Synthesis, characterisation and crystal structure of 1,2-bis(6-methylpyridin-2-yl)ethene-1,2-diol

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From the condensation reaction of (6-methylpyridin-2-yl)methanol and pyridine-2-carbaldehyde at 130 °C without catalyst or solvent was isolated an unexpected compound 1,2-bis(6-methylpyridin-2-yl)ethene-1,2-diol, in crystal form. The new compound was characterised by mass spectroscopy, IR, ^{1}H NMR, UV-Vis and single crystal X-ray diffraction showing that it is a symmetrical molecule with two intramolecular hydrogen bonds. The molecular and crystalline structure of 1,2-bis(6-methylpyridin-2-yl)ethene-1,2-diol indicated that the molecule crystallised in a monoclinic crystal system and belongs to $P2_1/c$ space group with two molecules per unit cell. Within the accuracy of the analysis the molecule is planar and there are two moderate intramolecular O–H···N hydrogen bonds. We think that the presence of two moderate intramolecular hydrogen bonds gives stabilisation to the crystal structure, making isolation of a single crystal form possible.

Keywords: 1,2-bis(6-methylpyridin-2-yl)ethene-1,2-diol, (6-methylpyridin-2-yl)methanol derivative, crystal structure, tautomer, ethenediol

From the benzoin condensation of pyridine-2-carbaldehyde Buehler *et al.*[1] reported that instead of the expected benzoin (2-hydroxy[1,2-di(pyridin-2-yl)]ethane-1-one), 1,2-di(pyridin-2-yl)ethene-1,2-diol was produced. The authors proposed that chelation (one type of hydrogen bond) is an important factor in increasing the stability of the three enediols studied, (Fig. 1). They observed a decreasing order of stability as follows: 1,2-di(pyridin-2-yl)ethene-1,2-diol (two chelate rings) > 1-phenyl-2-(pyridin-2-yl)ethene-1,2-diol (one chelate ring) > 1-phenyl-2-(pyridin-4-yl)ethene1,2-diol (no chelate ring).

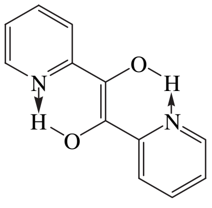


Fig. 1 *Trans*-chelated structure of 1,2-di(pyridin-2-yl)ethene-1,2-diol.

Furthermore, the benzoin condensation of quinoline-2-carbaldehyde in the presence of KCN and pyridine also does not give the expected benzoin product,[2] but instead the stable 1,2-di(quinolin-2-yl)ethane-1,2-diol (a) and its reduction product 1,2-di(quinolin-2-yl)ethene-1,2-diol (b) were obtained, (Fig. 2). Compound (a) was assigned the *trans*-chelated structure from its physical and chemical properties, and its stability was attributed to conjugation and steric hindrance. Additional support for the chelated structure (two intramolecular hydrogen bonds between N···H–O) was deduced by IR spectroscopy because the absorption band for the hydroxyl group was missing.

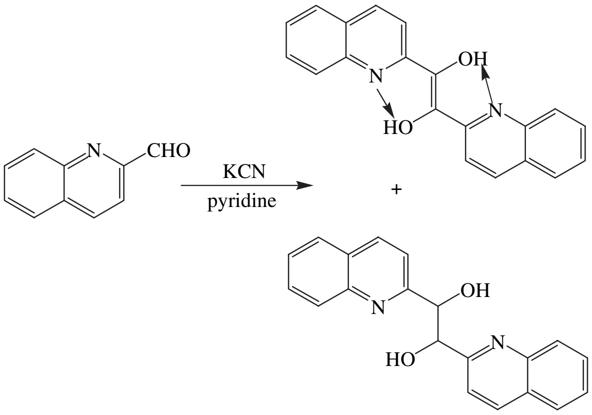
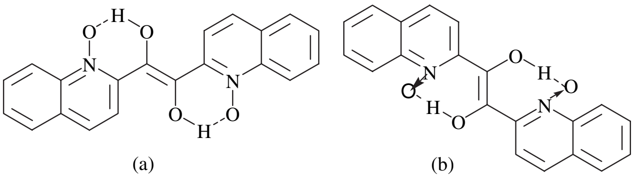


Fig. 2 Benzoin condensation of quinolin-2-carbaldehyde.

