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Self-recognition in a flexible bis(pyrrole) Schiff base derivative: formation of a one-dimensional hydrogen-bonded polymer

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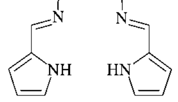
The title Schiff base compound, *N*,*N*′-bis(pyrrol-2-ylmethylene)propane-1,2-diamine, $C_{13}H_{16}N_4$, forms an interesting supramolecular structure (a one-dimensional ladder-like polymer) in the solid state that is based on the existence of complementary intermolecular $N-H\cdots N=C$ hydrogen bonds between the monomer units. The polymer axis is collinear with the *c* axis of the orthorhombic unit cell. Quantum-chemical AM1 calculations clearly indicate that self-recognition in this system by hydrogen bonding is favoured on electrostatic grounds, since the partial atomic charge on the H atom of the pyrrole NH group (0.274 e) complements the partial atomic charge of the N atom of the C=N group (−0.239 e) on a neighbouring molecule.

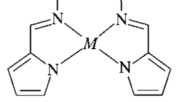
Comment

Although tetradentate Schiff base ligands comprising two pyrrole groups bridged by a synthetically variable di(azomethine) unit *X* [structure (I)] have been known for several decades (Weber, 1967), studies aimed at elucidating the chemistry (Jones & McCleverty, 1971; Van Stein *et al.*, 1984) and structures of both free bases and metal-containing coordination complexes of these synthetically feasible compounds are quite limited. Coordination of type (I) ligands to metal ions typically occurs with concomitant deprotonation of the two pyrrole NH H atoms, to give structures of type (II), where *M* represents a divalent metal ion (or any other feasible oxidation state). Structurally characterized examples of systems belonging to type (II) include complexes of Ru^{II} (Stern *et al.*, 2000), Pd^{II} (Bacchi *et al.*, 2003), Ni^{II} (Bailey & Hull, 1976), Mn^{II} (Franceschi *et al.*, 2001), Sm^{II} (Berube *et al.*, 2003) and Co^{III} (Mueller-Westerhoff *et al.*, 1996; Allen, 2002).

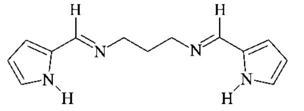
Although mononuclear coordination complexes are generally anticipated from reactions of (I) with divalent metal ions, *e.g.* Ni*L*, where *L* is the *N*,*N*′-bis(pyrrol-2-ylmethylene)ethane-1,2-diamine dianion (Kabuto *et al.*, 1984), recent structural studies have shown that even a relatively rigid derivative of (I), in which fragment *X* is based on 1,2-diamino-3,4-dimethylbenzene, is capable of conformational twisting to form binuclear complexes with a metal–ligand stoichiometry of 1:1 and the general formula M_2L_2 (Franceschi *et al.*, 2001).



(I)



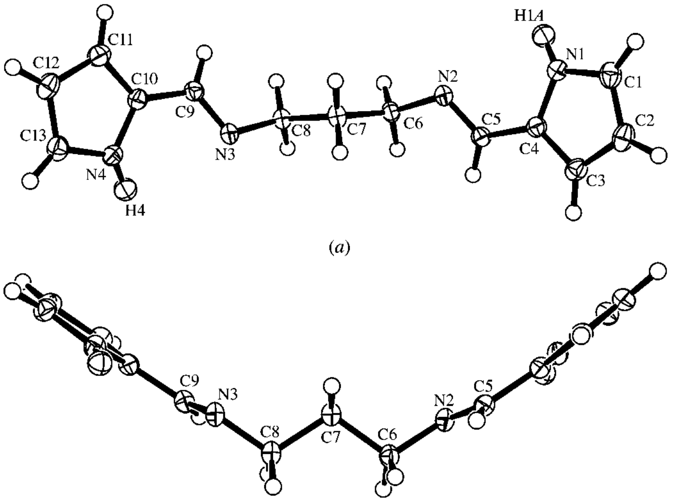
(II)



(III)

