large number of reflexions (2863) compared with the relatively small number of parameters (164). The low temperature is also a very important factor in attaining a large accuracy.

Discussion of the structure and packing

The bond distances and bond angles calculated from the positional parameters in Table 4 and uncorrected for thermal motions are shown in Fig. 4. The respective mean positional standard deviations $\sigma(r)$ are 0·0031 Å for N, O(1), O(2) and O(3), 0·0036 Å for C(1), C(2),... C(7) and 0·0041 Å for the remaining atoms C(8)... C(13). The C–C, C–O and N–O bonds in the benzoquinone part have standard deviations of 0·0051 Å,

Table 3. *A survey of the applied refinement procedures*

Cycle	R (%)	Procedure	Description
1	53·2	Structure factors only	
1*a*		$\varrho(xyz)$	$\Delta x=1/180$, $\Delta y=1/90$, $\Delta z=1/60$.
2	33·5	Least squares;	3 × 3 positional blocks; one 2 × 2
3	24·7	one B overall.	$k-B$ overall block; k = scale
4	21·4		factor.
5	20·9	Least squares;	3 × 3 pos. blocks; 1 × 1 B blocks;
6	20·8	individual	one 2 × 2 $k-B$ overall block.
7	20·6	B's.	
7*a*		Print out of structure factors; weight scheme adopted; discard of b-axis reflexions; rescaling of levels $l=0, 1, \ldots 10$.	
8	17·6	Least squares, individual B's; $n=11$ separate scale factors.	3 × 3 pos. blocks; 1 × 1 B blocks; one $(n+1)\times(n+1)$ block for n scale factors $+B$ overall.
8*a*		Difference Fourier	Hydrogen atoms located.
9	16·7	same as cycle 8	Hydrogen atoms introduced at calculated positions and kept fixed during refinement.
10	14·6	Anisotropic	3 × 3 pos. blocks; 6 × 6 U_{ij}
11	13·1	refinement; H atoms	blocks; one $(n+1)\times(n+1)$ block for
12	12·4	at fixed positions	scale factors and B overall
13	12·0		

Table 4. *Final positional parameters (fractions of cell edges) and their standard deviations* (Å) *p-methoxy-indophenol N-oxide*

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
N	0·1470	0·1200	0·1874	0·0028	0·0034	0·0031
O(1)	0·1563	0·1179	0·0190	0·0028	0·0033	0·0028
O(2)	0·3175	0·1222	0·6726	0·0027	0·0033	0·0038
O(3)	−0·0776	0·0915	0·3817	0·0028	0·0037	0·0036
C(1)	0·1887	0·1236	0·3117	0·0031	0·0037	0·0034
C(2)	0·2454	0·1321	0·2490	0·0033	0·0039	0·0039
C(3)	0·2884	0·1307	0·3689	0·0034	0·0040	0·0040
C(4)	0·2781	0·1228	0·5621	0·0032	0·0038	0·0040
C(5)	0·2203	0·1150	0·6223	0·0032	0·0038	0·0036
C(6)	0·1775	0·1143	0·5019	0·0031	0·0039	0·0034
C(7)	0·0888	0·1167	0·2414	0·0030	0·0039	0·0034
C(8)	0·0573	0·0271	0·1865	0·0036	0·0043	0·0042
C(9)	0·0011	0·0217	0·2365	0·0040	0·0044	0·0042
C(10)	−0·0227	0·1064	0·3394	0·0034	0·0046	0·0036
C(11)	0·0090	0·1963	0·3906	0·0035	0·0045	0·0038
C(11)	0·0090	0·1963	0·3906	0·0035	0·0045	0·0038
C(12)	0·0653	0·2016	0·3410	0·0033	0·0041	0·0035
C(13)	−0·1038	0·1752	0·4992	0·0043	0·0059	0·0049
H(1)*	0·253	0·139	0·117			
H(2)*	0·328	0·136	0·318			
H(3)*	0·213	0·113	0·751			
H(4)*	0·138	0·100	0·549			
H(5)*	0·075	−0·027	0·117			
H(6)*	−0·027	−0·037	0·190			
H(7)*	−0·005	0·257	0·452			
H(8)*	0·006	0·267	0·366			
H(9)*	−0·078	0·195	0·608			
H(10)*	−0·133	0·144	0·542			
H(11)*	−0·108	0·242	0·400			

* Hydrogen parameters for calculated positions.