Another similar study was made by Buehler *et al.*[3] where they showed that 6-methylquinoline-2-carbaldehyde gave 1,2-bis (6-methylquinoline-2-yl)ethene-1,2-diol, 1,2-bis(-(6-methylquinoline-2-yl)ethane-1,2-diol and 6-methylquinoline-2-carboxylic acid. The enediol was also assigned a *trans*-chelated structure. In order to study the influence of chelation on the stability of enediols Buehler *et al.*[4] during the benzoin condensation of quinolin-2-aldehyde *N*-oxide found that the oxygen atom did not prevent the formation of 1,2-di(quinolin-2-yl)ethane-1,2-diol *N,N'*-dioxide. The probable structures proposed for the enediols are *trans*-configurations which may be written as shown in (Fig. 3). Buehler[5] has suggested that for the stability of hindered enediols two factors are responsible: (1) the system is highly conjugated, the two rings being in conjugation through the double bond of the enediol group and (2) the substituents in the *ortho* positions are of sufficient size to interfere with the normal reactivity of the hydroxyl groups.



(a) (b)

Fig. 3 The probable *trans*-configuration for the 1,2-di(quinolin-2-yl)ethene-1,2-diol N,N'-dioxide with six-members (a) or seven-members (b) chelate rings.

In recent studies to obtain styrylpyridines,[6-8] it was found that the condensation reaction of 2-methylpyridine with pyridine-2-carbaldehyde without catalyst or solvent at 140 °C, produced the expected compound 1,2-di(pyridin-2-yl) ethene and also the enediol (1,2-di(pyridin-2-yl)ethane-1,2-diol), the latter in the form of an orange crystalline solid.

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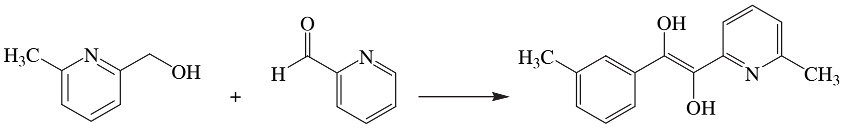

Fig. 4 Condensation reaction of (6-methylpyridin-2-yl)methanol and pyridine-2-carbaldehyde.

The physical properties and crystal structure of the enediol agreed with those previously reported[9] by Ashida *et al.* in 1965. The authors showed that the molecule possesses a center of symmetry with a *trans*-configuration around the central C=C double bond and had two intramolecular O–H···N hydrogen bonds.

We now report the synthesis, characterisation and molecular structure of a new enediol 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol, which was obtained when the (6-methylpyridin-2-yl)methanol was reacted with the aromaticaldehyde without catalyst or solvent at 140 °C.

The formation of the title compound opens the opportunity for a new path of study for the synthesis of very stable enediols and it is also important because, to the best of our knowledge, the crystal structure of the title compound has not been reported.

Experimental

General procedure

IR spectra were recorded on a Nicolet Magna model 750 FT-IR spectrophotometer, using KBr compressed tablets. The ^{1}H NMR spectrum was obtained on a Jeol Eclipse 400 MHz NMR-spectrometer in d_6-DMSO. The electron impact (EI) ionisation mass spectra was acquired on a JEOL JMS-AX505 HA mass spectrometer operated in the positive ion mode. The acquisition conditions were: ion source temperature 230 °C, ionisation energy of 70 eV, emission current of 0. 14 μA and ionisation current of 100 mA. Melting points were measured using a Fisher-Johns (0–300 °C) apparatus and are uncorrected. The UV-Vis was recorded on a Beckman DU 7500 spectrophotometer.

The crystal structure was determined using a Siemens P4/Pc Diffractometer with a graphite monochromator and a Mo-Kα radiation ($\lambda = 0.71073$ Å).

The 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol was synthesised according to the scheme in Fig. 4.

(6-Methylpyridin-2-yl)methanol (4.13 mmol) and 4.13 mmol of pyridine-2-carbaldehyde were heated at 140 °C. The mixture was magnetically stirred during 40 h, in this time the mixture turned oily and developed a brown colour. The reaction mixture was treated with 400 ml of 2N NaOH solution to precipitate the product. The brown precipitate was removed by vacuum filtration and washed with water until the pH was neutral. By crystallisation from cyclohexene, orange crystals were formed with a yield 28.10 %. The melting point was 179–180 °C.

