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The Crystal and Molecular Structures of Heterocyclic Compounds. II. α-Phenazine

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Following its analysis from three-dimensional data (Part I), the crystal structure of α-phenazine is discussed with reference to the molecular packing, the thermal vibrations, and the optical and magnetic properties of the crystal. The principal molecular susceptibilities are calculated from the measured (Lonsdale) values of the principal crystal susceptibilities.

The bond lengths are compared with bond lengths calculated by the method of molecular orbitals. Despite the approximations in the theoretical computations, agreement between measured and calculated bond lengths is good, the r.m.s. discrepancy being 0·006 Å.

The comparison of observed and calculated bond lengths is extended to those nitrogen heterocyclics for which both experimental and theoretical results are available. The method of molecular orbitals predicts the length of C–C bonds to within 0·02 Å, but is less successful in the treatment of the C–N bond.

1. Introduction

The application of quantum-mechanical methods to the determination of the fine-structure of organic molecules has met with considerable success in recent years (see, for example, Report of Discussion Meeting of the Royal Society, 1951). In particular, much attention has been given to the evaluation of bond orders in homocyclic aromatic molecules, and the calculated bond lengths agree well with those measured by refined X-ray techniques (Robertson, 1951).

In the heterocyclic series, the theoretical calculations are less reliable because of the difficulty of allowing quantitatively for the effect of the substitution of a hetero-atom for a carbon atom. Several heterocyclic molecules have recently been analysed by accurate X-ray methods, but unfortunately many of these compounds (e.g. the pyrimidines and purines studied by Cochran and his co-workers) are too complex for reliable calculations of bond orders. Measured values of interatomic distances are available for comparison with calculation in melamine (Hughes, 1941), tetramethylpyrazine (Cromer, Ihde & Ritter, 1951) and thiophthen (Cox, Gillot & Jeffrey, 1949), although fully-refined three-dimensional results are available only for the last of these compounds. On the theoretical side, the first two present difficulties due to the probable interaction of the ring systems with their substituents (NH_2 and CH_3 respectively), while in thiophthen the theoretical work is open to other objections (Longuet-Higgins, 1950; Schomaker, 1951; Lennard-Jones, 1951).

The replacement of carbon by nitrogen in an aromatic system may be expected to cause only a small perturbation of that system, and thus a simple molecular-orbital treatment should be valid. In order to select compounds suitable for crystallographic analysis we have surveyed a number of heterocyclic molecules containing nitrogen in which the hetero-atom supplies only one electron to the π-electron system of the molecule. Because of its crystallographic and theoretical simplicity we have chosen the α-modification of phenazine as the subject of a three-dimensional analysis, details of which are reported in Part I (Herbstein & Schmidt, 1955). In the present paper we discuss, first, features of the crystal structure, and, secondly, the molecular dimensions, which are then compared with theoretical values.

2. The crystal structure of α-phenazine

1. *The molecular arrangement*

The arrangement of the molecules in the crystal, and the shorter intermolecular distances, are shown in Fig. 1. The main feature of the molecular packing may be visualised in terms of molecular 'stacks', which consist of molecules separated by unit translation along [010]. Each molecule has three kinds of close neighbours: those within its own stack, those in the stacks separated by unit translation along [001], and those in the stacks generated by the glide plane. Within each stack the molecules are parallel and separated by an interplanar distance of 3·49 Å; they are staggered in such a way as to minimize overlap of the atoms (Fig. 2). The shortest distance of approach between carbon atoms in molecules separated by the length of the *c* axis is 3·73 Å, and in molecules related by the glide plane 3·82 Å. The molecules are inclined

