The Crystal and Molecular Structure of 3,6-Di-(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine

By Mino R. Caira, Robin G. F. Giles and Luigi R. Nassimbeni

Department of Physical Chemistry, University of Cape Town, South Africa

George M. Sheldrick

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

and Rita Grønbaek Hazell

Department of Chemistry, Aarhus University, DK-8000 C, Denmark

$C_{12}H_{10}N_6$ is triclinic with $a=8\cdot358$ (5), $b=8\cdot922$ (5), $c=8\cdot317$ (5) Å, $\alpha=111\cdot9$ (2)°, $\beta=90\cdot9$ (2)°, $\gamma=101\cdot5$ (2)°, space group $P\bar{1}$, $Z=2$. The structure was determined by direct methods in which an 'average structure' obtained from an E map was successfully refined with diffractometer data ($R=0\cdot043$ for 815 reflexions). The terminal pyridine rings are each inclined ($\sim20°$) to the tetrazine system which has a boat-like conformation. The pyridine N atoms are in the *anti* conformation. Torsion between adjacent rings is minimized by two intramolecular $N-H\cdots N$ hydrogen bonds.

Introduction

There are two features of the title compound, previously formulated as shown in Fig. 1 (Geldard & Lions, 1965), which have not been determined to date: firstly whether the molecule exists as the 1,2-dihydro form as shown in Fig. 1 or rather as the 1,4-dihydro-*s*-tetrazine, and secondly whether the pyridine N atoms are *syn* or *anti* with respect to one another. These ambiguities have been resolved for the compound in the crystalline form.

Experimental

The compound was prepared as described by Geldard & Lions (1965).

Microanalysis yielded the following results:

	%C	%H	%N
Found	60·3	4·2	35·2
Calculated for $C_{12}H_{10}N_6$	60·5	4·2	35·3

The crystals are prismatic needles, and a single crystal ($0\cdot12 \times 0\cdot16 \times 0\cdot24$ mm) was used for data collection. The lattice constants were obtained from least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation.

The crystal data are listed in Table 1.

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the $\omega-2\theta$ scan mode (scan width $1\cdot0°$ θ, scan speed $0\cdot03°$ θ s^{-1}). With graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å) 1039 reflexions up to
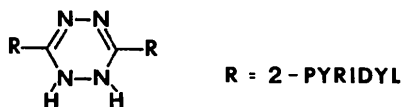

Fig. 1. Proposed structural formula of the compound (Geldard & Lions, 1965).

Table 1. *Crystal data*

$C_{12}H_{10}N_6$
M.W. 238·1
Space group $P\bar{1}$

$a=8\cdot358$ (5) Å	$D_m=1\cdot40$ g cm^{-3}
$b=8\cdot922$ (5)	$D_c=1\cdot41$ for $Z=2$
$c=8\cdot317$ (5)	$\mu(\text{Mo }K\alpha)=0\cdot56$ cm^{-1}
$\alpha=111\cdot9$ (2)°	$F(000)=248$
$\beta=90\cdot9$ (2)	
$\gamma=101\cdot5$ (2)	
$V=561\cdot05$ Å^3	

$2\theta=40°$ were measured. With the criterion $F_{rel}>1\cdot65\sigma(F_{rel})$ for an observed reflexion, 224 reflexions were omitted as unobserved. The remaining 815 reflexions were employed in the analysis. The data were corrected for Lorentz–polarization effects but not for absorption.

Solution and refinement of the structure

The structure was solved by the automatic centrosymmetric direct methods program incorporated in the XCSD system written for the Nova and Eclipse mini-computer with 32K 16-bit word core store (Sheldrick, 1976). Several E maps gave two shifted molecules, and attempts at refining either of the individual molecules or using the Patterson map to seek prominent vectors which would dictate appropriate shifts of the molecule, failed. The structure was solved by taking the 'average structure' of two shifted molecules given by an E map, as shown in Fig. 2 (Hazell & Hazell, 1975).