Results and discussion

The characteristic IR bands[10,11] for the title compound were: a band at 3449 cm^{-1} assigned to νO–H weak absorption due to an intramolecular hydrogen bond between O–H···N, the low intensity band at 1649 cm^{-1} was assigned to –C=C– stretching vibration double bond, two absorption peaks at 1590 and 1569 cm^{-1} assigned to –C=N–and –C=C– of pyridine rings, the band at 1226 cm^{-1} assigned to νC–O and the absorption peak at 1180 cm^{-1} to deformation vibration of O–H groups. ^{1}H NMR spectrum analysis showed a very symmetric molecule with a singlet at 2.5 ppm assigned to three protons of the $-CH_3$ in the pyridine ring 6-position. The signals for the three protons of the pyridine ring were: a doublet between 7.26 and 7.24 with J= 7.68 Hz, another doublet at 7.62–7.60 with J= 8.08 Hz and multiplet between 8.02–7.87 ppm with J= 8.08, and 7.68 Hz and the signal for the proton O–H was missing. The mass spectrum gave the molecular ion 242 *m/z* (M$^+$), which corresponded to the theoretical molecular weight of 242 for the 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol. The ultraviolet absorption spectrum of title compound was very similar to other reports,[3,12,13] that support the presence of the ethylenic double bond conjugated with ring systems. The spectrum showed three λ_{max} at 246, 282, 383 nm.

From the X-ray results the molecular structure of the title compound is shown in Fig. 5. From the molecular structure one can observe that the pyridine ring is located trans to the other pyridine ring relative to the double bond.

The crystal data and pertinent details of the experimental conditions are summarised in Table 1. The bond lengths and angles for 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol are listed in Table 2. Since the crystal belongs to space group $P2_1/c$ and the number of molecules in a unit cell are two, each molecule has 2/m symmetry with a mirror plane coinciding

Table 1 Crystallographic data of the 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol

Empirical formula	$C_{14}H_{14}N_2O_2$
Colour, habit	Colourless, prismatic
Crystal size	0.54 × 0.36 × 0.02 mm^3
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.2157(16)
b(Å)	13.451(2)
c (Å)	6.6686(14)
α (°)	90
β (°)	110.327(19)
γ (°)	90
Volume Å^3	606.9(2)
Z	2
Formula weight	242.27
Density (calc.)	1.326 g cm^{-3}
Absorption coefficient	0.090 mm^{-1}
F(000)	256
Diffractometer/scan used	Siemens P4 (PC) / ω
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Monochromator	Highly oriented graphite crystal
2θ Range	6.74 – 59.98°
Scan type	ω
Scan speed	Variable speed, 3 to 60°. mn^{-1} in ω
Index ranges	$-9 \leq h \leq 10, -1 \leq k \leq 18, -9 \leq l \leq 1$
Reflections collected	2329
Independent reflections [(a)]	1760 (R_{int} = 8.18 %)
Reflections with $F_o > 4\ \sigma(F_o)$	589
$< I / \sigma(I) >$ (all data)	4.64
Absorption correction	none
Software used	SHELXTL 5.03 and SHELX97
Wilson's statistics	$<\vert E^2 - 1\vert> = 1.042$
Solution	Direct methods and difference Fourier maps
Refinement method	Full matrix least-squares
Extinction correction	$x = 0.007(10)$ where $F_c^* = kF_c[1 + 0.001\ xF_c^2\lambda^3/\mathrm{Sin}(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w = [\sigma^2 (F_o^2) + (0.09640P)^2 + 0\ P]^{-1}$ $P = (\max [F_o^2,0] + 2\ F_c^2) / 3$
Parameters refined	83
Final R indices ($I > 2\ \sigma(I)$)	R_1 = 6.93 %, wR_2 = 17.19 %
Final R indices (all data)	R_1 = 20.71 %, wR_2 = 23.31 %
Goodness-of-fit	0.921
Largest and mean Δ/σ	0.000,0.000
Data-to-parameters ratio	1760/ 83
Largest difference peak / hole	0.195 e Å^{-3} / –0.229 e sÅ^{-3}

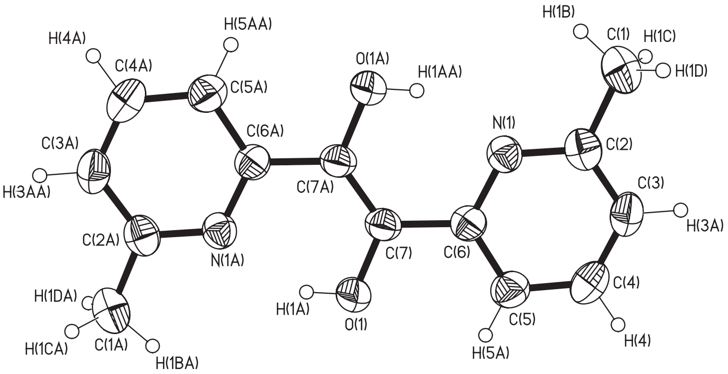

Fig. 5 The molecular structure of 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol, thermal ellipsoids is drawn at the 50 % probability level.

