The Crystal Structure of Phenazine 5, 10-Dioxide

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This paper describes part of an investigation of the structure of the *N*-oxides of heterocyclic compounds. Here we present the results of an analysis of the crystal and molecular structure of phenazine 5, 10-dioxide. In the course of the present investigation, a paper on the structure of the same substance was published[1]. Though the space group and the general scheme of the structure remain the same, the unit cell dimensions, and hence the interatomic distances, are different.

Experimental

Sample.—Phenazine 5, 10-dioxide was synthesized by the oxidation of phenazine 5-oxide using hydrogen peroxide and a acetic acid mixture. Single crystals were obtained from acetic acid solutions. Ethanol solutions of these crystals did not show any trace of absorption lines due to phenazine 5-oxide. Single crystals are elongated needle-like in the direction of the b-axis, are red in color and have predominant faces at {100} and $\{10\bar{2}\}$.

Crystal Data.—The unit cell dimensions were determined from oscillation photographs by recording the same reflections on both sides of the film, while the radius of the camera used was calibrated by superimposing a powder pattern of pure sodium chloride.

The density was measured by the pycnometer method using water as the medium.

Phenazine 5, 10-dioxide, $C_{12}H_8N_2O_2$, M. wt.=212. D. p.=190°C

Monoclinic;

$a = 7.83 \pm 0.02$ $\quad b = 3.95 \pm 0.02$

$c = 15.50 \pm 0.05$ Å $\quad \beta = 104°48' \pm 10'$

Volume of the unit cell: 463.47 Å^3

Density: Obs. 1.52 g. cm^{-3}, calcd. (with $z=2$) 1.519 g. cm^{-3}

Linear absorption coefficient for X-ray ($\lambda=1.542$ Å): $\mu=10.1$ cm^{-1}

Total number of electrons per unit cell: $F(000)=220$

The extinction rules were found to be $(h0l)$ for l odd and $(0kl)$ for k odd. Accordingly, the space group was determined as $P\,2_1/c-C^5{}_{2h}$.

It may be added here that on extremely long-exposured films there appeared several weak reflections which did not agree with the extinctions mentioned above. However, the shape of these reflections differ from the rest, and their indices (101), (201), $(20\bar{1})$ and (203) can be interpreted as due to double reflections arising from the following combinations of indices whose intensities are all very strong:

(101) : (013) ; $(1\bar{1}\bar{2})$ $\quad$ (201) : (311) ; $(\bar{1}\bar{1}0)$

$(20\bar{1})$: $(\bar{1}13)$; $(3\bar{1}\bar{4})$ $\quad$ (203) : (310) ; $(\bar{1}\bar{1}3)$

It is to be noted that similar double reflections have also been reported in the cases of anthraquinone[2] and other crystals[3] consisting of planar molecule.

Intensity Data.—The intensity data were obtained from equi-inclination Weissenberg photographs

1) R. Curti and V. Riganti, *Rend. it. Lombardo Sci., Pt. I. Classe Sci. mat e nat.*, **94A**, 117 (1960).

2) B. V. Murty, *Acta Cryst.*, **8**, 113 (1955).

3) H. Watase, K. Osaki and I. Nitta, This Bulletin, **30**, 532 (1957).

(*h*0*l*) and (0*kl*) taken by means of CuK_α radiation filtered through nickel foil.

The multiple-film technique was used, and the intensities were estimated visually by comparison with a calibrated scale prepared with the same crystal. The range of intensities measured was 1~6000 for the two zones, and the number of reflections observed were 107 for (*h*0*l*) and 48 for (0*kl*). These figures correspond to 75% and 70% of the total number of reciprocal lattice points included within the sphere of reflection.

The intensities were corrected for Lorentz and polarization factors to obtain the relative values of $|F|^2$.

No absorption corrections were applied, as the cross-sections of the crystals used were 0.2 mm.× 0.2 mm. for *h*0*l* (μr=0.2) and 0.5 mm.×0.5 mm. for 0*kl* (μr=0.5) respectively.

