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A comparison of the intramolecular and intermolecular hydrogen bonding of *N*,*N*′-ethylenebis(aminobenzylidene) in the solid state with its salen analogue

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Abstract

The crystal structure of H_2amben has been elucidated for the first time. The close NH···N contact between neighbouring molecules supports strongly the notion that *inter*molecular hydrogen bonding exists within the crystal lattice, creating a series of molecular chains, which are crosslinked in a three-dimensional array. This *inter*molecular bonding is suggested to account for the anomalously high melting point of H_2amben (176–178 °C) compared to its H_2salen counterpart (126–128 °C). Although strong intramolecular forces are present in both ligands, H_2salen contains no *inter*molecular hydrogen bonds.

Keywords: Aminobenzylidene; Intermolecular; Intramolecular; Hydrogen bonding; Amben; Salen; Schiff base

1. Introduction

Schiff bases, or imines, $R_2C{=}NR$—the condensation products of aldehydes and ketones reacting with primary amines—have been used extensively in the preparation of metal complexes [1–3]. Such ligands possess interesting photo-physical properties with potential applications as organic materials for reversible optical data storage [4]. Since these photo-physical properties, including thermochromism and photochromism, are governed strongly by the presence of intramolecular hydrogen bonds, several studies have focused on the nature of the hydrogen bonding in such materials [5–9]. A large number of Schiff base ligands, pertaining to the salicylidene family, have been prepared, with modification of the simple H_2salen ligand (*N*,*N*′-ethylenebis(salicylideneimine) proving relatively straightforward in most cases. Generally, the salicylidene ligands are prepared in situ, rather than being isolated in the solid state, and then reacted with the metal ion to yield the desired complex. As a result, most of the crystallographic data reported for H_2salen and its derivatives are those of metal complexes rather than the free ligands themselves.

For the N_4 quadridentate ligand, *N*,*N*′-ethylenebis(aminobenzylidene), or H_2amben, modifications to its aromatic groups have been limited, and unlike the analogous salicylidene Schiff bases, the chemical and physical properties of H_2amben and its derivatives are relatively unexplored. Whereas strong intramolecular hydrogen bonding is reported to exist within the crystalline lattice of H_2salen, governing a number of its properties [10], no crystallographic data have been reported thus far for H_2amben, although strong intramolecular hydrogen bonds have been reported for macrocyclic amben derivatives and N_4 porphyrins [11,12]. A renewed interest in these systems has resulted in the preparation of ligands derived from tosylaminobenzaldehyde and various diamines, where crystallographic data indicate the presence of both intramolecular and intermolecular interactions [13–15].

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2. Experimental

2.1. Methodology

An ethanolic solution of 30% w/w ethylenediamine hydrate (16 mmol) and 2-aminobenzaldehyde (34 mmol) was refluxed for one hour. The solution was then cooled and allowed to stand overnight. The white, plate-like crystals of H_2amben which separated were filtered and allowed to air-dry as reported previously [16,17]. Recrystallization from a solution of tetrahydrofuran and ether (1:9) yielded white plates that were dried in vacuum over P_2O_5 (3.14 g, 70%).

2.2. X-ray diffraction analyses

Data were collected on a Bruker Smart Apex diffractometer, equipped with a CCD detector. The structures were solved by the direct method, SHELXTL [18], and refined by a full matrix least squares method, SHELXL97 [19]. Thermal ellipsoid plots were drawn using ORTEP [20], whilst diagrams of the unit cell were created using Mercury [21]. Details of the data collected are provided in Table 1.

Table 1
Details of the X-ray crystal structure analysis for the H_2amben molecule

Empirical formula	$C_{16}H_{18}N_4$
Formula weight (g/mol)	266.35
Melting point (°C)	176–178
Crystal color	Colorless
Crystal description	Plate
Crystal class	Monoclinic
Space group	$P2_1/n$
a (Å)	5.7472(11)
b (Å)	7.7478(14)
c (Å)	31.595(6)
α (°)	90.00
β (°)	94.245(3)
γ (°)	90.00
Density (g/m^3)	1.261
Crystal size (mm)	0.40, 0.20, 0.03
Volume (Å^3)	1403.0
Z	4
μ (mm^{-1})	0.078
F(000) (e)	568
θ range (°)	2.59–25.0
Index ranges	$-6\leq h\leq 6$, $-8\leq k\leq 9$, $-24\leq l\leq 37$,
Reflections collected/unique	6940/2472 [R(int) = 0.1129)
Data/restraints/parameters	2472/0/197
Goodness of fit on F^2	0.982
Final R indices [$I>2\sigma(I)$]	$R1=0.0579$, $wR2=0.1464$
R indices (all data)	$R1=0.0813$, $wR2=0.1584$

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition No. 248810. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk or on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336033).

