

Variation of Physical Properties with Composition of Phenazine-N-oxyphenazine Mixed Crystals

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V. VARIATION OF PHYSICAL PROPERTIES WITH COMPOSITION OF PHENAZINE- *N*-OXYPHENAZINE MIXED CRYSTALS

BY A. M. GLAZER

[Plate 12]

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Examination of properties of the phenazine-*N*-oxyphenazine system has revealed that abnormal behaviour is observed approximately in a region of composition between 10 and 40 mole % *N*-oxyphenazine. This is consistent with the suggestion of the presence of a miscibility gap. The composition of the eutectic seems to be about 28 mole % *N*-oxyphenazine. Data are given for melting points, morphologies, refractive indices, unit-cell dimensions, packing densities, densities and thermal expansion coefficients.

INTRODUCTION

In this paper we shall consider ways in which certain physical properties of the phenazine-*N*-oxyphenazine system vary with respect to composition.

In mixed-crystal series, generally, large changes in physical properties often occur as the composition is varied. This is hardly surprising, since incorporation of impurity 'sites' into a perfectly or near-perfectly ordered 'host' lattice, will decrease the order and hence increase the entropy of the system. This means that cooperative interactions, such as van der Waals forces, will be affected. The effects are probably most apparent when considering spectroscopic properties of mixed crystals (as in the phenomenon of energy transfer (Lipsett 1967)). Moreover, it is known that incorporation of impurity has an especially big effect on the physical properties of very pure, perfect crystals. However, it should be noted that the crystals with which we are dealing here are neither of the highest purity nor are they crystallographically perfect.

Physical properties of mixed crystals tend to vary in a continuous manner with change in composition, except in the neighbourhood of regions of immiscibility gaps and phase transitions, where discontinuous changes are often found. In determining phase diagrams, use is made of these changes in physical properties. Phase diagrams are normally determined by thermal methods, such as by using cooling curves or melting-point data. However, this is not always possible, and variation in other physical properties, such as unit-cell parameters, density, etc., may be needed to allow the construction of phase diagrams.

Kitaigorodskii (1957) has investigated the conditions for mixed-crystal formation and suggests the following rules:

(1) If molecules A and B are approximately the same in form or dimension, molecules A can, in principle, replace molecules B in the crystal (and vice versa). A continuous mixed-crystal series is possible if (a) the symmetry of the distribution of molecules in A and B is the same, or (b) if the symmetries of the distribution of molecules in A and B differ, but the symmetry of the distribution of molecules in B changes discontinuously with the introduction of molecules of A (this applies to the solution of asymmetric molecules in a racemate).

(2) If the symmetries of the distribution of molecules A and B differ and, in addition, molecules of A enter B without changing the symmetry in B and molecules of B enter A without changing the symmetry in A, then two phases must exist, i.e. a miscibility gap occurs.

This theory was used by Curti, Riganti & Locchi (1961) to provide evidence for the occurrence of an average centre of symmetry for molecules in the crystal structure of *N*-oxyphenazine, by growing mixed crystals of *N*-oxyphenazine with phenazine. However, the use of this as a criterion for the determination of a centre of symmetry is only valid if the series is continuous. As will be shown here, there is considerable evidence that this is not so in this case.

The following physical properties have been examined: (1) melting points, (2) optical properties and variation in crystal habit, (3) unit-cell parameters, (4) densities, (5) thermal expansion.

MELTING POINTS OF THE MIXED CRYSTALS

Preliminary experiments were carried out to find the best method of observing the melting of the crystals. It was found that the most consistent results were obtained with a hot-stage microscope, especially when the material was enclosed in a sealed glass tube.

One or two crystals were selected from each batch of mixed crystals and the temperatures were noted at which the first droplets of liquid melt were observed, to give the solidus points on the phase diagram. The temperatures at which no solid remained provided the liquidus points. Crystals with compositions of more than about 30 mole % *N*-oxyphenazine turned brown and appeared to decompose on heating.

It was, however, possible by this means to obtain only a rather approximate phase diagram (figure 1). This shows a minimum somewhere between about 10 and 30 mole % *N*-oxyphenazine.

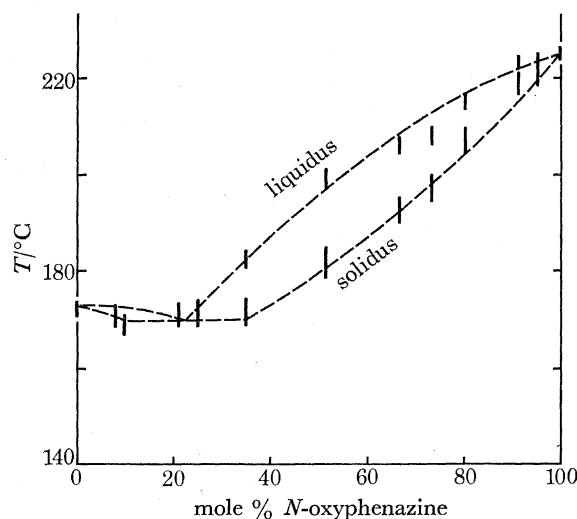


FIGURE 1. Melting-point data for the phenazine-*N*-oxyphenazine mixed-crystal series. The dotted line shows one of several interpretations that can be put on the results.