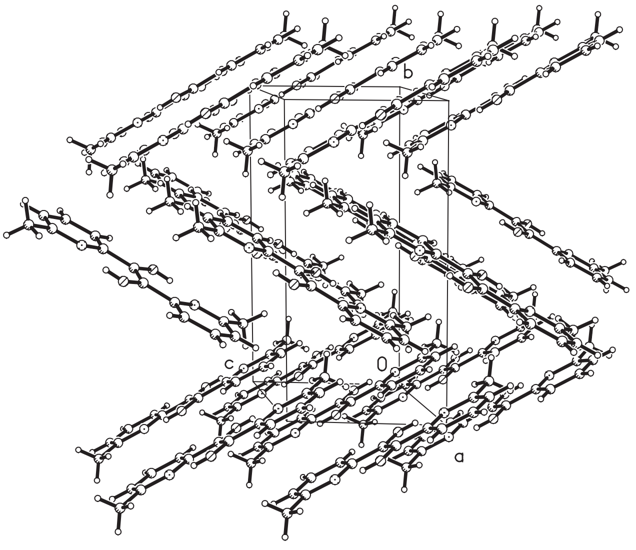

Fig. 6 Crystal package view for the 1,2-bis(6-methylpyridin-2-yl)]ethene-1,2-diol.

Table 2 Bond lengths (Å) and bond angles [°] for 1,2-bis (6-methylpyridin-2-yl)]ethene-1,2-diol

Bond	Length/Å	Bond	Angles/°
N(1)–C(2)	1.341(4)	C(2)–N(1)–C(6)	119.7(3)
N(1)–C(6)	1.352(3)	N(1)–C(2)–C(3)	121.1(3)
O(1)–C(7)	1.359(3)	N(1)–C(2)–C(1)	116.9(3)
C(1)–C(2)	1.489(4)	C(3)–C(2)–C(1)	122.0(3)
C(2)–C(3)	1.386(4)	C(4)–C(3)–C(2)	119.3(3)
C(3)–C(4)	1.365(4)	C(3)–C(4)–C(5)	121.0(3)
C(4)–C(5)	1.382(4)	C(4)–C(5)–C(6)	117.1(3)
C(5)–C(6)	1.405(4)	N(1)–C(6)–C(5)	121.7(3)
C(6)–C(7)	1.464(4)	N(1)–C(6)–C(7)	117.2(2)
C(7)–C(7)	1.356(5)	C(5)–C(6)–C(7)	121.0(3)
		C(7)^a–C(7)–O(1)	122.8(3)
		C(7)^a–C(7)–C(6)	123.8(3)
		O(1)–C(7)–C(6)	113.4(2)

Symmetry transformations used to generate equivalent atoms.
^{a} $-x+1, -y, -z+1$

with the molecular plane. The twofold axis is perpendicular to the molecular plane, passing across the inversion centre located in the middle C(7)–C(7A) bond.

There are two intramolecular hydrogen bonds between each protonated oxygen of the enediol and the nitrogen atom of the pyridine ring O–H···N (O···N 2.580(3)Å, (O(1)–H(1A)···N(1) 148.89 °) where the N···H distance is 1.854 Å and O–H is 0.820 Å helping the enediol crystal formation. The intramolecular hydrogen bond distance was shorter than a typical O–H···N hydrogen bond (2.8 Å). The hydrogen bonds complete an almost coplanar six member ring and from Fig. 6 it can be appreciated that the molecules are planar showing parallel crystal packing. The crystal structure gives no indication, either of interaction between the individual stacks or of intermolecular hydrogen bridging.

The molecular structure shows a much larger than normal double bond distance (1.336±0.005Å) for the C(7)–C(7A) bond, length 1.356(5)Å. The C(7)–O(1) bond distance 1.359(3)Å was shorter than a typical single bond (1.43Å). The difference between the expected bond lengths may be explained by delocalisation of the π electrons through the whole molecule.

