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Proton transfer and $N^{(+)}$–H···$S^{(-)}$ hydrogen bonds in the crystal structure of 4-aminothiophenol†

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4-Aminothiophenol exists as 4-ammonio-1-benzenethiolate in the solid and liquid state. The crystal structure is characterised by a tetrahedral β-As type network which is the driving force for the proton transfer.

Hydrogen bonds (bridges) with sulfur as a donor (S–H) are not well studied and lie at the border between strong and weak interactions.[1] The S–H group is a significantly weaker donor than the O–H group. Therefore, S–H···X (X = O, N, S, π) hydrogen bonds occur in crystals very rarely even in compounds that contain the pertinent functionalities.[2] We carried out computations on the H_2S–NH_3 and thiophenol–aniline systems (Spartan, RHF/6-31G**; GAMESS, RHF/6-31G** after BSSE correction) and concluded that S–H···N is a weak interaction with a stabilisation in the range −1.5 to −3.5 kcal mol^{-1} and an S···N distance of 3.70 Å (see ESI†).

Along these lines, we determined the crystal structure of 4-aminothiophenol, **1**. In the related 4-aminophenol, **2**, a two-dimensional network of O–H···N and N–H···O hydrogen bonds that resembles a supramolecular chair cyclohexane (β-As sheet) fully satisfies the hydrogen bonding capabilities of the –OH and $–NH_2$ functionalities.[3,4] The idea was that a corresponding combination of S–H···N and N–H···S hydrogen bonds in crystalline **1** would also result in the formation of the β-As network. Compound **1** (mp 45.7 °C) liquefies easily, and was crystallised by cooling the neat liquid in the refrigerator. The crystal was transferred to the diffractometer on a small block of dry ice (approximate temperature −60 °C) and fixed with grease at −30 °C. The data collection was carried out at −70 °C.‡

As in **2**, the N and S-atoms in **1** form a β-As network§ seemingly confirming our hypothesis (Figs. 1 and 2).[5] However, there was also clear evidence that rather than a combination of S–H···N and N–H···S hydrogen bonds in this network, a proton transfer had occurred from the S-atom to the N-atom so that only $N^{(+)}$–H···$S^{(-)}$ hydrogen bonds are present. The difference maps and the smooth refinement of the H-atoms clearly show that they are bonded to N, and the N···S distances (3.14, 3.19, 3.20 Å) are unusually short (ESI†). Fig. 1 shows the arrangement around S- and N-atoms while Fig. 2 shows the β-As sheet. The three N···S distances are nearly the same, unlike in **2**, where the N···O separations are quite different (2.77, 3.14, 3.25 Å) corresponding to O–H···N and N–H···O hydrogen bonds, respectively. This near equality of N···S distances occurs because all the three hydrogen bonds in **1** are equivalent and are of the $N^{(+)}$–H···$S^{(-)}$ type.

A recent paper by Becker *et al.* shows that proton transfer from S–H to N across an S···N bridge is facile in some ammonium silanethiolates.[6] The coordination around the N- and S-atoms in these silanethiolates and compound **1** is the same. In both cases, any N- or S-atom is connected to three S- and N-atoms, respectively, *via* strong, electrostatic hydrogen bonds of the $N^{(+)}$–H···$S^{(-)}$ type. While the resulting arrangement is a cube in the silanethiolates, it is a (β-As) sheet in 4-aminothiophenol, now more accurately termed 4-ammonio-1-benzenethiolate.

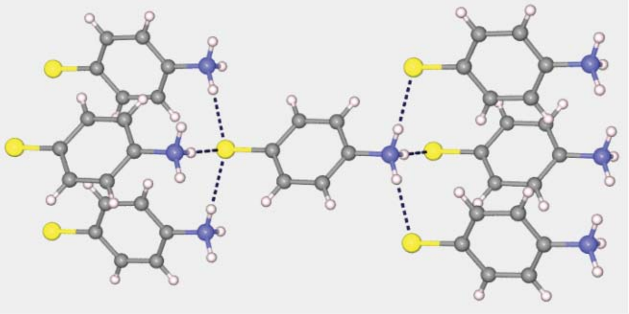

Fig. 1 Tetrahedral environment around S- and N-atoms in 4-aminothiophenol (4-ammonio-1-benzenethiolate).

A CSD search revealed only three hits that could possibly correspond to S–H···N interactions. In 2,5-mercaptothiadiazole (DMCTDZ), there is an appropriate S···N geometry but it is not clear if the H-atom is bonded to the S-atom or to the N-atom.[7] In 1,4-diamino-2,2′,6,6′-tetramercaptobiphenyl (HIPMUO), there are two S···N contacts which might correspond to weak S–H···N interactions.[8] In 1-formyl-3-thiosemicarbazide (SOJNAG), there is a weak S–H···N interaction.[9] From these structures we assign an S···N distance (*D*) range of 3.60–4.00 Å for this interaction in agreement with our computed value of 3.70 Å. In contrast, there are around 59 examples of the $N^{(+)}$–H···$S^{(-)}$ bridge in the CSD, with 11 being formed by aromatic amine thiolates (see ESI†). The N···S distance range for this interaction is much shorter (3.00–3.60 Å) as might be expected.

