

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

O(1)—C(2)	1.444 (7)	C(6)—C(11)	1.529 (7)
O(1)—C(6)	1.427 (6)	O(7)—C(8)	1.426 (7)
C(2)—C(3)	1.502 (9)	C(8)—C(9)	1.528 (8)
C(3)—O(4)	1.443 (8)	C(9)—C(10)	1.496 (9)
O(4)—C(5)	1.437 (7)	C(10)—C(11)	1.498 (8)
C(5)—C(6)	1.519 (8)	C(10)—O(12)	1.203 (6)
C(6)—O(7)	1.417 (6)		
C(2)—O(1)—C(6)	112.2 (4)	C(5)—C(6)—C(11)	111.2 (5)
O(1)—C(2)—C(3)	109.9 (5)	O(7)—C(6)—C(11)	111.2 (4)
C(2)—C(3)—O(4)	111.1 (5)	C(6)—O(7)—C(8)	113.6 (4)
C(3)—O(4)—C(5)	108.8 (4)	O(7)—C(8)—C(9)	110.5 (5)
O(4)—C(5)—C(6)	112.3 (5)	C(8)—C(9)—C(10)	111.4 (5)
O(1)—C(6)—C(5)	110.7 (4)	C(9)—C(10)—C(11)	115.3 (4)
O(1)—C(6)—O(7)	110.9 (4)	C(9)—C(10)—O(12)	122.7 (5)
O(1)—C(6)—C(11)	105.7 (4)	C(11)—C(10)—O(12)	122.0 (5)
C(5)—C(6)—O(7)	107.3 (4)	C(6)—C(11)—C(10)	111.5 (5)

The dioxolane ring with $Q = 0.554 (6) \text{ \AA}$, $\theta = 176.1 (6)$ and $\varphi = 49 (8)^\circ$ has the 6C_3 chair conformation. The conformation of the whole molecule with the axial positions of the O(1) and O(7) atoms with regard to the pyranoid and dioxolane rings, respectively, as well as the mutual orientation of both chair rings [the dihedral angles C(2)—O(1)—C(6)—O(7) and O(1)—C(6)—O(7)—C(8) are $-65.5 (5)$ and $-56.5 (5)^\circ$, respectively] is a result of the presence of the anomeric and *exo*-anomeric effects (Kirby, 1983).

The carbonyl oxygen has the pseudoequatorial orientation with an O(12)—C(10)—C(11)—C(6)

torsion angle of $-139.3 (5)^\circ$. There are no significant intermolecular steric interactions.

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Structure of Pyridazine at 100 K

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(Received 11 January 1990; accepted 25 February 1991)

Abstract. $C_4H_4N_2$, $M_r = 80.09$, monoclinic, $P2_1/n$, $a = 3.7870 (6)$, $b = 10.7415 (29)$, $c = 9.721 (6) \text{ \AA}$, $\beta = 91.401 (27)^\circ$, $V = 395.32 \text{ \AA}^3$, $Z = 4$, $D_x = 1.346 \text{ Mg m}^{-3}$, $\bar{\lambda}(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 0.083 \text{ mm}^{-1}$, $F(000) = 168$, $T = 100 \text{ K}$, $R = 0.0495$ for 1732 unique observed reflections. The observed valence angles agree very closely with those measured for free pyridazine studied by combined analysis of electron diffraction, microwave and liquid-crystal NMR data, but there are significant differences in bond lengths, which can probably be attributed to crystal packing effects.

Introduction. We have recently developed the technique whereby gas-phase structural data (electron diffraction and rotational constants) can be combined with dipolar couplings obtained for solutions in liquid-crystal solvents (Cradock, Liescheski, Rankin & Robertson, 1988; Liescheski & Rankin, 1989). In most cases the resulting structures depend on no geometrical assumptions other than the molecular symmetry, and all the parameters can be refined: nevertheless, the precision far exceeds that obtainable by either electron diffraction, rotational spectroscopy or NMR spectroscopy alone. Indeed,

the precision exceeds that achieved by any single technique for molecules containing more than three or four atoms. However, that precision presents a problem: if the precision is unprecedented, the accuracy is by definition incomparable, in the strict sense of that word. The new technique can only attain its potential value when the results can be verified independently.

There are three ways to set about obtaining such corroborative data: firstly by *ab initio* calculations of the highest quality which, although unlikely to give absolute distances to the required accuracy, should be reliable in respect of relative distances; secondly by comparison of structural details for a series of compounds which are chemically – and by implication structurally – related; and thirdly by experimental studies of molecules both by the new combined analyses and by some other method. As there are no widely applicable techniques other than electron diffraction and rotational spectroscopy for gases and liquid-crystal NMR spectroscopy for molecules in solution, diffraction techniques applied to crystals provide the only realistic alternative. Moreover, in using crystallographic results for the purposes of comparison, great care must be taken both to obtain data of the highest quality and to establish that no significant molecular distortion occurs on crystallization.

