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The Crystal and Molecular Structures of Heterocyclic Compounds. I. The Analysis of the Crystal Structure of α-Phenazine

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In a survey of heterocyclic compounds suited to both experimental and theoretical study of molecular dimensions, the crystallographic constants of two forms of phenazine and of four forms of acridine were measured. α-Phenazine was chosen as the most suitable crystal structure for a detailed X-ray analysis.

The intensities of 714 reflections (including 682 out of a possible total of 1024 within the limiting sphere for Cu $K\alpha$) were estimated visually. The structure problem was solved by the method of the molecular Fourier transform. Refinement was achieved in the $h0l$ zone by Fourier methods and in the $hk0$ and $0kl$ zones by the method of least squares. The coordinates from the two-dimensional analysis were refined by one least-squares treatment of the $F(hkl)$ to a new set of coordinates, which corresponded to $R(hkl) = 0{\cdot}16$. Final parameters were computed by one set of F_o and F_c differential syntheses. The electron-density distribution in the best plane through the atomic centres was calculated by a direct Fourier method.

The standard deviation $\sigma(x)$ of the final atomic coordinates was estimated to be 0·009 Å; within the limits of error the molecule has symmetry *mmm*.

The crystal and molecular structures of phenazine are discussed in Part II.

Introduction

While encouraging agreement has recently been reported between observed and calculated bond lengths in aromatic hydrocarbons, a similar comparison in the heterocyclic series is difficult because of the lack of accurate experimental results for compounds suitable for theoretical study. Thus, in choosing compounds for a detailed analysis by X-ray methods we have confined our attention to molecules in which the perturbations introduced by the hetero-atom may be assumed small, and where a comparative study of a related, fully-investigated homocyclic system might be expected to facilitate theoretical work. These requirements are satisfied by the series anthracene–acridine–phenazine.

The results of a crystallographic survey of several polymorphic modifications of acridine (see also Phillips, 1950; Lowde, Phillips & Wood, 1953) and phenazine are collected in Table 1. The cell constants listed in this table were obtained from the appropriate Weissenberg zero-level photographs, after extrapolation to $\theta = 90°$; the space groups were determined from zero- and n-level Weissenberg photographs. The data indicate that the most suitable compound for detailed study is α-phenazine, whose analysis by three-dimensional methods is reported in Part I of the present series. In Part II we discuss the crystal and molecular structures of phenazine and compare the experimental bond lengths with the theoretical values.

1. Previous work

Wood & Williams (1941) have recorded the crystallographic constants and refractive indices of this modification of phenazine; their measurements are in good agreement with those reported here. They also refer to (unpublished) magnetic measurements by Lonsdale; according to them 'there does not appear to be any correspondence between the optical and the magnetic properties'. Prof. Lonsdale has very kindly supplied us with her data, referred to in Part II, which we find to fit our conclusions.

2. Measurement and correction of intensities

The hkl reflexions were recorded on equi-inclination Weissenberg photographs taken about the needle ([010]) axis, and their intensities were measured in the usual way. Layers with $k \leqslant 4$ were recorded with Cu $K\alpha$ radiation; the fifth and sixth layers, whose equi-inclination angles for Cu radiation are outside the experimental limit of $\mu \sim 35°$ of the Weissenberg camera, were photographed with Mo $K\alpha$ radiation. Correlation between the intensities of these layer-line photographs was effected through photographs of the $hk0$ and $0kl$ zones from crystals cut to approximately cubic shape. Also, the $h0l$ spectra of a large crystal of approximately 1 mm.^{2} cross-section were recorded with both Cu $K\alpha$ and Mo $K\alpha$ radiation; a total of 106 $h0l$ spectra were thus observed, including 15 reflexions outside the limiting sphere for Cu radiation, up to a maximum of 1·66 Å^{-1} in $2 \sin \theta/\lambda$.