Structure Determination

Since the space group is $P\ 2_1/c$ and since the unit cell contains two molecules, it follows that the center of gravity of the molecules should be placed at one of the following four sets of equivalent positions:

(a) 0, 0, 0 ; 0, 1/2, 1/2

(b) 1/2, 0, 0 ; 1/2, 1/2, 1/2

(c) 0, 0, 1/2 ; 0, 1/2, 0

(d) 1/2, 0, 1/2 ; 1/2, 1/2, 0

It is immaterial which set is chosen ; hence, case (a) was chosen.

The fact that the length of the b-axis of the unit cell is comparable to the van der Waals' contact between condensed rings (3.5Å) suggests that the molecular planes have to be almost parallel to the (010)-plane. Therefore, if we designate the molecular axes by L and M, where L is the longest axis joining the centers of the three hexagons of the phenazine ring and M is the one along the N–O bonds, it is anticipated that the orientations of these molecular axes with respect to the a- and c-axes may be found easily by an optical Fourier transform of a single molecule.

The b-Axis Projection.—With a model of a planar molecule having the bond lengths 1.4 Å, 1.4 Å, 1.3 Å for C–C, C–N and N–O respectively and a bond angles of 120° for all, Fraunhofer diffraction patterns for various inclinations of the molecular axes to the b-plane were prepared. Comparing these Fraunhofer diffraction patterns with the (*h*0*l*) weighted reciprocal lattice, it was found that the molecular axis L points in the [102] direction. Furthermore, using the superposition method proposed by Otsuka and Watanabe[4], signs of the structure factors for several reflections

4) T. Watanabe and M. Otsuka, *Acta Cryst.*, **10**, 377 (1957).

SIGNS FOUND BY THE OPTICAL METHOD

h 0 *l*	Sign	*h* 0 *l*	Sign
1 0 6	−	4 0 10	+
2 0 14	+	5 0 8	+
3 0 2	−	5 0 10	+
3 0 6	−	6 0 4	+
3 0 14	+	7 0 4	+
4 0 0	−	0 0 8	−
4 0 2	−		

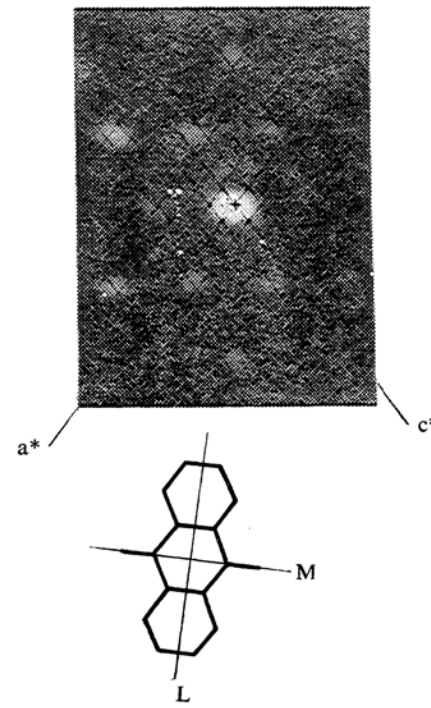

Fig. 1. Optical transform of the (0*l*0) projection and projected molecule giving optical transform.

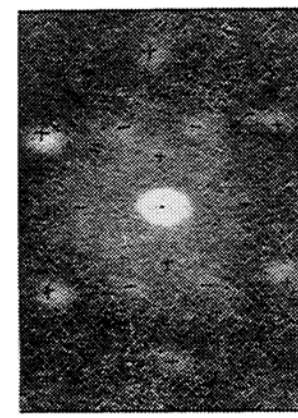

Fig. 2. Optical transform using superposition method, the enhancement of the positive regions are observed.