Despite the interesting coordination possibilities offered by derivatives of (I), only two free bases belonging to this group of compounds have been structurally characterized, namely *N*,*N*′-(1,2-cyclohexylene)bis(1*H*-pyrrol-2-ylmethyleneamine) (Bacchi *et al.*, 2003) and 4,5-dimethyl-*N*,*N*′-bis(1*H*-pyrrol-2-ylmethylene)benzene-1,2-diamine (Franceschi *et al.*, 2001). The structure of the latter derivative is quite remarkable, since it forms a hydrogen-bonded dimer in which each C-shaped molecule becomes interlocked by hydrogen-bonding as a result of self-recognition. Indeed, we have recently found that self-recognition seems to be favoured in such systems, *e.g.* *N*-(1*H*-pyrrol-2-ylmethylene)benzene-1,2-diamine, as a result of the combination of one or more hydrogen-bond donor (pyrrole NH group) and acceptor sites (C=N group) within the molecule (Munro *et al.*, 2003). In this paper, we report the X-ray structural characterization of the title compound, (III), the first example of a one-dimensional hydrogen-bonded homopolymeric free base derivative belonging to group (I).

The X-ray crystal structure of (III) reveals that the geometry around each azomethine or imine group is exclu-



(*a*)

(*b*)

Figure 1
(*a*) A labelled 'top' view of (III) at 120 (2) K. (*b*) A partly labelled side view of (III), illustrating the W-shaped conformation of the molecule. In both diagrams, displacement ellipsoids are drawn at the 60% probability level and H atoms are shown as small spheres of arbitrary radii.

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sively the E isomer, consistent with the fact that the Z isomer would lead to unfavourable steric interactions between the pyrrole NH groups and the adjacent methylene groups of the propyl bridge (Fig. 1). The mean pyrrole α-C—N, α-C—β-C and β-C—β-C bond lengths are 1.373 (7), 1.384 (5) and 1.413 (4) Å, respectively (Table 1). The pair of imine C=N bond lengths average 1.280 (1) Å, while the mean pyrrole α-C—(C=N) bond length is 1.446 (1) Å. The mean C—C bond length of the aliphatic chain is 1.528 (2) Å. The mean bond angles subtended at the N atoms of (III) are 109.0 (1) (α-C—N—α-C), 125.0 (5) (H—N—α-C) and 116.9 (1)° (C=N—CH_2). Collectively, these mean distances and angles compare favourably with those reported for similar derivatives of (I) (Franceschi *et al.*, 2001; Bacchi *et al.*, 2003).

With six torsional degrees of freedom, many potentially stable conformations are possible for (III). However, the conformation favoured in the crystal structure exhibits an all-staggered conformation for the methylene groups of the propyl chain and an *anti* configuration for the two (1*H*-pyrrol-2-ylmethylene)amine units at either end of the molecule. The reason for this particular conformational preference in (III) becomes apparent upon inspection of the supramolecular structure (see below). Furthermore, although there is no formal or crystallographically imposed symmetry on the conformation of (III), it is clear that the molecule has approximate C_2 symmetry, with the twofold axis running through atom C7 along the bisector of the C6—C7—C8 backbone angle and in the plane of these three atoms (Fig. 1*b*). The latter projection of the molecular structure also illustrates the rather interesting W-shaped conformation for (III).

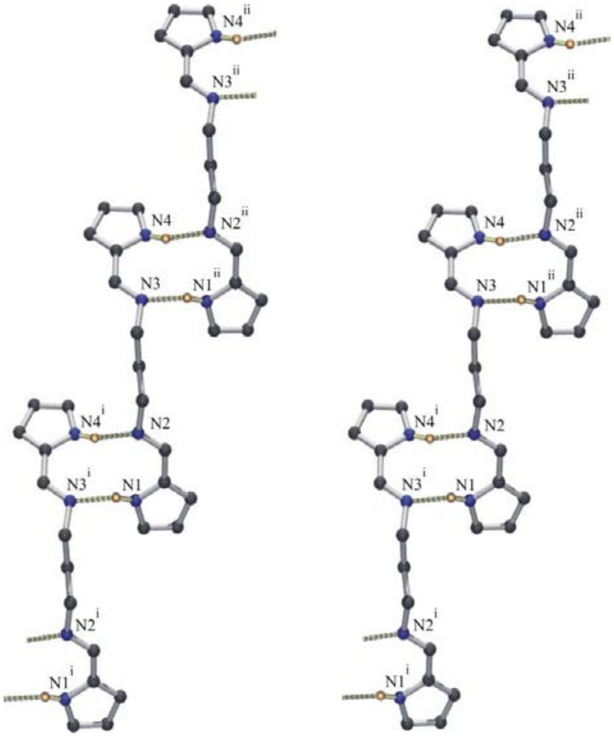

Figure 2
A stereoscopic view of three molecules forming part of an infinite one-dimensional hydrogen-bonded polymer in the crystal lattice of (III). The polymer axis is collinear with the *c* axis of the unit cell (symmetry codes are as given in Table 2).