Absorption corrections were not considered neces-

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Table 1. *Crystallographic constants of some heterocyclic compounds*

Compound	a (Å)	b (Å)	c (Å)	β	n	$D_{\text{flot.}}$	$D_{\text{X-ray}}$	Space group	Crystal habit
α-Phenazine	13·22 ±0·01	5·061 ±0·005	7·088 ±0·007	109° 13′ ±15′	2	1·34	1·33	$P2_1/a$	Needles elongated along [010], showing {100}, {001}, {$20\bar{1}$}
β-Phenazine	11·64 ±0·04	11·58 ±0·07	6·88 ±0·02	99° 19′ ±1°	4	1·24	1·28	$P2_1/n$	Needles elongated along [001], showing {110}
α-Acridine	16·18 ±0·04	18·88 ±0·05	6·08 ±0·02	95° 40′ ±30′	8	1·28	1·27	$P2_1/a$	Needles elongated along [001], showing {110} and {100}
β-Acridine	16·37 ±0·04	5·95 ±0·02	30·01 ±0·10	141° 20′ ±30′	8	1·26	1·29	Aa	Plates showing {100} and {110}
γ-Acridine	17·45 ±0·06	8·89 ±0·03	26·37 ±0·10	—	16	1·10	1·15	$Pnab$	Laths elongated along [010], showing {001}
δ-Acridine	15·61 ±0·04	6·22 ±0·02	29·34 ±0·04	—	12	1·20	1·24	$P2_12_12_1$	Laths elongated along [010], showing {130}

sary because of the nearly cylindrical cross-sections of the crystals; we found it imperative to allow for the compaction and extension of spots on the n-level photographs (Buerger, 1942) by making measurements on both sides of the films and taking the mean values of the intensities. The Lorentz, polarization, and rotation corrections were evaluated by means of the device described by Goldschmidt & Pitt (1948) and modified according to a suggestion of one of us (Herbstein, 1951). The F_o values were put on an absolute scale by comparison with calculated structure factors; large discrepancies were found between the observed and calculated values of the strongest spectra (200, 001, $20\bar{1}$, 210, 310, 011, 111, 211). These extinction errors were corrected satisfactorily by the re-measurement of the intensities from a small crystal which had been dipped into liquid air. The accuracy of the observed structure factors was estimated by comparison of intensity measurements from three different crystals; for the $h0l$ spectra, which were estimated independently by each of us, the standard deviation $\sigma(F_o)$ was 0·5; for all reflections $\sigma(F_o) = 0{\cdot}7$. The latter figure is somewhat higher because of the uncertainty in the spot-shape correction.

The total number of spectra observed is 714; these include 682 lying within the limiting sphere for Cu$K\alpha$ radiation or 67% of the possible total of 1024, compared with 77% recorded for naphthalene (Abrahams, Robertson & White, 1949) and 64% for anthracene (Mathieson, Robertson & Sinclair, 1950).

3. The signs of the structure factors: application of the Fourier-transform method

The theory of the Fourier-transform (F.-T.) method and its application to the determination of molecular orientation and position have been described by several authors (Ewald, 1935; Hettich, 1935; Knott, 1940; Klug, 1950; and others) and consequently need no further elaboration here. Our own experience with the molecular F.-T. technique in a number of structure analyses is being summarised in a separate publication (Harnik, Herbstein, Hirshfeld & Schmidt, to be published); the following details are relevant here:

As the phenazine molecule is centrosymmetric and may be assumed planar the molecular F.-T. is given by a real two-dimensional function. Its computation by means of Beevers–Lipson strips is simplified by the further assumption that the molecule consists of weighted atoms placed at the corners of regular hexagons of side 1·40 Å. The idealised F.-T. now becomes

$$T(X,\,Y,\,Z) = 2\sum_{i=1}^{7} N_i \cos 2\pi(x_iX+y_iY)\,,$$

where x_i, y_i are the coordinates of the seven atoms in the asymmetric unit, referred to orthogonal molecular axes, L, M, N (see Fig. 1), and X, Y, Z are referred to orthogonal axes in reciprocal space. N_i is the weighting factor of the ith atom and is put equal to its atomic number.

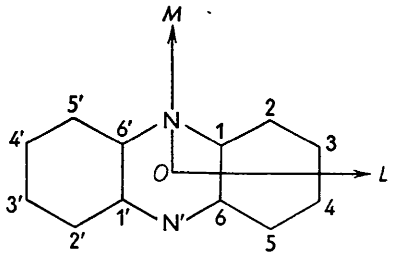

Fig. 1. Phenazine: molecular axes and nomenclature of atoms.