TABLE I. ATOMIC PARAMETERS WITH STANDARD DEVIATIONS

Atom	x	s. d.	y	s. d.	z	s. d.	B, Å^2
O	−0.229	0.0009	0.061	0.003	0.1053	0.0004	7.1
N	−0.115	0.001	0.030	0.004	0.0545	0.0005	5.1
C	0.048	0.001	0.164	0.004	0.0802	0.0005	5.2
C	0.106	0.001	0.337	0.005	0.1644	0.0005	5.7
C	0.271	0.001	0.473	0.006	0.1891	0.0005	6.3
C	0.393	0.001	0.444	0.006	0.1338	0.0005	6.4
C	0.341	0.001	0.277	0.005	0.0526	0.0005	6.2
C	0.173	0.001	0.136	0.004	0.0244	0.0005	5.4

with strong intensities, as are shown in the following table were obtained.

Signs of the structure factors not determined by the above method were obtained by calculations of structure factors based on the atomic coordinates derived from the molecular orientation found by the optical method.

The first Fourier map $\rho(xz)$ was prepared, by using about 70 terms whose calculated structure factors showed a fairly good agreement with the observed F values. All the atoms were well resolved in this projection. The refinement was made successively by Fourier syntheses and by difference syntheses, which gave a disagreement index R 18 %.

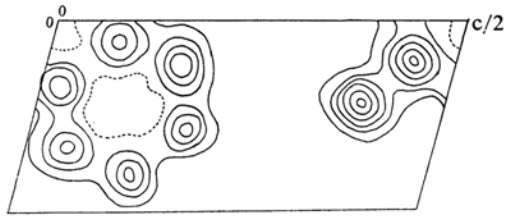

Fig. 3. Electron-density projection along [010].

***y*-Coordinates.**—There remained two possible sets of y-coordinates of all the atoms to be determined. Calculations of the structure factors, $(0kl)$, were carried out for the two structures. It was possible to eliminate one of the two structures from the disagreements between F_c and F_o, even for lower order reflections.

The successive refinement of the y-coordinates was accomplished by the trial and error method with the aid of the structure factor maps[5], while keeping the z-coordinates unchanged from the positions already obtained from the analyses of the (010) projection.

In the calculation of structure factors, the atomic scattering factors given by Berghuis et al.[6] were used throughout.

Final refinements of the positional- and isotropic temperature- parameters of individual atoms were made by least squares calculations[7] for $(h0l)$ and $(0kl)$ zones respectively, the contributions of hydrogen atoms being, however, omitted.

The final positional- and isotropic temperature-parameters with standard deviations, are listed in Table I.

TABLE II. BOND LENGTHS AND BOND ANGLES

Bond length, Å		Bond angle	
O—N	1.34	$\angle ONC_1$	121°
N—C_1	1.34	$\angle NC_1C_2$	120°
C_1—C_2	1.44	$\angle C_1C_2C_3$	120°
C_2—C_3	1.36	$\angle C_2C_3C_4$	121°
C_3—C_4	1.44	$\angle C_3C_4C_5$	119°
C_4—C_5	1.39	$\angle C_4C_5C_6$	119°
C_5—C_6	1.37	$\angle C_5C_6C_1$	119°
C_6—C_1	1.45	$\angle C_6C_1C_2$	118°
C_6—N	1.39	$\angle C_6C_1N$	121°
		$\angle C_1N\,C_6'$	122°
		$\angle ONC_6'$	117°
		$\angle C_1C_6N'$	117°
		$\angle C_5C_6N'$	122°

The disagreement index, R, for the final coordinates was 16% for $(h0l)$ and 15% for $(0kl)$. The comparison of the observed structure factors with the calculated ones is shown in Table III.

Discussion of the Structure

Molecular Structure.—The phenazine-ring skeleton found in this investigation is practically the same as those for α-phenazine[8] and phenazine 5-oxide[9]. The bond distances and valency angles found in these three compounds are shown in Table IV.