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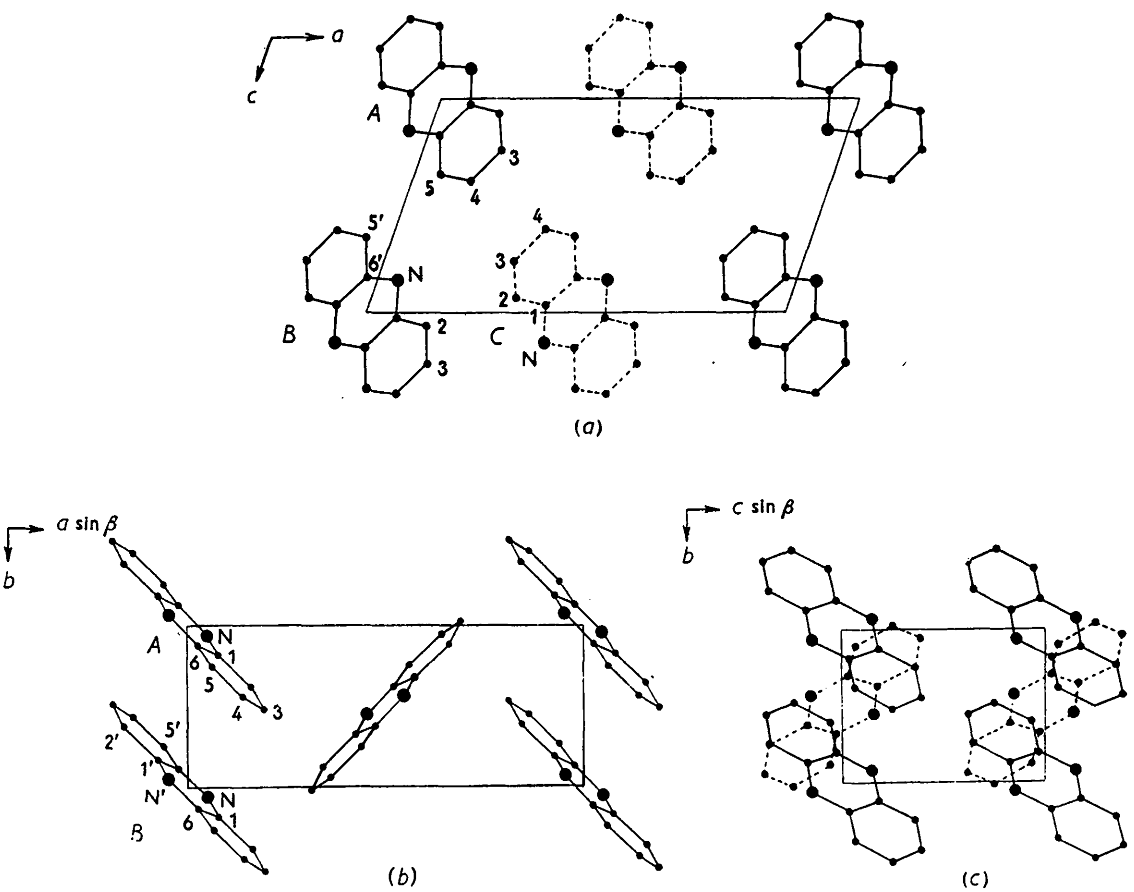

Fig. 1. (*a*) The projection of the unit-cell contents down [010]. Intermolecular distances (Å):

A–B		*B–C*		*A–C*	
5–5′	4·07	2–2	3·88	3–3	4·30
5–6′	4·38	2–3	4·72	4–3	4·02
5–N	3·73	3–N	3·82	4–4	3·83
4–N	4·37	3–1	4·20		
4–2	4·72	3–2	3·94		

(*b*) The projection of the unit-cell contents down [001]. Intermolecular distances (Å):

A–B		*A–B*		*A–B*	
1–1′	3·72	3–1	3·81	5–2′	3·82
1–2′	3·66	3–6	3·69	5–5′	3·81
1–5′	3·88	4–N′	3·49	6–1′	3·84
3–N	3·90	4–1′	3·80	6–2′	3·49

(*c*) The projection of the unit-cell contents down [100].

to the (010) plane at an angle of about 45°, and thus molecules in stacks related by the glide plane are approximately perpendicular.

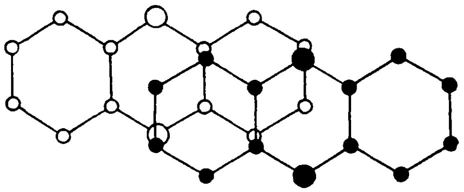

Fig. 2. The normal projection of two molecules in the same stack separated by unit translation along [010].