The F.-T. τ of the unit cell as a whole is obtained by the addition of the contributions from the two molecules in the unit cell, after allowance has been made for the phase differences between them. To each atom in one molecule, with coordinates u, v, w, corresponds a similar atom in the other molecule at $\frac{1}{2}+u$,

$\frac{1}{2}-v, w$. The contributions of these two atoms to the structure factor hkl contain geometric factors $\cos 2\pi(hu+kv+lw)$ and $\cos 2\pi(hu-kv+lw+\frac{1}{2}h+\frac{1}{2}k)$ respectively. The latter factor is equal to $\pm\cos 2\pi \times(\bar{h}u+kv+\bar{l}w)$, where the sign is positive for $h+k$ even and negative for $h+k$ odd. Thus, for any assumed orientation of the reciprocal axes relative to the plot of the molecular transform, we may read the corresponding contributions of the two molecules to $\tau(hkl)$ at the points hkl and $\bar{h}k\bar{l}$, adding or subtracting them depending upon the parity of $h+k$.

For $k = 0$, since $F(h0l) = F(\bar{h}0\bar{l})$, the signs of the structure factors were deduced by the method outlined by Knott (1940); an approximate molecular orientation based on the optical data of the crystal (Wood & Williams, 1941) was adjusted so as to yield the best agreement between the observed structure factors and the values read from the transform plot. The projection of the a^*–c^* reciprocal net on to the plane of the transform was thus determined. For $k \neq 0$ the origin of the a^*–c^* net was shifted from the transform origin (the position appropriate to the $h0l$ reflexions) to the point originally occupied by $0k0$, the contributions of the two molecules then being read off at the points $h0l$ and $\bar{h}0\bar{l}$, respectively, of the a^*–c^* net. Thus the transform values for all points in the kth layer were determined from one setting of the a^*–c^* net on the transform plot.

Because of the approximations inherent in the F.-T. method as above outlined, the values of the structure factors derived from the transform are not very accurate. For example, in the $h0l$ zone the agreement factor, R, is 0·28. However, the signs deduced from the transform are in good agreement with those calculated from the final atomic coordinates (see Table 2).

Table 2. *Comparison of transform signs with those from final atomic coordinates*

Class of reflexions	No. of spectra recorded	No. of signs from final F_c	No. of signs from transform	No. for which F.-T. agreed with F_c
$h0l$	106	103	98	91
$hk0$	57	56	54	47
$0kl$	37	37	35	32
all hkl	714	671	659	602

4. Refinement of coordinates by two-dimensional analysis

Ninety $h0l$ reflexions, with signs derived from the Fourier transform, were included in a Fourier summation of the electron-density projection on (010). This first projection, in which all seven atoms of the asymmetric unit were clearly resolved, was refined by conventional methods until there were no further sign changes of the calculated structure factors. The final projection, which includes all but three, very weak, observed $F(h0l)$, is shown in Fig. 2. The x and z coordinates (columns (A) of Table 3) derived from this projection were corrected by one (F_o-F_c) synthesis (columns (B)); the r.m.s. shift was 0·02 Å, with a maximum shift of 0·03 Å. These corrected x and z coordinates were used in the first calculation of hkl structure factors.

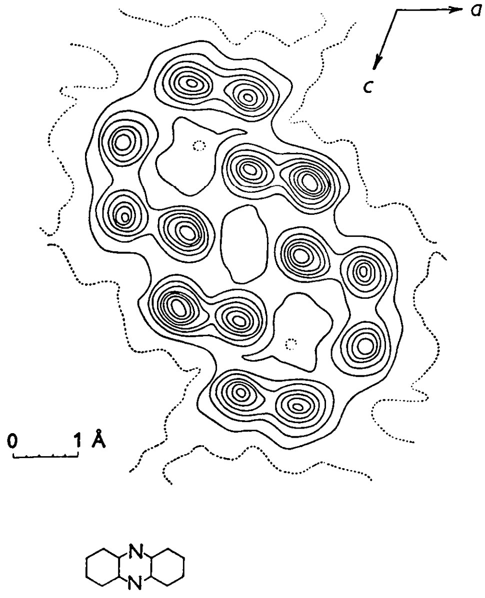

Fig. 2. Electron-density projection down [010]. The contours are drawn at intervals of 1 e.Å^{-2}, with the one-electron contour broken.

Table 3. *Comparison of two sets of x, z coordinates from the two-dimensional analysis*

The coordinates are given to 0·001 Å to facilitate comparison.

