than Li. The lowering of charge at the centre of the octahedron as a consequence of the incomplete occupancy of this site seems in fact to be insufficient to explain this lengthening, the mean M(1)–O distance being 2·20 Å in heterosite where the M(1) site is empty.

The results of the refinement indicate isomorphous substitution between Mn^{2+} and Fe^{3+} in the M(2) site in spite of the strong difference in ionic radii (25%) and the simplicity of the structure. The very low value of the final residual index ($R = 2·7\%$) and the normal values of the temperature factors leave no doubt on the subject.

The distortion of the coordination polyhedra in the structure can be explained in terms of the strong imbalance of the bond strengths to the anions. According to the Ferguson (1974) method the bond strengths to O(1) and O(2) are 1·85 and to O(3) 2·15, whereas for natrophilite they are 1·93, 1·94 and 2·06; for lithiophilite 1·90, 1·95 and 2·08; for triphylite 1·91, 1·94 and 2·07; for heterosite 1·80, 1·80 and 2·20. Ferrisicklerite is therefore an intermediate member of the group natrophilite, lithiophilite, triphylite and heterosite. In fact the variations in the O–cation distances tend to decrease the imbalance of the bond strengths but not by such a drastic amount as in heterosite, thus confirming the statement of Eventoff, Martin & Peacor (1972): 'during the oxidation and leaching of triphylite there is a gradual and continuous change in the average geometry of the $(Fe, Mn)O_6$ octahedron in response to charge redistribution'.

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Structures of Nitrogen-Containing Aromatic Compounds.
II. 2,5-Diphenylpyrazine

BY MICHAEL LAING AND POLLY SOMMERVILLE
Chemistry Department, University of Natal, Durban, South Africa

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2,5-Diphenylpyrazine is monoclinic, $P2_1/c$, $a = 13·42$ (2), $b = 5·73$ (1), $c = 7·66$ (1) Å, $\beta = 93·4$ (2)°, $Z = 2$. $R = 0·052$ for 761 observed data (diffractometer, monochromated Mo $K\alpha$); all C and N anisotropic, 6 H included. Mean C–C in the phenyl ring is 1·386 Å (not corrected for thermal motion which is relatively large). In the pyrazine ring, C–C = 1·389, C–N = 1·336, 1·331 Å. The structure is closely isostructural with those of terphenyl and the dimer of phenyl isocyanate. A discussion is given of the solution of the structure by direct methods.

Introduction

A crystallographic study of 2,5-diphenylpyrazine was begun at the University, Glasgow, in 1948 with the aim of obtaining the bonding parameters in the pyrazine ring. The cell dimensions and space group were established but no further work was done because of the limitations of facilities and time. The availability of automatic data collection on a diffractometer and vastly improved computing facilities have now made this a viable project. In addition, the crystal structures of the parent compound pyrazine (Wheatley, 1957) and the geometrically similar *p*-terphenyl (Rietveld, Maslen & Clews, 1970) have been reported; so the structure determination has now been undertaken both to obtain accurate bond lengths and angles in the pyrazine ring and to compare the molecular packing with that found in *p*-terphenyl.

Experimental

Suitable crystals were grown from an ethyl acetate solution. Cell dimensions (Table 1) were obtained by least-squares refinement of 2θ, χ and φ angles for 25 reflexions measured on a Philips four-circle diffractometer. Intensities were measured for a crystal 0·4 × 0·7 × 0·4 mm with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) for θ between 3 and 25°. The ω–2θ scan technique was used; the scan width was 1·5°, the scan time 37·5 s, and the background was counted for 37·5 s for each reflexion. Three reflexions were used as standards and remeasured after every 60 reflexions; no crystal decomposition occurred. Of the 1149 reflexions measured (including space-group extinctions), 761 were classed as observed, *i.e.* $I > 1{\cdot}65\sigma(I)$. Only Lorentz–polarization corrections were applied.

Table 1. *Crystal data*

$C_{16}N_2H_{12}$, monoclinic $P2_1/c$

a = 13·42 (2) Å	V = 589 Å^3
b = 5·73 (1)	Z = 2
c = 7·66 (1)	D_m = 1·32 g cm^{-3}
β = 93·4 (2)°	M = 232

A Patterson map immediately yielded the orientation of the six-membered rings, the direction of the long axis of the molecule, and hence the approximate x and z coordinates of the atoms. The y coordinates could not be deduced unambiguously because of overlap about the origin of the intramolecular vectors of the phenyl and pyrazine rings. The first trial structure, with the pyrazine ring roughly parallel to the xz plane and the phenyl ring tilted out of it, could not be refined. The second model, with the pyrazine ring tilted out of the xz plane and the phenyl ring roughly parallel to it, proved to be correct and was refined isotropically from R = 0·50 to 0·14 by block-diagonal least squares.

