

## The Crystal Structure of N-oxypyphenazine

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Crystals of N-oxypyphenazine are monoclinic holohedral, space group  $C_{2h}^5-P2_1/c$  with two molecules in the unit cell. The unsymmetrical molecules are statistically arranged about two possible  $180^\circ$  orientations, so giving the crystal a higher symmetry than that normally expected from this asymmetrical molecule.

### Introduction

N-oxypyphenazine and other N-oxides and halogen derivatives have been polarographically examined by Curti, Locchi & Landini (1953, 1954, 1955*a, b, c*) in order to determine the reactivity conditions of the N-O group. A detailed X-ray structural analysis of these crystals should throw some light on the bond characters of the molecule, particularly the N-O group. In the course of this analysis, however, we find that the asymmetric molecules of N-oxypyphenazine take up two possible orientations about centres of symmetry related by the space group in the crystal, thus putting the crystal into a higher class.

### Experimental data

Preliminary optical and X-ray investigations on N-oxypyphenazine  $C_{12}H_8N_2O$  have already been published (Curti & Riganti, 1960). The crystals are monoclinic with the unit-cell dimensions

$$a = 7.37 \pm 0.02, \quad b = 4.60 \pm 0.02, \quad c = 14.34 \pm 0.03 \text{ \AA};$$

$$\beta = 108^\circ 59' \pm 8'.$$

The volume of the unit cell is  $459.7 \text{ \AA}^3$ . The measured crystal density is  $1.42 \text{ g.cm.}^{-3}$ , giving 2 molecules per unit cell. The calculated density is  $1.417 \text{ g.cm.}^{-3}$ .

The following reflexions were observed:  $hkl$  in all orders,  $h0l$  for  $l=2n$ , and  $0k0$  for  $k=2n$ , suggesting the space group  $C_{2h}^5-P2_1/c$ . Using the multiple-film technique the intensities of the  $h0l$ ,  $h1l$  and  $h2l$  reflexions were obtained with the Wiebenga Integrating Weissenberg, using  $Cu K\alpha$  radiation. The cross-section of the crystal normal to the rotation axis was  $0.04 \times 0.03 \text{ mm.}$ ; no absorption correction was made. The intensities of the  $hk0$  reflexions were recorded in the same way. The intensities of all reflexions were measured with a Nonius-Delft microphotometer, and in this way 76  $h0l$ , 87  $h1l$ , 58  $h2l$  and 29  $hk0$  independent reflexions were recorded—representing 67, 50, 49 and 68% respectively of the total possible for these layer lines. In addition the  $hk0$  reflexions were recorded with a precession camera, using  $Mo K\alpha$  radiation. Finally all the intensities were corrected for Lorentz and polarization factors, then put on to an approx-

imately absolute scale by the Wilson statistical method, and later correlated with the calculated structure factors using scattering curves recorded in 'Tabellen zur Röntgenstrukturanalyse' (Sagel, 1958).

### Detection of the centre of symmetry

The X-ray absences and the crystal density show that the space group is  $P2_1/c$  with 2 molecules in the unit cell, although the N-oxypyphenazine molecule itself is non-centrosymmetrical. The above conclusion was tested by the following arguments:

(1) It was assumed that the  $0k0$  planes were accidentally halved; so we tried the space group  $C_s^2-Pc$ , but could not satisfactorily place the molecules to explain the absent X-ray reflexions. We concluded, therefore, that the halving was not accidental and that the molecules were statistically distributed in two  $180^\circ$  orientations. This means in effect that the oxygen atom is statistically distributed between two positions. So for that matter is the nitrogen, but this does not affect the argument so much.

(2) We carried out several tests for piezo-electricity with an instrument described by Stokes (1947) and another built by Crystal Structures of Cambridge. No appreciable effect was recorded by either instrument.