	(A)		(B)	
Atom	x	z	x	z
C_1	0·993	0·182	1·026	0·188
C_2	2·066	0·419	2·065	0·434
C_3	2·504	1·711	2·525	1·727
C_4	1·828	2·752	1·840	2·748
C_5	0·814	2·501	0·813	2·519
C_6	0·373	1·238	0·368	1·240
N	0·635	−1·085	0·625	−1·062

Overlap of atomic peaks in both the $hk0$ and $0kl$ projections makes refinement of the y coordinates by Fourier methods impractical; instead, we have had recourse to the method of least squares first used by Hughes (1941). Approximate y coordinates were calculated from the final x and z coordinates for a planar molecule with chemically-reasonable bond lengths. After three successive operations carried out on the combined $hk0$ and $0kl$ structure factors, a set of y coordinates was obtained (Table 4, column (B)) which gave satisfactory values of the R factors. Nevertheless, these coordinates were unacceptable because they implied mean deviations of atomic centres of 0·025 Å

Table 4. *y coordinates obtained by least-squares analysis with and without assumption of molecular planarity*

Atom	(*A*) *y* assuming planarity (Å)	(*B*) *y* not assuming planarity (Å)	Deviation from best plane (Å)
C_1	0·957	0·946	−0·022
C_2	1·940	1·959	0·000
C_3	2·641	2·606	−0·046
C_4	2·260	2·272	+0·020
C_5	1·292	1·250	−0·025
C_6	0·605	0·653	+0·057
N	0·319	0·344	+0·006

	(*A*)	(*B*)
$R(hk0)$ including $F_o = 0$	0·18	0·19
$R(hk0)$ excluding $F_o = 0$	0·16	0·17
$R(0kl)$ including $F_o = 0$	0·16	0·16
$R(0kl)$ excluding $F_o = 0$	0·12	0·14

from the best molecular plane, with a maximum deviation of 0·06 Å. As these deviations were not systematic, and as a non-planar molecule is unlikely on chemical grounds, we repeated the least-squares refinement with the added restriction that the molecule be planar. The resulting *y* coordinates (Table 4, column (*A*)) gave equally good values for the *R* factor, and were taken as final for the two-dimensional analysis. The final coordinates derived from the subsequent three-dimensional analysis differed from these by a mean value of 0·04 Å and a maximum of 0·08 Å, and gave *R* factors for the *hk*0 and 0*kl* zones as acceptable as those of the two previous solutions. It must be concluded that the agreement factor does not necessarily provide an unambiguous criterion for the correctness of a set of atomic coordinates derived from overlapped zones.

An electron-density projection down [001], including 53 terms, was calculated with the signs from the final *u*, *v* coordinates (Fig. 3).

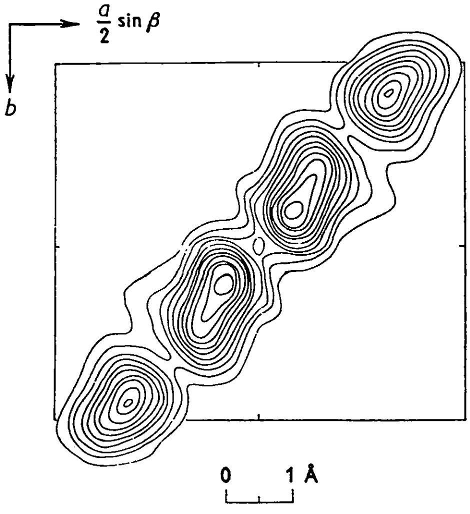

Fig. 3. Electron-density projection down [001]. The contours are drawn at intervals of 1 e.Å^{-2}, the lowest contour being the one-electron line.

5. Discussion of two-dimensional analysis

Following Cruickshank (1949*a*), we estimate the random errors in the *x*, *z* coordinates to be about 0·015 Å; the r.m.s. difference between the two-dimensional and final three-dimensional *x*, *z* coordinates is 0·011 Å. No objective assessment of the errors in the *y* coordinates is possible, but an estimate can be made from the mean difference between sets of coordinates giving the same *R* factor; the standard deviation of a *y* coordinate is therefore taken as 0·03 Å. The s.d. of the bond lengths is then found to be 0·03 Å, which is slightly greater than would be supposed from the internal consistency of the results or from a comparison with the bond lengths determined from the three-dimensional analysis.