The 'parallel-disc' packing (Hodgkin, 1951) found in α-phenazine is closely similar to the molecular arrangement in coronene (Robertson & White, 1945), the resemblance being emphasized by the comparable densities of the two compounds, which are considerably higher than those of other analogous substances. However, parallel-disc packing appears to be the exception rather than the rule among the eight polymorphic modifications of the three comparable molecules, anthracene, acridine and phenazine listed in Table 1, Part I; a more typical packing of molecules of this shape is the arrangement found in anthracene, acridine III (Phillips, 1950) and β-phenazine, though

Table 1. *A list of the more intense diffuse spectra*

200	001	$20\bar{1}$	$40\bar{2}$	$60\bar{3}$	$20\bar{6}$	203
210	310	410	520	620		
011	013	022	023			
111	211	411	421			

the reason for its preference is not clear as the utilization of space is more efficient in the parallel-disc packing than in the other types.

The face development of the crystals of α-phenazine follows simply from the molecular arrangement; from the $h0l$ projection it is clear that the three most densely-populated planes are (100), (001) and ($20\bar{1}$), and it is these faces that are most prominently developed in all the crystals examined.

2. *Thermal vibrations in the crystal*

Thermal vibration of the molecules in the crystal is indicated by the diffuse spectra accompanying a number of Bragg reflexions on well-exposed Weissenberg and Laue photographs. A list of the most intense diffuse spectra is given in Table 1; in Fig. 3 the traces of the diffuse zonal reflexions are superimposed on the appropriate projections of the molecule.

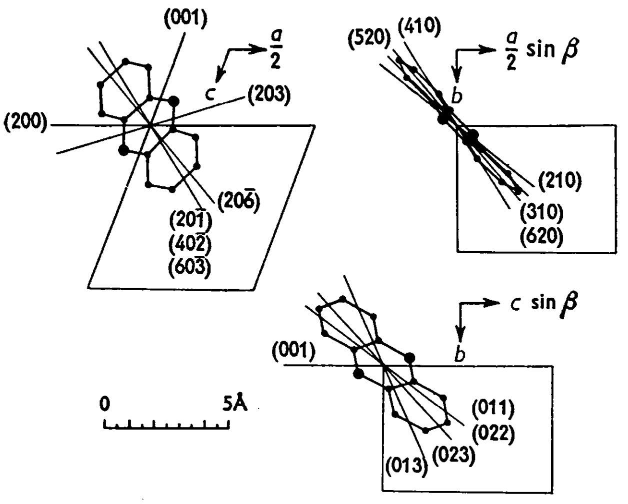

Fig. 3. The comparison of the molecular projections down the three principal crystallographic axes with the traces of the zonal planes showing intense diffuse reflexions.

A novel feature is presented by an $h0l$ photograph of a thick crystal of 1 mm.^{2} cross-section, taken with Mo $K\alpha$ radiation, which shows several areas of diffuse scattering outside the range of resolved Bragg spectra; these areas occur in regions of reciprocal space where large unitary structure factors may be expected (Table 2). The interpretation of these areas of diffuse scattering as Bragg reflexions broadened by thermal movement has been supported by their resolution into individual spectra at the temperature of liquid nitrogen (Hirshfeld & Schmidt, 1954).

Table 2. *Diffuse high-angle spectra resolved at low temperature*

$h0l$	$2 \sin \theta / \lambda$	U_c
$10,0,\bar{9}$	1·78	0·76
$18,0,\bar{14}$	2·11	0·91
$26,0,\bar{4}$	1·98	0·67
$28,0,\bar{10}$	2·25	0·59

3. *The optical properties*

Wood & Williams (1941) reported the following optical data for phenazine:

$\alpha=1{\cdot}73$, $\beta=1{\cdot}82$, $\gamma=1{\cdot}96$; $2V=83°$; $\gamma:[001]=40°$.

Direct calculation of the molecular polarizabilities from the optical properties of the crystal is not possible because of the mutual interaction of the molecules; one can, however, obtain a qualitative correlation of the principal refractive indices with the molecular arrangement.