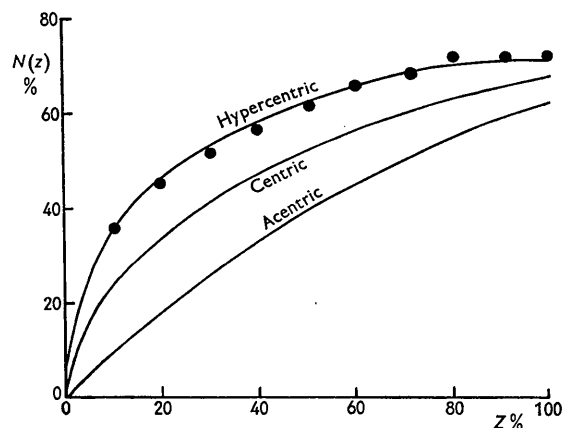
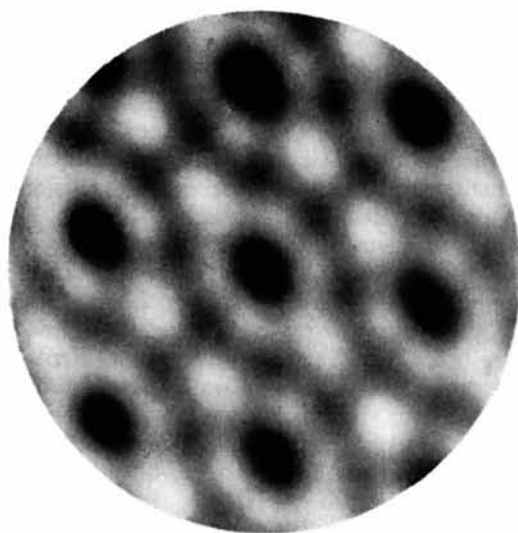


Fig. 1.  $h0l$  distribution curve for N-oxypyphenazine, compared with the curves for acentric, centric and hypercentric zones.

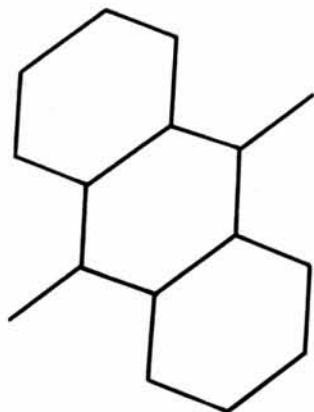
The same result was obtained with the device of Iitaka (1953) in the Mineralogical Institute of Tokyo University (Iitaka, private communication). Nevertheless, these negative tests must not be taken necessarily to mean the presence of a centre of symmetry in the crystal.

(3) All recorded reflexions were submitted to the Howells, Phillips & Rogers  $N(z)$  test (1950); the experimentally determined points for this test lie close to a hypercentric distribution curve (Lipson & Woolfson, 1952), see Fig. 1.

(4) The density of the crystals and the dimensions of the unit cells are very similar in phenazine and N-oxyphenazine respectively. As regards the crystallography and structure of phenazine reference should be made to the studies of Schmidt *et al.* (1952, 1954, 1955*a, b*, 1957). We prepared numerous solid solutions of phenazine and N-oxyphenazine in different ratios



(a)



(b)

Fig. 2. (a) Optical transform of the [010] projection of N-oxyphenazine. (b) Projected molecule giving optical transform in (a).

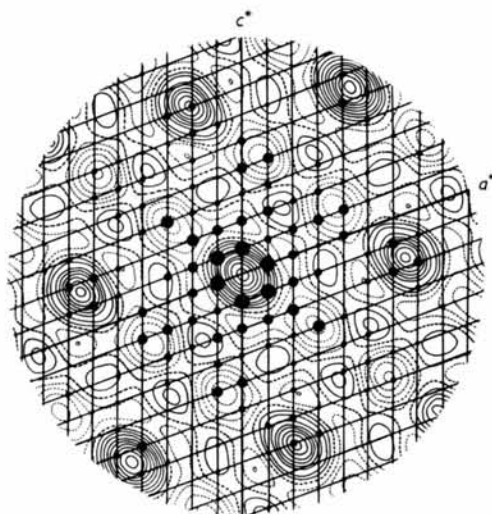


Fig. 3. The final agreement. The Fourier transform of the N-oxyphenazine with superimposed the  $h0l$  section of the weighted reciprocal lattice. Zero and negative contours broken.