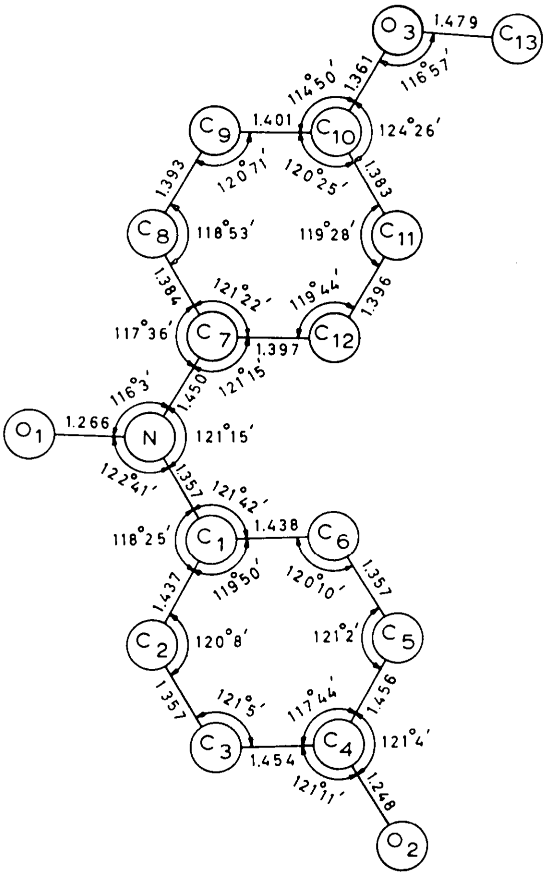

Fig. 4. Bond distances (Å) and bond angles of *p*-methoxyindophenol *N*-oxide.

0·0047 Å and 0·0044 Å, respectively. The C–C and C–O bonds in the other part of the molecule have standard deviations of 0·0058 and 0·0051 Å. The influence of small errors in unit-cell dimensions can be neglected. The standard deviation in the bond angles is about 30′.

The bond distances and bond angles in the anisylic benzene ring are quite normal. Their average value (1·392 Å with average s.d. 0·0024 Å) differs by 0·005 Å from the accepted value (1·397 Å) for the C–C bond in benzene. The difference, although insignificant in a statistical sense, might be due to the neglected libration effect. The C–O bonds in the methoxyl group are asymmetric with the shorter one (1·361 Å) attached to the benzene ring and the longer one (1·479 Å) to the methyl group. The same phenomenon was observed in *β*-5-n-propoxy-*o*-quinone-2-oxime (1·344 and 1·451 Å respectively; Romers, 1964) and in *α*-5-(2′-chloroethoxy)-*o*-quinone-2-oxime (1·343 and 1·448 Å, respectively; van Oijen & Romers, 1966). The bonds C(7)–N and C(10)–O(3) are not collinear, but make an angle of 172° 56′. The deviation of collinearity is caused by the angle C(11)–C(10)–O(3) (124° 26′) inside the quadrangle C(11), C(10), O(3), C(13) which is significantly larger than the outside angle C(9)–C(10)–O(3) (114° 50′). The same effect was observed in *β*-5-n-propoxy-*o*-quinone-2-oxime (124° 19′ and 116° 32′), in *α*-5-(2′-chloroethoxy)-*o*-quinone-2-oxime (125° 53′ and 114° 18′) and in the two forms of 2-chloro-*p*-benzoquinone-4-oxime acetate (127°, 114° and 125°, 116°, respectively; Fischmann, MacGillavry & Romers, 1961*a*, *b*). The difference between the inside and the outside angles can be interpreted as a steric effect of the hydrogen atom at-

Table 5. *Thermal parameters* (Å^2) *of p-methoxyindophenol N-oxide*

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
N	0·0126	0·0204	0·0077	0·0025	0·0012	0·0048
O(1)	0·0200	0·0308	0·0069	0·0079	0·0011	0·0079
O(2)	0·0138	0·0267	0·0209	0·0003	−0·0045	−0·0131
O(3)	0·0121	0·0442	0·0212	−0·0103	0·0128	0·0050
C(1)	0·0117	0·0165	0·0084	0·0024	0·0040	0·0038
C(2)	0·0125	0·0226	0·0113	0·0046	0·0077	0·0098
C(3)	0·0120	0·0211	0·0160	0·0045	0·0032	0·0074
C(4)	0·0116	0·0135	0·0186	0·0021	0·0006	−0·0044
C(5)	0·0138	0·0185	0·0100	0·0013	0·0004	−0·0008
C(6)	0·0125	0·0200	0·0063	−0·0016	0·0058	0·0050
C(7)	0·0109	0·0237	0·0062	0·0019	0·0024	0·0006
C(8)	0·0161	0·0240	0·0152	−0·0033	0·0027	−0·0019
C(9)	0·0182	0·0292	0·0155	−0·0102	0·0013	−0·0050
C(10)	0·0116	0·0368	0·0071	−0·0030	0·0122	−0·0016
C(11)	0·0138	0·0315	0·0097	0·0050	0·0027	0·0010
C(12)	0·0122	0·0278	0·0070	−0·0011	0·0005	0·0022
C(13)	0·0174	0·0502	0·0186	−0·0041	0·0186	0·0028
H(1)	1·28*					
H(2)	1·34*					
H(3)	1·26*					
H(4)	1·17*					
H(5)	1·59*					
H(6)	1·78*					
H(7)	1·52*					
H(8)	1·36*					
H(9)	2·02*					
H(10)	2·02*					
H(11)	2·02*					

* Isotropic *B* values.

tached to C(11) and the carbon atom C(13) on the oxygen atom O(3) thus inducing a non-linear overlap of σ-orbitals (Coppens & Schmidt, 1965, Hirshfeld, 1964).

