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The Crystal Structure of 1, 6-Dimethoxy Phenazine*[1]

Hiroshi YAJI, Taiichi HIGUCHI and Akira SHIMADA

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

and Yoshiyuki NAMBA and Tsutomu ODA

Laboratory of Physical Chemistry, Osaka University of Liberal Arts and Education, Tennoji-ku, Osaka

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The crystal structure of 1, 6-dimethoxy phenazine was solved by the method of the molecular Fourier transform, and a refinement based on the two-dimensional data was achieved by the Fourier method and also by the least-squares method. The space group is $P2_1/n$ with two molecules in the unit cell. The lattice constants are $a=8.60$ Å, $b=12.59$ Å, $c=5.17$ Å, and $\beta=93.5°$. The molecule has an exact center of symmetry and lies approximately on a plane, with the exception of the methyl groups, which are 0.21 Å outside the plane of the molecule. As for the phenazine ring, almost all the bond distances and angles exhibit normal values. The bond distances around the oxygen atom seem to indicate that the lone-pair electrons in this atom flow into the π-electron system of a phenazine ring. The planar molecules are stacked parallel to each other along the c axis, with an inter-planar spacing of 3.41 Å.

Much attention has been paid in recent years to the elucidation of the crystal structures in heterocyclic aromatic compounds, among which are phenazine[1] and some of its derivatives[2,3]. These works have shown that the phenazine ring is planar and that the ring structure is in accordance with the molecular orbital calculations. Moreover, some interesting features of the molecular packing in the crystals have been revealed in these studies, as compared with the packing of the homocyclic aromatic compounds. In connection with these findings, a study of the crystal and molecular structure of 1, 6-dimethoxy phenazine by the X-ray diffraction method was undertaken to establish the effect of two methoxy groups on the packing mode of the molecules in the crystal. This work will also be of interest from the standpoint of molecular interactions in the crystal, since this crystal is known to show fluorescence and also photoconductivity.

Experimental

The specimens were prepared from *o*-anisidine and *o*-nitroanisole and were kindly supplied by Professor Eizo Matsumura and Dr. Hisao Takeda, Osaka University of Liberal Arts and Education. Suitable crystals were crystallized in yellow plates elongated along the c axis by the slow evaporation of a benzene solution.

Oscillation and Weissenberg photographs were taken around the three principal axes using Cu$K\alpha$ radiation. They showed that the unit cell is monoclinic with the following dimensions:

$$a = 8.60,\ b = 12.59,\ c = 5.17\ \text{Å},\ \beta = 93.5°$$

These values were determined from high-angle axial reflections in Weissenberg photographs, with a powder pattern of sodium chloride superimposed. Assuming two molecules in the unit cell, the density of the crystal was calculated to be 1.429 g cm^{-3}, which is in good agreement with 1.42 g cm^{-3}, the value measured by the pycnometer. The extinction rules were found to be $h0l$ for $h+l$ odd and $0k0$ for k odd; this suggested that the space group was $P2_1/n$.

Reflections of the $hk0$, $h0l$ and $0kl$ types along the principal axes were obtained from the zero-layer Weissenberg photographs by making use of the multiple-film technique. The intensities were estimated visually by comparison with a calibrated scale prepared with the same crystal; they ranged from 1 to 6000. 99 reflections were observed for the $hk0$ zone, while 68 and 39 reflections were observed for $0kl$ and $h0l$ zones respectively. These figures correspond to 69, 80 and 64% of the possible reflections. They were corrected for Lorentz and polarization factors in the usual way. No absorption correction was applied, however, because the linear absorption coefficient, μ, was rather small ($\mu=9.19$ cm^{-1} for the Cu$K\alpha$ radiation). The preliminary values of the scale factors and the temperature factors, derived by Wilson's method,[4] were improved during the later stages of refinement.

Structure Determination

Since two molecules exist in the unit cell with the space group, $P2_1/n$, it follows that the center of gravity of the molecule will lie at a center of

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*[1] A part of this paper was read at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[1] L. F. Hirshfeld and G. M. Schmidt, *Acta Cryst.*, **7**, 129 (1954); *ibid.*, **8**, 399, 406 (1955); *ibid.*, **9**, 233 (1956).