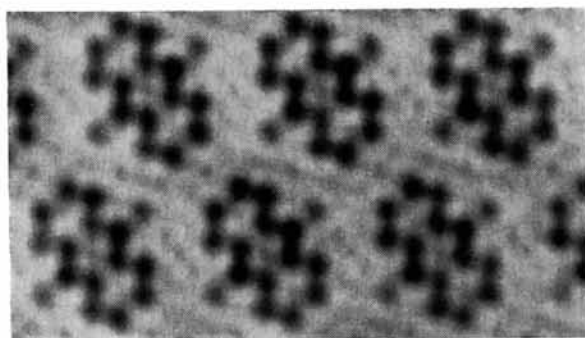


Fig. 4. (010) Fourier synthesis with signs allotted to the coefficients according to the Fourier transform.

by crystallization from methylethylketone; it was noticed that the unit cell of the solid solutions underwent a gradual change as one component was varied between the extremes of crystalline phenazine on the one hand and crystalline N-oxyphenazine on the other. A corresponding change in the intensities of the reflexions of these crystals was also observed. From all this, we feel some justification in stating that the space group of N-oxyphenazine is  $C_{2h}^5-P2_1/c$ .

#### Molecular orientation in the unit cell determined by the Fourier-transform method

Assuming a planar molecule with reasonable bond lengths and with the contribution of the oxygen atoms divided equally between two positions linked by a centre of symmetry, the orientation of the molecule on the  $b$  plane was determined from optically derived transforms using a v. Eller 'photosommateur'. The optical diffraction patterns for various orientations of