The first three cycles of full-matrix least-squares refinement were carried out with all heavy atoms treated as C atoms. Subsequent analysis of the isotropic temperature factors clearly differentiated the C and N atoms and a further three cycles of refinement, together with a difference map yielded the positions of

all the H atoms. The latter were finally refined in constrained positions (C–H = 1·08 Å, N–H = 1·00 ± 0·01 Å) and were given a common isotropic temperature factor which refined to 0·08 Å^2 (Sheldrick, 1976). Final refinement (four cycles) was carried out with the weighting scheme $w = (1/\sigma^2)F + gF^2$, where g refined to 0·00453 and gave the best analysis of variance* (Table 2). The final residuals were $R = 0·043$ and $R_w = 0·049$. The scattering factors employed were those of Cromer & Mann (1968).

The final atomic positions and thermal parameters are listed in Tables 3 and 4.

Description of the structure and discussion

Fig. 3 shows a perspective view of the molecule with atomic nomenclature. The hydrogen bonds are shown as broken lines. The molecule exists as the 1,4-dihydro form with the pyridine N atoms in the *anti* conformation.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31455 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Hydrogen atomic positions (calculated)* × 10^3

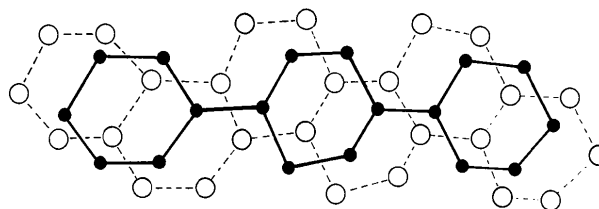|	x	y	z
H(1)	30	829	850
H(2)	−119	556	651
H(5)	346	591	1032
H(6)	270	848	1040
H(8)	5	147	636
H(11)	431	102	925
H(14)	261	−243	389
H(15)	456	−423	281
H(16)	704	−382	472
H(17)	741	−173	770

Fig. 2. Projection on the least-squares plane through peaks in the E map. The two shifted molecules are shown as open circles and the 'average structure' as full circles.

Table 2. *Analysis of variance*

(a) By parity groups

	ggg	ugg	gug	uug	ggu	ugu	guu	uuu	All
N	104	100	95	108	95	106	101	106	815
V	40	40	36	34	33	41	32	41	37

(b) As a function of sin θ

sin θ	0·00 − 0·16	− 0·20	− 0·22	− 0·25	− 0·27	− 0·28	− 0·30	− 0·32	− 0·33	− 0·35
N	91	90	63	104	91	53	88	108	57	70
V	40	37	35	41	35	33	35	36	39	39

(c) As a function of $\sqrt{F/F_{max}}$

$\sqrt{F/F_{max}}$	0·00 − 0·18	− 0·20	− 0·23	− 0·26	− 0·28	− 0·31	− 0·34	− 0·39	− 0·46	− 1·00
N	90	79	91	81	67	95	74	77	81	80
V	52	48	41	36	39	31	32	29	23	31

Table 3. *Fractional atomic positions* (× 10^4) *and their e.s.d.'s for non-hydrogen atoms*