In the (010) projection, the average peak height of the carbon atoms is 8·3 e.Å^{-2}, while the nitrogen peak height is 10·3 e.Å^{-2}. If only the terms within the range of Cu *K* radiation are included in this summation, these figures fall to 7·3 and 9·7 e.Å^{-2}. The effect of the Mo terms on the sharpening of the peaks is further indicated by the value of *p* in the expression

$$\varrho(r) = \varrho(0)\exp(-pr^2)$$

taken as a representation of the atomic electron-density maxima; for the Cu terms alone $p = 5·4$ Å^{-2}, averaged for all atoms, which rises to 6·7 Å^{-2} after the inclusion of the Mo terms.

6. Three-dimensional analysis

(*a*) *Introduction*

The limited computing facilities available to us at the time precluded the use of Fourier methods of refinement (three-dimensional sections, lines; differential syntheses); instead it was decided to refine the structure by the least-squares technique. The total amount of work in a three-dimensional least-squares treatment, involving the solution of a determinant of order 21, was substantially reduced, without significant loss of accuracy, by the following two approximations. First, all but the diagonal terms of the full determinant were neglected; Shoemaker, Donohue, Schomaker & Corey (1950), in their three-dimensional analysis of L_s-threonine, showed that the error in bond lengths introduced by this approximation was less than 0·01 Å. Secondly, since none of the atoms of phenazine is at a special position in the unit cell, the diagonal terms themselves were computed on the assumption that the squares of the trigonometric functions could be replaced by their mean value (= 0·5) (Cruickshank, 1949*a*); we have checked that the values of the diagonal terms obtained from this approximation, and hence the *corrections* to the atomic coordinates, do not differ by more than 5% from the true values.

(b) *Structure-factor calculations*

$F_c(hkl)$ for the space group $P2_1/a$ may be written (Lonsdale, 1936)

$$\begin{aligned} F_c(hkl) = 4fA(hkl) &= 4f\sum_i N_i \cos 2\pi(hu_i+lw_i)\cos 2\pi kv_i \quad \text{for } h+k \text{ even} \\ &= -4f\sum_i N_i \sin 2\pi(hu_i+lw_i)\sin 2\pi kv_i \text{ for } h+k \text{ odd.} \end{aligned}$$

The cosine and sine values were read quickly and conveniently to two-figure accuracy from the circular trigonometric slide rule described by one of us (Schmidt, 1951). $A(hkl)$ were calculated on an additive multiplying machine (fully-automatic Fridén) at the rate of 100 values per day.

The atomic scattering factor f was obtained from the table given by Robertson (1935), for both carbon and nitrogen. An attempt to use the James & Brindley (1931) carbon curve, modified by a temperature factor of the form $\exp(-B\sin^2\theta/\lambda^2)$, led to a value of $B = 3{\cdot}46$ Å^2 derived from a least-squares analysis of the $h0l$ spectra; but this curve resulted in slightly poorer agreement between F_o and F_c than the Robertson curve. However, this may not be significant as the two curves differ appreciably only in the region of $\sin\theta < 0{\cdot}4$, in which there are several strong reflexions for which the extinction errors have perhaps not been fully corrected. No attempt was made to allow for anisotropic thermal vibrations; also the hydrogen contributions were completely neglected.

The R factor for the hkl reflexions, based on the u, v, w coordinates from the two-dimensional analysis, was 0·21 (or 0·26 if terms with $F_o = 0$ are included).

(c) *The least-squares computations*

We require a new set of atomic coordinates $(u_iv_iw_i)$ such that

$$\sum_{hkl} ws(F_o-F_c)^2$$

is a minimum. Here w is the weight ascribed to the value of (F_o-F_c) for a given plane hkl and s the multiplicity factor of that plane. For want of a better criterion, we have put $w = 1$ for all planes except those with $F_o = 0$, for which we have assumed $w = \frac{1}{2}$.