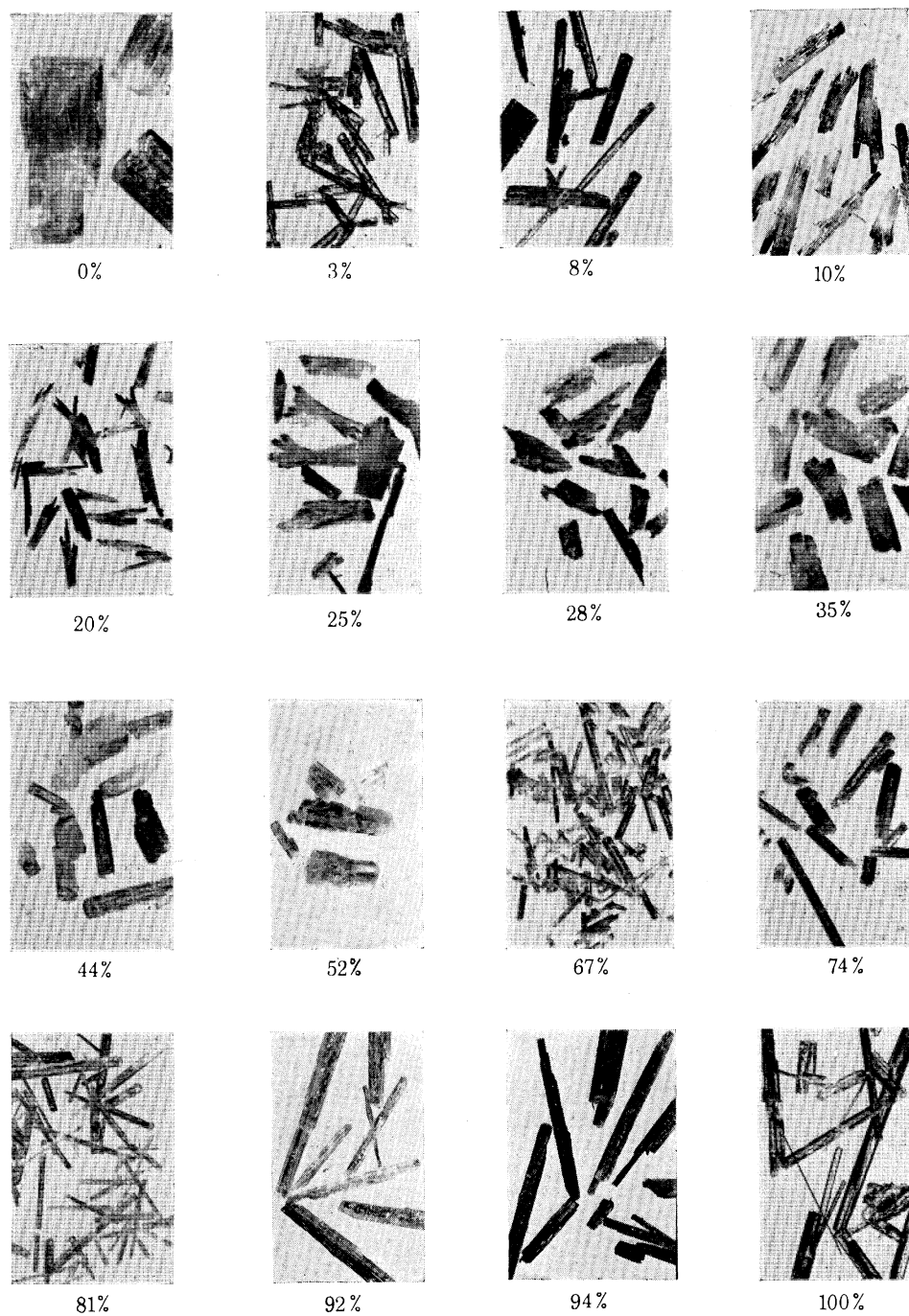


FIGURE 2. Photographs of the crystals in the series phenazine-*N*-oxyphenazine, showing the poor development of crystal faces between 10 and 40 mole % *N*-oxyphenazine.

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It is not possible to state from these results whether this represents a continuous solid solution with a minimum or a solid solution with a miscibility gap. The melting ranges and other detailed numerical data are given by Glazer (1968).

In an attempt to gain more thermal information about the series, some attempts were made using the technique of differential thermal analysis (d.t.a.) (see, for example, Mackenzie & Mitchell 1962). However, the results were again rather ambiguous, because of the decomposition of *N*-oxyphenazine with heating. This occurred even when the experiment was carried out in an atmosphere of neon, nitrogen or argon. It became clear that other physical properties would have to be examined in order to supply information about the solubility of the two components in one another.