The NO and the methoxyl group are *trans* with respect to the benzene ring. The atoms N, C(7), C(8), ... C(12) define a plane (I)

$$-0{\cdot}25256X+0{\cdot}47623Y-0{\cdot}84227Z+1{\cdot}3576=0 \quad \text{(I)}$$

in which X, Y and Z coincide with a, b and c. This plane was calculated according to the method of Schomaker, Waser, Marsh & Bergman (1959). The atoms C(13) and O(1) are 0·11 and 0·98 Å respectively above this plane, while O(3) is 0·025 Å under it.

The distribution of long and short bond distances in the second moiety of the molecule indicates a predominant benzoquinone character. By kind permission of the authors (Mulder & van der Lugt, 1966) we cite the results of π bond order calculations of PMI according to the self-consistent field method of Pople (1953). The intramolecular distances derived from the bond orders p compare favourably (Table 6) with those found in this analysis. In this calculation the angle $\varphi=64°$ (see below) between the two benzene rings has been incorporated.

The atoms O(2), C(1), C(2)... C(6) are within 0·01 Å coplanar and define a plane (II):

$$0{\cdot}05108X-0{\cdot}99664Y-0{\cdot}06407Z+1{\cdot}4525=0\,. \quad \text{(II)}$$

The atoms N and O(1) are at the respective distances of 0·05 and 0·16 Å under this plane. The atoms C(1, C(7), N and O(1) are exactly planar and define a third plane (III):

$$-0{\cdot}03053X+0{\cdot}99932Y-0{\cdot}02084Z-1{\cdot}3160=0\,. \quad \text{(III)}$$

The angle between planes (I) and (II) is 64°, in agreement with the prediction by Vroom. It is surprising that O(1) is outside plane (II). The angle between planes (II) and (III) is 174° and that between (I) and (III) is 60°.

Table 7. *A few intermolecular distances between atoms of the reference molecule and atoms of symmetry-related molecules*

Atom of molecule *xyz*	Atom of other molecule	Symmetry relation	Distance
N	O(2)	$\frac{1}{2}-x,\ -y,\ -\frac{1}{2}+z$	3·06 Å
O(1)	O(2)	$\frac{1}{2}-x,\ -y,\ -\frac{1}{2}+z$	3·19
O(1)	C(4)	$\frac{1}{2}-x,\ -y,\ -\frac{1}{2}+z$	3·33
O(1)	C(5)	$x,\ y,\ -1+z$	3·31
O(1)	C(6)	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$	3·29
O(2)	C(13)	$\frac{1}{2}+x,\ y,\ 1+\frac{1}{2}-z$	3·14
C(2)	C(5)	$\frac{1}{2}-x,\ -y,\ -\frac{1}{2}+z$	3·25
C(2)	C(5)	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$	3·27
O(2)	C(1)	$\frac{1}{2}-x,\ -y,\ \frac{1}{2}+z$	3·16

Table 6. *Bond distances in* PMI *derived from bond order calculations.*

Bond	p	d(calc)	d(obs)	Bond	p	d(calc)	d(obs)
C(1)–C(2)	0·379	1·443	1·437	C(7)–N	0·204	1·432	1·450
C(2)–C(3)	0·853	1·354	1·357	C(7)–C(8)	0·636	1·392	1·384
C(3)–C(4)	0·422	1·433	1·454	C(8)–C(9)	0·688	1·382	1·393
C(4)–C(5)	0·425	1·433	1·456	C(9)–C(10)	0·616	1·395	1·401
C(5)–C(6)	0·849	1·355	1·357	C(10)–C(11)	0·615	1·395	1·383
C(1)–C(6)	0·387	1·441	1·438	C(11)–C(12)	0·688	1·382	1·396
C(1)–N	0·593	1·357	1·357	C(7)–C(12)	0·636	1·392	1·397
C(4)–O(2)	0·762	1·269	1·248	C(10)–O(3)	0·354	1·354	1·361
N–O(1)	0·656	1·265	1·266				