Simultaneously, the solution was attempted by direct methods, because it seemed likely that this structure with its planar six-membered rings could well prove to be anomalous. This idea was confirmed by the Wilson plot which had the expected zigzag shape. The intensity statistics were typical of a hypersymmetric structure containing planar six-membered rings: $\langle|E|\rangle = 0{\cdot}70$, $\langle|E^2|\rangle = 0{\cdot}97$, $\langle|E^2 - 1|\rangle = 1{\cdot}14$; $|E| > 1 = 20\%$, $|E| > 2 = 4\%$, $|E| > 3 = 1{\cdot}3\%$. 129 E's > 1·50 were used in program *SAYRE* (Long, 1965) to solve the structure. The program failed to yield a correct solution when operated in the automatic mode, but when the appropriate set of reflexions (Table 2) was used as origin definers and variables (NBACK = 1, NSORT = 1), the correct solution was obtained. The E map had nine large peaks whose coordinates were the same as those of the C and N atoms which had been deduced from the second Patterson model. The correct solution had several peculiarities: the origin definers, the four variables and the 12 largest E's remaining (all above 2·90) had positive signs; it had the second highest consistency index (0·929) and it was obtained after seven cycles. The solution with the highest consistency index (0·972) was also obtained after seven cycles. It gave an E map with a large peak at the origin, equivalent to a Patterson map.

Table 2. *Reflexions used as the starting set in program SAYRE*

h k l	E	Signs	
1 0 2	4·71	+	fixed
−9 3 3	3·82	+	
2 1 4	2·84	+	
−10 3 1	3·73	a	variables
−9 2 2	4·25	b	
3 3 7	3·46	c	
1 5 1	3·74	d	

Two further aspects of the correct solution are of interest. 72 signs were +, only 57 were −; and one of the trial solutions suffered a change of sign of variable d from − to + to yield the correct combination of signs also after seven cycles but with a consistency index of only 0·85 (the sixth highest). The experience described above emphasizes the power of Long's (1965) program, especially when used in the manual mode with a suitable set of reflexions as origin definers and variables. Some simple criteria for choosing these reflexions have been given (Laing, 1976).

The structure was refined isotropically, and the difference map at R = 0·11 clearly showed the H atoms. They were included in the refinement, the N and C atoms were made anisotropic and the structure was refined to convergence. R = 0·052 for 761 observed reflexions.* The scattering factors were for neutral atoms, taken from *International Tables for X-ray Crystallography* (1962). The weights were proportional to $1/\sigma(F)$.

The fractional atomic coordinates and thermal parameters are given in Table 3. The molecule as a whole does not behave as a rigid body, but the phenyl ring and C(1) can be handled by this simple approximation (Cruickshank, 1956) and the τ and ω parameters which are derived are physically reasonable. Table 4 lists the parameters for the thermal ellipsoids of all N and C atoms. The numbering system and the bond

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31813 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Atomic coordinates and thermal parameters*

Fractional atomic coordinates (× 10^4 for N and C; × 10^3 for H) and isotropic thermal parameters.

	x	y	z	B (Å^2)
N	9514 (1)	−2021 (3)	467 (2)	
C(1)	9041 (1)	31 (4)	465 (2)	
C(2)	9544 (2)	2029 (4)	−12 (3)	
C(3)	7996 (1)	41 (4)	958 (2)	
C(4)	7342 (2)	1848 (4)	470 (3)	
C(5)	6359 (2)	1784 (4)	903 (3)	
C(6)	6010 (2)	−65 (4)	1850 (3)	
C(7)	6650 (2)	−1859 (4)	2360 (3)	
C(8)	7631 (2)	−1807 (4)	1919 (3)	
H(2)	918 (2)	357 (4)	−2 (3)	2·0 (5)
H(4)	759 (1)	320 (3)	−22 (2)	1·0 (4)
H(5)	590 (1)	314 (4)	49 (3)	1·6 (5)
H(6)	530 (1)	−13 (3)	213 (2)	0·9 (4)
H(7)	641 (1)	−325 (4)	308 (3)	1·8 (5)
H(8)	811 (1)	−310 (3)	223 (2)	0·7 (4)