In crystals of those aromatic compounds in which the molecules are all approximately parallel, a direct, if rough, correlation exists between the magnitudes of the principal refractive indices and the molecular polarizabilities; thus, in anthracene (Sundararajan, 1936) for instance, γ lies along the molecular length, which is the direction of maximum polarizability, β is in the direction of the molecular width, and α is approximately normal to the molecular plane. In α-phenazine, too, γ lies close to the direction of the long axis OL of the molecule (Fig. 4; for nomenclature of the molecular axes see Fig. 1, Part I); α, on the other hand, is roughly in the direction of the molecular width OM. This difference between the two crystals is due to the criss-cross arrangement of the molecules in α-phenazine: because of the inclination of the molecules to [010], the 'component' of OL along [010]

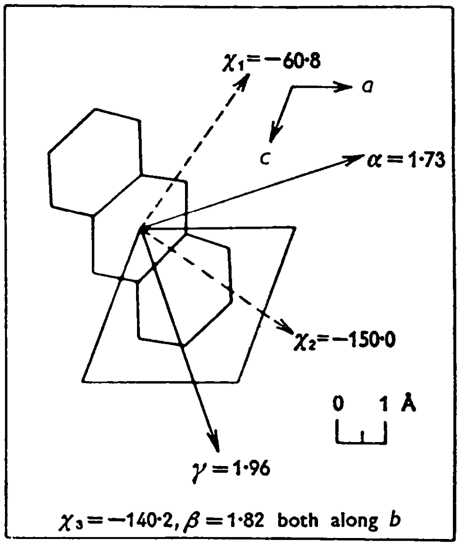

Fig. 4. The relation of the principal refractive indices and principal crystal susceptibilities to the molecular orientation.

is greater than OM; hence the direction of minimum polarizability is approximately in the direction of the molecular width. As a further consequence of the criss-cross packing in α-phenazine its birefringence ($\gamma - \alpha = 0{\cdot}23$) is less than that of anthracene (0·40) for, although the values of γ for the two compounds are very similar, α in phenazine lies along the molecular width and is thus greater than in anthracene, where it is approximately normal to the molecular plane.

4. *The magnetic properties*

Measurements of the diamagnetic susceptibilities of α-phenazine were made by Lonsdale (1952), who has very kindly allowed us to include her unpublished results in this paper.

'Measurements were made on a number of crystals of which the largest, weighing 0·01164 g., gave the most consistent results when set in four directions in the magnetic field. The values found (in units of 10^{-6} c.g.s.e.m.u.) were:

$$\chi_1 - \chi_2 = 89{\cdot}2, \quad \chi_1 - \chi_3 = 79{\cdot}4;$$

$$\psi = \text{angle } \chi_1 : [001] \text{ (measured positive in obtuse } \beta) = -14{\cdot}8^\circ;$$

χ_3 lies along [010] for reasons of symmetry.

The absolute susceptibility was not measured but can be estimated by means of Pascal's additivity rule.

$$\begin{aligned} \bar{\chi} \text{ for anthracene} &= -129{\cdot}2; \\ \bar{\chi} \text{ for acridine} &= -123; \\ \text{hence } \bar{\chi} \text{ for phenazine} &= -117. \end{aligned}$$

$$\text{(Note: } \bar{\chi} = \tfrac{1}{3}(\chi_1 + \chi_2 + \chi_3).)$$

Hence

$$\chi_1 = -60{\cdot}8 \pm 2, \quad \chi_2 = -150{\cdot}0 \pm 2, \quad \chi_3 = -140{\cdot}2 \pm 2.$$

$$\chi_1 : [001] = -14{\cdot}8^\circ, \quad \chi_2 : [001] = 75{\cdot}2^\circ.\text{'}$$

The principal crystal susceptibilities are compared with the molecular arrangement projected on to (010) in Fig. 4.