The value 1.33Å for the N–O bond indicates that it has some double bond character. In Table V, several N–O bond distances previously

5) W. L. Bragg and H. Lipson, *Z. Krist.*, **95**, 323 (1936).
6) J. Berghuis, I. J. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).
7) K. Osaki, The Programme of Least Squares Calculations in X-Ray Crystallography by the NIAC-2203 Computer (EOI-3330, Nippon Electric Co. (1962)).
8) L. F. Hirshfeld and G. M. Schmidt, *Acta Cryst.*, **7**, 129 (1954); ibid., **9**, 233 (1956); F. H. Herbstein and G. M. Schmidt, ibid., **8**, 399 (1955).
9) R. Curti, V. Riganti and S. Lochi, ibid., **14**, 133 (1961).

TABLE III. OBSERVED AND CALCULATED STRUCTURE FACTORS

$h\,k\,l$	$F_o/4$	$F_c/4$	$h\,k\,l$	$F_o/4$	$F_c/4$	$h\,k\,l$	$F_o/4$	$F_c/4$	$h\,k\,l$	$F_o/4$	$F_c/4$
0 0 2	40.7	44.4	8	8.2	10.0	6	11.1	− 9.2	6	12.2	−12.4
4	27.1	−27.3	10	4.2	6.4	8	4.7	− 6.2	7	14.7	−14.6
6	3.2	− 4.1	12	0.1	0.1	10	9.7	7.5	8	6.7	− 6.0
8	15.6	−14.7	6 0 0	1.9	− 4.9	12	2.5	3.0	9	3.8	3.9
10	4.4	− 4.7	2	1.6	2.3	14	2.5	− 2.6	10	2.9	3.3
12	0.9	− 2.2	4	0.6	− 0.9	16	2.2	− 2.0	11	1.1	− 1.4
14	2.8	− 2.6	6	0.6	− 2.2	18	2.8	− 2.1	12	0.4	0.4
16	0.5	0.5	8	0.3	− 0.5	$\bar{5}$ 0 2	0.5	0.5	13	0.6	− 0.8
18	0.1	0.1	10	0.3	− 1.0	4	10.1	− 9.4	14	1.3	− 1.3
1 0 0	37.9	35.3	7 0 0	2.2	− 2.0	6	1.6	1.9	15	0.5	− 1.1
2	3.5	− 1.4	2	2.2	− 3.6	8	11.5	9.4	16	0.1	0.1
4	22.3	22.7	4	4.7	− 5.9	10	1.3	− 1.8	0 2 0	12.6	12.1
6	26.8	−27.5	6	2.6	− 1.3	12	7.3	− 4.8	1	2.9	3.2
8	29.7	−30.5	8	0.2	0.2	14	2.5	− 0.4	2	5.9	− 5.5
10	0.9	0.9	8 0 0	0.9	1.6	16	0.6	0.7	3	12.6	−12.6
12	3.8	4.4	2	1.9	− 4.0	18	1.3	− 1.4	4	8.0	− 8.5
14	1.6	− 1.2	4	1.3	− 2.6	$\bar{6}$ 0 2	9.0	8.1	5	16.8	−15.6