Anisotropic temperature factors are of the form

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^3\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	669 (4)	7184 (5)	8475 (5)	53 (3)	49 (3)	73 (3)	11 (2)	2 (2)	24 (2)
C(2)	−171 (4)	5644 (5)	7381 (5)	56 (3)	54 (3)	61 (3)	17 (2)	−9 (2)	25 (2)
N(3)	194 (4)	4227 (3)	7321 (4)	51 (2)	50 (2)	52 (2)	14 (2)	−11 (1)	14 (2)
C(4)	1472 (4)	4345 (4)	8377 (4)	36 (2)	42 (2)	37 (2)	14 (2)	−1 (2)	11 (2)
C(5)	2416 (4)	5856 (4)	9501 (5)	48 (2)	45 (3)	52 (2)	6 (2)	−10 (2)	10 (2)
C(6)	1994 (5)	7285 (4)	9540 (5)	54 (3)	42 (3)	68 (3)	4 (2)	−1 (2)	12 (2)
C(7)	1821 (4)	2763 (4)	8276 (4)	38 (2)	42 (2)	34 (2)	8 (2)	−3 (2)	11 (2)
N(8)	805 (3)	1271 (3)	7152 (4)	40 (2)	42 (2)	46 (2)	11 (2)	−9 (2)	9 (2)
N(9)	1669 (3)	64 (3)	6191 (4)	43 (2)	39 (2)	46 (2)	12 (1)	−7 (2)	12 (2)
C(10)	2885 (4)	23 (4)	7130 (4)	46 (2)	41 (2)	37 (2)	13 (2)	−5 (2)	14 (2)
N(11)	3196 (3)	1089 (4)	8886 (4)	56 (2)	51 (2)	41 (2)	21 (2)	−9 (1)	12 (2)
N(12)	3075 (3)	2746 (3)	9177 (3)	48 (2)	47 (2)	39 (2)	15 (1)	−8 (2)	10 (1)
C(13)	3971 (4)	−1103 (4)	6402 (4)	40 (2)	39 (2)	42 (2)	6 (2)	−5 (2)	17 (2)
C(14)	3681 (4)	−2293 (4)	4711 (4)	43 (2)	46 (2)	49 (3)	10 (2)	−7 (2)	15 (2)
C(15)	4770 (4)	−3285 (4)	4110 (5)	56 (2)	51 (2)	51 (2)	15 (2)	−1 (2)	16 (2)
C(16)	6148 (4)	−3077 (5)	5175 (5)	54 (3)	66 (3)	55 (3)	22 (2)	8 (2)	26 (2)
C(17)	6345 (5)	−1884 (5)	6851 (5)	53 (3)	74 (3)	53 (3)	31 (2)	−3 (2)	23 (2)
N(18)	5295 (4)	−913 (4)	7465 (4)	50 (2)	64 (2)	47 (2)	24 (2)	−12 (2)	14 (2)

Table 5. *Intramolecular bond lengths* (Å)
(*all e.s.d.'s* 0·01 Å)

C(1)—C(2)	1·37	N(11)–N(12)	1·43
C(2)—N(3)	1·34	N(12)–C(7)	1·28
N(3)–C(4)	1·33	C(10)–C(13)	1·46
C(4)—C(5)	1·39	C(13)–C(14)	1·39
C(5)—C(6)	1·38	C(14)–C(15)	1·37
C(6)—C(1)	1·37	C(15)–C(16)	1·38
C(4)—C(7)	1·47	C(16)–C(17)	1·38
C(7)—N(8)	1·40	C(17)–N(18)	1·33
N(8)—N(9)	1·42	N(18)–C(13)	1·35
N(9)—C(10)	1·29	N(8)—H(8)	0·99
C(10)–N(11)	1·40	N(11)–H(11)	0·99

Table 6. *Intramolecular bond angles* (°)
(*all e.s.d.'s* 0·1°)

C(6)—C(1)–C(2)	117·9	N(9)—C(10)–N(11)	119·9
C(1)—C(2)–N(3)	123·9	C(10)–N(11)–N(12)	113·1
C(2)—N(3)–C(4)	117·4	N(11)–N(12)–C(7)	111·4
N(3)—C(4)–C(5)	122·6	N(9)—C(10)–C(13)	121·4
C(4)—C(5)–C(6)	118·4	N(11)–C(10)–C(13)	118·7
C(5)—C(6)–C(1)	119·8	N(18)–C(13)–C(10)	115·9
N(3)—C(4)–C(7)	115·6	C(10)–C(13)–C(14)	122·6
C(5)—C(4)–C(7)	121·9	N(18)–C(13)–C(14)	121·6
C(4)—C(7)–N(8)	119·6	C(13)–C(14)–C(15)	119·2
C(4)—C(7)–N(12)	120·2	C(14)–C(15)–C(16)	119·7
N(12)–C(7)–N(8)	120·1	C(15)–C(16)–C(17)	118·0
C(7)—N(8)–N(9)	113·9	C(16)–C(17)–N(18)	123·3
N(8)—N(9)–C(10)	111·9	C(17)–N(18)–C(13)	118·3