In view of the neglect of non-diagonal terms in the least-squares treatment one needs to compute the expressions

$$x_{io} = \begin{cases} -\sum\limits_h^{h+k \text{ even}} h \sum\limits_k \sum\limits_l \sin 2\pi(hu_i+lw_i)\cos 2\pi kv_i \,.\, \Delta_{hkl} \\ -\sum\limits_h^{h+k \text{ odd}} h \sum\limits_k \sum\limits_l \cos 2\pi(hu_i+lw_i)\sin 2\pi kv_i \,.\, \Delta_{hkl} \end{cases}$$

where $\Delta_{hkl} = (F_o-F_c)/4fN_i$; while the terms

$$x_{ii} = \begin{cases} \sum\limits_h^{h+k \text{ even}} h^2 \sum\limits_k \sum\limits_l [\sin 2\pi(hu_i+lw_i)\cos 2\pi kv_i]^2 \\ +\sum\limits_h^{h+k \text{ odd}} h^2 \sum\limits_k \sum\limits_l [\cos 2\pi(hu_i+lw_i)\sin 2\pi kv_i]^2 \end{cases}$$

can be set equal to $\frac{1}{4}\sum\limits_h h^2N_h$, where N_h is the number of observed reflexions of equal h. Similar expressions hold for y_{ii} and z_{ii}. In order to obtain the corrections δu_i, δv_i, and δw_i one has to solve equations of the type

$$2\pi x_{ii}\,.\,\delta u_i = x_{io} \quad 2\pi y_{ii}\,.\,\delta v_i = y_{io} \quad 2\pi z_{ii}\,.\,\delta w_i = z_{io}\,.$$

In setting up the normal equations, observations from 892 planes were used, for 221 of which F_o was zero, while 43 reflexions could not be included in the calculations because of uncertainties in their signs. With two-figure trigonometric values taken from the structure-factor calculations, the 21 equations were set up in approximately two weeks.

The shifts obtained for the x and z coordinates were small, with mean value 0·007 Å, maximum value 0·02 Å, while the shifts in the y coordinates were rather larger, with a mean value of 0·03 Å and a maximum value of 0·06 Å. A new set of structure factors was calculated with the previous values of $\cos(\sin)2\pi \times(hu_i+lw_i)$ and new values of $\cos(\sin)\,2\pi kv_i$; the resulting R factor was 0·16 (0·22 if terms with $F_o = 0$ are included). The observed and calculated structure factors are listed in Table 7.*†

(d) *Refinement by differential synthesis*

In view of the approximations made in the refinement of the atomic coordinates by the least-squares method, it was considered desirable to carry out a final refinement by an independent method. By courtesy of Prof. E. G. Cox, three-dimensional differential syntheses (Booth, 1948) were computed on the B. T. M. installation at the University of Leeds and afterwards checked, and extended, by computations on the electronic computer at the University of Manchester.

The u, w coordinates from the two-dimensional analysis and the v coordinates from the three-dimensional least-squares refinement (i.e. the coordinates used for the calculation of the final set of hkl structure factors) served as the initial coordinates for the differential syntheses. A set of corrections, computed with F_o, was added to the initial coordinates to give atomic positions equivalent to those that would be obtained from a three-dimensional Fourier synthesis. The Fourier coordinates were then corrected for termination-of-series and overlap errors by subtraction of the differential shifts calculated with F_c (Booth, 1946). The largest of the latter corrections was 0·018 Å.

The differential corrections were calculated with neglect of the non-diagonal terms A_{hk} etc. Inclusion of these small terms would have caused only negligible

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† See *Note added in proof*, p. 405.

changes in the differential shifts. The final atomic coordinates are listed in Table 5. The r.m.s. difference between these coordinates and those computed by least squares was 0·008 Å in x, 0·012 Å in y, and 0·008 Å in z.

Table 5. *The final atomic coordinates and perpendicular distances of atoms from the best molecular plane*

These values were obtained from the three-dimensional differential syntheses and have been corrected for termination-of-series errors

Atom	x (Å)	y (Å)	z (Å)	Normal distance from best plane (Å)
C_1	1·022	0·945	0·191	−0·003
C_2	2·064	1·943	0·438	+0·009
C_3	2·493	2·614	1·717	−0·014
C_4	1·842	2·339	2·749	+0·011
C_5	0·828	1·371	2·528	−0·002
C_6	0·379	0·648	1·244	−0·002
N	0·624	0·281	−1·059	+0·001

The observed electron-density values ϱ_o at the atomic maxima, derived from the F_o synthesis (column (A) of Table 6), show systematic variations with the distances of the atoms from the molecular centre. That these variations are partly due to termination-of-series and overlap errors is shown by similar variations in ϱ_c (column (B)), derived from the F_c synthesis. In order to arrive at a meaningful comparison of the peak heights of the various atoms it is necessary to correct for these spurious variations; following Cruickshank (1949*a*), we therefore subtract from each of the ϱ_o a correction equal to the difference between the corresponding ϱ_c and the average of all ϱ_c. (In this treatment ϱ_c of nitrogen was multiplied by $\frac{6}{7}$ before being averaged in with the carbon peaks.) The corrected values of ϱ_o are given in column (C).