Table 1. *Measured and calculated structure factors*

<i>hkl</i>	$F_c$	$F_o$	<i>hkl</i>	$F_c$	$F_o$	<i>hkl</i>	$F_c$	$F_o$	<i>hkl</i>	$F_c$	$F_o$
100	41.0	35.1	104	-15.7	20.7	420	-2.8	3.0	312	-6.4	9.5
200	-20.0	17.2	204	-32.7	34.7	520	-0.1	<2.5	313	0.8	<3.1
300	3.2	2.6	304	-15.6	10.0	620	-8.5	5.0	314	1.2	<3.1
400	-12.1	15.7	404	0.1	<1.6	720	2.5	3.5	315	-2.5	<3.1
500	0.2	<2.1	504	-10.0	9.1	820	5.9	3.0	316	-0.6	<3.1
600	-1.6	<2.4	604	19.9	18.4				317	1.9	<3.1
700	-1.6	<2.6	704	19.9	18.8	130	7.4	8.2	318	6.0	11.5
800	3.0	3.2				230	-1.0	<2.5	319	11.5	10.5
			106	8.7	7.4	330	-5.2	3.8	3,1,10	6.0	6.6
002	47.2	40.7	206	-11.2	8.7	430	2.0	4.1	3,1,11	1.5	<3.1
102	-10.7	13.8	306	-35.5	30.2	530	0.7	<2.5	3,1,12	1.2	<3.1
202	12.0	15.5	406	-4.1	9.3	630	-1.1	<2.5			
302	-23.4	27.8	506	3.5	<2.6	730	0.2	<2.5	411	1.1	<3.1
402	-22.8	25.3	606	-3.7	<2.8				412	2.6	4.8
502	-1.3	3.1	706	5.9	6.6	140	-6.0	9.4	413	-7.8	10.6
602	2.1	<2.6	806	1.7	3.7	240	-3.8	4.1	414	5.3	8.2
702	1.1	<2.6				340	3.1	4.1	415	-9.5	9.7
802	-1.2	<2.8	108	3.9	3.5	440	-0.5	<2.5	416	7.4	7.8
			208	4.0	6.0	540	0.5	<2.5	417	10.2	14.6
004	-22.1	20.2	308	-5.8	2.6				418	9.6	11.7
104	20.6	23.2	408	-5.0	9.1	150	6.3	6.1	419	6.2	4.2
204	10.1	9.6	508	7.7	9.1	250	8.1	7.9	4,1,10	3.2	3.0
304	-13.7	14.7	608	1.2	<2.4	350	0.5	<2.5	4,1,11	-0.3	<3.1
404	-4.1	2.6	708	-3.3	<2.8						
504	3.3	2.6	808	-4.1	5.6	020	20.0	18.6	511	2.6	<3.1
604	0.3	<2.6							512	4.3	4.2
704	-7.0	6.5	1,0,10	-3.5	<2.6	040	3.0	2.5	513	-4.1	6.5
			2,0,10	-7.6	8.1				514	0.8	<3.1
006	0.4	4.1	3,0,10	0.9	<2.6	011	17.6	14.4	515	-2.7	<3.1
106	-12.0	14.8	4,0,10	6.6	9.5	012	-38.7	39.8	516	1.0	<3.1
206	-1.2	<1.7	5,0,10	-6.4	6.0	013	51.9	47.2	517	1.4	<3.1
306	8.4	8.1	6,0,10	-4.9	6.1	014	-30.9	30.4	518	1.6	<3.1
406	-3.2	2.3	7,0,10	1.0	3.6	015	-14.6	18.7	519	-1.1	<3.1
506	-3.5	2.7				016	-13.3	16.8			
606	-5.7	4.2	1,0,12	7.8	8.6	017	-17.1	19.2	611	4.5	4.2
706	-4.8	3.4	2,0,12	15.3	11.7	018	-7.2	5.5	612	-4.6	4.2
			3,0,12	-1.0	2.3	019	2.4	<3.1	613	-5.4	4.3
008	-20.0	21.9	4,0,12	2.1	2.8	0,1,10	3.5	<3.1	614	-4.9	4.3
108	-24.2	23.8	5,0,12	-3.2	3.8	0,1,11	-1.6	<3.1	615	-1.2	<3.1
208	1.8	<2.1	6,0,12	-10.7	8.8	0,1,12	2.4	<3.1	616	-2.3	<3.1
308	-1.6	<2.4				0,1,13	-1.5	<3.1	617	-0.9	<3.1
408	0.5	<2.6	1,0,14	-0.2	2.4	0,1,14	-1.8	<3.1			
508	5.6	9.3	2,0,14	17.7	14.1				711	-1.8	<3.1
			3,0,14	11.6	11.9	111	68.4	53.4	712	-2.6	<3.1
0,0,10	-11.9	11.8	4,0,14	-2.6	<2.6	112	-34.0	33.5	713	-2.5	<3.1
1,0,10	-1.8	<2.1	5,0,14	1.3	<2.8	113	29.2	28.6	714	-1.5	<3.1
2,0,10	-2.6	<2.4				114	-9.8	9.3			
3,0,10	-0.8	<2.6	1,0,16	-0.6	<2.8	115	-13.6	17.7	111	-9.4	9.9
4,0,10	15.7	15.3	2,0,16	1.2	<2.8	116	-4.1	7.8	112	-1.0	<3.1
5,0,10	7.5	6.7	3,0,16	6.2	3.4	117	-2.0	<3.1	113	-8.1	7.9
			4,0,16	-1.7	<2.8	118	2.1	<3.1	114	2.6	3.5
0,0,12	-1.3	<2.4	5,0,16	-0.7	<2.8	119	-5.2	9.1	115	-0.6	3.6
1,0,12	4.2	3.0				1,1,10	8.8	8.9	116	1.6	3.1
2,0,12	-2.5	<2.6	1,0,18	3.0	2.8	1,1,11	-8.0	5.5	117	-12.0	12.6
3,0,12	5.1	4.2	2,0,18	-2.8	<2.8	1,1,12	0.3	<3.1	118	-5.7	3.2
4,0,12	7.5	9.1	3,0,18	-1.4	<2.8				119	2.0	<3.1
			4,0,18	-2.8	2.8	211	-14.8	10.1	1,1,10	-1.2	<3.1
0,0,14	-0.6	<2.6				212	-2.2	<3.1	1,1,11	-3.0	<3.1
1,0,14	-1.1	<2.8	110	-26.4	24.3	213	-4.6	4.3	1,1,12	-1.1	<3.1
			210	-5.9	6.3	214	5.1	5.1	1,1,13	0.8	<3.1
1,0,16	-4.3	3.4	310	-17.3	20.3	215	13.7	15.4			
			410	-10.3	9.2	216	4.5	4.3	211	-4.3	6.6
102	56.2	43.5	510	3.0	4.4	217	-0.3	<3.1	212	-10.2	14.8
202	-19.7	21.8	610	-5.9	5.5	218	0.5	<3.1	213	-7.0	7.3
302	13.0	13.8	710	-6.8	4.8	219	-7.1	6.5	214	5.1	5.3
402	0.4	<1.6	810	-0.4	<2.5	2,1,10	3.1	<3.1	215	2.3	<3.1
502	5.6	5.3				2,1,11	-1.3	<3.1	216	14.4	15.1
602	22.6	18.4	120	-3.0	2.5	2,1,12	-1.8	<3.1	217	-19.7	16.6
702	4.5	6.5	220	-14.6	14.1				218	8.7	10.1
			320	-11.1	12.6	311	-18.3	22.2	219	1.2	<3.1

