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Two novel bis-azomethines derived from quinoxaline-2-carbaldehyde

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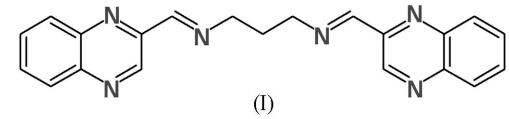
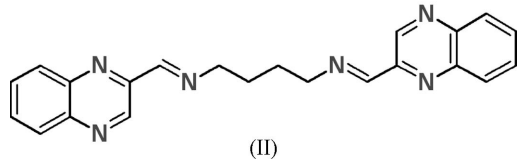
The Schiff base compounds *N*,*N*′-bis[(*E*)-quinoxalin-2-ylmethylidene]propane-1,3-diamine, $C_{21}H_{18}N_6$, (I), and *N*,*N*′-bis[(*E*)-quinoxalin-2-ylmethylidene]butane-1,4-diamine, $C_{22}H_{20}N_6$, (II), crystallize in the monoclinic crystal system. These molecules have crystallographically imposed symmetry. Compound (I) is located on a crystallographic twofold axis and (II) is located on an inversion centre. The molecular conformations of these crystal structures are stabilized by aromatic π–π stacking interactions.

Comment

The importance of Schiff bases is related to the common presence of a C═N bond in natural systems as well as to their easy formation and ability to form metal complexes with different structures. There exists a vast literature dealing with their biological activities, including antibacterial (Karia & Parsania, 1999), antifungal (Singh & Dash, 1988), anticancer (Desai *et al.*, 2001) and herbicidal (Samadhiya & Halve, 2001). Schiff bases are also becoming increasingly important in the dye, plastic, electronic and pharmaceutical industries. Multidentate Schiff base ligands and their metal complexes have been extensively studied for many years (Xavier *et al.*, 2004). Schiff bases derived from quinoxaline-2-carbaldehyde and diamines constitute one of the most important ligand systems (Arun, Robinson *et al.*, 2009). Interestingly, the size or length of the chain on the diamine clearly plays a role in the complexation with transition metal ions. Our results are of interest for the following reasons: (i) only a few crystal structures of free quinoxaline-based Schiff bases have been reported in the literature, (ii) many drug candidates bearing quinoxaline core structures are in clinical trials in antibacterial, antiviral (Harmenberg *et al.*, 1991), anticancer and central nervous system therapeutic areas (Naylor *et al.*, 1993), and (iii) Schiff base complexes act as catalysts in a variety of reactions including hydrogenation (Arun, Sridevi *et al.*, 2009) and oxidation (Chittilappilly *et al.*, 2008). In addition, we recently reported the X-ray crystal structure of the Schiff base formed between quinoxaline-2-carbaldehyde and diamine (Varghese *et al.*, 2009). This study is part of our ongoing effort to design and characterize an extensive series of Schiff bases derived from quinoxaline-2-carbaldehyde and their complexes. Keeping this goal in mind, we have synthesized two novel Schiff base compounds, namely *N*,*N*′-bis[(*E*)-quinoxalin-2-ylmethylidene]propane-1,3-diamine, (I), and *N*,*N*′-bis[(*E*)-quinoxalin-2-ylmethylidene]butane-1,4-diamine, (II), and we report here their crystal structures. This study of (I) and (II) was undertaken in order to obtain a clear understanding of the coordination geometries of these potential ligands.


(I)


(II)

In (I) (Fig. 1), one half of the molecule is related to the other half by a twofold axis passing through atom C11. The value of the N3—C10—C11—C10*A* torsion angle [180.0 (2)°] implies a *trans* alignment of the quinoxaline ring systems with respect to the azomethine C═N bond (*i.e.* C9—N3) (Philip *et al.*, 2004). The quinoxaline systems are nearly planar, with a maximum deviation of 0.0021 Å from the mean plane. The dihedral angle between the two quinoxaline ring systems is 87.97 (3)°. The N3—C10 and N3—C9 bond lengths are 1.459 (3) and 1.256 (3) Å, which are typical of C—N single-bond and C═N double-bond lengths, respectively. The N3—C9—C8, C9—N3—C10, N3—C10—C11 and C10—C11—C10*A* angles are 122.3 (2), 116.7 (2), 110.3 (2) and 112.3 (3)°, respectively. The crystal structure cohesion is reinforced by π–π stacking interactions, forming a zigzag pattern along the *c* axis, with a mean $Cg1\cdots Cg1(-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1)$ distance of 3.784 (14) Å (*Cg*1 is the centroid of the six-membered ring that includes atoms C2–C7; Fig. 2). The perpendicular distance between the rings is 3.4737 (8) Å.