Table 6. *Peak electron densities from the* $F_o(A)$ *and* $F_c(B)$ *syntheses*

The corrected ϱ_0 values are given in Column C

	(A)	(B)	(C)
C_1	8·216	8·062	7·757
C_2	6·949	7·384	7·168
C_3	6·377	7·067	6·913
C_4	6·617	7·148	7·072
C_5	7·085	7·651	7·037
C_6	8·174	8·052	7·725
N	9·322	9·162	9·030

7. The electron-density section in the molecular plane

In previously-published structures the electron-density distribution within the molecular plane was derived by interpolation from sections parallel to a principal crystallographic plane, required *ipso facto* for the refinement of atomic coordinates. We preferred a somewhat different technique, which permitted direct calculation of the section through the atomic centres.

The general expression for the electron density at a point (u, v, w) in the unit cell is

$$\varrho(u, v, w) = \frac{1}{V} \Sigma\Sigma\Sigma F(hkl) \cos 2\pi(hu+kv+lw)\,, \quad (1)$$

which can be written in the more convenient form

$$\varrho(u, v, w) = \frac{1}{V}\left[\sum_k C_k(u, w) \cos 2\pi kv - \sum_k S_k(u, w) \sin 2\pi kv\right], \quad (2)$$

where

$$C_k(u, w) = \overset{h+k \text{ even}}{\sum_h \sum_l} F(hkl) \cos 2\pi(hu+lw)\,; \quad S_k(u, w) = \overset{h+k \text{ odd}}{\sum_h \sum_l} F(hkl) \sin 2\pi(hu+lw)\,.$$

$C_k(u, w)$ and $S_k(u, w)$ were evaluated at intervals of 60ths in u and 30ths in w, with the aid of Beevers–Lipson strips.

The final summation, over k, was required only for points in the molecular plane, this being achieved by the substitution in (2) of the values of v determined from equation (3) (see § 9), i.e.

$$\varrho(u, Pu+Qw, w) = \frac{1}{V} \sum_k \left[C_k(u, w) \cos 2\pi k(Pu+Qw) - S_k(u, w) \sin 2\pi k(Pu+Qw)\right],$$

where

$$P = 0{\cdot}8807a/b = 2{\cdot}3000\,,$$
$$Q = 0{\cdot}2553c/b = 0{\cdot}3576\,.$$

The functions cos (sin) $2\pi k(Pu+Qw)$ were evaluated by means of the trigonometric slide rule at those values of u, w necessary to include the entire molecule; the final summations were carried out with an additive multiplying machine. This gave the function $\varrho(u, v, w)$ on a grid in the molecular plane with intervals of 0·293 Å parallel to the (001) face, and 0·243 Å parallel to (100), the grid axes intersecting at an angle of 96° 11′. Electron-density contours at intervals of 0·5 e.Å^{-3} were then drawn by graphical interpolation between the summation totals, and are shown in Fig. 6 of Part II. It is seen that the largest irregularities in the background, in regions far removed from any atomic maxima, are 0·6 e.Å^{-3}, while negative regions do not fall below −0·2 e.Å^{-3}.

8. Accuracy of the three-dimensional analysis

The r.m.s. value $\sigma(x)$ of the error in an atomic coordinate due to random errors in the F_o and in the atomic scattering factors was calculated (Cruickshank, 1949*a*) to be 0·009 Å. Thus the standard deviation of the distance between two independent atoms is $\sqrt{2} \times 0{\cdot}009$ Å $= 0{\cdot}013$ Å; if lengths of two chemically-similar bonds are averaged then the s.d. of the average bond length is 0·009 Å. The measured bond lengths differ from the averaged values by a mean of 0·007 Å and a maximum of 0·010 Å. A similar analysis indicates that the s.d. of a bond angle is 0·6°, while the s.d. of an averaged bond angle is about 0·4°. The measured bond angles differ from the averaged values for symmetry-related angles by a mean of 0·6° and a maximum of 1·1°.