Table 1 (cont.)

$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$
$\bar{2},1,10$	10.8	10.1	$\bar{5}18$	2.3	<3.3	227	5.1	3.9	$\bar{2}27$	1.4	<3.3
$\bar{2},1,11$	10.2	10.4	$\bar{6}11$	4.2	4.2	321	5.1	4.3	$\bar{2}28$	1.6	<3.6
$\bar{2},1,12$	7.3	9.1	$\bar{6}12$	1.9	<3.1	322	-7.6	7.8	$\bar{2}29$	8.0	7.3
$\bar{2},1,13$	-0.5	<3.3	$\bar{6}13$	-0.6	<3.1	323	-0.8	<3.3	$\bar{2},2,10$	-9.4	7.9
$\bar{3}11$	-21.9	24.6	$\bar{6}14$	-9.8	7.3	324	-1.0	<3.3	$\bar{2},2,11$	2.4	<3.6
$\bar{3}12$	-10.3	8.7	$\bar{6}15$	16.1	13.6	325	19.2	17.3	$\bar{3}21$	-0.4	<3.1
$\bar{3}13$	-14.1	16.4	$\bar{6}16$	-12.0	9.8	326	17.5	17.2	$\bar{3}22$	14.6	15.1
$\bar{3}14$	-19.6	17.0	$\bar{6}17$	9.2	9.9	327	10.2	11.1	$\bar{3}23$	14.2	12.9
$\bar{3}15$	-0.5	<3.1	$\bar{7}11$	10.9	9.0	421	-0.8	<3.3	$\bar{3}24$	-4.2	3.5
$\bar{3}16$	-0.1	<3.1	$\bar{7}12$	8.9	8.1	422	-1.7	<3.6	$\bar{3}25$	-0.7	<3.3
$\bar{3}17$	-5.9	7.7	$\bar{7}13$	3.5	4.2	423	-2.1	<3.3	$\bar{3}26$	-4.3	3.5
$\bar{3}18$	3.8	3.1	$\bar{7}14$	1.4	<3.3	424	7.4	6.8	$\bar{3}27$	2.5	3.3
$\bar{3}19$	-9.6	12.0	021	0.6	<2.5	425	12.7	10.9	$\bar{3}28$	10.5	8.1
$\bar{3},1,10$	8.3	10.5	022	-9.5	11.0	521	-4.5	4.2	$\bar{3}29$	15.1	12.9
$\bar{3},1,11$	13.7	11.8	023	-12.5	13.6	522	-2.2	<3.9	$\bar{3},2,10$	12.8	9.2
$\bar{3},1,12$	11.8	10.8	024	-8.7	10.1	523	-3.7	<3.9	$\bar{3},2,11$	6.3	8.5
$\bar{3},1,13$	10.9	8.2	025	-17.4	19.5	$\bar{1}21$	-5.9	4.2	$\bar{4}21$	-13.1	11.4
$\bar{4}11$	-3.4	<3.1	026	8.3	9.3	$\bar{1}22$	2.1	4.2	$\bar{4}22$	-9.7	8.9
$\bar{4}12$	4.0	7.5	027	-1.3	<3.3	$\bar{1}23$	-6.3	7.8	$\bar{4}23$	-4.2	6.6
$\bar{4}13$	-8.2	7.0	028	1.6	<3.3	$\bar{1}24$	-18.4	15.9	$\bar{4}24$	-2.2	<3.3
$\bar{4}14$	-9.3	10.1	121	4.6	5.9	$\bar{1}25$	-7.2	9.3	$\bar{4}25$	-2.1	<3.3
$\bar{4}15$	-14.8	15.0	122	9.6	11.8	$\bar{1}26$	-10.9	9.8	$\bar{4}26$	2.9	<3.3
$\bar{4}16$	0.0	<3.1	123	21.4	24.8	$\bar{1}27$	2.1	<3.1	$\bar{4}27$	-3.2	<3.3
$\bar{4}17$	1.1	<3.1	124	32.3	32.4	$\bar{1}28$	-6.3	4.1	$\bar{4}28$	-2.1	<3.6
$\bar{4}18$	1.2	<3.3	125	-23.7	23.2	$\bar{1}29$	4.9	3.4	$\bar{4}29$	8.2	9.6
$\bar{4}19$	6.7	4.3	126	8.3	9.1	$\bar{1},2,10$	-3.4	<3.3	$\bar{4},2,10$	10.1	8.5
$\bar{4},1,10$	-2.2	<3.3	127	-1.8	<3.6	$\bar{1},2,11$	0.5	<3.6	$\bar{4},2,11$	6.0	8.9
$\bar{4},1,11$	0.9	<3.3	128	-5.7	4.1	$\bar{2}21$	13.2	12.7	$\bar{5}21$	-2.7	<3.3
$\bar{5}11$	-7.1	4.3	221	-0.3	<3.0	$\bar{2}22$	6.7	11.1	$\bar{5}22$	0.1	<3.3
$\bar{5}12$	-3.5	<3.1	222	16.7	17.5	$\bar{2}23$	11.7	10.1	$\bar{5}23$	-2.4	<3.6
$\bar{5}13$	8.3	6.1	223	-11.5	14.6	$\bar{2}24$	1.8	<3.3	$\bar{5}24$	-3.3	<3.9
$\bar{5}14$	-8.7	7.9	224	8.5	8.3	$\bar{2}25$	-7.3	4.1	$\bar{5}25$	0.8	<3.9
$\bar{5}15$	10.2	8.6	225	-4.6	3.9	$\bar{2}26$	3.0	<3.3	$\bar{5}26$	13.9	8.9
$\bar{5}16$	-2.3	<3.1	226	0.3	<3.3				$\bar{5}27$	-10.1	8.2
$\bar{5}17$	-2.4	<3.3							$\bar{5}28$	11.8	10.2