OPTICAL EXAMINATION OF THE MIXED CRYSTALS

The crystals were examined under the microscope. Their colour varies from light yellow at the phenazine-rich end to orange-yellow at the *N*-oxyphenazine-rich end of the series. In figure 2, plate 12, are shown photographs of the crystals at various compositions. Crystals of composition approximately between 10 and 40 mole % *N*-oxyphenazine are rather opaque and poorly formed. These crystals tend to grow in 'clumps', to produce small, misoriented, fibrous masses. Crystals of compositions outside this region are well developed, with relatively smooth, clean crystal faces.

At all compositions, it is found that the crystals tend to be lath-like in appearance (figure 3), although sometimes slight variations in the development of the crystal faces are observed. All the crystals are elongated along [010]. Any attempts at cutting them tend to cause cleavage parallel to this direction. The crystals have been obtained in a range of sizes within any batch, the average size being approximately $1 \times 0.2 \times 0.05 \text{ mm}^3$.

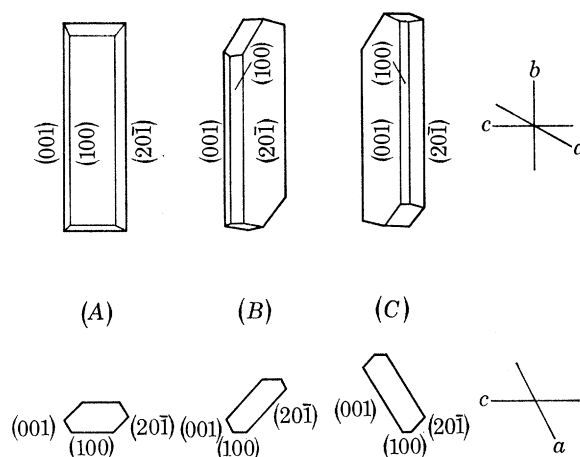


FIGURE 3. Habit changes of the crystals in the series phenazine-*N*-oxyphenazine. Compositions, in mole % *N*-oxyphenazine are (A) 0%; (B) 3 to 28%; also occasionally found for 0%; (C) from about 28 to 100%.

Because of their lath-like shape, the crystals, when placed on a microscope slide, present their most prominent face. They were examined between crossed polars for extinction. It was found that straight extinction occurred, i.e. the extinction directions lay parallel to the length and breadth of the largest face.

Using sodium light, the conoscopic figures were examined. All the crystals showed that the

refractive indices were represented by a biaxial indicatrix. However, whilst it was possible to identify the indicatrix section for phenazine, it was not possible to decide where the various bisectrices were in the *N*-oxyphenazine-rich crystals. This was because the interference figures could only be observed from one direction, due to the blade-like shape of the crystals (see Glazer (1968) for photographs of the interference figures).

It was thought that the most useful optical study of these crystals would be of the refractive indices. The experimental method and results have been given elsewhere (Glazer & Pramatus 1968 *a, b*; Glazer 1968). Because of the high refractive indices, it was difficult to find a suitable immersion medium. A final choice was made of a mixture of arsenic tribromide, triiodide and sulphide (Borgström 1929; Meyrowitz 1955). It was found that this liquid gave refractive indices far higher than those for other liquid mixtures (greater than 1.93). There was a tendency to dissolve the crystals, but this was slow enough to permit observation of the Becke line. Measurements of the refractive indices were made in the plane of the largest crystal face in each case, one being along [010], the other at right angles to [010]. The resulting refractive indices were then plotted against composition (see figure 4, and Glazer 1968).

Oscillation photographs were used to determine the morphology of the crystal faces for crystals at each composition. It was found (Glazer & Pramatus 1968 *b*) that the morphology of the crystals changed across the series (figure 3). The large faces found were for:

0 mole % <i>N</i> -oxyphenazine	(100)
0 mole % <i>N</i> -oxyphenazine	occasionally (20 $\bar{1}$)
up to about 28 mole % <i>N</i> -oxyphenazine	(20 $\bar{1}$)
28–100 mole % <i>N</i> -oxyphenazine	(001)

Two crystals from the 28 mole % *N*-oxyphenazine batch were examined and found to have in one case (20 $\bar{1}$) as the largest face and (001) in the other. (It is not known whether the composition is *identical* in the two cases although they came from the same batch.) This means that the refractive indices measured perpendicular to [010] but in the plane of the largest face were for:

0 mole % <i>N</i> -oxyphenazine along	[001]
3 to 28 mole % <i>N</i> -oxyphenazine along	[102]
28 to 100 mole % <i>N</i> -oxyphenazine along	[100]

It follows, therefore, that the refractive index curve perpendicular to [010] includes and needs interpretation in the light of the habit change with composition. Habit changes of mixed crystals indicate the occurrence of different phases, such as those produced by a miscibility gap. This behaviour has been observed in other systems (Kitaigorodskii & Myasnikova 1958; Kitaigorodskii, Myasnikova & Samarskaya 1963; Kolosov 1958), whereas in continuous-mixed-crystal series no habit change is observed (see, for example, Donnay & Storm 1967).

The presence of a miscibility gap is also indicated by the refractive-index measurements along [010] (figure 4), where a discontinuity appears, starting at about 8 mole % *N*-oxyphenazine and ending at about 30 mole %.