Anisotropic thermal parameters (× 10^4). The form of the expression is:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	45 (1)	196 (7)	192 (4)	1 (5)	30 (3)	54 (9)
C(1)	39 (1)	146 (7)	86 (3)	4 (6)	−3 (3)	1 (10)
C(2)	42 (1)	155 (8)	185 (5)	18 (6)	25 (4)	32 (11)
C(3)	39 (1)	162 (7)	73 (3)	−8 (6)	−7 (3)	−35 (10)
C(4)	46 (1)	197 (8)	108 (4)	6 (6)	13 (4)	17 (10)
C(5)	47 (1)	263 (9)	125 (4)	45 (6)	10 (4)	−11 (11)
C(6)	39 (1)	334 (9)	114 (4)	−15 (7)	12 (4)	−52 (12)
C(7)	47 (1)	266 (9)	114 (4)	−32 (6)	13 (4)	40 (11)
C(8)	42 (1)	206 (8)	107 (4)	−5 (6)	−1 (4)	37 (10)

lengths and angles (uncorrected for thermal motion) are given in Fig. 1. Fig. 2 is a projection of the molecule down **b**.

Discussion

Molecular geometry

The phenyl rings are twisted out of the plane of the pyrazine ring by about 20°, thus reducing intramolecular H···H repulsions to a minimum. The lengths in the pyrazine ring are close to the expected values of about 1·34 for C–N and 1·39 Å for C–C. The C–C distances in the phenyl ring illustrate the foreshortening caused by the relatively large thermal motion of the ring which appears to be undergoing oscillations of approximately 5° about the axis C(1)–C(6) (Table 4). The pyrazine ring cannot be treated as a rigid body because C(2) and N have far larger amplitudes of vibration than C(1). This apparent motion corresponds to a breathing of the pyrazine ring parallel to the long axis of the molecule but could actually be a scissoring of the two C–N bonds about the flexible N atom. This motion could in turn produce a non-planar (twist-boat or chair) conformation of the pyrazine ring. The observed thermal motion could therefore be an artefact caused by a continuous inversion between two slightly non-planar conformations of the pyrazine ring. This implies that the centre of symmetry is only a time-average and could disappear if the crystal were sufficiently cooled. This occurs in p-terphenyl (Baudour & Charbonneau, 1974).

Packing and isomorphism

In addition to p-terphenyl, the dimer of phenyl isocyanate is also isostructural with 2,5-diphenylpyrazine (Baudour, Delugeard & Sanquer, 1974). Although all atoms in p-terphenyl appear to be coplanar at room temperature, the torsion angle between the planar rings is 11·5° in the dimer of phenyl isocyanate while

Table 4. *Thermal motion*

Observed thermal ellipsoids

	$\sqrt{\bar{U}^2}$ (Å)	Direction cosines referred to a	b	c^*
N	0·24	0·235	0·217	0·947
	0·20	−0·954	0·237	0·183
	0·17	−0·185	−0·947	0·262
C(1)	0·19	0·976	0·043	−0·211
	0·16	−0·215	0·141	−0·966
	0·16	−0·011	0·989	0·147
C(2)	0·24	0·173	0·150	0·973
	0·19	−0·965	−0·173	0·198
	0·16	0·198	−0·973	0·115
C(3)	0·19	0·980	−0·045	−0·195
	0·17	−0·045	0·900	−0·434
	0·14	0·195	0·434	0·880
C(4)	0·20	0·967	0·238	0·091
	0·18	−0·255	0·907	0·336
	0·18	−0·003	−0·348	0·937
C(5)	0·23	0·690	0·724	−0·019
	0·19	−0·407	0·366	−0·837
	0·18	−0·598	0·585	0·547
C(6)	0·23	0·132	−0·962	0·240
	0·19	0·991	0·130	−0·022
	0·18	−0·010	0·241	0·970
C(7)	0·23	0·594	−0·786	−0·173
	0·20	0·756	0·472	0·453
	0·18	−0·275	−0·400	0·874
C(8)	0·20	0·817	−0·516	−0·256
	0·19	0·571	0·671	0·472
	0·17	−0·071	−0·532	0·844

Angular motion of the phenyl ring

Oscillation angle (°)	Direction cosines referred to a	b	c^*
5·6	0·961	0·018	−0·275
1·9	−0·025	0·999	−0·022
1·4	0·275	0·028	0·961

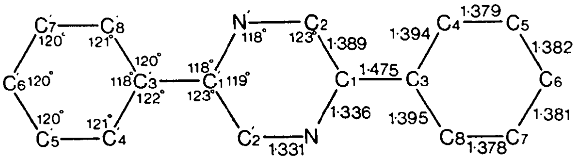

Fig. 1. Bond lengths (Å) and angles (°) (not corrected for thermal motion).