For (II) (Fig. 3), the central C—C bond lies on a crystallographic inversion centre and the two halves of the molecule

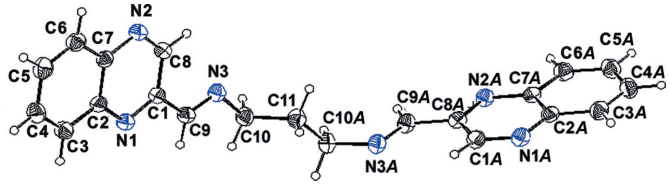


Figure 1
A displacement ellipsoid plot (drawn at the 50% probability level) of (I) with the atomic labelling scheme. Atoms labelled with the suffix *A* are at the symmetry position $(-x, y, -z+\frac{1}{2})$.

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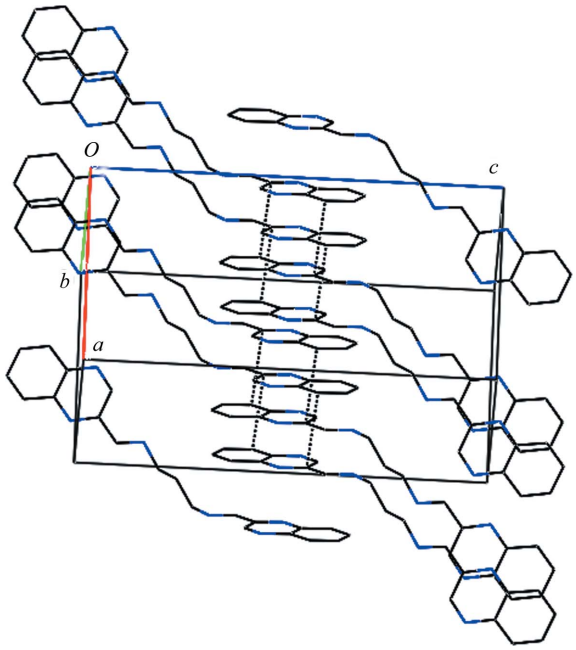

Figure 2
π–π stacking interactions of (I), forming chains. H atoms have been omitted for clarity.

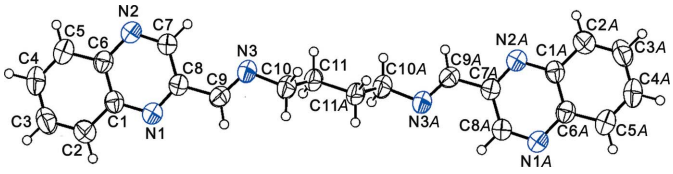

Figure 3
A displacement ellipsoid plot (drawn at the 50% probability level) of (II) with the atomic labelling scheme. Atoms labelled with the suffix *A* are at the symmetry position $(-x+1, -y-1, -z)$.

are in a *trans* orientation. The quinoxalidene ring systems and the C=N imine bonds are coplanar, as indicated by the C10—N3—C9—C8 torsion angle [−179.2 (2)°]. The central N3—C10—C11—C11*A* fragment is planar [177.3 (3)°]. The quinoxaline systems are nearly planar, with a maximum deviation of 0.0022 Å from the mean plane. The two quinoxaline ring systems are parallel. The N3—C10 and N3—C9 bond lengths are 1.463 (3) and 1.255 (3) Å. The N3—C9—C8, C9—N3—C10, N3—C10—C11 and C10—C11—C11*A* angles are 121.8 (2), 116.3 (2), 110.8 (2) and 113.1 (3)°, respectively. The crystal structure of this compound is also stabilized by π–π stacking interactions, in this case along the *b* axis, with a mean centroid–centroid distance of 4.243 (18) Å (Fig. 4).The perpendicular distance between adjacent rings is 3.165 Å.