The occurrence of crystals in the 28 mole % *N*-oxyphenazine batch with two different morphologies could indicate the presence of a eutectic composition.

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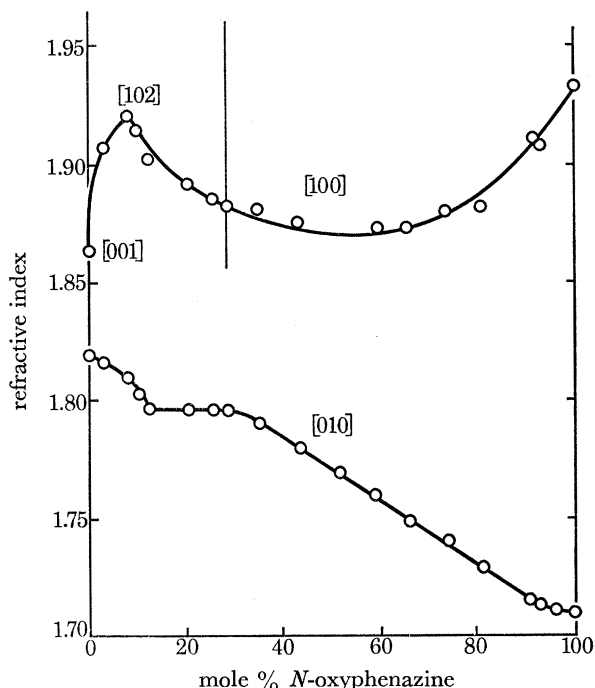


FIGURE 4. The variation of refractive index with composition along and perpendicular to [010] in the plane of the largest face.

UNIT-CELL DIMENSIONS

Good, clear crystals were selected from each batch, the average size of the crystals being approximately $1 \times 0.2 \times 0.05 \text{ mm}^3$. Because of the difficulty in cutting the crystals, it was decided to measure the unit-cell parameters from one crystal setting.

The b -axis dimension was obtained from X-ray photographs taken with the film-holder inclined at an angle of 43° to the incident beam direction. Cu $K\alpha$ radiation was used and the film radius was determined from a set of aluminium diffraction rings superimposed on the photographs. Layer-line measurements were made from zero to fourth layer, using a travelling microscope. This method is better than the normal-beam layerline method, because reflexions from further out in reciprocal space can be recorded, and these are relatively undistorted (Milledge 1963).

The a , c and β dimensions were obtained using the Straumanis method with Cu and Co radiations. Generally, it was difficult to obtain clear high-order reflexions above $\theta = 70^\circ$ because of strong background (long exposures were needed). In one case (35 mole % *N*-oxyphenazine) the crystal produced such poor reflexions that it was easier to use a zero-layer Weissenberg photograph.

The results of the measurements were combined by the least-squares method. The final computed cell dimensions are given by Glazer (1968), with their estimated errors. These have been plotted against composition in figures 5 and 6.

In order to give some explanation of the changes in the parameters observed, intermolecular contacts were calculated for a 'hypothetical' mixed crystal, by using the fractional coordinates and unit cell for *phenazine* and with oxygen atoms attached to the nitrogen atoms at a distance of 1.2 Å. The important (hypothetical) contacts are given in table 1.

(1) 000 to 001

Two contacts are apparently well below the van der Waals limit. These are O'—H 4' and O'—C 5'. Therefore, on addition of a molecule of *N*-oxyphenazine, it would be expected that *c* should increase; but since these two contacts are inclined somewhat to *b* (table 1) the increase is slightly reduced.

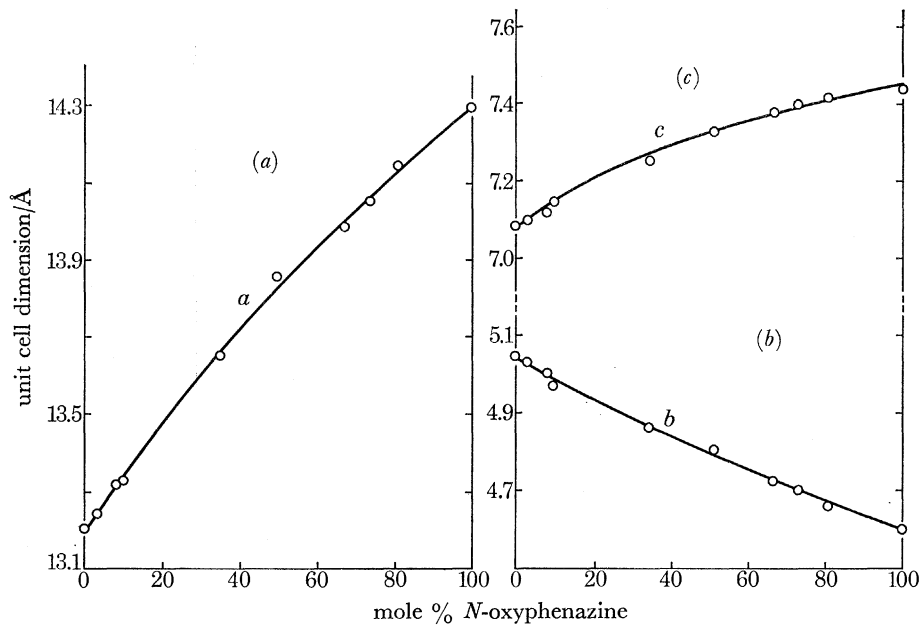


FIGURE 5. Unit-cell dimensions across the mixed-crystal series: (a) *a* axis, (b) *b* axis, (c) *c* axis.