We are attempting to validate the method of combined analysis in all three of these ways. In this paper we present the results of an X-ray crystallography study of pyridazine, which has recently been the subject of a structural analysis based on electron diffraction, microwave and liquid-crystal NMR data (Cradock, Purves & Rankin, 1990), and we present a comparison of the two sets of geometrical parameters.

Experimental. A sample of pyridazine (m.p. 266 K), sealed in a Pyrex capillary tube mounted in an insulating Tufnol pip, was cooled on a Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986). The entire sample was first frozen, then warmed to melt all but one seed crystal: slow cooling afforded a colourless cylindrical crystal, $0.46 \times 0.46 \times 0.77$ mm, which was maintained at $100.0(1)$ K for the duration of the experiment. STADI-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values of 25 reflections measured at $\pm\omega$ ($31 < 2\theta < 35^\circ$). For data collection, ω - 2θ scans using the learnt-profile method (Clegg, 1981), $2\theta_{\max} = 80^\circ$, $h - 6 \rightarrow 6$, $k 0 \rightarrow 16$, $l 0 \rightarrow 17$, no significant crystal movement or decay, no absorption correction, 2431 unique reflections, giving 1732 with $F > 6\sigma(F)$ for structure solution [by automatic direct methods (Sheldrick, 1986)]

Table 1. *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$U_{\text{iso}}(\text{Å}^2)$
N(1)	-0.05097 (19)	0.85367 (6)	0.38368 (6)	0.0212 (3)
N(2)	-0.12681 (19)	0.75374 (6)	0.30488 (7)	0.0212 (3)
C(3)	-0.05254 (21)	0.75721 (7)	0.17242 (7)	0.0201 (3)
C(4)	0.10718 (21)	0.85826 (7)	0.10871 (7)	0.0202 (3)
C(5)	0.18383 (21)	0.96010 (7)	0.18908 (7)	0.0200 (3)
C(6)	0.09752 (21)	0.95277 (7)	0.32697 (7)	0.0204 (3)
H(3)	-0.117 (4)	0.6827 (14)	0.1196 (15)	0.036 (3)
H(4)	0.156 (3)	0.8550 (10)	0.0151 (13)	0.025 (3)
H(5)	0.294 (3)	1.0328 (12)	0.1562 (13)	0.026 (3)
H(6)	0.153 (4)	1.0229 (14)	0.3896 (15)	0.037 (4)

Table 2. *Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses*

N(1)—N(2)	1.3456 (9)	C(4)—C(5)	1.3712 (11)
N(1)—C(6)	1.3298 (10)	C(4)—H(4)	0.933 (12)
N(2)—C(3)	1.3252 (10)	C(5)—H(6)	1.3897 (11)
C(3)—C(4)	1.3950 (11)	C(5)—H(5)	0.945 (13)
C(3)—H(3)	0.978 (15)	C(6)—H(6)	0.988 (15)
N(2)—N(1)—C(6)	119.28 (6)	C(5)—C(4)—H(4)	122.8 (8)
N(1)—N(2)—C(3)	118.90 (7)	C(4)—C(5)—C(6)	116.93 (7)
N(2)—C(3)—C(4)	123.91 (7)	C(4)—C(5)—H(5)	123.8 (8)
N(2)—C(3)—H(3)	115.5 (9)	C(6)—C(5)—H(3)	119.3 (8)
C(4)—C(3)—H(3)	120.6 (9)	N(1)—C(6)—C(5)	123.85 (7)
C(3)—C(4)—C(5)	117.12 (7)	N(1)—C(6)—H(6)	116.1 (9)
C(3)—C(4)—H(4)	120.1 (8)	C(5)—C(6)—H(6)	120.0 (9)
C(6)—N(1)—N(2)—C(3)	-0.30 (11)	C(3)—C(4)—C(5)—C(6)	0.48 (11)
N(2)—N(1)—C(6)—C(5)	-0.46 (11)	C(3)—C(4)—C(5)—H(5)	179.2 (10)
N(2)—N(1)—C(6)—H(6)	-178.7 (10)	H(4)—C(4)—C(5)—C(6)	-179.9 (9)
N(1)—N(2)—C(3)—C(4)	1.20 (11)	H(4)—C(4)—C(5)—H(5)	-1.2 (13)
N(1)—N(2)—C(3)—H(3)	-179.0 (10)	C(4)—C(5)—C(6)—N(1)	0.36 (11)
N(2)—C(3)—C(4)—C(5)	-1.27 (12)	C(4)—C(5)—C(6)—H(6)	178.6 (10)
N(2)—C(3)—C(4)—H(4)	179.1 (9)	H(5)—C(5)—C(6)—N(1)	-178.5 (9)
H(3)—C(3)—C(4)—C(5)	179.0 (10)	H(5)—C(5)—C(6)—H(6)	-0.3 (14)
H(3)—C(3)—C(4)—H(4)	-0.6 (14)		