[2] R. Curti, V. Riganti and S. Lochi, *ibid.*, **14**, 133 (1961).

[3] Y. Namba, T. Oda and T. Watanabé, This Bulletin, **36**, 79 (1963).

[4] A. J. C. Wilson, *Nature, Lond.*, **150**, 152 (1942).

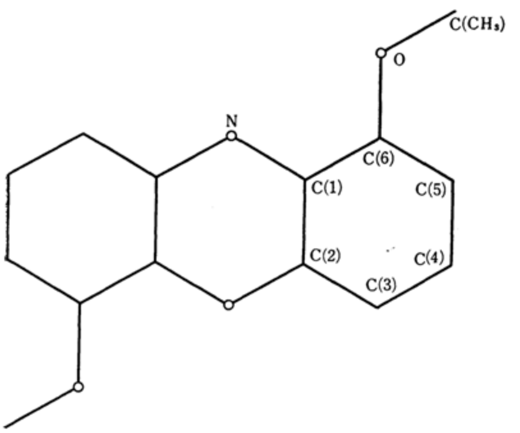

Fig. 1. Assumed molecular model with the nomenclature of atoms.

symmetry. Consequently, it is only necessary to find the parameters of nine atoms of half a molecule in an asymmetric unit, excluding hydrogen atoms. The designation of the atoms is shown in Fig. 1.

Because of the short *c* axis, it was expected that an approximate structure might appear in the electron-density projection along this axis, without any complication due to the overlappings of atoms. The Patterson projection along this axis was calculated and found to have a train of peaks in the [110] direction. This fact seemed to suggest that the long axis of a molecule lies in the [110] direction in the (001) projection, but several trial models based on this clue did not yield structure factors consistent with the observations. Hence, an attempt was made to solve the structure by the Fourier-transform method, with the aid of the above feature in the Patterson map.

In the application of this method, all the atoms in a molecule were assumed to lie on the plane of a phenazine ring consisting of three regular hexagons. The computation of a molecular Fourier-transform was simplified by the further assumption that all the bond distances were 1.40 Å and that all the bond angles were 120°, as is shown in Fig. 1. Various projections of the *hk*0 reciprocal nets onto the plane of the molecular transform were tried and adjusted so as to give a good agreement between the observed unitary structure factors and the values from the transform plot, where the transform of an unit cell was calculated by the interaction of two transforms of the molecules. In this manner, three molecular orientations were found to be promising, and the corresponding electron-density maps were computed with the signs of the structure factors derived by the above method. It was not hard to pick out the best molecular orientation through several cycles of successive Fourier refinements. All the atoms in a molecule were well-resolved in this electron-density map, as Fig. 2 shows. Further refinement by the difference-synthesis technique quickly reduced *R*, the reliability index of *hk*0 reflections, to 0.20.

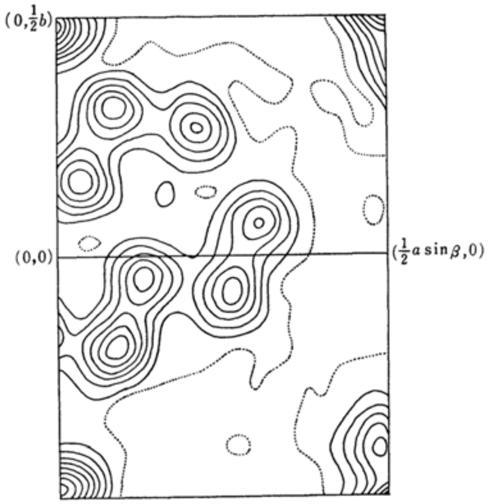

Fig. 2. Electron density projected along the *c* axis, contours are drawn in an arbitrary scale.