On the basis of these results Prof. Lonsdale has suggested to us a molecular orientation which we find to be in good agreement with our results. As the mutual magnetic interaction of the molecules can be neglected, it is possible to calculate the molecular susceptibilities from a knowledge of the principal crystal susceptibilities χ_1, χ_2 and χ_3, and the molecular orientation. We have obtained the following values for the molecular susceptibilities referred to the L, M, N axes:

$|K_1| = 46{\cdot}2$ (along molecular length OL),
$|K_2| = 61{\cdot}8$ (along molecular width OM),
$|K_3| = 243{\cdot}0$ (along normal, ON, to molecular plane).

It is generally assumed (Lonsdale, 1937) that the excess of diamagnetism in the direction normal to the molecular plane is due to the precession of the π-electron orbits only. Thus $\Delta K_M \,(= |K_3| - \tfrac{1}{2}(|K_1| + |K_2|))$ is a measure of the delocalization of the π-electrons in the molecule; the similarity of the values of ΔK_M for anthracene (Lonsdale & Krishnan, 1936) and phenazine (182·6 and 189·0, respectively) shows that the degree of delocalization is similar in these molecules. This conclusion is supported by the equality of the experimental resonance energies of the two compounds (105 Kcal./mole; Willis, 1947). There remains an unexplained difference between the principal molecular susceptibilities of anthracene and phenazine: for the former $|K_2| < |K_1|$, while the reverse holds for the latter.

3. The molecular structure of phenazine

The molecular dimensions of phenazine were derived and their limits of error were estimated in Part I, where it was shown that adjustment of bond lengths and angles to give a model of symmetry *mmm* required shifts from the observed coordinates whose magnitudes were less than the estimated experimental error. The dimensions of the 'regularized' model are shown in Fig. 5; comparison with calculated bond lengths (§ 4) refers to these averaged bond lengths. The standard deviations of the averaged bond lengths 1–2, 2–3, N–1 were estimated (§ 8, Part I) to be 0·009 Å, while the s.d. of the bond lengths 1–6 and 3–4, for which only single measurements are available, were estimated to be 0·013 Å. The s.d. of an averaged bond angle was estimated as 0·6°.

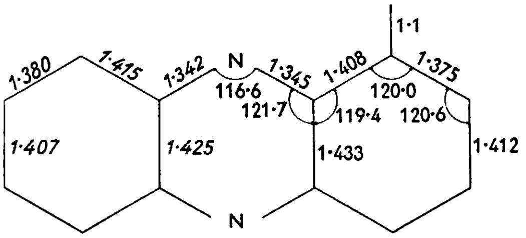

Fig. 5. Molecular dimensions after averaging in accordance with assumed molecular symmetry *mmm*. Theoretical bond lengths (Pullman) are given in italics in the left half of the figure. All bond lengths are in Ångström units.

The computation of the electron-density distribution through the atomic centres (Fig. 6) was described in Part I, where it was also indicated how correction was made for spurious differences in atomic peak heights due to termination-of-series errors. The corrected peak electron densities of the carbon atoms fall off with increasing distance from the centre of the molecule (Fig. 4, Part I). This effect is similar to that observed in naphthalene and anthracene and ascribed to thermal oscillations about the molecular centre. The central curvatures, evaluated in connection with the differential syntheses and similarly corrected, show this same tendency. For each atom the three components of curvature are equal to within a few per cent, indicating that the thermal vibrations are approximately isotropic.