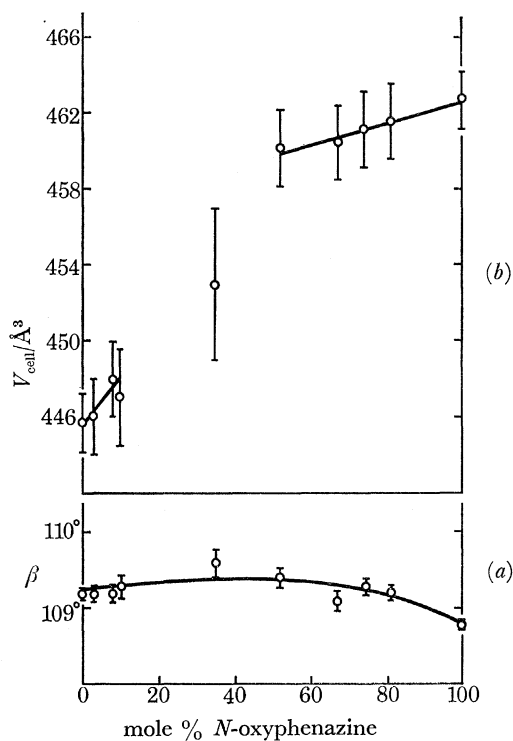


FIGURE 6. (a) β -angle variation; (b) cell-volume variation across the mixed-crystal series.

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(2) 000 to $\frac{1}{2}\frac{1}{2}0$

Again, two contacts are below the van der Waals limit and therefore indicate some expansion of a with increasing concentration of N -oxyphenazine. This time the contacts are more nearly perpendicular to [010], and parallel to [100].

TABLE I. SHORTEST INTERMOLECULAR CONTACTS FOR AN N -OXYPHENAZINE MOLECULE IN A UNIT CELL OF PHENAZINE

Only contacts to the oxygen atom are given				
	length	a	b	c^*
000 to 001				
O'-H 3'	3.04 Å	62°	40°	116°
O'-H 4'	1.84	99	69	157
O'-C 4'	3.19	64	55	134
O'-C 5'	2.64	80	71	158
000 to $\frac{1}{2}\frac{1}{2}0$				
O-H 1	3.14	132	73	134
O-H 2	2.10	171	99	93
O-C 3	2.88	170	81	95
000 to 010				
O-H 1'	3.84	79	153	66
O-H 3'	3.62	40	117	63
O-H 4'	3.74	73	153	70
O-C 4'	3.59	40	127	78
O-C 5'	3.66	60	149	82
van der Waals limits (Kitaigorodskii (1957))				
O-H	2.35-2.85 Å			
O-C	2.95-3.35 Å			

(3) 000 to 010

All the contacts are well outside the upper limits for van der Waals contacts. This means that b can decrease, in order to maintain a minimum cell volume, i.e. the highest packing density. This is accomplished by turning the molecules approximately about their M -inertia axes (Glazer 1968 and part IV, above), thus setting up strain between the molecules at 000 and $\frac{1}{2}\frac{1}{2}1$. This is related to the general expansion in (010).

It can be seen, from figure 6 (a), that the variation in the β -angle is very small, and thus hardly affects the argument dealing with the changes in a , b and c .

The variation in cell volume is also shown in figure 6 (b). The circles indicate the cell volumes calculated from the measurements of a , b , c and β . The heavy vertical lines represent the approximate estimated errors. It appears that there are two distinct regions in this graph, i.e. 0 to 10 and 52 to 100 mole % N -oxyphenazine. The crystal at 35 mole % N -oxyphenazine was poorly developed and hence the result for this crystal is much less accurate than the others. It is possible that this cell volume represents the average of two or more cell volumes, if one assumes that this crystal is heterogeneous, i.e. composed of crystallites of several compositions.

