Trimorphism of an asymmetric disulfonamide Schiff base†

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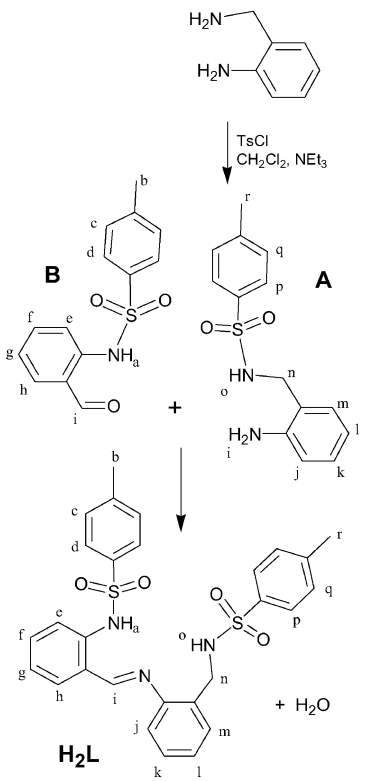
An asymmetric Schiff base, **H_2L**, has been prepared by condensation of the selectively functionalised 2-(tosylaminomethyl)aniline (**A**) with 2-tosylaminobenzaldehyde (**B**). **H_2L** has been characterised by elemental analysis, FAB-MS, NMR and FTIR techniques. The molecular structure of **A** has been elucidated by X-ray diffraction methods, as well as four different conformational isomers of **H_2L**, which are present in the three polymorphic forms solved (**T_a**, **T_c** and **M**). Two of these polymorphs (**T_c** and **M**) are based on similar dimeric units, which are connected *via* two intermolecular N–H···O bonds, along with some edge-to-face and face-to-face interactions. Molecules corresponding to **T_a** are differently conformed, and display two intramolecular N–H···O and N–H···N bonds. In this crystal structure, pairs of neighbouring molecules are connected through simultaneous face-to-face interactions between their two tosyl groups.

Introduction

Both free and coordinated sulfonamides, and *N*-tosylamine derivatives in particular, have been successfully employed in such fields as bioinorganic chemistry,[1] organic synthesis,[2] catalysis,[3] heavy metal extraction,[4] photosensible and luminescent materials,[5] dyes,[6] or pharmaceuticals.[7] In some of these areas, polymorphism can be a source of substantial benefits or problems.[8]

Since crystals can be regarded as "supramolecular assemblies *par excellence*",[9] polymorphism occurs when a slightly different balance of subtle intermolecular interactions is recognised. This can lead to the packing of rigid molecules into different arrangements, or to the packing of different conformers into identical or different packing motifs. This second case was termed *conformational polymorphism*,[10] and its study provides relevant structure–property relationships that depend only on crystal packing or molecular conformation, as the chemical composition remains identical. Therefore, systems having many polymorphs are beneficial to such studies, and allow a broader exploration of this phenomenon.[11]

Continuing with our studies on ditosylamine-functionalised Schiff bases,[12,13] this paper deals with an asymmetric tridentate imine (**H_2L**, Scheme 1) that exhibits three polymorphic forms at least.



Scheme 1 Synthesis of **A** and **H_2L**, including the labelling schemes used for the assignment of NMR signals corresponding to **A**, **B** and **H_2L**.

Results and discussion

With the aim of preventing a double condensation[13d] of 2-aminobenzylamine with 2-tosylaminobenzaldehyde[14] (**B**),

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† Electronic supplementary information (ESI) available: Representations of NOESY and HMQC spectra for **A** and **B**, respectively, and secondary interactions of the crystal packing schemes. See DOI: 10.1039/b704195k

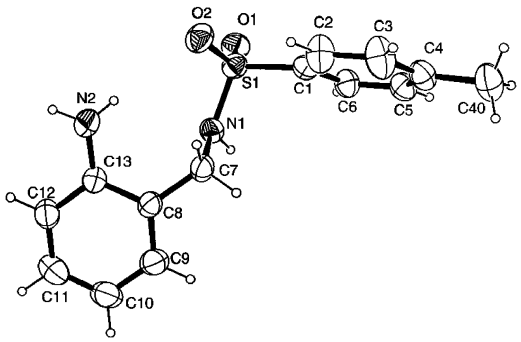


Fig. 1 ORTEP view of the molecular structure of **A**, showing 30% probability displacement ellipsoids.

firstly, we proceeded to the mono-tosylation of the diamine. This functionalisation occurred selectively on the benzylamine group, and gave rise to 2-(tosylaminomethyl)aniline (**A**). This compound was isolated and satisfactorily characterised.

Finally, a classic Schiff condensation of **A** and **B** yielded $\mathbf{H_2L}$ (Scheme 1), which was conveniently characterised as well.

Single crystal X-ray diffraction studies‡

Crystal structure of 2-(tosylaminomethyl)aniline (A). Slow evaporation of a methanol solution of **A** afforded colourless prismatic crystals suitable for X-ray diffraction studies. Its molecular structure was elucidated, and an ORTEP view of **A** is shown in Fig. 1, along with the numbering scheme used.