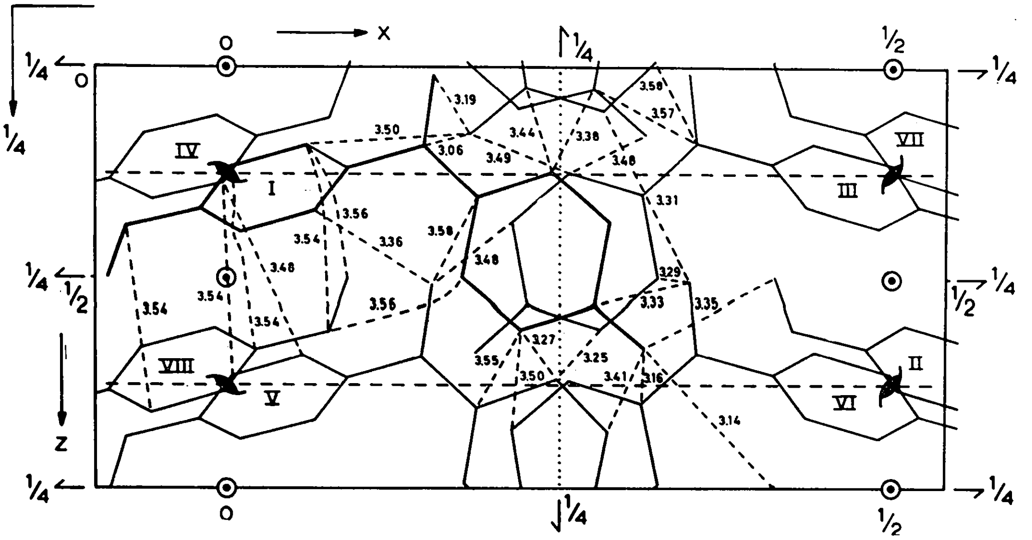

Fig. 5. The crystal structure of PMI viewed along the b axis. The roman numbers indicate the molecules at x, y, z (I); $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$ (II); $\frac{1}{2}-x$, $\frac{1}{2}+y$, z (III); $-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$ (IV); x, $\frac{1}{2}-y$, $\frac{1}{2}+z$ (V); $\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$ (VI); $\frac{1}{2}+x$, y, $\frac{1}{2}-z$ (VII) and $-x$, $-y$, $-z$ (VIII).

The packing of the molecules is illustrated in a projection along [010] in Fig. 5. Only intermolecular distances less than 3·60 Å between the heavy atoms are indicated. A few very short distances are listed in Table 7. Very small intermolecular C–O distances have also been reported by other authors (Davies & Blum, 1955; Chu, Jeffrey & Sakurai, 1962; Romers, 1964) and their existence is less exceptional than might be expected on the basis of spherical van der Waals radii of atoms.

All calculations mentioned in this paper were carried out on the X1 computer of the University of Leiden with programs devised by:

1. Elisabeth W. M. Rutten, Fourier and structure factor-least-squares programs (Rutten, 1963).
2. Mr W. M. H. Rutten, correlation and scaling of different zones and also 'best least-squares' planes.
3. Dr H. Geise, reduction of reflexion intensities to structure factors (Geise, 1964).
4. The second author (B.H.), computation of intramolecular bond distances and bond angles and intermolecular bond distances.

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Isomerism of Benzoquinone Monoximes (Nitrosophenols).

XIV. The Crystal Structure of α-5-(2′-Chloroethoxy)-*o*-quinone-2-oxime at −180 °C*

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Crystals of α-5-(2′-chloroethoxy)-*o*-quinone-2-oxime are monoclinic with space group $P2_1/c$ and $Z=4$. The lattice constants at −180 °C are $a=4{\cdot}01$, $b=10{\cdot}87$, $c=20{\cdot}08$ Å, $\beta=103°\ 36'$. The structure was refined by the least-squares method; the data used were integrated reflexions recorded at −180 °C with a Weissenberg goniometer and measured with an automatic recording microdensitometer. The final R value is 6·77 %.

The molecule has an oxime structure with CO and NOH groups in the *anti* configuration. Intermolecular hydrogen bridges connect CO and NOH groups of different molecules by means of a screw axis operation. The $\mathrm{Cl{-}C_2H_4{-}O}$ group has the *gauche* conformation.

Introduction

In an earlier paper of this series Romers & Umans (1960) published an investigation of 5-alkoxy-*o*-quinone-2-oximes occurring in two modifications α and β that were discovered by Henrich & Eisenach (Henrich, 1904; Henrich & Eisenach, 1904). Romers & Umans reported that in the β modification an intramolecular hydrogen bridge exists between the CO(H) and NO(H) groups in the *syn* configuration and that intermolecular hydrogen bonds connect CO and NOH groups of dif-

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* Part XIII: Romers & Hesper, 1966.