An indication of the existence of two separate phases is further shown by calculating the packing density. This quantity is defined (Kitaigorodskii 1947) as

$$k = zV_{\text{mol}}/V_{\text{cell}}$$

where k is the packing density, z the number of molecules/unit cell, and V_{mol} the volume of the

molecule, calculated using van der Waals radii. The values for V_{mol} and k are given in table 2. When packing density is plotted against composition (figure 7) it can be seen that addition of up to about 10 mole % *N*-oxyphenazine does not alter the packing density significantly. Similarly, addition of up to 48 mole % phenazine into the *N*-oxyphenazine structure only slightly

TABLE 2. UNIT-CELL AND MOLECULAR VOLUMES AND PACKING DENSITIES FOR THE MIXED-CRYSTAL SERIES

x^\dagger	$V_{\text{cell}}/\text{\AA}^3$	error	$V_{\text{mol}}/\text{\AA}^3$	k	error	$V_{\text{cell}} - zV_{\text{mol}}$
0	445.8	1.5	170.6	0.765	0.002	104.6
3	446.1	2.0	170.7	0.765	0.003	104.7
8	448.0	2.0	170.9	0.763	0.003	106.2
10	447.1	2.5	170.9	0.765	0.005	104.9
35	453.0	4.0	171.9	0.760	0.007	109.2
52	460.2	2.0	172.5	0.750	0.003	115.2
67	460.5	2.0	173.1	0.752	0.003	114.4
74	461.3	2.0	173.3	0.751	0.003	114.7
81	461.6	2.0	173.6	0.752	0.003	114.5
100	462.8	1.5	174.3	0.753	0.002	114.3

† Mole % *N*-oxyphenazine.

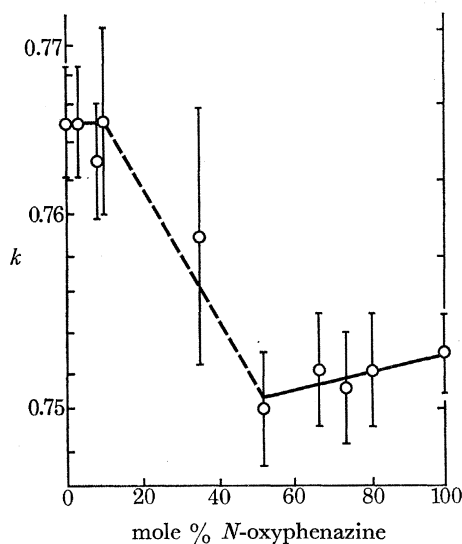


FIGURE 7. Variation in packing density with composition.

lowers the packing density. Between 10 and 52 mole % *N*-oxyphenazine there is therefore a large change in packing density, indicating a region of immiscibility in the solid state. Here, again, the crystal containing 35 mole % *N*-oxyphenazine is probably the average of two or more packing densities.

DENSITY

The density of the crystals was obtained by the density-gradient column method.

A concentrated solution of sodium iodide in water was placed in the bottom half of a test-tube and a density-gradient column was made by carefully mixing with a more dilute solution of sodium iodide (Glazer 1968). One or two of the mixed crystals were crushed, mixed with a little sodium iodide solution to wet the surfaces, and added to the density-gradient column. After

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centrifuging for 2 min, the yellow powder had settled at the point where its density was the same as that of the liquid. A drop of the liquid at this point was withdrawn and its refractive index was measured with an Abbé refractometer. The refractive index versus density had been previously calibrated for sodium iodide in water, by making solutions of known density. The densities determined by this method were accurate to $\pm 0.005 \text{ g cm}^{-3}$, and are given in figure 8, plotted against composition (see Glazer (1968) for numerical data).

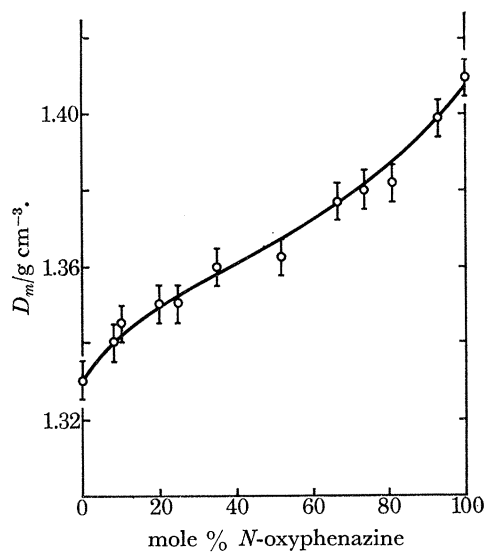


FIGURE 8. Variation in measured density D_m with composition (20 °C).

It can be seen that there is a gradual increase in density with increasing concentration of *N*-oxyphenazine. Because of the sizes of the errors it is not possible to see any real effect due to a miscibility gap.

THERMAL EXPANSION

Very little is known about the thermal expansion of organic mixed crystals. However, it is possible that the thermal expansion of such crystals will show variations similar to those found in inorganic solid solutions.