A consists of crystallographically independent molecules, whose geometric parameters (Table 1) are within typical ranges observed for other free tosylamine-functionalised Schiff base ligands.[12,15–20] Hence, it does not merit further discussion.

Intramolecular N(2)–H(2B)···O(2) bonds can be observed for **A**, while its crystal packing appears mostly controlled by two intermolecular H-bonds (Table 2), among other weaker interactions (Table S1 in ESI†). Intermolecular N(1)–H(1A)···O(1)$^{\#1}$ bonds connect adjacent molecules to form infinite chains along the *b* direction (Fig. 2), and these parallel chains interact through N(2)–H(2A)···O(2)$^{\#2}$ bonds.

Crystal structures of $\mathbf{H_2L}$ ($\mathbf{T_a}$, $\mathbf{T_c}$ and M). Saturated chloroform and acetonitrile solutions of $\mathbf{H_2L}$ were slowly evaporated, and afforded both yellow (triclinic) and colourless (monoclinic) single crystals. The yellow crystalline forms isolated from both solutions proved to be conformational polymorphs, while monoclinic crystals were identical. Accordingly, three polymorphic forms of $\mathbf{H_2L}$ could be studied. These polymorphs have been labelled as $\mathbf{T_a}$ (triclinic$_{\text{acetonitrile}}$, $P\bar{1}$, yellow), $\mathbf{T_c}$ (triclinic$_{\text{chloroform}}$, $P\bar{1}$, yellow) and **M** (monoclinic$_{\text{(chloroform or acetonitrile)}}$, $P2_1/n$, colourless). Crystals of the $\mathbf{T_c}$ type were also later found in an acetonitrile solution. Consequently, solvent does not appear to be a key factor for crystallisation selectivity.

Asymmetric units of $\mathbf{T_a}$, $\mathbf{T_c}$, and **M** contain one crystallographically independent molecule of $\mathbf{H_2L}$ (Fig. 3). One of them has also been represented by an ORTEP diagram (Fig. 4) to show the atom labelling scheme used, while the pairs of conformers present in $\mathbf{T_c}$ and $\mathbf{T_a}$ are shown in Fig. 5.

‡ CCDC reference numbers 646377–646380. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704195k

Table 1 Selected geometric parameters for **A** and $\mathbf{H_2L}$ ($\mathbf{T_a}$, $\mathbf{T_c}$ and **M**)

	A	$\mathbf{T_a}$	$\mathbf{T_c}$	**M**
Bond distance/Å				
N(1)–C(7)	1.474(4)	1.467(3)	1.478(3)	1.483(3)
C(1)–S(1)	1.744(4)	1.764(3)	1.766(2)	1.755(2)
N(1)–S(1)	1.620(4)	1.615(2)	1.6194(18)	1.615(2)
N(2)–C(13)	1.365(6)	1.422(2)	1.416(2)	1.411(3)
N(2)–C(14)		1.281(3)	1.271(3)	1.279(3)
N(3)–C(20)		1.404(3)	1.399(3)	1.406(3)
N(3)–S(2)		1.610(2)	1.6242(18)	1.625(2)
Angle/°				
C(1)–S(1)–N(1)	108.44(18)	107.27(11)	107.60(10)	107.30(10)
C(7)–N(1)–S(1)	121.1(3)	118.66(17)	119.20(13)	119.93(16)
O(1)–S(1)–O(2)	120.2(2)	120.01(17)	119.66(11)	119.36(10)
N(2)–C(14)–C(15)		123.99(19)	123.84(18)	124.0(2)
C(13)–N(2)–C(14)		120.32(18)	120.40(17)	120.73(19)
C(20)–N(3)–S(2)		128.81(16)	127.98(15)	126.19(18)
O(3)–S(2)–O(4)		118.70(11)	120.00(11)	119.96(12)
Torsion angle/°				
S(1)–N(1)–C(7)–C(8)	142.9(3)	−122.23(18)	−135.79(16)	−128.96(18)
N(1)–C(7)–C(8)–C(13)	−72.2(5)	−100.5(2)	−71.7(2)	−70.7(3)
C(7)–C(8)–C(13)–N(2)	−4.4(6)	2.0(3)	−1.5(3)	6.1(3)
C(13)–N(2)–C(14)–C(15)		−176.30(18)	172.5(2)	174.74(19)
C(15)–C(20)–N(3)–S(2)		168.22(18)	170.69(17)	152.43(19)
C(20)–N(3)–S(2)–C(21)		72.1(2)	−67.2(2)	−54.1(2)

Selected bond lengths and angles are listed in Table 1, together with those corresponding to **A** for comparison. As expected, bond parameters observed for $\mathbf{T_a}$, $\mathbf{T_c}$ and **M** are similar, and can be considered within usual ranges reported for other free tosylamine Schiff bases.[12,15–20] Their differences are mostly based on torsion angles (Table 1), especially for $\mathbf{T_a}$ compared to $\mathbf{T_c}$ or **M**.

Some structural features such as conformation, H-bonding scheme and crystal packing will be discussed below.

Conformation. Some significant torsional degrees of freedom are associated with single bonds corresponding to the methylene and sulfonamide groups of $\mathbf{H_2L}$.