the molecule in the unit cell were in turn superimposed on the  $h0l$  weighted reciprocal lattice directly, and Fig. 2 shows, with the corresponding molecular orientation, the optical transform that yielded the best agreement. The contour lines in the calculated transform, Fig. 3, allowed the signs of 69 structure factors to be determined, of which only three, the weakest ones, were in disagreement with the signs of the structure factors calculated from the final atomic coordinates. Fig. 4 shows a Fourier projection on (010) and from this we obtained a further refinement which gave a disagreement index  $R$  of 0.32, taking an isotropic temperature factor  $B=3.5 \text{ \AA}^2$  for all the atoms.

#### (010) Projection and refinement

In the electron-density map on (010) all the atoms are well resolved. Later refinements proceeded by computing four successive  $F_o - F_c$  syntheses and by shifting the atoms in order to minimize the slopes at the atomic centres, new individual temperature parameters being chosen to minimize the differences between the observed and calculated peak electron densities and curvatures. Recalculation of structure factors for all the observed  $h0l$  reflexions showed that

the disagreement factor  $R$  had been reduced to 0.19. Because of the statistical distribution of molecules, we thought it was advisable not to proceed with further refinement.

An electron-density projection along the  $b$  axis (using all the observed  $h0l$  reflexions) is shown in Fig. 5.