16	3.5	− 3.9	6	0.5	0.5	4	21.9	21.1	6	0.3	0.3
18	0.6	− 0.8	9 0 0	0.1	0.1	6	8.0	4.8	7	3.8	5.5
2 0 0	27.8	−27.2	2	0.3	0.4	8	0.9	1.3	8	0.8	1.0
2	18.1	15.4	$\bar{1}$ 0 2	39.3	41.7	10	5.7	− 2.7	9	1.3	0.6
4	15.7	18.5	4	22.3	−21.8	12	9.5	− 7.3	10	1.7	1.3
6	0.6	0.9	6	14.3	14.0	14	1.9	− 2.0	11	2.5	− 2.9
8	2.2	− 2.9	8	5.9	6.5	16	1.6	0.8	12	2.9	− 3.4
10	2.2	− 3.0	10	1.9	− 1.3	18	0.1	− 0.1	13	1.7	− 1.9
12	0.9	− 1.4	12	7.6	6.4	$\bar{7}$ 0 2	1.6	0.0	14	0.6	− 1.3
14	4.2	− 3.0	14	1.6	0.1	4	17.7	15.7	15	0.6	− 1.1
16	2.2	− 1.7	16	0.9	1.1	6	12.5	10.7	0 3 1	0.8	1.1
3 0 0	2.8	− 2.3	18	1.3	1.5	8	2.5	− 2.7	2	7.1	− 7.0
2	37.2	−33.2	$\bar{2}$ 0 2	22.3	−21.5	10	1.6	0.1	3	0.8	− 0.6
4	7.6	− 5.7	4	25.4	−26.2	12	0.2	− 0.2	4	0.6	1.0
6	11.8	12.3	6	3.5	− 4.2	14	0.1	− 0.1	5	0.8	− 1.5
8	0.9	0.5	8	0.6	− 1.7	$\bar{8}$ 0 2	1.9	2.0	6	1.7	1.6
10	0.7	− 0.8	10	11.8	−12.1	4	0.8	− 0.8	7	0.5	− 0.5
12	0.1	− 0.1	12	13.6	12.8	6	0.4	0.4	8	0.4	− 0.4
14	1.6	− 0.8	14	21.2	18.4	8	2.5	− 2.5	9	0.8	− 3.5
16	0.6	0.8	16	1.9	2.3	10	0.0	0.0	10	0.8	− 1.8
4 0 0	9.7	−10.9	18	0.3	0.3	12	1.6	0.7	11	2.1	− 2.1
2	19.0	−22.4	$\bar{3}$ 0 2	19.8	18.5	$\bar{9}$ 0 2	0.1	0.1	12	0.8	− 1.3
4	1.9	− 4.9	4	0.4	− 0.4	4	0.4	− 0.4	0 4 0	0.6	0.6
6	2.5	− 3.4	6	36.9	−39.3	6	1.2	− 0.5	1	0.3	− 0.3
8	4.2	7.8	8	15.6	−13.7	8	1.9	− 2.1	2	0.6	0.8
10	10.8	14.6	10	1.9	1.7	10	2.2	− 2.7	3	0.6	− 1.0
12	2.6	2.3	12	3.8	1.4	12	0.9	− 0.7	4	0.2	− 0.2
14	0.3	− 0.8	14	12.3	9.4	0 1 1	23.5	25.6	5	0.6	− 0.6
5 0 0	1.6	− 1.7	19	2.5	3.5	2	43.7	−57.7	6	0.7	− 1.1
2	2.5	5.2	18	1.9	− 0.9	3	39.9	42.1	7	0.7	0.9
4	0.6	0.0	$\bar{4}$ 0 2	2.5	2.8	4	19.3	−22.0	8	1.4	− 1.7
6	1.6	− 3.1	4	3.8	− 4.6	5	21.4	−23.3	9	0.5	− 0.6