Table 2 H-bonds for **A** and $\mathbf{H_2L}$ ($\mathbf{T_a}$, $\mathbf{T_c}$ and **M**)

	d(D–H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	(D–H···A)/°
A				
N(1)–H(1A)···O(1)^a	0.96(4)	2.05(4)	2.993(4)	168(3)
N(2)–H(2A)···O(2)^b	0.84(6)	2.30(6)	3.091(5)	158(6)
N(2)–H(2B)···O(2)	0.81(5)	2.44(5)	3.235(6)	166(5)
$\mathbf{T_a}$				
N(1)–H(1A)···O(3)	0.82(3)	2.38(3)	3.137(3)	154(3)
N(3)–H(3A)···N(2)	0.82(3)	1.93(3)	2.634(3)	143(3)
$\mathbf{T_c}$				
N(1)–H(1A)···O(2)^c	0.99	1.99	2.977(3)	175
N(3)–H(3A)···N(2)	0.92	1.91	2.665(3)	138
M				
N(1)–H(1A)···O(2)^d	0.80(3)	2.24(3)	3.038(3)	176(2)
N(3)–H(3A)···N(2)	0.85(2)	1.95(3)	2.660(3)	141(3)

^{a} $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$. ^{b} $1-x, 1-y, 1-z$. ^{c} $1-x, -y+2, 1-z$. ^{d} $-x-1, -y, -z$.

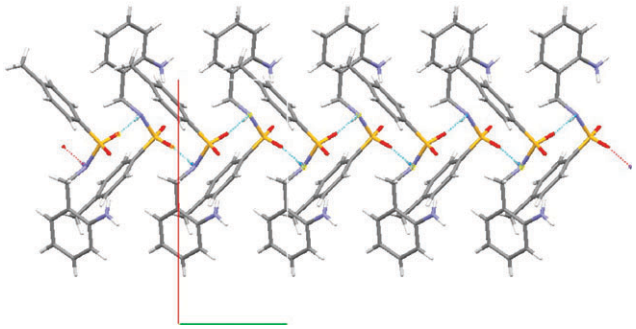


Fig. 2 Packing view of **A**.

Newman projections of the N(1)–C(7) bonds (Fig. 6) indicate that S(1) and C(8) might prefer to adopt *anti* conformations, both in **A** and $\mathbf{H_2L}$, with torsion angles in the range 122–143°. The nearly eclipsed conformations shown by polymorphs of $\mathbf{H_2L}$ may be related to the participation of N(1) in intra- ($\mathbf{T_a}$) or intermolecular ($\mathbf{T_c}$ and **M**) H-bonds (Table 2).[21]

H-bonding scheme. Conformers found for $\mathbf{H_2L}$ display intramolecular N–H···N connections between a sulfonamide group and the contiguous imine one (Scheme 2a, Table 2), as described for some other mono-[15,16,18,19] and di-[12,17] tosylamino-functionalised Schiff bases. The presence of these intramolecular interactions likely favours a typical (*E*)-configuration of the azomethine group.[12,15–20,22]

These intramolecular N–H···N bonds, as well as other intra- ($\mathbf{T_a}$, Fig. 4) or intermolecular N–H···O contacts ($\mathbf{T_c}$ and **M**, Fig. 7) contribute to polarise the sulfonamide N–H groups of $\mathbf{H_2L}$, facilitating the deprotonation of the Schiff base. This polarisation can occur by charge flow through π-bonds (Schemes 2a and 2b), which could be assisted by a partial sp^2 nature of the sulfonamide N atoms. This type of interaction is typical of amide derivatives,[8d,11a,21,23] and can also be considered as an example of π-bond cooperativity,[21a] or "resonance-assisted hydrogen bonding" (RAHB).[24] In addition, polarisation of these N–H bonds might increase the donor ability of $\mathbf{H_2L}$ to behave as a ligand, since it also favours zwitterionic resonance forms of the type depicted in Scheme 2c, although the weight of the neutral forms always dominates.[21,23]

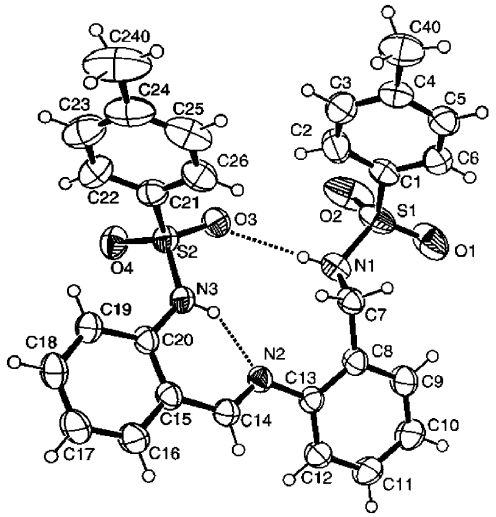


Fig. 4 ORTEP diagram of $\mathbf{T_a}$, showing intramolecular H-bonds and ellipsoids at 50% probability.