and refinement [using full-matrix least squares on F (Sheldrick, 1976) with anisotropic thermal parameters for C and N atoms, isotropic for H atoms]. At final convergence, $R = 0.0495$, $wR = 0.0643$, $S = 1.139$ for 71 parameters, $(\Delta/\sigma)_{\max}$ in final cycle 0.02, max., min. residues in final ΔF synthesis 0.73, $-0.26 e \text{ Å}^{-3}$, respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000321F^2$ gave satisfactory agreement analyses. [A high-angle refinement, using only those data with $50 \leq 2\theta \leq 80^\circ$, showed no systematic differences in molecular parameters, suggesting that librational parameters are not significant. All results and discussion refer to the refinement using the complete data set.] Scattering factors were inlaid (Sheldrick, 1976); atom coordinates and isotropic thermal parameters are given in Table 1 while bond lengths, valence angles and torsion angles appear in Table 2.* The atom-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54031 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985); packing diagrams of the structure, produced by *PLUTO* (Motherwell, 1976) appear as Fig. 2. Molecular geometry calculations

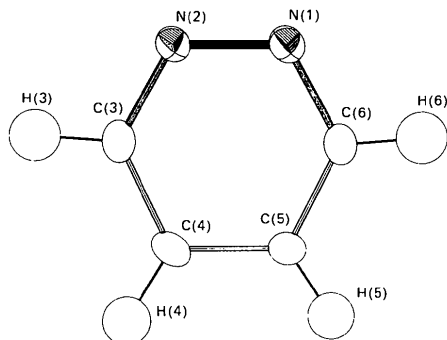


Fig. 1. A general view of the molecule showing the atom-numbering scheme: thermal ellipsoids are drawn at the 30% probability level.

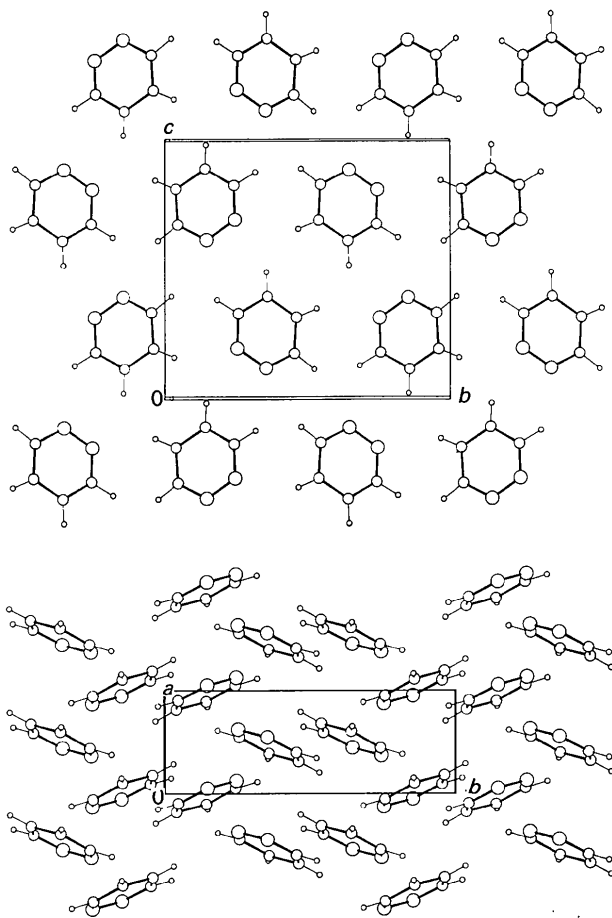


Fig. 2. Packing diagrams for the structure as viewed along the *a* and *c* directions.

Table 3. Comparison of gas-phase and crystal structures

Bond lengths in Å, angles in °.			
	Pyridazine Combined ED + MW + NMR*	Pyridazine Crystal X-ray†‡	Pyridazine-3,6- dicarboxylic acid Crystal X-ray†§
N—N	1.337 (2)	1.346 (1)	1.337 (6)
C—N	1.338 (2)	1.328 (3)	1.330 (4)
C(3)—C(4)	1.400 (1)	1.392 (3)	1.391 (5)
C(4)—C(5)	1.385 (2)	1.371 (1)	1.376 (9)
N—N—C	119.4 (1)	119.1 (2)	119.2 (5)
N—C—C	123.8 (1)	123.9 (1)	123.9 (6)
C—C—C	116.9 (1)	117.0 (1)	116.9 (8)
N—C—R¶	114.9 (2) (R=H)	115.8 (9) (R=H)	116.7 (6) (R=CO ₂ H)

* Cradock, Purves & Rankin (1990).