reported are given. The value of 1.42 Å found for trimethylamine *N*-oxide hydrochloride[15] can be taken as the standard single bond distance. The N–O bond distances in *N*-heteroconjugate ring compounds are shorter than that of trimethylamine *N*-oxide; this indicates that there exists a resonance between lone-pair electrons in the oxygen atom and the π-electron system in conjugate rings. If we assume 1.16 and 1.43 Å for the single and double bonds for N–O, the total bond order N[10] for the N–O bond in phenazine 5, 10-dioxide is

10) W. J. Orville-Thomas, *Chem. Revs.*, **57**, 1179 (1957).

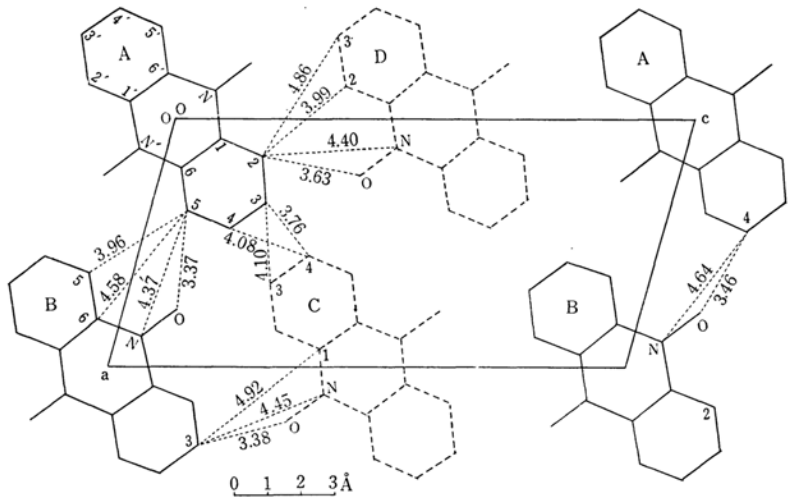

Fig. 4. Projection of the unit-cell contents on (010).

TABLE IV. BOND DISTANCES AND VALENCY ANGLES IN RELATED CRYSTALS

	α-Phenazine	5-Oxide	5, 10-Dioxide
N—C_1	1.355 Å	1.34 Å	1.34 Å
C_1—C_2	1.415 Å	1.40 Å	1.44 Å
C_2—C_3	1.382 Å	1.38 Å	1.36 Å
C_3—C_4	1.412 Å	1.39 Å	1.44 Å
C_4—C_5	1.367 Å	1.36 Å	1.39 Å
C_5—C_6	1.412 Å	1.38 Å	1.37 Å
C_6—C_1	1.433 Å	1.43 Å	1.45 Å
N—O		1.24 Å	1.34 Å
∠N C_1C_6	121.7°	120°	121°
∠$C_6C_1C_2$	119.4°	119°	118°
∠$C_1C_2C_3$	120.0°	119°	120°
∠$C_2C_3C_4$	120.6°	122°	121°
∠$C_3C_4C_5$	121.0°	120°	119°
∠$C_4C_5C_6$	120.4°	121°	119°
∠$C_5C_6C_1$	118.5°	119°	119°
∠C_1C_6N	122.7°	121°	117°
∠C N C	116.6°	119°	122°

calculated to be 1.3, which can be compared to the value $N=1.17$ assigned for the N–O bond in pyridine *N*-oxide hydrochloride[11,12]. The distance, 1.37 Å, found for the N–O bond in pyridine *N*-oxide hydrochloride, which is somewhat longer than that of any other pyridine derivatives, would indicate that the n-π resonance here is weakened by the addition of a proton to oxygen*.

Arrangement of the Molecules.—The arrangement of the molecules and the packing between nearest neighbors are shown in Figs. 4 and 5, which are the b- and c-axes projections of the structure respectively. The packing of the molecules is found to be quite similar to those for α-phenazine[8], phenazine 5-oxide[9] and anthraquinone[16]. It can be said that these are iso-structural.

The shortest intermolecular distance between

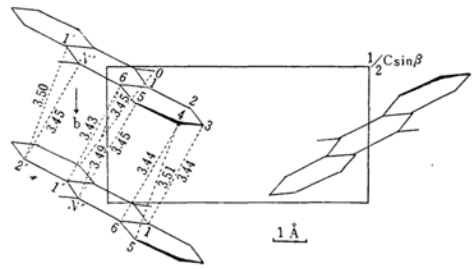

Fig. 5. Projection of the half unit-cell contents down [100].

TABLE V. N–O BOND LENGTHS IN RELATED COMPOUNDS

	N-Oxides	N–O Bond length, Å
	Pyridine *N*-oxide hydrochloride	1.37[11,12]
A	4, 4-*trans*-Azopyridine *N*-oxide	1.28[13]
	4-Nitropyridine *N*-oxide	1.26[14]
	Phenazine 5-oxide	1.24[9]
B	Trimethylaminoxide hydrochloride	1.42[15]

* The crystal structure of pyridine *N*-oxide has not yet been determined. As the result of an infrared absorption study, it was reported by Dr. Kubota et at. of Shionogi Research Laboratory at the 5th Meeting for Infrared and Raman Spectra that the distance of the N-O bond in it was 1.27~1.29 Å.