9. The molecular dimensions

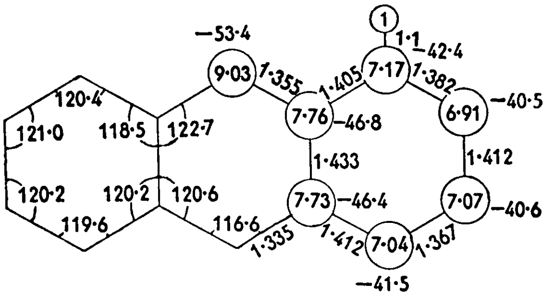

Fig. 4. Experimental bond lengths (in Å) and bond angles (in °). Figures in circles are peak electron densities (in e.Å^{-3}); figures beside circles are central curvatures (in e.Å^{-5}).

The molecular dimensions (see Fig. 4) were calculated from the atomic coordinates obtained from the three-dimensional differential syntheses (see Table 5). The best plane through the atomic centres, calculated by a least-squares method, has the form

$$0{\cdot}8807x-y+0{\cdot}2553z = 0\,, \qquad (3)$$

where x, y, z are measured in Ångström units with respect to the coordinate axes of the unit cell. The perpendicular distances of the atoms from this plane are also listed in Table 5. As these deviations are not significant, there is no justification for assuming that the molecule is not planar. Furthermore, the differences between chemically-similar bonds, bond angles, and peak electron densities are also small and within the limits of error. Thus in the discussion of the molecular dimensions in Part II of this series the molecule has been taken to be planar with dimensions averaged from the measured values in accordance with assumed molecular symmetry *mmm*.

10. Further work

The photographic measurements of intensities have been repeated on crystals held in a stream of boiling nitrogen (Hirshfeld & Schmidt, 1954). Work is also in progress on the second modification of phenazine in an attempt to measure the molecular dimensions from an entirely new set of crystallographic data and to investigate the effect of intermolecular forces on molecular structure.

Note added in proof, 12 *June* 1955.—It is now recognized that the equations actually solved imply a weighting factor proportional to $1/f^2$. Such a procedure, which heavily discriminates against the low-angle terms, is difficult to justify except by the results obtained.

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References

Abrahams, S. C., Robertson, J. M. & White, J. G. (1949). *Acta Cryst.* **2**, 233.

Booth, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.

Booth, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis*. Cambridge: University Press.

Buerger, M. J. (1942). *X-ray Crystallography*. New York: Wiley.

Cruickshank, D. W. J. (1949*a*). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1949*b*). *Acta Cryst.* **2**, 154.

Ewald, P. P. (1935). *Z. Kristallogr.* **90**, 493.

Goldschmidt, G. H. & Pitt, G. J. (1948). *J. Sci. Instrum.* **25**, 397.

Herbstein, F. H. (1951). *Acta Cryst.* **4**, 185.

Hettich, A. (1935). *Z. Kristallogr.* **90**, 483.

Hirshfeld, F. L. & Schmidt, G. M. J. (1954). *Acta Cryst.* **7**, 129.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* (7), **12**, 81.

Klug, A. (1950). *Acta Cryst.* **3**, 176.

Knott, G. (1940). *Proc. Phys. Soc. Lond.* **52**, 229.

Lonsdale, K. (1936). *Structure Factor Tables*. London: Bell.

Lowde, R. D., Phillips, D. C. & Wood, R. G. (1953). *Acta Cryst.* **6**, 553.

Mathieson, A. McL., Robertson, J. M. & Sinclair, V. C. (1950). *Acta Cryst.* **3**, 245.

Phillips, D. C. (1950). *Research*, **3**, 578.

Robertson, J. M. (1935). *Proc. Roy. Soc.* A, **150**, 106.

Schmidt, G. M. J. (1951). *Acta Cryst.* **4**, 186.

Shoemaker, D. P., Donohue, J., Schomaker, V. & Corey, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.

Wood, R. G. & Williams, G. (1941). *Phil. Mag.* (7), **31**, 115.