3. Results and discussion

3.1. Molecular structure of H_2amben

After many unsuccessful attempts using a variety of mixed solvents, crystallization of H_2amben (in a form suitable for analysis by single crystal X-ray diffraction) was finally achieved using a 1:9 tetrahydrofuran:diethyl ether mixture. An X-ray analysis of H_2amben shows the amino groups to be trans, as are the hydroxy groups in H_2salen [10], and confirms the long-held belief that it is an extended molecule with the two aromatic rings lying in parallel planes (0.2° displacement) [22,23]. The distance between these planes is 1.37 Å. The molecular point group symmetry is *Ci* (previously termed S_2) with an inversion center (Fig. 1). Selected bond lengths and angles from the analysis are presented in Table 2. Bond lengths within the aromatic rings are consistent with those expected for sp^2 aromatic carbon atoms [24–26]. The slightly longer bond lengths of the carbon atoms connected to the imine and amine moieties [C(2)–C(1) (1.409(3) Å), C(11)–C(12), (1.408(3) Å)] are not unexpected for Schiff bases, as substitution of aromatic rings can lead to minor distortions within the aromatic moiety [5,10,27,28].

Bond angles, which range from 118.38 to 121.80° in the aromatic moieties, are consistent with mean literature values [24]. The C(1)–C(7) (1.454(3) Å) and C(10)–C(11) (1.462(3) Å) distances are consistent with single bonds between sp^2 hybridized carbon atoms, whilst the bond length of 1.277(2) Å for each imine group, C(7)–N(2) and C(10)–N(3), is in agreement with those reported for H_2salen, H_2tosylamben and H_2salphen [10,14,29].

The imine nitrogen atoms, N(2) and N(3), bond angles of 117.49(17) and 117.05(17)°, respectively, confirms their sp^2 character, whilst the bond lengths of 1.463(2) and 1.458(2) Å for C(8)–N(2) and C(9)–N(3), respectively, are consistent with C(sp^3)–N(sp^2) single bonds. Bond lengths of 1.372(2) and 1.370(2) Å for the C(sp^2)–N(sp^3) single bonds

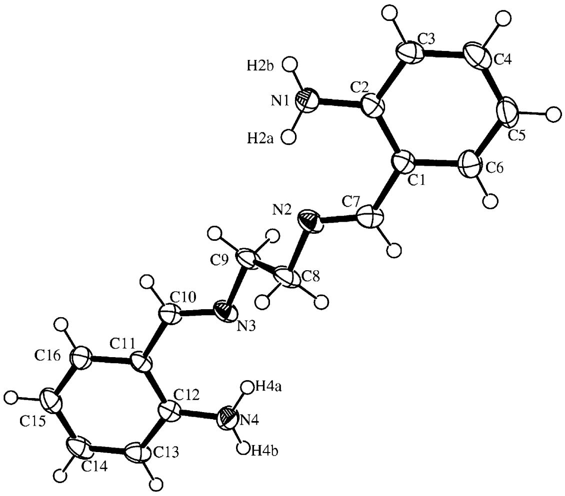

Fig. 1. Molecular structure of H_2amben (50% ellipsoid probability).