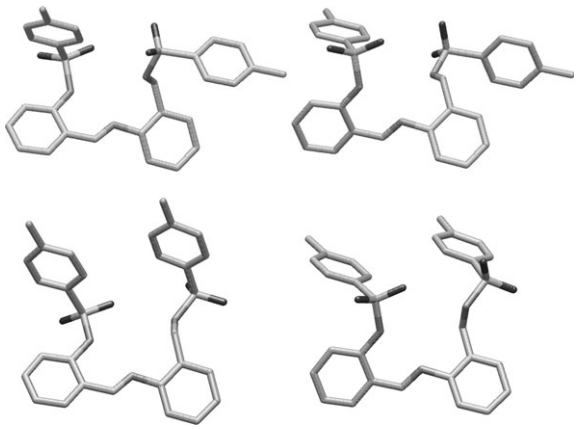


Fig. 5 Stick representations of the two conformers coexisting in $\mathbf{T_c}$ (*top*) and $\mathbf{T_a}$ (*bottom*).

Packing scheme. The close resemblance between the molecular conformations found for $\mathbf{T_c}$ and **M** (Fig. 3) leads to a similar pairing of their molecules (Fig. 7). Thus, both dimers of $\mathbf{T_c}$ and **M** are associated *via* two bifurcated hydrogen bonds,[21] where their N(1) atoms interact with a sulfonyl O atom of an adjacent molecule (major component), and with

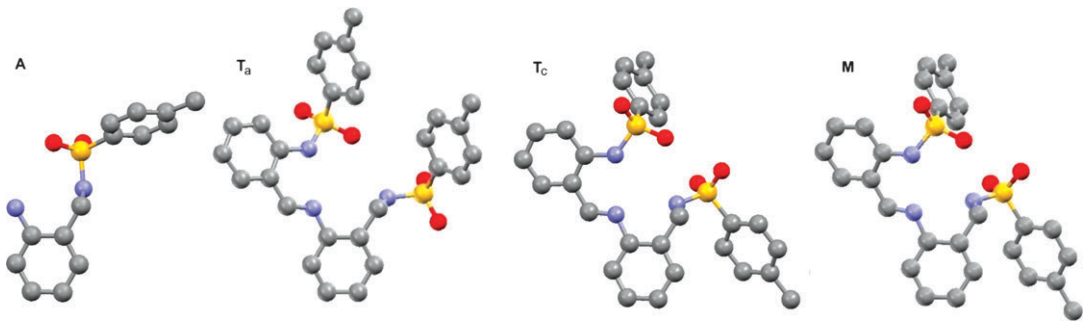


Fig. 3 Ball and stick representations of the molecular structures elucidated for **A** and the three polymorphs of $\mathbf{H_2L}$. Molecules have been chosen such that their N(1)–C(7)–C(8)–C(13) torsions have the same sign (Table 1) and consequently, the 2-aminobenzylamine residues could be similarly positioned for comparison. H atoms have been omitted for clarity.

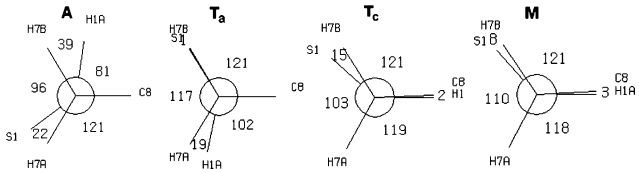
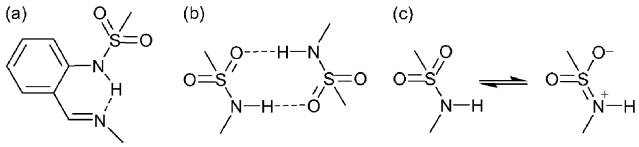


Fig. 6 Newman projections of the N(1)–C(7) bonds keeping the same positions for substituents on C(7).



Scheme 2 (a) Intramolecular H-bonds in conformers of $\mathbf{H_2L}$; (b) rings formed by dimers of $\mathbf{T_c}$, **M** and some other tosylamine Schiff base ligands;[19,20] (c) resonance forms for sulfonamide groups.

the imine N(2) atom of its own molecule (minor component). Likewise, analogous combinations of face-to-face and edge-to-face interactions seem to exist between contiguous aromatic rings in $\mathbf{T_c}$ and **M** dimers (Tables S3 and S4 in ESI†), with interplanar mean distances of about 4.1–4.3 Å, and C–H···centroid distances of about 2.8 Å.

As a result, $\mathbf{T_c}$ and **M** are constructed from similar dimeric units as "building-blocks" or supramolecular synthons,[25] but with different crystal packing schemes (Fig. 8 and 9, respectively). This latter might be explained on the basis of their slightly different torsions (Table 1), especially around single bonds. Among other minor differences (Tables S3 and S4 in ESI†), C–H···O interactions are intramolecular in the case of **M**, while in $\mathbf{T_c}$, an additional and well-oriented C(3)–H(3A)···O(3) interaction occurs between two molecules. Moreover, the packing scheme of $\mathbf{T_c}$ involves two C–H···π interactions, while **M** only displays one of this type. These apparently subtle divergences are probably enough to lead to polymorphism.

