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3-Methyl-1*H*-quinoxalin-2-one

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In the crystal structure of the title compound, $C_9H_7N_2O$, one-dimensional chains of planarmolecules are interlocked at a dihedral angle of about 30° and display weak aromatic interactions, consistent with π–π stacking. The distance between quinoxaline rings in two neighbouring planes is 3.972 (6) Å. Within a chain, molecular dimers, which are held together by a pair of strong intermolecular $N—H\cdots O$ hydrogen-bonding interactions at a distance of 2.792 (4) Å, are linked by weak ditopic hydrogen-bonding interactions $C—H\cdots N$ at a distance of 3.560 (6) Å.

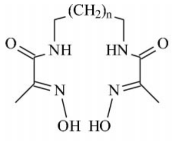
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.058
wR factor = 0.167
Data-to-parameter ratio = 22.2

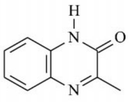
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The synthesis and structures of a family of novel tetradentate oxime/amide ligands that show a high affinity for divalent transition metal ions, (I) (n = 0, 1, 2), have been reported recently in the literature (Duda *et al.*, 1997; Fritsky *et al.*, 1999). The key and final step of the synthetic route to compounds (I) involves condensation of 2-hydroxyiminopropionic acid ethyl ester (ethylpyruvate oxime, epo) with the appropriate diamine. Following a procedure similar to that of Fritsky *et al.* (1999), we have successfully synthesized ligands (I) with three aliphatic spacers with a particular goal of studying the thermodynamics of their protonation and metallation reactions in aqueous solutions. However, all our attempts to link two epo moieties with an aromatic spacer (aromatic diamine) have failed, despite the use of a range of solvents, catalysts, and reaction conditions. No identifiable products were recovered with such reactants as 1,3- and 1,4-diaminobenzene, while the reaction with 1,2-diaminobenzene dihydrochloride in tetrahydrofuran (THF), toluene, and methanol yielded only 3-methyl-1*H*-quinoxalin-2-one, (II), which was characterized by IR and NMR spectroscopy. The molecular and crystal structure of (II) was definitively established from a single-crystal X-ray diffraction experiment, the results of which are reported in this paper.



(I)



(II)

In our view, the formation of (II) reflects the effect of steric hindrance on the condensation reaction of epo with 1,2-diaminobenzene. Specifically, once the first amino group has reacted with epo, the adjacent position of the second amino group in 1,2-diaminobenzene is probably too crowded to react

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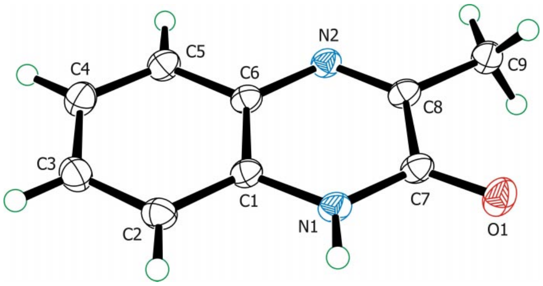


Figure 1
An *ORTEP*-3 (Farrugia, 1997) view of the molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level.