Table 2
Selected bond lengths (Å) and angles (°) for H_2amben

C1–C2	1.409(3)
C1–C7	1.454(3)
C2–N1	1.372(2)
C7–N2	1.277(2)
C8–N2	1.463(2)
C8–C9	1.513(3)
C9–N3	1.459(2)
C10–N3	1.277(2)
C10–C11	1.462(3)
C11–C12	1.408(3)
C12–N4	1.370(2)
C6–C1–C7	117.96(18)
N1–C2–C3	120.06(18)
N1–C2–C1	120.95(18)
N2–C8–C9	109.83(16)
N3–C9–C8	109.87(16)
C16–C11–C10	117.45(18)
N4–C12–C13	120.46(19)
N4–C12–C11	121.13(18)
C7–N2–C8	117.49(17)
C10–N3–C9	117.05(17)
C2–N1–H2A	113.04(15)
C2–NI–H2B	116.91(13)
C12–N4–H4A	115.95(14)
C12–N4–H4B	117.57(14)
H2A–N1–H2B	128.72(19)
H4A–N4–H2B	124.70(02)

Esd's are given in parentheses.

for C(2)–N(1) and C(12)–N(4), respectively, are in excellent agreement with the mean bond length of 1.375 Å reported previously [24]. The ethylene bridge is in the *trans* conformation and the C(8)–C(9) distance of 1.513(3) Å is consistent with a single bond between sp^3 carbon atoms. Furthermore, C(8) and C(9) deviate from C(1)–C(6) by ±0.11 Å and C(11)–C(16) by ±0.12 Å, respectively, whilst the dihedral angle for N(2)–C(8)–C(9)–N(3) is ± 179°. Torsion angles indicate that the molecule is strictly planar about the aromatic ring and imine group, although free rotation is possible about C(8)–C(9) in the ethylenediamine bridge.

On average, the bond angles around the two amino nitrogen atoms, N(1) and N(4) are closer to sp^2 than to sp^3 hybridization. For example, the angles C(2)–N(1)–H(2A) [113.04(15)°] and C(2)–N(1)–H(2B), [116.91(13)°] and C(12)–N(4)–H(4A) [115.95(14)°] and C(12)–N(4)–H(4B) [117.57(14)°], indicate considerable flattening of the $-NH_2$ moiety in order to optimize both intra- and inter-molecular hydrogen bonding.

The distances between N(1)–N(2) and N(4)–N(3), of 2.731 and 2.745 Å, respectively, and the close proximity of H(2A)···N(2) (=1.994 Å) and H(4A)···N(3) (=2.037 Å) in Fig. 1, suggest strong intramolecular hydrogen bonding. Similar distances are observed between the aminic (NH_2) and iminic nitrogen (C=N) atoms in the free ligands of *N*,*N*′-bis(2-tosylaminobenzylidene)1,2-ethanediamine and *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-propanediamine [13,14]. Likewise, the molecular interactions in H_2salen are dominated by two strong intramolecular hydrogen bonds within the unit cell, indicated by the close approach of the phenolic oxygens and imine nitrogens (2.596 and 2.598 Å for the two pairs) [10].

3.2. The unit cell

Four molecules are contained within the unit cell of H_2amben (Fig. 2), which is marginally larger than the analogous H_2salen unit cell. For the pair of molecules on the right of the unit cell, the distances are 6.405 and 3.542 Å between N(1)–N(4) at their right- and left-hand ends, respectively. These distances are reversed for the pair of