With regard to $\mathbf{T_a}$, substantial intramolecular H-bonds (Fig. 4, Table 2) seem to control its spatial conformation, whereas its crystal packing appears based on weaker interactions than classic H-bonds (Table S2 in ESI†). For instance, significant face-to-face π-stacking interactions between the

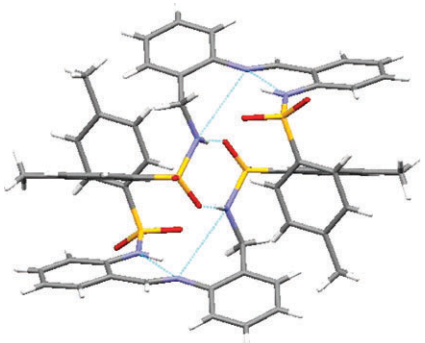


Fig. 7 Stick diagram of the centrosymmetric dimers present in $\mathbf{T_c}$, and equivalently in **M**, which are based on intermolecular H-bonds and π-interactions.

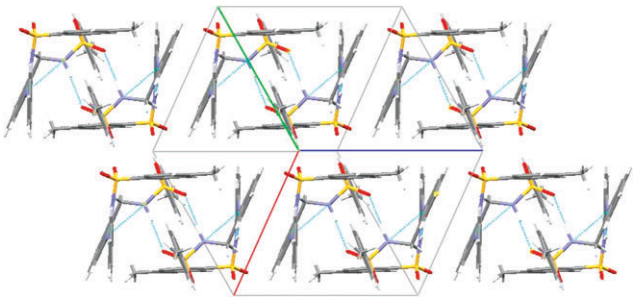


Fig. 8 Crystal packing of $\mathbf{T_c}$. All the dimers are identically orientated and stacked parallel to *c*.

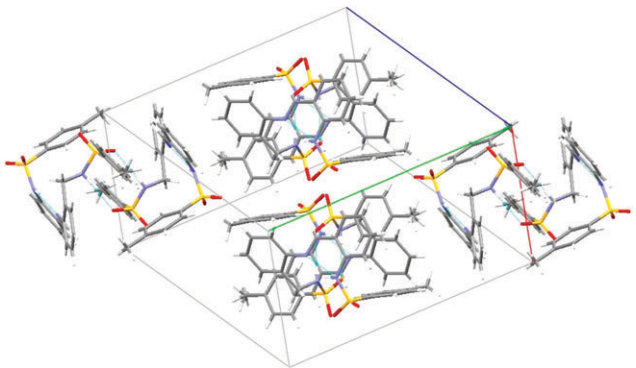


Fig. 9 Packing scheme of **M**.

p-tolyl residues of adjacent molecules (Fig. 10) also result in the formation of dimers.

Comparison of these three packing schemes appears to indicate that the two different conformations that give rise to conformational polymorphism mainly differ in an intramolecular N–H···O hydrogen bond.

Energy calculations. The semi-empirical molecular orbital program MOPAC 2000[26] has been used to calculate AM1 heats of formation[27] for the three polymorphic forms. These calculations resulted in the following values: −16.28, −15.45 and −14.90 kcal mol^{-1}, for $\mathbf{T_a}$, $\mathbf{T_c}$ and **M**, respectively. Additionally, some basic MM2[28] calculations were also made to estimate their corresponding E_{steric} values, resulting in differences between polymorphs of less than 0.5 kcal mol^{-1} (1 cal = 4.18 J).

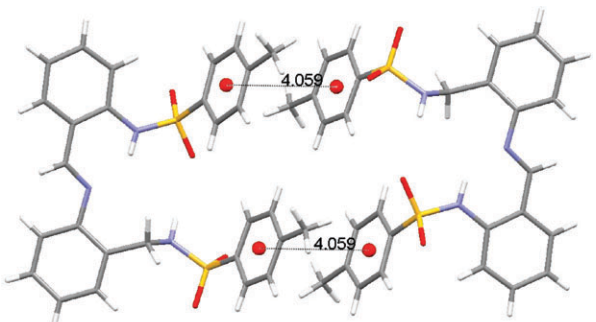


Fig. 10 Stick diagram to show the pairing of molecules in $\mathbf{T_a}$ *via* face-to-face π-stacking interactions, with distances between centroids.

Judging by these values, calculated energy barriers seem insufficient to avoid interconversion in solution at room temperature, and this could also explain the co-crystallisation of at least two of the polymorphs in each solution studied.

NMR studies

The spontaneous selectivity of the mono-tosylation of 2-aminobenzylamine became evident with the observation of a ^{1}H NMR spectrum of the crude solid isolated after this reaction as, even without further purification, the number and multiplicity of its signals corresponded to an unmixed compound.

Although the methylene and methyl proton signals of **A** could be unequivocally assigned in a simple 1D-spectrum, a detailed assignment of ^{1}H and ^{13}C signals in the aromatic region required the use of 2D-spectra. In consequence, NOESY (nuclear Overhauser enhanced spectroscopy), COSY (correlation spectroscopy) and HMQC (heteronuclear multiple quantum correlation) experiments were also performed. These techniques were also used to assign signals corresponding to **B**.