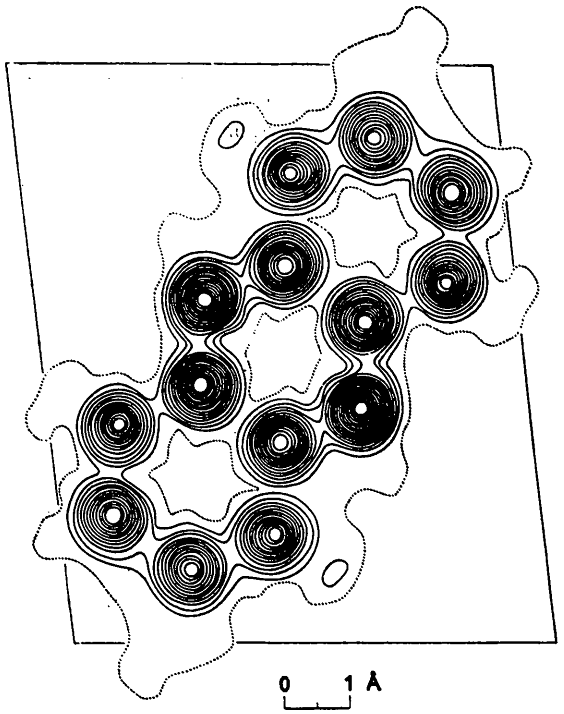

Fig. 6. The electron-density distribution in the molecular plane. The contours are drawn at intervals of $\frac{1}{2}$e.Å^{-3}, with the half-electron contour broken.

Table 3. *Comparison of measured and calculated bond lengths*

	Pullman ($H_{NN} = \alpha+0{\cdot}6\beta$)		Present authors ($H_{NN} = \alpha+2\beta$)		
Bond	(*A*) Mobile bond order	(*B*) Bond length (Å)	(*C*) Mobile bond order	(*D*) Bond length (Å)	Averaged observed bond lengths (Å)
1–N	0·603	1·342	0·521	1·356	1·345
1–2	0·536	1·415	0·562	1·410	1·409
2–3	0·737	1·380	0·728	1·381	1·375
3–4	0·584	1·407	0·546	1·414	1·412
1–6	0·480	1·425	0·418	1·437	1·433
R.m.s. difference between calculated and measured lengths		$0{\cdot}005_6$		$0{\cdot}006_0$	

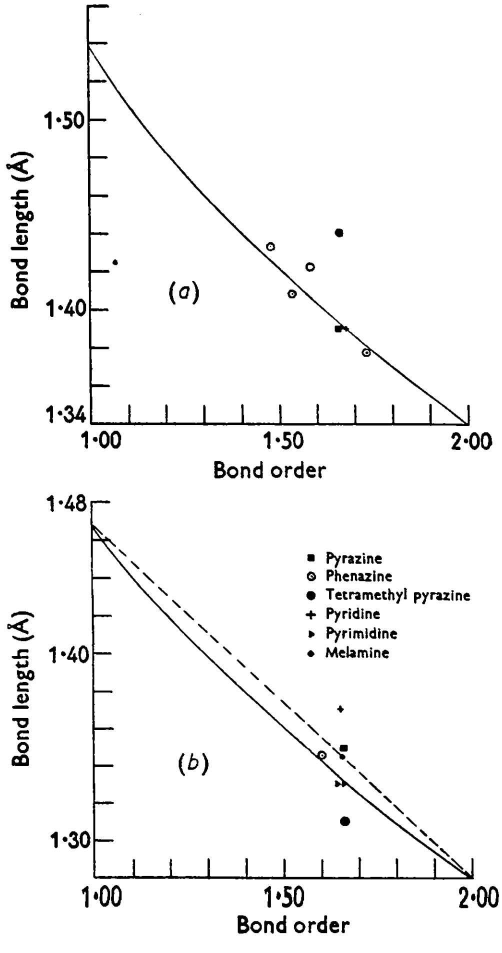

Fig. 7. (*a*) Curve showing variation of bond length with bond order (Coulson, 1951) for C–C bonds.

(*b*) Variation of bond length with bond order for C–N bonds. The broken line was given by Cox & Jeffrey (1951), while the full line is the modified curve suggested by the present authors.

4. The application of the method of molecular orbitals

In the calculation of bond orders and electron densities in heterocyclic molecules, quantitative allowance must be made for the increased electronegativity of the hetero-atoms and their influence on neighbouring atoms, i.e. numerical values assigned to the Coulomb integrals of the hetero-atoms and their neighbours. Figures for the Coulomb integral of nitrogen, H_{NN}, range from the earlier values of $(\alpha+2\beta)$ (Wheland & Pauling, 1935; Longuet-Higgins & Coulson, 1947) through $(\alpha+\beta)$ (Orgel, Cottrell, Dick & Sutton, 1951) to $(\alpha+0{\cdot}6\beta)$ (Chalvet & Sandorfy, 1949; Löwdin, 1951). In this standard notation α is the Coulomb integral of the carbon atom in the benzene molecule; β is the resonance integral of the carbon–carbon bond in benzene. In addition, the earlier workers assumed that the Coulomb integral of the carbon atoms bonded to nitrogen atoms was changed to $(\alpha+\frac{1}{4}\beta)$ by an inductive effect, which was ignored by the later authors. In all computations the resonance integral of the C–N bond was assumed equal to β.