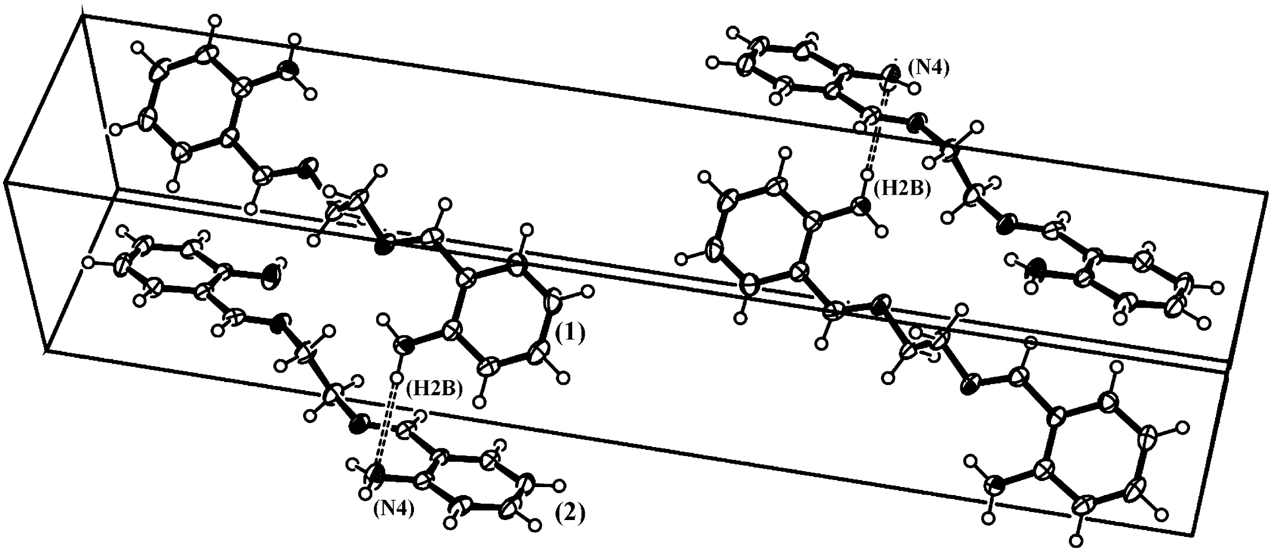

Fig. 2. Intermolecular hydrogen bonding (H(2B)···N(4)) within the unit cell of H_2amben.

molecules on the left of the unit cell. It is noteworthy, in contrast to H_2salen, that two intermolecular hydrogen bonds, (which are parallel to, and separated by, (002) planes) are contained fully within each unit cell. On the left half of Fig. 2, the hydrogen bond is from H(2B) in the upper molecule to N(4) in the lower, while on the right half, it is from H(2B) in the lower to N(4) in the upper molecule. The distance between the intermolecular hydrogen-bonded molecules within the unit cell is 2.673 Å (H(2B)···N(4)). The complete hydrogen-bonding pattern, taking into account intermolecular hydrogen bonds which are shared between adjacent unit cells, is much more extensive. Indeed, each molecule participates in four hydrogen bonds involving N(1), H(2B), N(4) and H(4B), as indicated in Fig. 3. All the resulting hydrogen bonds are in directions parallel to the (002) crystallographic planes. This enables the extended hydrogen-bond structure to be described completely by referring only to the left-hand side of Fig. 2 (this side is reproduced as the middle section of Fig. 3). As an aid to interpretation, the molecules have been numbered in each of Figs. 2–4 in the same way. A molecule with the same orientation as the upper molecule on the left-hand side of the unit cell will be found in the unit cell immediately below (only the upper left half of this unit cell is shown), while one with the same orientation as the lower molecule will be found in the unit cell immediately above (only the lower left half of this unit cell is shown). Thus, a chain of molecules, 8-1-2-7, can be traced by their intermolecular hydrogen bonding from N(1) in the upper unit cell to H(4B) in the lower unit cell, which is then repeated throughout the crystal lattice. In this chain, it can be seen that the resulting hydrogen bonds alternate between N(1)···H(4B) and H(2B)···N(4) in opposite parts of the molecule. The direction in which the molecular chain propagates is [110], and chains extend throughout the solid crystal. Fig. 4 depicts three molecular chains. As in Fig. 3, the chain 8-1-2-7 propagates in the [110] direction. Thus, any given molecule that is hydrogen-bonded via nitrogen H(2B)···N(4) in the [110] direction is also simultaneously hydrogen-bonded to a molecule in another chain, that being 5-1-3 and 6-2-4 which propagate in the $[1\bar{1}0]$ direction (as seen in Fig. 4). These crosslinked hydrogen-bonded chains constitute a two-dimensional network.