† Where parameters are related by molecular symmetry but are crystallographically independent, their mean and its e.s.d. are given.

‡ This work.

§ Abraham, Bremard, Lagrence & Sueur (1987).

¶ Exocyclic angles.

were performed using *CALC* (Gould & Taylor, 1985).

Discussion. The major geometrical parameters for pyridazine as a free molecule in the vapour or in solution (Cradock, Purves & Rankin, 1990) and in the crystalline phase, and for pyridazine-3,6-dicarboxylic acid monohydrate in the crystalline phase (Abraham, Bremard, Lagrence & Sueur, 1987) are compared in Table 3. The two sets of angles for pyridazine are in remarkably close agreement and indicate that the accuracy of each study is as good as the low estimated standard deviations suggest. The ring angles in the dicarboxylic acid derivative are almost identical to those in the parent compound: the exocyclic N—C—C angle is 1–2° larger than the corresponding N—C—H angle in pyridazine, but the substituents at C(3) and C(6) are nevertheless bent substantially towards nitrogen.

The differences between bond lengths are more significant. In the first place, the average of the six ring distances is 0.006 Å more in the isolated pyridazine molecule than in either of the crystal structures, a systematic difference between the r_{α}° nuclear positions and the centres of electron density located by X-ray diffraction. In the second place, bond lengths which are related by molecular symmetry but which are crystallographically independent differ by ca 0.005 Å. This provides us with a lower limit estimate of the effect of crystal packing, which is not sufficient to account for the third effect, an apparent shortening of the C—N and C(4)—C(5) bonds relative to the other ring bonds. This would imply that pyridazine is rather less aromatic in the solid phase

at 100 K than as a free molecule, delocalization of the π electrons being reduced by the local electric field which each molecule experiences in the crystal. It is interesting that the ring distances in the dicarboxylic acid derivative are intermediate between the two sets for pyridazine itself.

Overall, the crystal structure provides good evidence that the accuracy of the combined analysis method matches its precision insofar as angles are concerned. For bond lengths, it is not possible to tell from this study alone how accurate the results are. The errors are certainly not more than 0.01 Å, but as the e.s.d.'s are 0.002 Å or less, further comparative studies are needed.

We thank the SERC for funding towards the purchase of a diffractometer and Professor G. M. Sheldrick for helpful discussions.

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Structure of 1-(3-Methyl-1-butenyl)piperidin-2-one

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Abstract. $C_{10}H_{17}NO$, $M_r = 167.25$, monoclinic, $P2_1$, $a = 6.619(1)$, $b = 7.339(1)$, $c = 11.284(2)$ Å, $\beta = 103.63(1)^\circ$, $V = 532.72(14)$ Å³, $Z = 2$, $D_x = 1.043$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.06$ mm⁻¹, $F(000) = 184$, $T = 250$ K, final $R = 0.082$ for 838 observed reflections. Although disorder occurs in the six-membered lactam ring and the isopropyl group, the antiperiplanar conformation of the vinyl group relative to the amide system in the title compound is established. The crystal structure is stabilized by intermolecular hydrogen bonds between the vinylic β -H atom and the carbonyl O atom of the next molecule, with a distance of 2.5 Å.

Introduction. The pyramidality of a N atom in a conjugated system is a measure of its hybridization.

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For enamines various investigations based on photoelectron spectroscopy (PES) (Brown, 1976; Domelsmith, Houk & Rouge, 1977; Müller, Previdoli & Desilvestro 1981; Lafon, Gonbeau, Pfister-Guillouzo, Lasne, Ripoll & Denis, 1986), semi-empirical calculations (Müller & Brown, 1978; Saebö & Radom, 1982) and structural studies (Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, 1978) show a pyramidal N atom for most of the investigated compounds. The largest pyramidality was found in six-membered ring systems such as piperidine and morpholine.

Conformational analyses of the amide linkage of acyclic and cyclic systems (Kitano & Kuchitsu, 1974; Hoesterey, Neely & Worley, 1983; Norskov-Lauritsen, Bürgi, Hofmann & Schmidt, 1985; Treschanke & Rademacher, 1985; Marstokk, Möllendal, Samdal & Uggerud, 1989) have shown a