It is difficult to arrive at a decision among the three sets of values for the nitrogen Coulomb integral on the basis of bond-length measurements as the variation of the empirical parameters from $(\alpha+2\beta)$ to $(\alpha+0{\cdot}6\beta)$ produces maximum changes in mobile bond order of approximately 0·10, corresponding to differences in bond lengths of 0·02 Å. A more sensitive test of the value to be assigned to H_{NN} is provided by a calculation of the contribution of the π-electrons to the dipole moment. Löwdin (1951) has shown that, with $H_{NN} =$

$\alpha+0{\cdot}6\beta$, calculated values of the dipole moment in good agreement with experiment are obtained for a number of heterocyclics, while $H_{NN} = \alpha+2\beta$ gives calculated moments much larger than the measured values.

Bond orders of phenazine calculated by Pullman (1951) with $H_{NN} = \alpha+0{\cdot}6\beta$ are given in Column (*A*) of Table 3, while column (*C*) lists bond orders calculated by us with the values of the empirical parameters used by Longuet-Higgins & Coulson (1947). Bond lengths (Columns (*B*) and (*D*)) were derived for both sets of bond orders from empirical order–length curves. For C–C bonds the curve given by Coulson (1951) was used (Fig. 7(*a*)), while for the C–N bond it was found desirable to modify slightly the order–length curve given by Cox & Jeffrey (1951) (Fig. 7(*b*)).* The results of the two calculations differ by a maximum of 0·014 Å (for the C–N bond), which is of the order of magnitude of the uncertainty in our measurements.

As we have anticipated, the observed bond lengths (Column (*E*)) do not distinguish between the two sets of theoretical figures; Columns (*B*) and (*D*) both agree with (*E*) to within a r.m.s. deviation of 0·006 Å. This compares with the r.m.s. difference of 0·007 Å in the refined determination of the bond lengths of anthracene (Ahmed & Cruickshank, 1952). In view of the approximations made in the calculations on phenazine, and because of the existence of a number of further corrections of magnitudes varying up to 0·015 Å (Coulson, Daudel & Robertson, 1951), the excellent agreement obtained here between observed and calculated bond lengths must be considered to be to a certain extent fortuitous.

It is of interest to extend this comparison of theoretical and measured bond lengths to other heterocyclic compounds. Three-dimensional bond-length measurements (without correction for termination-of-series error) have been made on tetramethylpyrazine (Cromer *et al.*, 1951), while the bond lengths of the pyrimidine ring have been deduced from the analysis of a number of substituted pyrimidines (Clews & Cochran, 1949). Electron-diffraction measurements are available for pyridine and pyrazine (Schomaker & Pauling, 1939). Bond orders have been calculated for pyridine, pyrimidine and pyrazine by Chalvet & Sandorfy (1949).

A concise method of comparing theoretical results with experimental values employs the plot of bond order against bond length; if agreement between these values is good then the corresponding points should not deviate from an accepted order–length curve by more than the experimental error (approximately 0·02 Å). The graphs obtained are shown in Fig. 7; agreement for C–C bonds is good in all compounds studied, with the exception of tetramethylpyrazine. For the C–N bond, on the other hand, the position is not as satisfactory. The order–length curve suggested here is based primarily on the bond lengths of pyrimidine, melamine and phenazine, which were derived from careful X-ray analyses and are likely to be more accurate than the electron-diffraction results for pyridine and pyrazine. The C–N bond lengths of tetramethylpyrazine, again, do not fit this curve too well, though the deviations here are not as large as for the C–C curve. Complete correspondence cannot be expected as the bond orders are those calculated for pyrazine itself, though it is doubtful whether the effect of the methyl groups on the dimensions of the substituted compound would be sufficiently large to account for all discrepancies. The X-ray analysis of pyrazine would be helpful in clarifying this point.