2-Tosylaminobenzaldehyde (B). Although a rough ^{1}H NMR characterisation had been already reported for **B**,[14] additional ^{1}H and ^{13}C data have now been included in the Experimental section, not only to accomplish its full characterisation, but to facilitate its comparison to **H_2L**. The HMQC spectrum has been included in the ESI as Fig. S1.†

2-(Tosylaminomethyl)aniline (A). The methylene signal (H_n, Scheme 1) was a clear reference in the COSY spectrum of **A**. Its coupling with the sulfonamide H_o proton led to the unequivocal identification of this broad signal, and demonstrated the tosyl-functionalisation of the benzylamine group.

It could be worth mentioning that the influence of the solvent ($CDCl_3$ or DMSO-d_6) on the chemical shift of each proton signal is noticeable, becoming more evident for those H atoms bonded to N atoms. Thus, the sulfonamide H_o proton undergoes a significant downfield shift (about 3 ppm) when the spectrum is measured in DMSO-d_6.

Regarding the NOESY experiment (Fig. S2 in ESI†), the coupling of the methylene signal (H_n) with an aromatic proton of the aniline residue evidenced the location of the H_m signal, since this is the only proton suitable to interact with H_n. As a result, the assignment of the remaining aniline aromatic protons was based on successive couplings: H_m–H_l, H_l–H_k, and H_k–H_j. In addition, location of *p*-tolyl protons was facilitated by the coupling between signals of the methyl group (H_r) and H_q protons.

An HMQC spectrum was also registered, but the assignment of some non-quaternary C-atom signals was not possible, in $CDCl_3$ solution at least, since some signals were indistinguishable (C_q–C_k and C_l–C_j) despite being chemically not equivalent.

H_2L. Condensation of **A** and **B** yielded the expected ligand (Scheme 1), with disappearance of those signals corresponding to the amine and aldehyde protons, and formation of an azomethine group. The new signal, at about 8.4 ppm in $CDCl_3$ solution, was assigned to the imine proton.[12–20,22] The Schiff condensation led to a noticeable downfield shift of the sulfonamide protons, which became more evident for the aldehyde residue H_a (about 2 ppm) than for the diamine one, H_o (about 0.6 ppm).

It should be noted that, as in the case of **A**, the methylene signal (H_n) was observed as a doublet, while that attributed to the sulfonamide H_o proton appeared as a triplet in the DMSO-d_6 spectrum. These multiplicities were interpreted as a result of the expected H_n–H_o coupling.

The twelve non-equivalent aromatic protons display very similar chemical shifts in DMSO-d_6 solution, so their full assignment was not possible. Something similar occurred when an HMQC experiment was performed with the intention of assigning the ^{13}C signals.

Conclusions

Mono-tosylation of 2-aminobenzylamine occurred selectively on the benzylamine group to yield 2-(tosylaminomethyl)-aniline, which forms infinite chains in the solid state, through N–H···O interactions.

2-(Tosylaminomethyl)aniline was condensed with 2-tosylaminobenzaldehyde to obtain **H_2L**. Three polymorphic forms (**T_a**, **T_c** and **M**) of this imine have been found, but the compound does not seem to present polymorphic selectivity of crystallisation in chloroform or in acetonitrile.

Sulfonamide H atoms corresponding to the aldehyde residue form equivalent intramolecular N–H···N bonds with adjacent azomethine N atoms in **T_a**, **T_c** and **M**. The remaining sulfonamide H atom participates in intra- (**T_a**) or intermolecular (**T_c** and **M**) N–H···O bonds. This divergence seems to be the key factor in the clearly different conformation of **T_a**, with respect to **T_c** or **M**.

Noteworthy face-to-face interactions exist between both tosyl groups of adjacent **H_2L** molecules in **T_a**, this stacking being one of the most remarkable features of the packing scheme of **T_a**.

In contrast, crystal construction of **T_c** and **M** seems based on analogous dimers, which are connected by two N–H···O bonds, in conjunction with face-to-face and edge-to-face interactions. Despite this equivalence between the "building blocks" packed in **T_c** and **M**, some subtle divergences within their molecular arrays lead to differences that cause polymorphism. Thus, an additional C–H···π interaction in **M**, or a supplementary intermolecular C–H···O bond in **T_c**, are likely responsible for their different crystal packings.

Experimental

Materials and methods

Chemicals of the highest commercial grade available (Aldrich) were used as received, without further purification. Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on Bruker spectrometers, using DMSO-d_6 or $CDCl_3$ as solvents. FTIR spectra were recorded using KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. FAB mass spectra were recorded on a Micromass Autospec spectrometer in the range 200–2000

m/z, employing *m*-nitrobenzyl alcohol as matrix. Characterisation analyses were performed by the in-house services (CACTUS).