We may arbitrarily define the average coefficient of linear expansion over a range of temperature of a set of crystal planes (hkl) by

$$\alpha(hkl) = \frac{1}{d(hkl)} \frac{\Delta d(hkl)}{\Delta T} \text{ K}^{-1}$$

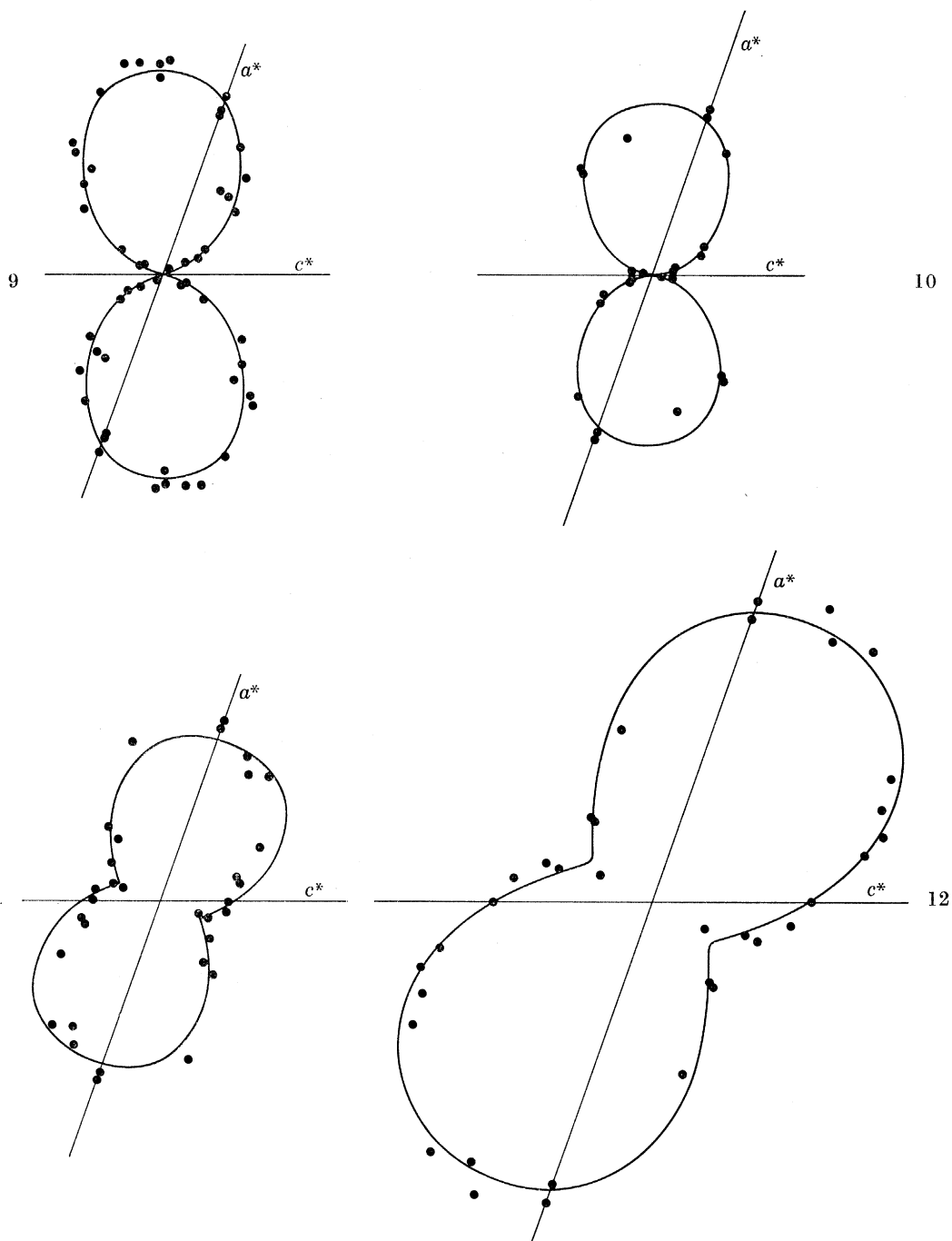
where $d(hkl)$ = the interplanar spacing at the lower temperature T_1 , $\Delta d(hkl)$ = the change in this spacing with temperature rise from T_1 to T_2 , $\Delta T = T_2 - T_1$.

Use was made of the formula

$$\frac{\Delta d(hkl)}{d(hkl)} = \frac{\text{cosec}(\theta - \Delta\theta)}{\text{cosec} \theta} - 1.$$

The thermal expansion of a crystal is represented by a second rank symmetric tensor, which can be considered in terms of a quadric. In the monoclinic system, this is characterized by four components:

$$\alpha_{11} \quad \alpha_{22} \quad \alpha_{33} \quad \phi.$$



FIGURES 9 to 12. Thermal expansion coefficient figures for $\{h0l\}$ planes.

FIGURE 9. Phenazine.

FIGURE 10. 8 mole % *N*-oxyphenazine in phenazine.

FIGURE 11. 67 mole % *N*-oxyphenazine in phenazine.

FIGURE 12. *N*-oxyphenazine.

All for the temperature range 20 to -120°C .

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The coefficient α_{22} lies along the unique axis [010]. The other two coefficients α_{11} and α_{33} lie in the plane (010). The direction of α_{11} is defined by the angle ϕ measured from the a axis in obtuse β .

To determine the thermal-expansion coefficients in (010), Weissenberg photographs were taken at 20 and -120°C , with the crystals rotating about [010]. Both exposures were made on the same film but shifted slightly to allow the differences to be seen. Measurements of the positions of the reflexions were made with a travelling microscope. Fuller details of the experimental procedure are given elsewhere (Glazer 1968).