In conclusion, there is only a little variation in bond lengths and angles between (I) and (II). The values are comparable to those in related structures (Varghese *et al.*, 2009; Varsha *et al.*, 2009; Leeju *et al.*, 2009). The crystal structures of these compounds are stabilized by π–π stacking interactions. For (I), the ring systems within the molecule are approximately perpendicular and those in (II) are parallel.

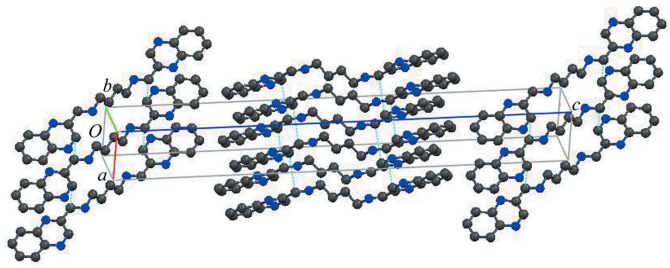

Figure 4
π–π stacking interactions of (II), forming chains in the [010] direction. H atoms have been omitted for clarity.

Experimental

Compounds (I) and (II) were synthesized by adopting a procedure similar to that used for the preparation of *N*,*N*′-bis[(*E*)-quinoxalin-2-ylmethylidene]ethane-1,2-diamine (Varghese *et al.*, 2009). Instead of ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane were used for the synthesis of (I) and (II), respectively. Compounds (I) and (II) were recrystallized from methanol. Analysis calculated for $C_{21}H_{18}N_6$, (I): C 71.17, H 5.12, N 23.71%; found: C 70.86, H 5.21, N 23.59%. Analysis calculated for $C_{22}H_{20}N_6$, (II): C 71.52, H 5.47, N 22.81%; found: C 71.12, H 5.95, N 22.95%. The melting point of (I) is 431 K and that of (II) is 426 K. The IR spectra of (I) and (II) exhibit strong bands at 1639 and 1637 cm^{-1}, respectively, due to the stretching of the azomethine bond in the Schiff base. Colourless single crystals of (I) and (II) suitable for X-ray diffraction were grown by slow evaporation from a solution in dichloromethane/toluene (1:1 *v*/*v*).

Compound (I)

Crystal data

$C_{21}H_{18}N_6$
M_r = 354.41
Monoclinic, $C2/c$
a = 10.371 (2) Å
b = 9.180 (2) Å
c = 19.084 (4) Å
β = 90.209 (4)°
V = 1817.0 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 K
0.45 × 0.35 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.964, T_{max} = 0.990
5277 measured reflections
2086 independent reflections
1695 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.169
S = 1.18
2086 reflections
159 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Compound (II)

Crystal data

$C_{22}H_{20}N_6$
M_r = 368.44
Monoclinic, $P2_1/c$
a = 4.4819 (12) Å
b = 5.3333 (14) Å
c = 39.456 (10) Å
β = 92.266 (4)°
V = 942.4 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 K
0.75 × 0.35 × 0.14 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.942, T_{max} = 0.989
5220 measured reflections
2132 independent reflections
1748 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.186
S = 1.14
2132 reflections
167 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

For compound (I), the space group $P2_1/c$ was uniquely assigned from systematic absences; for compound (II) the choice of space group $C2/c$ was confirmed by the subsequent analysis.All H-atom parameters were refined freely [C—H = 0.93 (3)–1.03 (3) Å in (I) and 0.94 (3)–1.02 (3) Å in (II)].

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2009).

The X-ray data were collected on the diffractometer facilities at the CSMCRI, Gujarat, provided by the Department of Science and Technology. The authors thank the Department of Science and Technology, India, for use of the Sophisticated Analytical Instrumentation Facility (SAIF) at STIC, Cochin University of Science and Technology, Cochin, for elemental analysis and FT–IR measurement. DV acknowledges the Council of Scientific and Industrial Research (CSIR), India, and MS thanks Kerala State Council for Science, Technology and the Environment, Trivandrum, Kerala, for financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3348). Services for accessing these data are described at the back of the journal.

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