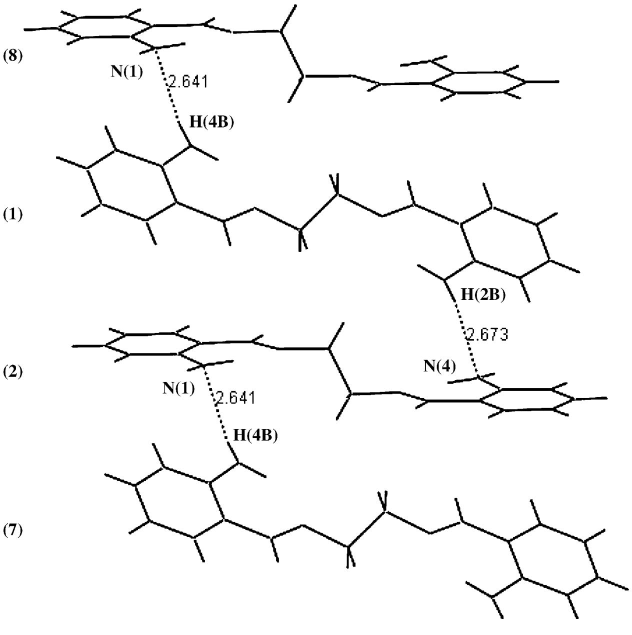

Fig. 3. Molecular chains (intermolecular hydrogen bonding) within H_2amben crystal lattice.

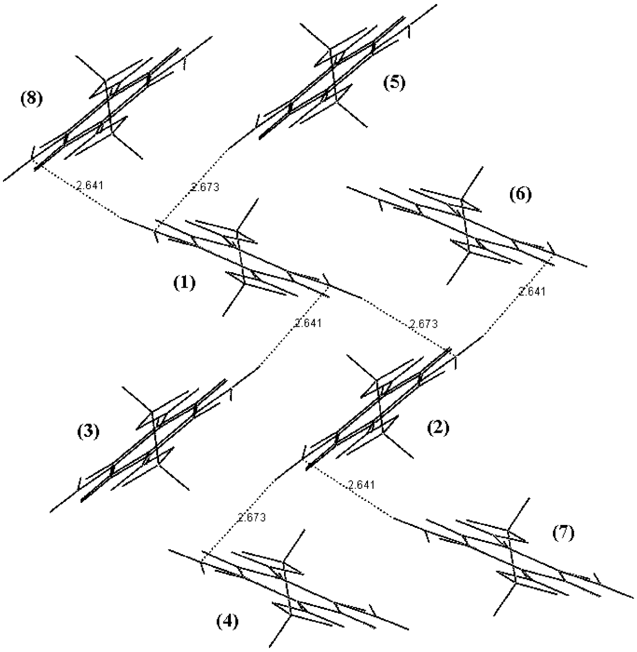

Fig. 4. Crosslinked intermolecular hydrogen bonding within the crystal lattice of H_2amben.

The long axes of the H_2amben molecules are close to perpendicular to the plane of the bonded network ($\beta = 94°$). The lattice of the H_2amben crystal is monoclinic, where the dimensions of the unit cell are 5.747 (Å) (a direction), 7.747 (Å) (b direction) and 31.595 (Å) (c direction). This compares to the marginally-smaller H_2salen unit cell with dimensions, 6.094 (Å) (a direction), 7.567 (Å) (b direction) and 30.680 (Å) (c direction). The directions, [110] (molecular chains) and $[1\bar{1}0]$ (crosslinked chains), are at 90°. With $a \neq b$, it might be expected that the chains in each direction are not equivalent. Such an expectation (which would hold for a closely similar orthorhombic lattice) is incorrect, as is apparent from Fig. 5(a) and (b). These show a portion of the H_2amben lattice, with the structural motif extended to a $3 \times 3 \times 3$ model. Comparison of Fig. 5(a), representing the molecular chains in the [110] direction, with Fig. 5(b), representing the crosslinked chains within the crystal lattice in the $[1\bar{1}0]$ direction, reveals that the chains propagating in each direction are equivalent. For comparison, views of H_2salen [10] in the same directions are shown in Fig. 6(a) and (b). The diagrams show the remarkable similarity of the H_2amben and H_2salen