Table 7. *Relevant torsion angles* (°)

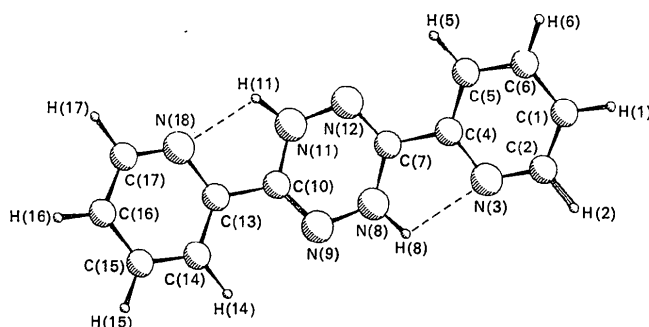| N(8)—N(9)—C(10)–N(11)	0·0
N(9)—C(10)–N(11)–N(12)	−44·0
C(10)–N(11)–N(12)–C(7)	43·0
N(8)—C(7)—N(12)–N(11)	−1·6
N(12)–C(7)—N(8)—N(9)	−41·9
C(7)—N(8)—N(9)—C(10)	41·1
N(9)—C(10)–C(13)–C(14)	−5·9
C(5)—C(4)—C(7)—N(12)	−3·5

Fig. 3. Molecular structure of the compound with atomic nomenclature.
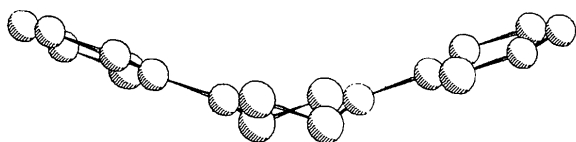

Fig. 4. The molecule viewed edge-on. Hydrogen atoms have been omitted for clarity.

Tables 5 and 6 list the bond lengths and angles, and Table 7 the torsion angles of the central ring, showing that it has a boat-like conformation. The torsion angles about C(4)–C(7) and C(10)–C(13) (−3·5°, −5·9°, Table 7) show that there is little twist between adjacent rings. This is attributed to the two intramolecular hydrogen bonds which are detailed in Table 8. In Fig. 4 the molecule is viewed edge-on illustrating that the three rings are inclined to one another. The angles between their least-squares planes are given in Table 9. There are no significant short intermolecular contacts.

Table 8. *Hydrogen bonds* (*distances in* Å, *angles in degrees*)

N(3)···N(8)	2·74	N(3)····H(8)—N(8)	107·9
N(3)···H(8)	2·27		
N(11)··N(18)	2·72	N(18)···H(11)–N(11)	116·1
N(18)··H(11)	2·13		

Table 9. *Least-squares planes and atom deviations* (Å)

The equations of the planes are expressed in direct space as $PI + QJ + RK = S$. The atoms listed are those included in the plane calculation.

Plane I: $-5·2308X - 1·6961Y + 6·5675Z = 3·9886$

C(1)	0·009	C(4)	0·006
C(2)	−0·009	C(5)	−0·006
N(3)	0·001	C(6)	−0·002

Plane II: $4·7825X + 4·4038Y - 6·1823Z = -3·1673$

C(7)	0·138	C(10)	0·149
N(8)	−0·310	N(11)	−0·318
N(9)	0·166	N(12)	0·174

Plane III: $3·2233X + 6·8520Y - 5·3366Z = -2·8982$

C(13)	0·006	C(16)	0·010
C(14)	0·000	C(17)	−0·004
C(15)	−0·008	N(18)	−0·005

Acute angles between normals to planes (°)

Planes I and II	20·1
Planes I and III	41·2
Planes II and III	21·3

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
GELDARD, J. F. & LIONS, F. (1965). *J. Org. Chem.* **30**, 318–319.
HAZELL, R. G. & HAZELL, A. C. (1975). *Acta Cryst.* A**31**, S 19.
SHELDRICK, G. M. (1976). To be published.