11) Y. Namba, T. Oda, H. Ito and T. Watanabe, This Bulletin, 33, 1618 (1960).
12) P. G. Tsoucaris, *Acta Cryst.*, **14**, 914 (1961).
13) E. L. Eichhorn, ibid., **12**, 746 (1959).
14) F. L. Eichhorn, ibid., **9**, 787 (1956).
15) C. Rerat, ibid., **13**, 63 (1960).
16) S. N. Sen, *Indian, J. Phys.*, **19**, 243 (1945); *Structure Report*, **11**.

neighboring molecules related by the translation parallel to the a-axis is 4.04 Å ($C_5\cdots C_{5'}$), while that between molecules related by the glide plane is 3.99 Å ($C_2\cdots C_2$), and that along a diagonal direction, 3.76 Å ($C_3\cdots C_4$).

These intermolecular distances are found to be very close to the corresponding intermolecular distances reported for α-phenazine, as is shown in Table VI.

TABLE VI. THE INTERMOLECULAR DISTANCES OF NEAREST NEIGHBORING MOLECULES

	$C_5\cdots C_{5'}$	$C_2\cdots C_2$	$C_3\cdots C_4$
This crystal	4.04 Å	3.99 Å	3.72 Å
α-Phenazine	4.07 Å	3.88 Å	4.02 Å

It is very interesting to see that in the structures of 5-oxide and 5, 10-dioxide the oxygen atoms can be said to lie in the holes resulting from the packing of the phenazine rings. Such holes, though small in size, can also be found in the structure of α-phenazine. The ratio of the number of oxygen atoms to the number of holes is 1 for 5, 10-dioxide crystal, whereas it is 1/2 for the 5-oxide crystal.

The angle of inclination of the molecule to the (010)-plane is about 30° for the longest molecular axis, L, and about 5° for the shorter one, M.

Let us now compare the structure of the 5, 10-dioxide crystal with those of related crystals. We notice that the unit cell dimensions of these crystals change by degrees with an increase in the number of oxygen atoms in a molecule, as is shown in Table VII.

TABLE VII. UNIT CELL DIMENSIONS OF RELATED CRYSTALS

	a, Å	b, Å	c, Å	β
α-Phenazine	7.088	5.061	13.22	109°13′
5-Oxide	7.37	4.60	14.34	108°59′
5, 10-Dioxide	7.85	3.95	15.50	104°48′
Anthraquinone	7.92	3.98	15.85	102°42′

The differences in the lengths of these b-axes correspond to the different inclinations of the molecular plane to the (010)-plane. However, it is to be emphasized that the interplanar distances between the neighboring molecular planes remain practically the same, about 3.5 Å, for all the compounds listed. The inclination of the molecular plane mentioned above is related to the mutual displacement of the molecular planes in the same stack. These features can well be seen in Fig. 6, where the structures projected onto their molecular planes are shown for α-phenazine and phenazine 5, 10-dioxide. We are now trying to elucidate the different inclinations of the molecular planes in these related structures, taking into account various interactions between molecules.

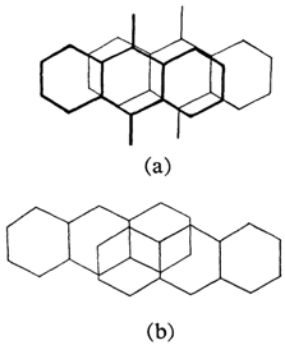

Fig. 6. Normal projection of two molecules in the same stack separated by unit translation along [0*l*0].
(a) Phenazine-5, 10-dioxide
(b) α-Phenazine (by Herbstein & Schmidt[8])

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