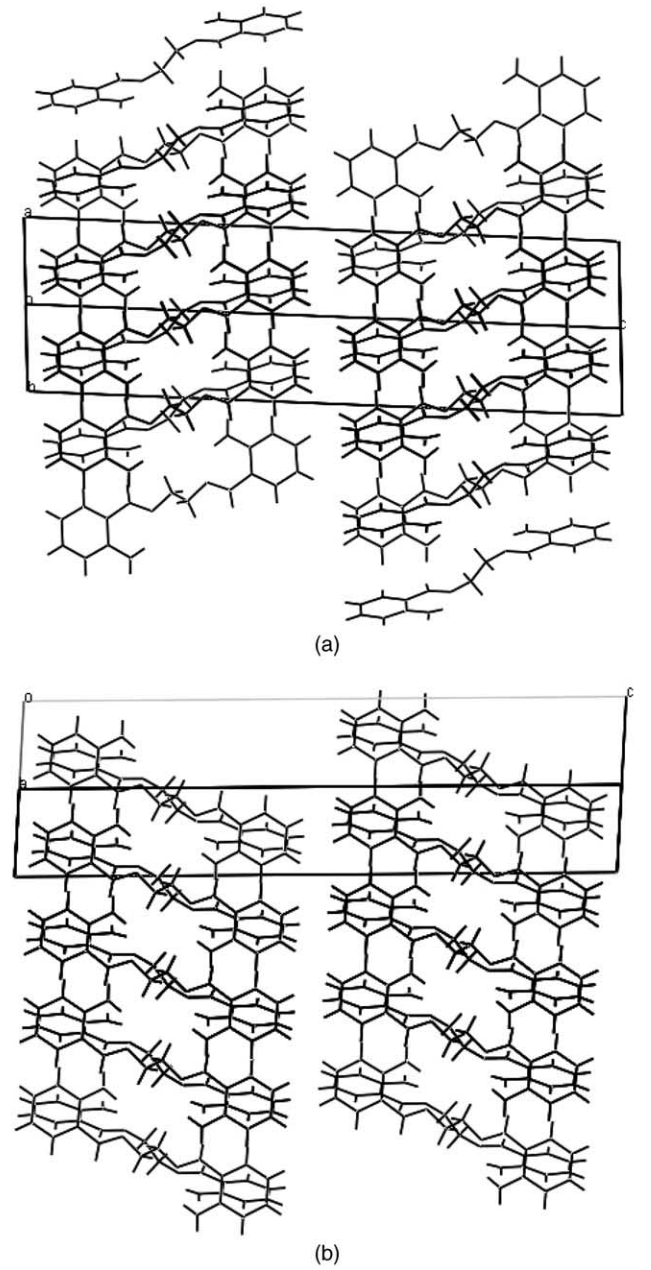

Fig. 5. A 3×3×3 structural motif of the H_2amben crystal lattice: (a) molecular chains (propagating in [110] direction) and (b) crosslinked chains (propagating in [1$\bar{1}$0] direction).