Syntheses

2-(Tosylaminomethyl)aniline (A). A dichloromethane solution (200 cm^3) of 2-aminobenzylamine (2 g, 16.37 mmol), tosyl chloride (3.12 g, 16.37 mmol) and triethylamine (2.27 cm^3, 16.27 mmol) was refluxed for 8 h. After cooling, the triethylamine hydrochloride was removed by filtration upon celite, and the resulting solution was extracted with acidic water (3 × 100 cm^3, pH = 5). The remaining dichloromethane solution was dried with anhydrous Na_2SO_4. The solid was removed by filtration, and the resulting solution was concentrated *in vacuo*, yielding a very pale beige powdery solid, which was subsequently characterised as **A** (1.96 g, 78%); mp 135 °C; anal. found: C, 61.2; H, 5.9; N, 10.2; S, 11.2%; $C_{14}H_{16}N_2O_2S$ (M, 276.1 g mol^{-1}) requires: C, 60.85; H, 5.80; N, 10.14; S, 11.59%; FTIR (KBr, cm^{-1}): ν(N–H) 3479(s), 3386(s), 3289(s), ν(C–N) 1322(vs), $\nu_{as}(SO_2)$ 1292(sh), $\nu_s(SO_2)$ 1157(vs), ν(C–S) 668(m); m/z (FAB): 276.1 (100%) [M^+]; δ_H (250 MHz, $CDCl_3$, ppm): 7.81 (2H, d, H_p); 7.29 (2H, d, H_q); 7.09 (1H, t, H_k); 6.84 (1H, d, H_m); 6.78 (1H, d, H_j); 6.72 (1H, t, H_l); 4.81 (1H, t, H_o); 4.10 (2H, s, H_i); 3.91 (2H, s, H_n); 2.42 (3H, s, H_r); (250 MHz, DMSO-d_6, ppm): 7.89 (1H, t, H_o); 7.75 (2H, d, H_p); 7.41 (2H, d, H_q); 6.97 (2H, d, H_l + H_j); 6.64 (1H, d, H_m); 6.50 (1H, t, H_k); 4.93 (2H, s, H_i); 3.79 (2H, d, H_n); 2.41 (3H, s, H_r); δ_C (75 MHz, Cl_3CD, ppm): 144.0 (1C); 136.34 (1C); 130.61 (1C, C_m); 130.08 (3C, C_q, C_k); 127.40 (2C, C_p); 121.10 (1C); 119.63 (1C); 117.44 (2C, C_l, C_j); 45.51 (1C, C_n); 21.79 (1C, C_r).

2-Tosylaminobenzaldehyde (B)[14]. δ_H (250 MHz, $CDCl_3$): 10.80 (1H, s, H_a); 9.79 (1H, s, H_i); 7.74 (2H, d, H_d); 7.64 (1H, d, H_e); 7.57 (1H, d, H_h); 7.48 (1H, t, H_f); 7.21 (2H, d, H_c); 7.13 (1H, t, H_g); 2.33 (3H, s, H_b); δ_C (75 MHz, $CDCl_3$, ppm): 195.0 (1C, C_i); 136.0 (2C, C_f, C_h); 129.7 (1C, C_c); 127.3 (1C, C_d); 122.9 (1C, C_g); 117.7 (1C, C_e); 21.6 (1C, C_b).

Synthesis of the Schiff base. H_2L was obtained by condensation of 2-(tosylaminomethyl)aniline (**A**) with 2-tosylaminobenzaldehyde[14] (**B**) (Scheme 1).

A chloroform solution (about 150 cm^3) of **A** (2.5 g, 9.1 mmol) and **B** (2.5 g, 9.1 mmol) was heated at reflux over a 6 h period. Concentration *in vacuo* of the solution obtained gave rise to an oily fluid. This was treated with dry diethyl ether to yield a yellowish powdery solid, which was collected by filtration, washed with dry methanol and diethyl ether, and finally, dried *in vacuo*. The solid was characterised as follows: yellowish powder (4.30 g, 87%); mp 165 °C; anal. found: C, 59.13; H, 5.39; N, 7.40; S, 10.15; O 16.85%. $C_{28}H_{27}N_3O_4S_2 \cdot 2H_2O$ (M, 569.65 g mol^{-1}) requires: C, 59.03; H, 5.48; N, 7.38; S, 11.26; O 16.12%; FTIR (KBr, cm^{-1}): ν(O–H) 3457(br), ν(N–H) 3257(m), ν(C=N) 1614(s), ν(C–N) 1338(m), $\nu_{as}(SO_2)$ 1291(s), $\nu_s(SO_2)$ 1157(vs), ν(C–S) 661(s); m/z (FAB): 534.2 (100%) [$M^+ - 2H_2O$]; δ_H (250 MHz, $CDCl_3$): 12.80 (1H, s, H_a); 8.41 (1H, s, H_i); 7.78 (2H, d, H_p); 7.71 (2H, d, H_d); 7.56 (1H, d, H_e); 7.50 (1H, d, H_h); 7.41 (1H, d, H_m); 7.35 (1H, d, H_j); 7.29 (2H, m, H_f + H_g); 7.25 (2H, d, H_q); 7.20 (2H, d, H_c); 7.09 (1H, t, H_k); 7.00 (1H, d, H_l); 5.50 (1H, t, H_o); 4.39 (2H, d, H_n); 2.39 (6H, s, H_b + H_r); (250 MHz, DMSO-d_6, ppm): 12.16 (2H, s, H_a); 8.59 (1H, s, H_i); 8.05 (1H, t, H_o); 7.77 (1H, d, H_e); 7.69 (2H, d, H_p); 7.66 (2H, d, H_d); 7.44 – 7.11 (11H, m, H_c + H_f + H_g + H_h + H_j + H_k + H_l + H_m + H_q), 4.23 (2H, d, H_n); 2.32, 2.29 (6H, 2 s, H_b, H_r); δ_C (125 MHz, $CDCl_3$, ppm): 162.5 (1C, C_i); 136.0 (2C, C_e, C_h); 134.5 (1C, C_m); 129.7 (2C, C_q, C_c); 127.2 (2C, C_p, C_d); 122.9 (1C, C_k); 117.7 (1C, C_l); 44.5 (1C, C_n); 21.6 (2C, C_b, C_r).