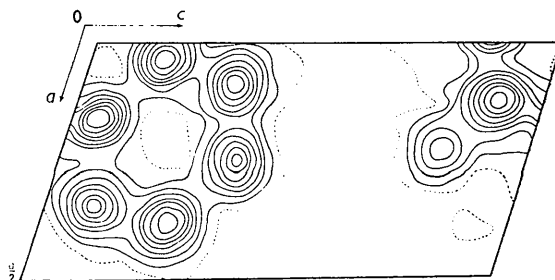


Fig. 5. Final (010) Fourier synthesis. Contours are drawn at equal intervals on an arbitrary scale with the zero contour broken.

#### Refinement of the $y$ coordinates

Overlap of atom peaks in the  $c$ -axis Fourier projection diminishes the efficacy of the syntheses  $F_o - F_c$

in refinement. For the same reason refinement on the  $a$ -axis projection is not reliable. The  $y$  coordinates were therefore calculated initially from the final  $x$  and  $z$  coordinates, assuming the molecule to be planar with reasonable bond lengths. The refinement was then carried out by the method of least squares using reflexions  $hk0$ ,  $h1l$  and  $h2l$ . At the end of the refining process the disagreement factors  $R$  were as follow:

$$\begin{aligned} R &= 0.17 \text{ for } hk0 \text{ planes,} \\ R &= 0.17 \text{ for } h1l \text{ planes,} \\ R &= 0.16 \text{ for } h2l \text{ planes.} \end{aligned}$$

Final  $F_c$  and  $F_o$  values for the  $h0l$ ,  $hk0$ ,  $h1l$ ,  $h2l$  reflexions are listed in Table 1.

### Final coordinates of the atoms

The final positional and temperature parameters of the atoms in one asymmetric unit are listed in Table 2, expressed as fractions of the unit-cell edges. The best plane through the carbon and nitrogen atoms, obtained by the least-squares method, is:

$$0.432X' - 0.749Y + 0.498Z' = 0,$$

where  $X'$ ,  $Y$  and  $Z'$  are coordinates expressed in Å units and referred to orthogonal axes  $a'$ ,  $b$  and  $c$ — $a'$  being perpendicular both to  $b$  and  $c$ ; atom deviations from this plane are given in Table 3.

The root-mean-square deviation of the carbon and nitrogen atoms from this plane is 0.016 Å. Deviation of the oxygen atom from the best plane amounts to 0.070 Å, this being considerably greater than the average deviation; this detail is of doubtful significance because the position of the oxygen atoms and length of N—O bond show limited accuracy.

Table 2. *Positional and temperature parameters*

Atom	$x$	$y$	$z$	$B$
C <sub>1</sub>	0.035	0.187	0.078	3.3 Å <sup>2</sup>
C <sub>2</sub>	0.083	0.372	0.160	3.5
C <sub>3</sub>	0.254	0.522	0.185	3.8
C <sub>4</sub>	0.385	0.480	0.135	3.8
C <sub>5</sub>	0.339	0.298	0.056	3.5
C <sub>6</sub>	0.170	0.144	0.027	3.3
N	-0.129	0.032	0.052	3.3
O	-0.240	0.063	0.101	5.0

Table 3. *Deviations from the mean plane*

Atom	Deviation from phenazine plane	Atom	Deviation from phenazine plane
C <sub>1</sub>	-0.024 Å	C <sub>5</sub>	-0.013 Å
C <sub>2</sub>	+0.011	C <sub>6</sub>	+0.006
C <sub>3</sub>	-0.015	N	+0.025
C <sub>4</sub>	+0.009	O	+0.070

The deviations calculated from Cruickshank's formulae (1949) are rather optimistic; more reliable values for the standard deviations of the mean bond lengths and valency angles are about 0.015–0.020 Å

for the aromatic bonds, 0.020–0.025 Å for the heterocyclic ones, 0.030 Å for the N—O bond, and 1°–2° for the angles.

Further interesting details concerning the N—O bond are expected from the structure of dioxyphenazine, which is being studied and should be completed before long.