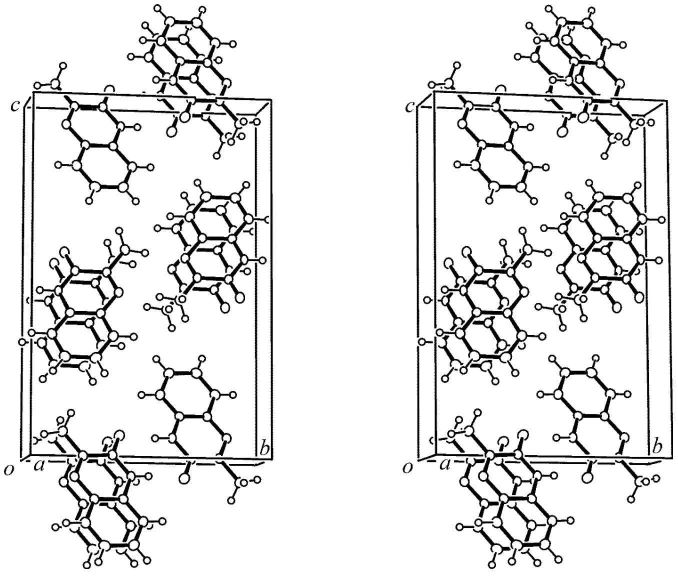
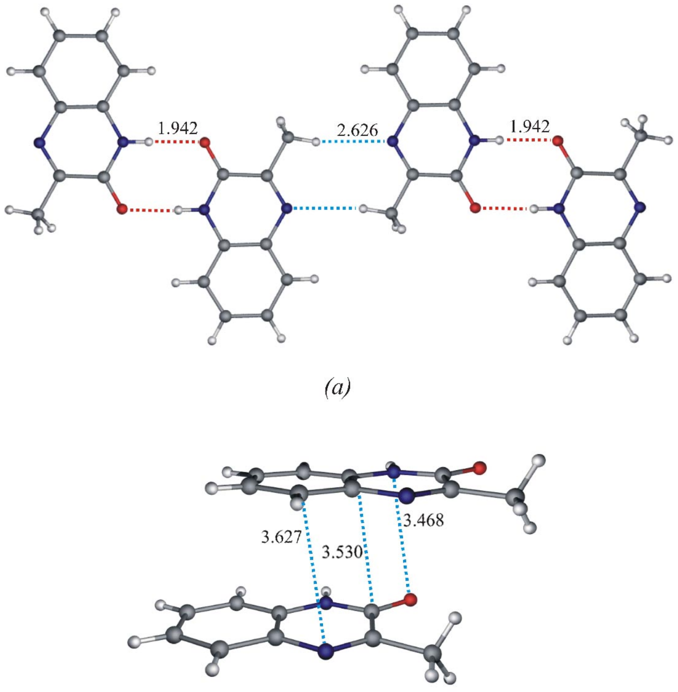


Figure 2
Packing diagram (cross-eye stereoview) for the crystal structure of (II).

with the second equivalent of epo, leading to a monoamide as the primary product. Thereafter, in the process of separation and recrystallization from water, the monosubstituted amide undergoes hydrolysis, losing the oxime group. This is then followed by an intramolecular condensation, which results in ring closure and formation of heterocycle (II).

The molecular structure of (II) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The bicyclic structure is clearly planar, consistent with sp^2 hybridization of N1 and N2 as well as the two outer C atoms of the ring. This suggests that the second amide-containing ring is fully conjugated with the benzene ring in (II). In the crystal packing diagram (Fig. 2), two sets of one-dimensional chains are clearly interlocked at a dihedral angle of about 30° and display weak aromatic interactions that are suggestive of π–π stacking (Fig. 3*b*). The distance between quinoxaline rings in two neighbouring planes is 3.972 (6) Å. The chains of molecules (Fig. 3*a*) are assembled from strongly associated dimers, which are held together by a pair of intermolecular hydrogen bonds, $N1—H\cdots O1^{i}$ at a distance of 2.792 (2) Å. The dimers are, in turn, linked by weak ditopic intermolecular hydrogen-bonding interactions, $C9—H\cdots N2^{ii}$ at a distance of 3.560 (6) Å; details are given in Table 2.



(*a*)

(*b*)

Figure 3
(*a*) Strong $N—H\cdots O$ and weak ditopic $C—H\cdots N$ hydrogen-bonding interactions responsible for the formation of the one-dimensional chain-like structure in (II). (*b*) Weak π–π stacking of the molecules.

The *in vacuo* molecular structure and the IR spectrum of (II) were simulated by density functional theory (DFT) calculations using *Spartan* '04 (Wavefunction Inc., 2003). At the B3LYP/6-311+G** level of theory, satisfactory agreement between the calculated and observed data for (II) was achieved (both the structural and spectroscopic features of (II) were reproduced in the simulations).