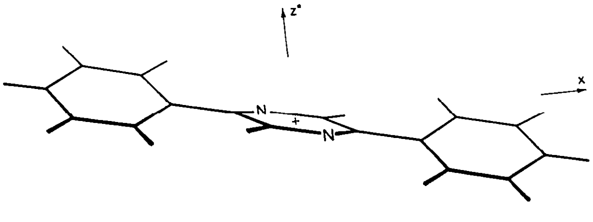

Fig. 2. A projection of the molecule down **b** showing the relative orientation of the rings.

Table 5. *Physical characteristics of the three isostructural crystals*

	p-Terphenyl	2,5-Diphenyl-pyrazine	Phenyl isocyanate dimer
a (Å)	13·61	13·42	12·75
b (Å)	5·61	5·73	5·52
c (Å)	8·11	7·66	8·08
β (°)	92·0	93·4	92·3
V (Å^3)	619	589	568
M.W.	230	232	248
Density (g cm^{-3})	1·22	1·32	1·40
M.p. (°C)	211	193	186
Vol./atom* (Å^3)	17·2	16·3	15·8
Effective volume of central ring (Å^3)	93	78	68
Atoms*/molecule	18	18	18

* Non-hydrogen.

it is even larger, 20°, in the present case. In all other respects, the mode of packing in these three crystals is similar, as is seen by comparison of the cell dimensions and related characteristics (Table 5).

The libration of the phenyl rings about the C–C single bonds in the three compounds is similar: 69(°)^2 in *p*-terphenyl, 32(°)^2 in 2,5-diphenylpyrazine and 27(°)^2 in phenyl isocyanate dimer. These amplitudes of oscillation parallel the similarities of the products $c \times b$ in the respective crystals: 45·5, 43·9 and 44·6 Å^2.

The effective volume of the central ring in each molecule (Table 5) can be estimated by subtracting the volumes of the two phenyl rings, which for simplicity will be taken as the effective volume/molecule of diphenyl (Kitaigorodsky, 1973). These volumes reflect both the real thermal motion and the (possible) disorder of the central ring in the crystalline structures. The decrease in unit-cell volume accompanies an increase in molecular weight and density. However, the most dense material has the lowest melting point, the least dense the highest. This appears to be a contradiction, *i.e.* the crystal with the closest packing appears to have the weakest intermolecular attractions in the solid state. The problem is resolved if the thermodynamics of the phase change are considered. The entropy change on melting, ΔS, is related to the enthalpy change, ΔH, and the melting point T by $\Delta S = \Delta H/T$. The entropy of the molecules, *i.e.* effective volume per atom, in the more loosely packed material will be greater than that of the molecules in the more tightly packed material. If ΔH of melting is approximately the same for each compound, then a decrease in ΔS between the solid and the melt automatically corresponds to an increase in melting point (Ubbelohde, 1965).

It is interesting to note that 3,6-diphenyl-*s*-tetrazine (Ahmed & Kitaigorodsky, 1972) is *not* isostructural with the three compounds in Table 5 although the molecule is closely similar in shape and size. The cell dimensions and mode of packing are different; but the density of 1·35 g cm^{-3} is normal and the volume/atom is 15·7 Å^3 which indicates that the structure is close-packed. The effective volume of the central tetrazine ring is 67 Å^3, significantly smaller than the value found for the pyrazine ring.

Conclusion

The present study has shown that the desired precision in the bonding parameters of the pyrazine system has not been attained because of the anomalous thermal behaviour of the atoms in the pyrazine ring. It thus seems apt to quote the final comments made by Wheatley (1957) in his study of pyrazine: 'if the main purpose of an X-ray analysis is the determination of accurate bond lengths, it would be better to work at low temperatures where the molecular motion is less important'.*

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* *Note added in proof:–* Details of the low-temperature ordered phase of *p*-terphenyl have now been published (Baudour, Delugeard & Cailleau, 1976), and they show that there are two types of molecule per cell, each of which retains a centre of symmetry, and the outer phenyl rings are twisted by either 16 or 25° out of the plane of the central ring. In pyrazinecarboxylic acid, the pyrazine ring was found to have a well-defined chair configuration (Takusagawa, Higuchi, Shimada, Tamura & Sasada, 1974). It therefore seems probable that the unusual thermal parameters of the pyrazine ring in 2,5-diphenylpyrazine are caused by a disordering between two different centrosymmetric chair conformations of the ring.

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