The unique conformational features of (III) may be attributed to the supramolecular structure of the compound. More specifically, as illustrated in Fig. 2, the pyrrole NH groups serve as hydrogen-bond donors and the azomethine groups as hydrogen-bond acceptors (Table 2). This pair of functional groups creates a structural motif that allows for 'recognition' of the complementary motif in a neighbouring molecule in the lattice. Indeed, self-recognition and dimer formation of this type have been observed previously in the structurally related system 2-(2-pyrrolyl)-1,3-benzothiazole (Davidović *et al.*, 1999). However, in (III), there are two hydrogen-bonding motifs at opposite ends of the molecule, such that self-recognition or complementary hydrogen-bonding favours the formation of one-dimensional polymeric chains, in which the polymer axis runs collinear with the *c* axis of the unit cell. The hydrogen bonding in this system is therefore characterized by the formation of stable ten-membered rings, in which the pairs of planar hydrogen-bonding motifs do not lie in the same plane but are canted at 67.8 (1)°, to produce a twist in the ten-membered ring. This twisting presumably minimizes unfavourable steric contacts between the pyrrole α-CH group on one molecule and the methylene group appended to the azomethine group of the neighbouring molecule.

The formation of complementary hydrogen bonds between neighbouring molecules in the lattice of (III) leads to a ladder-like structure, in which each step of the ladder is laterally displaced from the preceding step. The *anti* configuration of the two (1*H*-pyrrol-2-ylmethylene)amine units (hydrogen-bonding motifs) at either end of the molecule is thus clearly required to facilitate the formation of a stable polymer chain. Interestingly, in the recently reported X-ray crystal structure of *N*,*N*′-(1,2-cyclohexylene)bis(1*H*-pyrrol-2-ylmethylene)amine monohydrate, a hydrogen-bonded water molecule is effectively chelated by the (1*H*-pyrrol-2-ylmethylene)amine units to form a polymeric supramolecular structure (Bacchi *et al.*, 2003). Evidently, this structural unit (pyrrole NH/imine C=N) builds into such systems the intrinsic ability to form hydrogen-bonded networks. To date, therefore, two of the three structurally characterized examples of compounds belonging to group (I) are essentially one-dimensional polymeric structures. Although the hydrogen-bonding interactions are clearly complementary, the interaction angles are 12–16° narrower than the 'ideal' hydrogen-bonding angle of 180°, consistent with the specific architecture of the two interacting (1*H*-pyrrol-2-ylmethylene)amine units and their relative non-coplanar, or slightly twisted, orientation in space.

In order to understand better the supramolecular structure of (III), we have carried out a series of gas-phase quantum-chemical AM1 calculations (Dewar *et al.*, 1985) on the monomer structure of (III), as well as on its hydrogen-bonded trimer and pentamer supramolecular analogues. Our objectives were, firstly, to quantify the electrostatics of the intermolecular hydrogen-bonding interactions observed for (III) and, secondly, to assess how reliably one could simulate a complex hydrogen-bonded polymer using electronic structure theory methods. Since calculations on three or five interacting monomers are large scale to say the least, *ab initio* or density functional theory calculations at the required level of theory (6-31G* or better) were clearly unfeasible in this case. Notwithstanding the obvious theoretical limitations of a semi-empirical valence-electron-only method like AM1, we found that qualitatively sensible partial charge distributions were calculated for all structures considered (monomer, trimer and pentamer). This is shown in Fig. 3(*a*), which gives the partial charge distribution (*i.e.* Mulliken charges) for the centre molecule in the hydrogen-bonded trimer shown in Fig. 3(*b*). Clearly, the pyrrole NH H atom has the highest positive fractional charge, while the imine N atom has the largest negative fractional charge.

Thus, in terms of simple electrostatic arguments, the AM1 calculations readily explain the N—H···N═C hydrogen-bond complementarity observed in the X-ray crystal structure of (III). Moreover, as shown by the root-mean-square fit (0.460 Å for all atoms) of the geometry of the AM1-calculated trimer to that of the X-ray structure, a reasonable simulation of the hydrogen-bonded polymer is possible at this level of theory. The complementary N—H···N═C hydrogen bonds average 2.56 (2) Å in the calculated structure, compared with 2.07 (1) Å in the X-ray structure. However, the most significant deviations between the calculated and crystal structures are for the orientations of the pyrrole rings. This reflects the fact that each pyrrole ring packs rather closely with a neighbouring molecule in the experimental structure, a factor that has not been included in the simulations because a complete simulation of the lattice is unfeasible with our presently available computer resources.