Experimental

Compound (II) was synthesized as follows: epo (2.6 mmol), prepared using a literature method (Armand & Guette, 1969), was dissolved in dry THF and 1,2-diaminobenzene dihydrochloride (1.25 mmol, Aldrich) was added. The solution was refluxed under atmospheric pressure for about 5 h, the solvent removed on a rotary evaporator and the residue dissolved in hot water. Unreacted epo was extracted with diethyl ether prior to crystallization of compound (II) from the aqueous phase. After recrystallization from water, the dry yield of compound (II) was about 15% (melting point, 494 K). ^{1}H NMR (499.98 MHz): δ 2.399 (*s*, 3H, C9H$_3$), 7.264 (*t*, 1H, J = 8.86 Hz, C4H), 7.273 (*d*, 1H, J = 8.86 Hz, C2H), 7.463 (*dd*, 1H, J_{32} = 7.56 Hz, J_{34} = 7.82 Hz, C3H), 7.690 (*d*, 1H, J = 7.81 Hz, C5H), 12.294 (*s*, 1H, N1H). ^{13}C NMR (125.736 MHz): δ 20.51 (C9), 115.22 (C2), 123.04 (C3), 127.86 (C5), 129.31 (C3), 131.65 (C6), 131.91 (C1), 154.93 (C8), 159.22 (C7). IR (cm^{-1}): 1568 ν(C═N), 1663 ν(C═O), 2710, 2843, 2898, 2963, 3007 ν(C—H, aromatic), 3430 ν(N—H). Pale-yellow crystals of (II), suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of a saturated solution in ethyl acetate.

Crystal data

$C_9H_8N_2O$
$M_r = 160.17$
Monoclinic, $P2_1/c$
$a = 3.971$ (6) Å
$b = 11.238$ (4) Å
$c = 16.947$ (7) Å
$\beta = 91.24$ (7)°
$V = 756.2$ (12) Å^3
$Z = 4$
$D_x = 1.407$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 316 reflections
$\theta = 4$–31°
$\mu = 0.10$ mm^{-1}
$T = 120.0$ (10) K
Needle, yellow
0.6 × 0.2 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer
ω–2θ scans
Absorption correction: none
7654 measured reflections
2415 independent reflections
1491 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\rm max} = 31.7°$
$h = -3 \rightarrow 5$
$k = -16 \rightarrow 16$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.167$
$S = 0.95$
2415 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0984P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.51$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.381 (2)	C6—N2	1.3953 (18)
C1—C2	1.397 (2)	C7—O1	1.2487 (18)
C1—C6	1.409 (2)	C7—N1	1.3537 (18)
C2—C3	1.381 (2)	C7—C8	1.481 (2)
C3—C4	1.404 (2)	C8—N2	1.2989 (19)
C4—C5	1.379 (2)	C8—C9	1.489 (2)
C5—C6	1.401 (2)		
N1—C1—C2	121.65 (13)	C5—C6—C1	118.87 (13)
N1—C1—C6	117.77 (12)	O1—C7—N1	122.33 (13)
C2—C1—C6	120.58 (13)	O1—C7—C8	121.93 (13)
C3—C2—C1	119.19 (14)	N1—C7—C8	115.74 (13)
C2—C3—C4	121.03 (13)	N2—C8—C7	123.01 (13)
C5—C4—C3	119.58 (14)	N2—C8—C9	120.19 (13)
C4—C5—C6	120.71 (14)	C7—C8—C9	116.80 (12)
N2—C6—C5	119.70 (13)	C7—N1—C1	123.11 (12)
N2—C6—C1	121.43 (12)	C8—N2—C6	118.85 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1$^{\rm i}$	0.86	1.94	2.792 (4)	170
C9—H9$\cdots$N2$^{\rm ii}$	0.96	2.63	3.560 (6)	164

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

The H atoms were introduced at calculated positions as riding atoms, with bond lengths of 0.93 (CH-aromatic), 0.96 (CH_3) and 0.86 Å (NH). The displacement parameters were set equal to 1.2 (CH-aromatic and NH) and 1.5 (CH_3) times $U_{\rm eq}$ of the parent C or N atom.

Data collection: *CrysAlis CCD* 170 (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD* 170; data reduction: *CrysAlis RED* 170 (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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