### Discussion

A molecule of N-oxyphenazine has no centre of symmetry, but if two molecules are placed in such a way as to lie on parallel planes with their ring systems directly above one another and with the oxygen atoms in opposite positions then there must exist a centre of symmetry between the two molecules. The X-ray study of these crystals has clearly revealed that the packing of these molecules in the crystal takes place in two possible 180° orientations, as described above, and consequently has yielded a crystal possessing a higher symmetry than that expected. Some support for this is revealed by the X-ray study of solid solutions of phenazine and N-oxyphenazine, which may be interpreted as solid solutions in which the molecules of phenazine are statistically replaced by N-oxyphenazine. A similar possibility is suggested in the acridine–anthracene system studied by Kitaigorodskii (1955), where the acridine molecules can partially replace the anthracene ones, giving rise to a statistical distribution in the structure. We considered the possibility that the crystals of N-oxyphenazine might consist of blocks containing molecules with the O in one position and other blocks with the O in the opposite position, but there was no evidence for this. It is not unlikely that both orientations of the molecule could exist within a single unit cell.

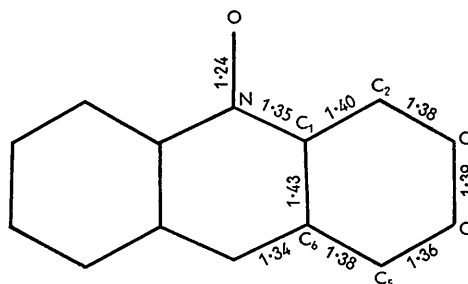


Fig. 6. Final bond lengths.

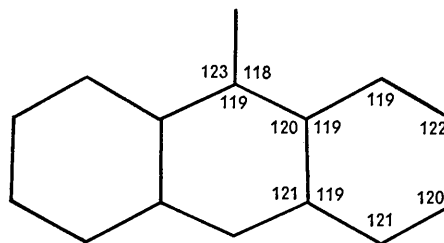


Fig. 7. Final valency angles.

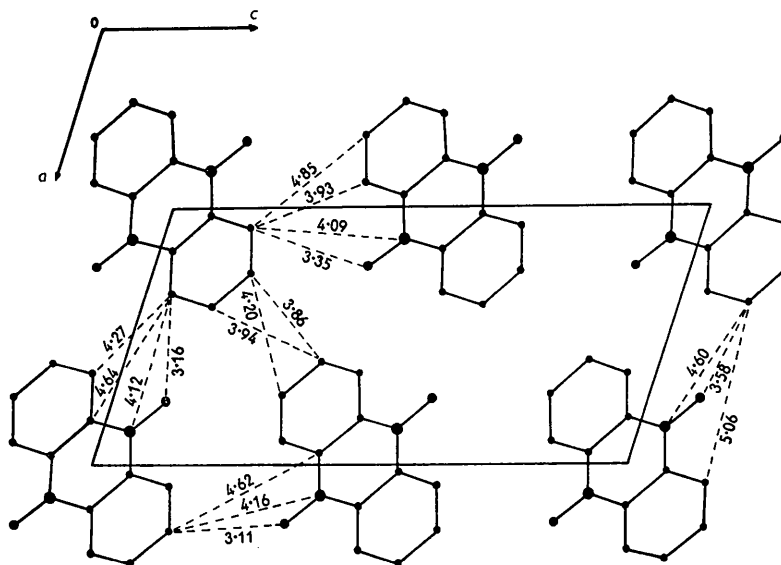


Fig. 8. Projection of the structure down [010], showing the shorter intermolecular contacts.

Bond lengths and valence angles in the molecule of N-oxypyphenazine (Figs. 6 and 7 respectively) were calculated from the coordinates given in Table 2, and the standard deviation (see above) suggests that neither the values of the bond lengths can be quoted to better than 0.01 Å, nor the valency angles better than 1°. Bond C<sub>1</sub>-C<sub>6</sub> is appreciably longer than the other aromatic ones; the average C-C length amounts to 1.39 Å. The N-O and N-C lengths and their connexion with the corresponding distances in other N-oxides will be discussed in detail elsewhere.

The shortest intermolecular distance in molecules separated by the length of the *a* axis is 3.16 Å and in molecules related by the glide plane is 3.11 Å. These distances are illustrated in Fig. 8. The shortest intermolecular distance in molecules separated by the length of the *b* axis is 3.52 Å.

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