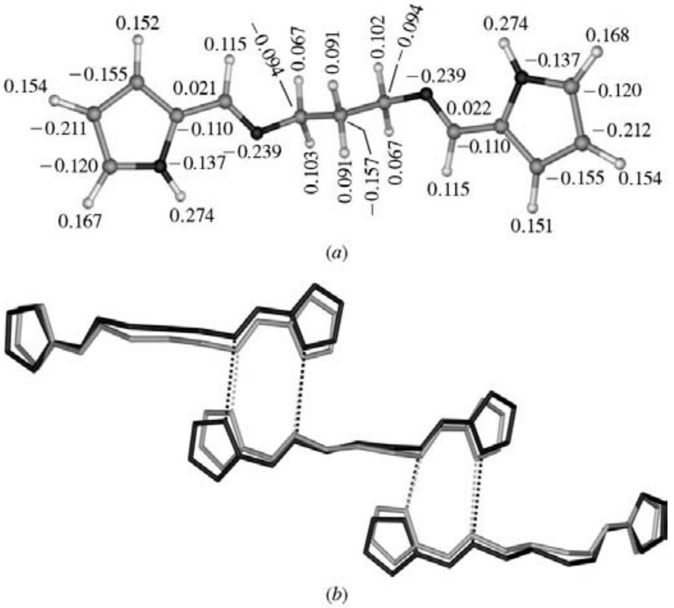

Figure 3
(*a*) The AM1-calculated Mulliken charges for (III). (*b*) The root-mean-square fit (0.460 Å) of the AM1-calculated structure of three consecutive hydrogen-bonded units of (III) to the X-ray crystal structure. The calculated Mulliken charges in (*a*) are taken from the centre molecule in (*b*).

Experimental

Hexane and dichloromethane (BDH) were distilled from sodium metal and calcium hydride, respectively, before use. Ethanol (96%, BDH) was used as received. Compound (III) was synthesized from propane-1,3-diamine and 1*H*-pyrrole-2-carbaldehyde (both from Aldrich) in refluxing ethanol, following the literature method of Jones (1994). ^{1}H and ^{13}C NMR spectroscopic data for (III) were consistent with those reported in the literature (Jones, 1994). Single crystals of (III) suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a dichloromethane solution of (III). AM1 geometry optimization calculations were carried out with the default singlet-state parameters in *HyperChem* (Hypercube, 2000).

Crystal data

$C_{13}H_{16}N_4$
$M_r = 228.3$
Orthorhombic, *Pccn*
$a = 15.469$ (3) Å
$b = 20.644$ (4) Å
$c = 7.997$ (4) Å
$V = 2554.0$ (14) Å^3
$Z = 8$
$D_x = 1.187$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 826 reflections
$\theta = 4$–32°
$\mu = 0.08$ mm^{-1}
$T = 120$ (2) K
Needle, yellow
0.75 × 0.25 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur2 CCD area-detector diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.879$, $T_{\max} = 0.985$
23 402 measured reflections
4144 independent reflections
3367 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 31.9°$
$h = -21 \rightarrow 22$
$k = -29 \rightarrow 29$
$l = -7 \rightarrow 11$

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.123$
$S = 1.10$
4144 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.6559P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.3665 (14)	C9—N3	1.2798 (14)
C4—N1	1.3776 (14)	C10—N4	1.3796 (14)
C5—N2	1.2806 (13)	C13—N4	1.3675 (14)
C6—N2	1.4680 (14)		
C1—N1—C4	109.08 (9)	C9—N3—C8	116.85 (9)
C5—N2—C6	117.04 (9)	C13—N4—C10	108.93 (9)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N3$^{\rm i}$	0.902 (14)	2.059 (14)	2.935 (2)	163.5 (13)
N4—H4···N2$^{\rm ii}$	0.889 (14)	2.073 (14)	2.949 (2)	168.4 (12)

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

A difference Fourier calculation, after anisotropic refinement of the C and N atoms of (III), located all of the H atoms in the molecule. We elected to refine the pyrrole NH H atoms isotropically without restraints; all other H atoms were calculated using the standard riding model of *SHELXL*97 (HFIX 23 and HFIX 43; Sheldrick, 1997).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (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: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1708). Services for accessing these data are described at the back of the journal.

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