By a comparison of the *x* and *y* coordinates in this projection with the planar phenazine ring, it was postulated that the short axis of the phenazine ring might lie approximately on this projection plane and that the long axis might make an angle of about 45° with this plane. The approximate *z* coordinates thus derived were confirmed by the Patterson projection *P(VW)* along the *a* axis. Several calculations of the Fourier transforms in

TABLE 1. POSITIONAL AND ISOTROPIC-TEMPERATURE PARAMETERS WITH STANDARD DEVIATIONS

Atom	*x*	s. d.	*y*	s. d.	*z*	s. d.	*B*(Å²)
C(1)	0.036	0.001	0.075	0.001	0.180	0.003	2.6
C(2)	0.126	0.001	−0.022	0.001	0.168	0.003	2.5
C(3)	0.258	0.002	−0.039	0.001	0.350	0.003	3.0
C(4)	0.296	0.002	0.034	0.001	0.538	0.003	3.4
C(5)	0.211	0.002	0.131	0.001	0.556	0.003	3.3
C(6)	0.081	0.001	0.150	0.001	0.386	0.003	2.7
$C(CH_3)$	0.021	0.002	0.307	0.001	0.607	0.003	4.1
N	−0.089	0.001	0.096	0.001	0.017	0.002	2.7
O	−0.007	0.001	0.238	0.001	0.381	0.002	3.5

the 0*kl* zone were enough to give fairly well-resolved electron-density maps, from which the *z* coordinates were successively refined. The *z* coordinates were then further refined by the difference syntheses. The projection along the *b* axis was then studied in order to confirm the results obtained in the other axes.

Final refinements of the positional and isotropic-temperature parameters for each atom were carried out by least-squares calculations⁵⁾ for *hk*0, 0*kl* and *h*0*l* zones, the contributions of the hydrogen atoms being discarded. The final parameters, with standard deviations, are listed in Table 1, the reliability index, *R*, being finally lowered to 0.16. The average standard deviation of the bond lengths is estimated to be 0.02 Å.

Description of the Structure

The dimensions of the molecule with a center of symmetry are given in Fig. 3. The equation of the mean plane through the phenazine ring was calculated by a least-squares method to be:

$$-0.602\,X - 0.450\,Y + 0.659\,Z = 0,$$

where Y and Z have the [010] and [001] directions respectively, and where X is perpendicular to the (100) plane. The deviation of each atom from the above plane is shown in Table 2. This result shows that only methyl groups exist out of the plane of the molecule, and that the bond between the oxygen atom and the methyl group is found to incline to the plane of the molecule at an angle of 8°. In connection with this fact, it will be noted that the methoxy groups attached to the rigid ring have rather large temperature factors. As for the phenazine ring, the bond distances and angles are found to be practically the same as those found in phenazine and its derivatives,³⁾ although each bond in this study is longer by around 0.02 Å than the conventional value. The bond distance, 1.47 Å, between the oxygen atom and the methyl group suggests that this bond might be single, but another bond distance connected with the oxygen atom, 1.34 Å, indicates that the lone-pair electrons in the oxygen atom flow into the π-electron system of a phenazine ring.

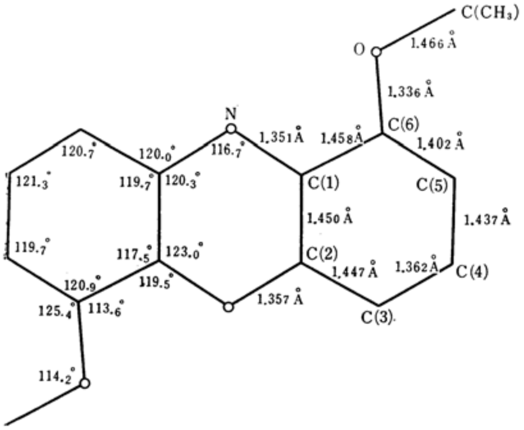

Fig. 3. Bond distances and angles in a molecule.

TABLE 2. DEVIATIONS OF ATOMS FROM THE MOLECULAR PLANE

Atom	Deviation (Å)
C(1)	−0.013
C(2)	+0.006
C(3)	−0.012
C(4)	+0.012
C(5)	−0.010
C(6)	+0.019
C(CH$_3$)	+0.211
N	−0.008
O	+0.004