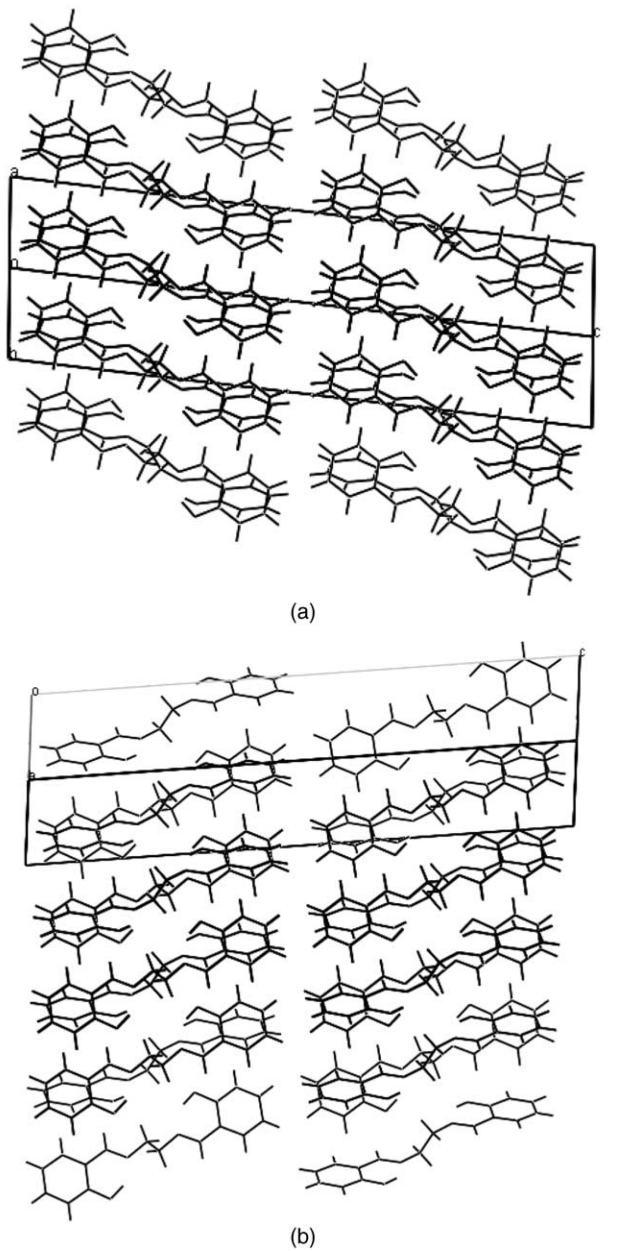

Fig. 6. A 3×3×3 structural motif of the H_2salen crystal lattice: (a) molecular units (propagating in [110] direction) and (b) molecular units (propagating in [1$\bar{1}$0] direction).

lattices, which arises from the similarity of the crystal packing requirements. However, it is noteworthy that the presence of additional intermolecular hydrogen bonding in H_2amben is accommodated through a moderate degree of rehybridization of the amino-nitrogen atoms, N(1) and N(4), as discussed earlier.

It is well accepted in the literature that strong intramolecular forces govern the properties exhibited by Schiff bases. In the case of H_2salen, similar strong intramolecular interactions are observed. Likewise, the structural behaviour of tosylamben derivatives is attributed not only to the presence of tosyl moieties (used to replace the hydrogen atom on the aromatic amine), but also to the strong intramolecular forces which are thought to minimize the steric hindrance of the tosyl groups [13]. Similar intramolecular forces are observed for H_2amben also; however, what is unique to this system is the presence of additional *intermolecular hydrogen bonds*. Molecules within the crystal lattice of H_2salen are held together only by van der Waals forces [10], whilst the presence of the intermolecular hydrogen bonds within the crystal lattice of H_2amben is expected to influence significantly the properties of the molecule.

4. Conclusion

The anomalously higher melting point of H_2amben (176–178 °C) compared to H_2salen (126–128 °C)—which has remained unexplained for more than 60 years—can now be attributed to the network of *inter*molecular hydrogen bonds present within the crystal lattice. The lower rate of dissolution of H_2amben, compared to H_2salen, in a variety of solvents is consistent with the extensive *inter*molecular hydrogen bonding present in the solid state. In addition, the manner in which molecules crystallize from solution is dictated strongly by hydrogen bonds formed within the molecule and the crystal lattice. In the case of H_2amben, the isolation of suitable crystals for X-ray analysis proved to be a challenging task, and numerous solvents and solvent mixtures were explored under varying conditions in an attempt to isolate a crystalline material suitable for X-ray analysis. Frequently, the H_2amben molecules grew preferentially in a 'pancake' arrangement, forming a sequence of thin, stacked platelets, unsuitable for analysis. This problem was solved eventually by using very slow evaporation in the chosen solvent mixture, which yielded crystalline plates of more uniform dimensions, appropriate for X-ray analysis. Based on the crystallographic data obtained in this work, it can be seen why the molecules stack in the *a* and *b* directions of the unit cell rather than the *c* direction (which would produce needle or rod shaped crystals), as intermolecular hydrogen bonding within the unit cell occurs in the *a* and *b* directions only. In addition, the spacing in H_2amben ($P2_1/n$) is less than that in H_2salen ($P2_1/c$), which accounts for the thinness of the platelets arising from rapid growth in the hydrogen-bonded directions.

Finally, it should be noted that the crystal structures for the nickel- and copper-amben complexes [30] as well as those for substituted amben analogues of Co(II) [23], Ni(II) [31] and Cu(II) [32], indicate the flexibility of the CH_2–CH(X) (X=H, CH_3) bridge, which allows the *trans*-configured ligand to readily adopt the *cis*-stereochemistry necessary to bind to a metal ion in a tetradentate manner.

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