From this summary it is clear that predictions of C–N bond lengths by the method of molecular orbitals will not be as reliable as those of C–C bond lengths; the present difficulties are due partly to a lack of knowledge of the correct values of the empirical parameters, and partly to the various approximations made in the calculations. These include the assumption that all the atoms in the molecule are trigonally hybridized; while this assumption is reasonable for phenazine, calculations on pyrimidine, for example, should take into account the deviations of the bond angles from 120°. Undoubtedly a more serious approximation, made in all the calculations reviewed here, is the neglect of overlap between adjacent atomic orbitals (Chirgwin & Coulson, 1950); these errors are supposed to be 'not very great' although their magnitudes are not known with certainty.

We are grateful to Prof. K. Lonsdale and to Dr B. Pullman for permission to include in this paper certain unpublished results, and to Prof. C. A. Coulson for helpful criticism of an earlier draft of this paper. We also wish to thank Mr R. Cohen of this Laboratory, who has drawn the diagrams for Parts I and II.

This work forms part of a thesis for the degree of Doctor of Philosophy submitted to the Senate of the Hebrew University, Jerusalem, by one of us (F. H. H.).

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* In a preliminary communication (Herbstein & Schmidt, 1952) the calculated length of the C–N bond is given incorrectly because of the use of a wrong order–length curve.

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Über die Struktur und Eigenschaften der Halbmetalle. VII.* Neubestimmung der Struktur des glasigen Selens nach verbesserten röntgenographischen Methoden

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The X-ray analyses of amorphous selenium, arsenic and antimony hitherto described in the literature do not agree with chemical conceptions. An improved experimental technique and the elimination of certain sources of error give atomic distribution curves which are now in good agreement with chemical ideas. Experiments on selenium and AsSe glass are described. In selenium glass the structural units are high- and low-molecular rings bound by van der Waals forces. The close packing of the chains in hexagonal selenium is destroyed.

1. Einleitung

Im Rahmen unserer Untersuchungen über die Allotropie der Halbmetalle beschäftigten wir uns auch mit den amorphen Modifikationen dieser Elemente (Krebs, 1951, 1953*b*). Die dabei nach chemischen Gesichtspunkten entwickelten Strukturmodelle stimmten nicht mit den in der Literatur angegebenen Ergebnissen der röntgenographischen Strukturanalyse überein. So fanden Hendus (1942) und Richter, Kulcke & Specht (1952) für das glasige Selen als erste Koordinationszahl 2,4 und nicht 2,0, wie man nach der Wertigkeit des Elementes erwarten sollte. Für das explosive Antimon erhielt Hendus (1942) 4,0 anstatt 3,0. Ferner leitete Richter aus seinen röntgenographischen Untersuchungen der amorphen Formen des Arsens und Antimons eine mehr kettenartige Verknüpfung der Atome ab (Richter & Breitling, 1951; Richter, Berkhemer & Breitling, 1954). Eine solche ist aber aus chemischen Gründen recht unwahrscheinlich, da diese Elemente dreiwertig sind und ein Teil der Valenzen ungesättigt bleiben müsste. Aus unseren chemischen Untersuchungen (Krebs, 1953*b*) liess sich schliessen, dass freie radikalartige Enden in diesen Substanzen nicht vorhanden sein können. Wir vermuteten daher, dass unbekannte bzw. nicht genügend beachtete Fehlerquellen die bisherigen röntgenographischen Analysen der erwähnten Substanzen verfälscht hatten (vgl. auch Prins, 1951). Das von Krebs & Thees (1953) entwickelte photomechanische Verfahren zur Umrechnung einer Streuintensitätsverteilung in eine Atomverteilung gestattete durch seine Schnelligkeit, die Strukturanalyse amorpher und flüssiger Substanzen auf Fehlerquellen hin zu untersuchen.

2. Experimentelle Methodik

Bisher wurde die Verteilungsfunktion der gestreuten Röntgenstrahlung photographisch aufgenommen. Wir

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* VI: Krebs, 1953*a*.