Table 3 Crystal and structure refinement data for **A** and **H_2L** (**T_a**, **T_c** and **M**)[2]‡

	A	**T_a**	**T_c**	**M**
Empirical formula	$C_{14}H_{16}N_2O_2S$	$C_{28}H_{27}N_3O_4S_2$	$C_{28}H_{27}N_3O_4S_2$	$C_{28}H_{27}N_3O_4S_2$
M_r	276.35	533.65	533.65	533.65
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group [No.]	$P2_1/n$ [14]	$P\bar{1}$ [2]	$P\bar{1}$ [2]	$P2_1/n$ [14]
Crystal dimensions/mm	0.52 × 0.32 × 0.24	0.40 × 0.36 × 0.32	0.52 × 0.48 × 0.44	0.41 × 0.31 × 0.27
Wavelength/Å (radiation)	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)	0.71073 (Mo-Kα)
Description	Prism, colourless	Prism, yellow	Prism, yellow	Prism, colourless
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	ω
$2\theta_{max}/°$	73.08	74.89	73.45	52.74
a/Å	13.184(3)	8.797(5)	10.206(1)	9.046(2)
b/Å	5.7697(10)	10.788(4)	10.734(1)	18.882(3)
c/Å	18.696(4)	14.713(8)	12.878(1)	16.057(3)
$\alpha/°$	90	100.53(5)	97.96(1)	90
$\beta/°$	100.833(16)	101.70(5)	95.36(1)	105.14(1)
$\gamma/°$	90	100.23(6)	108.69(1)	90
U/Å^3	1396.7(5)	1310.4(11)	1309.2(1)	2647.4(8)
D_c/g cm^3	1.314	1.352	1.354	1.339
Z	4	2	2	4
μ/mm^{-1}	2.060	2.169	2.171	0.240
Max. trans., min trans.	0.6377, 0.3186	0.6811, 0.2092	0.3830, 0.2157	1.000 , 0.7903
No. Ref. col./No. Ref. ind.	2872/2785	5691/5327	5742/5263	24691/5404
R_{int}	0.0680	0.0271	0.0973	0.0389
Data/restraints/parameters	2785/0/184	5327/0/343	5263/0/337	5404/0/344
R_1, wR_2 [$I > 2\sigma(I)$]	0.0632, 0.1395	0.0522, 0.1465	0.0555, 0.1596	0.0457, 0.1168
R_1, wR_2 (all data)	0.1731, 0.2117	0.0636, 0.1561	0.0581, 0.1627	0.0832, 0.1286
Residuals/e Å^{-3}	0.218, −0.353	0.288, −0.352	0.470, −0.811	0.219, −0.256

Single crystal X-ray diffraction studies

The crystal structures of **A**, $\mathbf{T_a}$, $\mathbf{T_c}$ and **M** have been determined. Diffraction data for **A**, $\mathbf{T_a}$ and $\mathbf{T_c}$ were collected in the in-house service (CACTUS) at room temperature on an Enraf Nonius Turbo CAD4 diffractometer, using graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å) from a fine focus sealed tube source. Data for **M** were collected on a Siemens CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). All the data sets were processed and corrected for Lorentz and polarisation effects. Decays were also corrected for **A** (6%), $\mathbf{T_a}$ (18%), $\mathbf{T_c}$ (10%) and **M** (1%). Absorption corrections were applied through either psi-scan (**A**, $\mathbf{T_a}$ and $\mathbf{T_c}$) or multi-scan[29] methods (**M**).

The structures were solved by direct methods using SIR-92 [30] ($\mathbf{T_a}$, $\mathbf{T_c}$ and **M**) or SHELXS-97 [31] (**A**), and refined by full-matrix least-squares techniques based on F^2 (SHELXL-97).[31] All non-hydrogen atoms were anisotropically treated. All hydrogen atoms were included in the model at geometrically calculated positions, and refined using a riding model (SHELXL-97),[31] except those bonded to amine or amide H atoms. These latter could be located on Fourier maps and then, either isotropically treated (**A**, $\mathbf{T_a}$ and **M**), or their coordinates were fixed with U_{eq} of 0.1 ($\mathbf{T_c}$). Molecular graphics were represented by Ortep-3 for Windows[32] or Mercury.[33] Packing schemes were studied with the help of PLATON.[34] (Table 3)

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