The C–C bond lengths vary between 1.365(4) and 1.464(4)Å and C–N between 1.341(4)Å and 1.352(3)Å, as can be seen from Table 2, indicating the existence of the π delocalisation in the rings across of double bond. The typical double bond values for C–C aromatic and C–N pyridine ring are 1.394±0.005Å and 1.339±0.005Å) respectively. The C(6)–C(7) 1.464 Å and C(7)–C(7A) 1.356 Å are in good agreement with those observed in conjugated systems.[14] The conclusion

Table 3 Mean plans in the molecule obtained by the least-squares method, rms, mean plane deviations (Å) and angles between defined planes(°)

Plane	Atoms	rms/Å	Deviations	Angles between planes/°			
				1	2	3	4
1	N(1),C(2),C(3),C(4),C(5),C(6)	0.0013	C(1)0.0245,C(7)–0.0456,H(1A)–0.0640				
2	N(1A),C(2A),C(3A),C(4A), C(5A), C(6A)	0.0013	C(1A) –0.0245, C(7A) 0.0456, H(1AA) 0.0641	0.0			
3	N(1),C(2),(3),C(4),C(5),C(6),C(7), C(7A),(1A),C(2A),C(3A),C(4A), C(5A),C(6A)	0.0185	C(1) 0.0170, C(1A) –0.0170, O(1) 0.0359, O(1A) –0.0359, (1A) 0.0218, H(1BA) –0.0218	1.2	1.2		
4	C(6), C(7), C(7A), O(1A), H(1AA), N(1)	0.0026	O(1) 0.0052, C(6A) 0.0091, C(5) –0.0563	2.5	2.5	1.4	
5	C(6A),C(7A),C(7),O(1)H(1A), N(1A)	0.0040	O(1A)–0.0157, C(5A) 0.548, C(6) –0.186	2.5	2.5	1.4	0.4

from the data is that within the accuracy of the analysis the molecule is planar. Table 3 shows several selected mean planes with their rms deviation from planarity, the bonded atoms distances deviations from the defined mean planes, calculated by least-squares method.

The analytical characterisation results indicated that the compound was the 1,2-bis(6-methylpyridin-2-yl)]ethene-1, 2-diol. Although the broad band for chelated hydrogen bond[10] at 3200–2500 cm^{-1} was not observed, the presence of the intramolecular hydrogen bond indicated by IR gave sufficient stability for the molecule to be isolated. This result was also corroborated by hydrogen bond distance determination by X-ray showing that intramolecular hydrogen bond was in the moderate category.[15] According to the categories defined by Jeffrey[16] hydrogen bonds may be called moderate because of the values found by X-ray analysis for the X…A 2.5–3.2 (Å) and the bond angle >130 (°).

Supplementary material

Crystallographic data (excluding structure factors) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 253709. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road. Cambridge CB2 IEZ, UK, (fax: +44-(0)1223-336033, E-mail: deposit@ccdc.cam.ac.uk).

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References

1 C.A. Buehler, J.W. Addleburg and D.M. Glenn, *J. Org. Chem.*, 1955, **20**, 1350.
2 C.A. Buehler and J.O. Harris, *J. Am. Chem. Soc.*, 1950, **72**, 5051.
3 C.A. Buehler and S.P. Edwards, *J. Am. Chem. Soc.*, 1950, **72**, 5015.
4 C.A. Buehler, A. Lloyd, L.A., Walker and P. García, *J. Org. Chem.*, 1961, **25**, 1410.
5 C.A. Buehler, *Chem. Rev*. 1964, **64**, 7.
6 Morales (Master Thesis) Reacciones de condensación de derivados de metilpiridinas con aldehídos aromáticos, Benemérita Universidad Autónoma de Puebla, México, 2000.
7 M.J. Percino, V.M. Chapela, M. Salmon, G. Espinoza-Pérez, A. M, Herrera and A. Flores, *J. Chem.Crys.*, 1997, **27**, 9.
8 V.M. Chapela, M.J. Percino and C. Rodríguez de Barbarín, *J. Chem. Cryst* 2003, **33**, 77.
9 T. Ashida, S. Hirokawa and Y. Okaya, *Acta Cryst*. 1965, **18**, 122
10 L.J. Bellamy, *The infra-red Spectra of Complex Molecules*, Third Edition, John Wiley and Sons, Inc., New York, 1975.
11 K. Nakanishi and P.H Solomon, *Infrared absorption spectroscopy*, 2nd edn, Holden-day, Inc., Oakland,1977.
12 Y. Hirschberg and F. Bergmann, *J. Am. Chem. Soc*., 1950, **72**, 5118.
13 J. Norman, *J. Am. Chem. Soc*., 1945, **67**, 1956.
14 F.H. Allen, I. Kennard, G.D. Watson, L. Brammer, A.G. Orpen and R.Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1-9
15 T. Steiner *Angew.Chem. Int*. Ed. Eng. 2002, **41**, 48.
16 G.A. Jeffrey, *An Introduction to hydrogen bonding*, Oxford University Press, 1997.