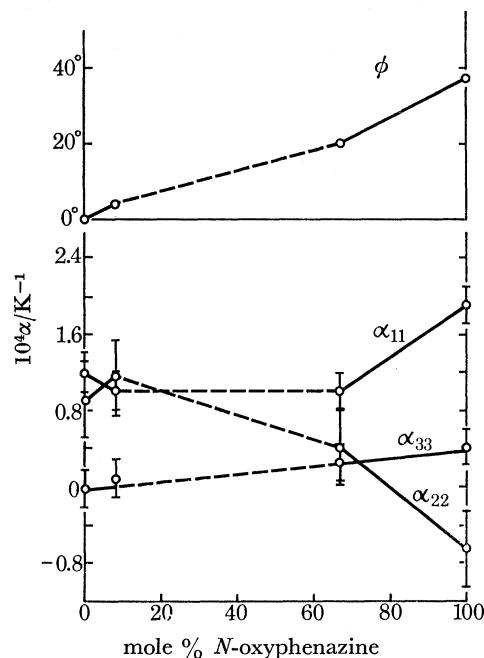


FIGURE 13. Variation with composition of thermal expansion coefficients α_{11} , α_{22} , α_{33} and of the angle ϕ (the angle between α_{11} and a in obtuse β). Temperature range 20 to -120°C .

Because of the difficulty of cutting the crystals without splitting, only the $\{h0l\}$ zone was measured for each crystal. To obtain a value for the thermal expansion coefficients along [010], i.e. α_{22} , it was decided to use the inclined-beam method. Again both exposures were made on the same film. In both methods, Cu $K\alpha$ radiation was used for 0 mole % N -oxyphenazine and Co $K\alpha$ radiation for the other crystals. It was thought that the low temperature was steady and measurable to $\pm 10^\circ\text{C}$. The experiment was carried out with crystals of composition 0, 8, 67 and 100 mole % N -oxyphenazine.

The values for the thermal-expansion coefficients normal to the set of planes were drawn out with reference to the crystallographic axes (figures 9 to 12). α_{11} , α_{33} and ϕ were calculated from these results by a least-squares method. The variations in thermal-expansion coefficient with composition are shown in figure 13. This shows that some large changes occur between 8 and 67 mole % N -oxyphenazine, in support of the hypothesis of the existence of a miscibility gap.

The correlation between thermal expansion and the crystal structures is dealt with elsewhere (Glazer 1968 and part IV above).

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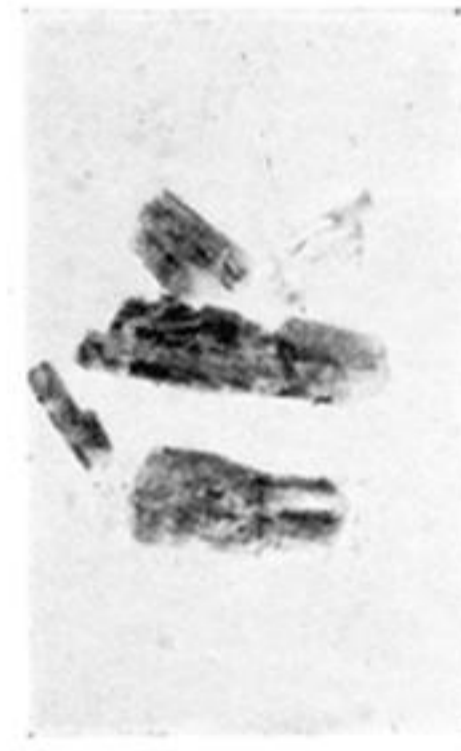


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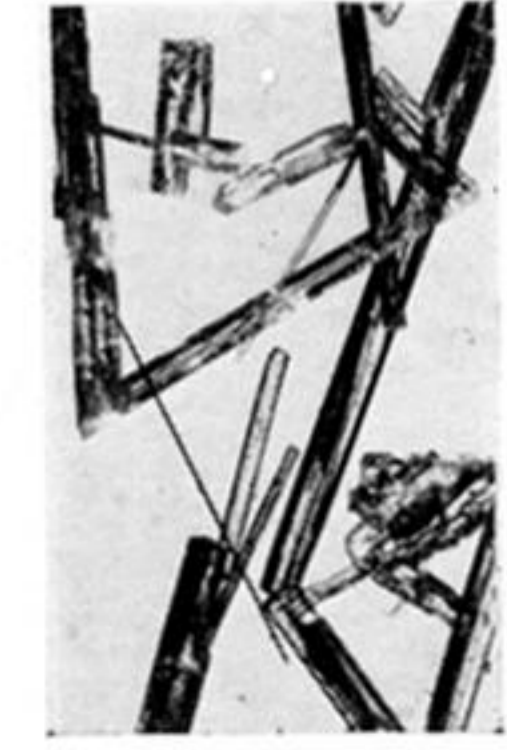
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FIGURE 2. Photographs of the crystals in the series phenazine-*N*-oxyphenazine, showing the poor development of crystal faces between 10 and 40 mole % *N*-oxyphenazine.