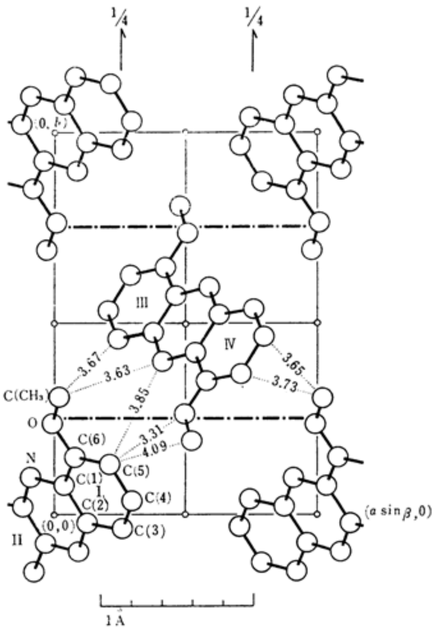

Fig. 4. Crystal structure projected along the *c* axis with some intermolecular distances.

The arrangement of the molecules and the mode of their packing may be seen in Figs. 4, 5 and 6, which are the projections of the structure along the principal axes. The shorter intermolecular distancs are also indicated in the figures. Each molecule is surrounded by six molecules in such a way that the methoxy groups take up the open spaces among the molecules. Four of the molecules are related by the glide plane, *n*, while two molecules are stacked along the *c* axis. The long axis of a phenazine ring is found to incline to the (001)

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5) K. Osaki, The Program of Least-squares Calculations in X-Ray Crystallography by the NEAC-2203 Computor (EOI-3330, Nippon Electric Co. (1962)).

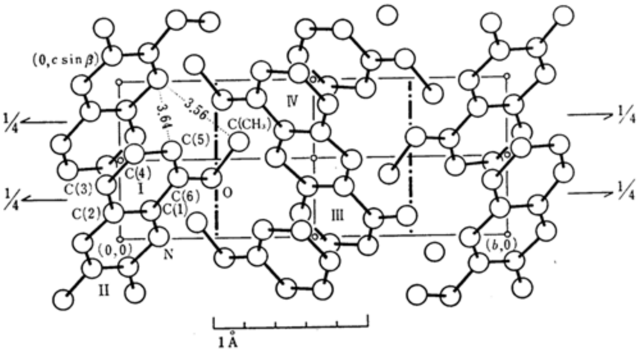

Fig. 5. Crystal structure projected along the *a* axis with some intermolecular distances.

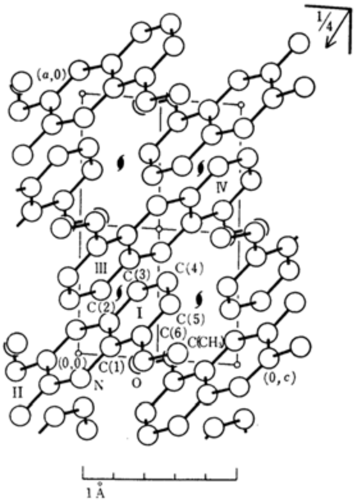

Fig. 6. Crystal structure projected along the *b* axis.

plane at an angle of around 49°. The perpendicular distance between adjacent rings along the *c* axis is 3.41 Å, which agrees well with the values found for various compounds of this type. Figuer 7 shows the normal projection of one phenazine ring on the plane of the adjacent molecule related by the translation along the *c* axis. This projection shows a close resemblance to that in the crystal of α-phenazine¹⁾ in such a way as to minimize

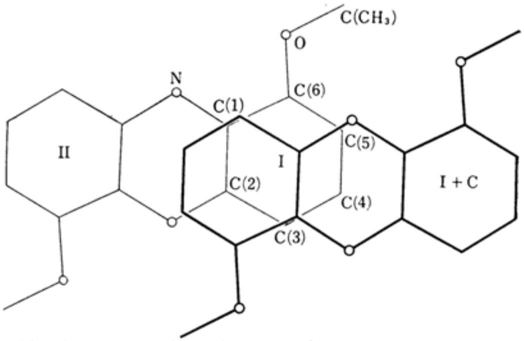

Fig. 7. Normal projection of two parallel molecules along the *c* axis.

the overlapping of atoms. In this regard, the molecules seem to be packed parallel along the *c* axis to give a columnar arrangement. Within a crystal, two kinds of columns of molecules are found, one at the corners, and the other at the centers, of the unit cells, as is shown in Fig. 4.

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