The IR spectrum of **1** was recorded at −63, −38, 25 and 33 °C with the sample being semi-solid in the last case. All four spectra are essentially the same and show that the compound exists predominantly in the zwitterion form.¶ We simulated these spectra with Gaussian03 at the RHF/6-31 + +G(d,p) level (ESI†). While there is good agreement between experiment and theory for the symmetric (3371 cm^{-1}) and asymmetric (3430 cm^{-1}) N–H stretches, there is an additional moderately strong band at 3210 cm^{-1}, which we assign to the $N^{(+)}$–H stretch. This cannot be modelled theoretically for the monomer but appears when the dimer is so modelled. This assignment is further supported by the presence of a band at 1598 cm^{-1} that corresponds to the NH_3^+ deformation bending. Unlike in thiophenol wherein a solvent shift corresponding to S–H···N hydrogen bonding was seen in MeCN,[10] no such effect was observed when the IR spectrum of **1** was recorded in MeCN. All these results show that compound **1** almost surely exists as a zwitterion, and also at elevated temperatures, thus qualifying for the descriptor 'ionic liquid'.

To estimate the energy of the $N^{(+)}$–H···$S^{(-)}$ interaction, we

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† Electronic supplementary information (ESI) available: (i) ORTEP plot drawn at 50% probability level for non-H atoms. (ii) Difference Fourier map for the H-atom positions around the N-atom. (iii) Pertinent intermolecular interactions for compound **1**. (iv) A CSD search on N–H···S interactions. (v) Computational details. (vi) Structure refinement parameters. (vii) Computation related references. (viii) IR spectra recorded at variable temperatures. See http://www.rsc.org/suppdata/cc/b4/b407319c/

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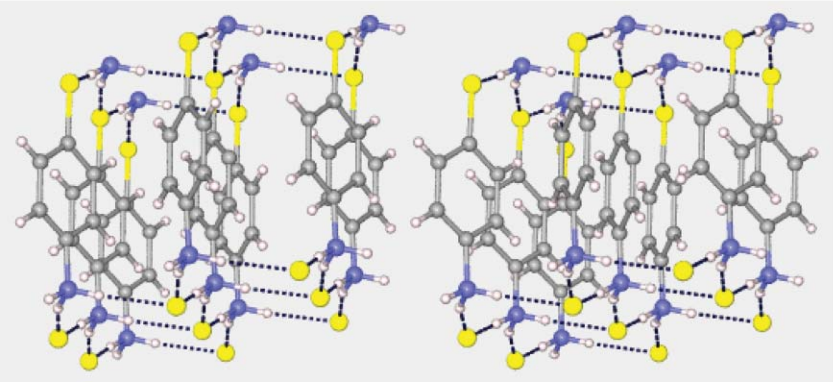
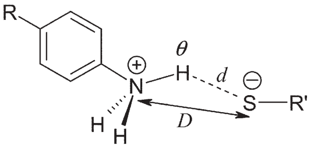


Fig. 2 Stereoview of the β-As network in the title compound.

Table 1 Calculation of the energy of the $\mathrm{N^{(+)}}$–H···$\mathrm{S^{(-)}}$ interaction (see also ESI†)

	D/Å	θ/°	Energy at $\theta \sim 90°$ (E_1)/a.u.	Energy at optimized geometry (E_2)/a.u.	($E_2 - E_1$)/ kcal mol^{-1}
3a	2.90254	157.60	−684.4470155	−684.463195	−10.1528
3b	2.93019	168.24	−914.0213227	−914.046990	−16.1065
3c	2.93462	168.76	−1366.6074755	−1366.628377	−12.1787

carried out computations with GAMESS (RHF/6-311G**) on the ammonium thiolate systems shown above (Table 1). In each case, the $\mathrm{X^{(+)}}$–H···$\mathrm{A^{(-)}}$ energy was computed for a geometry with the hydrogen bond angle (θ) being optimised and also for a geometry for which this angle was constrained to be around 90°. In both cases the X···A distance (D) was fixed at the optimised value. The energy for the latter case corresponds to the electrostatic stabilisation because hydrogen bonding vanishes when $\theta = 90°$. The energy for the optimised geometry gives both the electrostatic and hydrogen bonding components. This method gives a good idea of the $\mathrm{N^{(+)}}$–H···$\mathrm{S^{(-)}}$ energy, which is seen to lie in the 10–15 kcal mol^{-1} range.



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3a R = R' = H
3b R = H, R' = Ph
3c R = SH, R' = -C_6H_4-(p)- NH_2

Given that the optimum S···N separation for an S–H···N interaction is around 3.70 Å whereas the N···S separation for a typical $\mathrm{N^{(+)}}$–H···$\mathrm{S^{(-)}}$ interaction is around 3.30 Å, and both interactions correspond to energy minima we tried to estimate the barrier to the proton transfer reaction. An estimate is obtained by arguing that the stabilisation achieved from the herringbone interactions in the β-As sheet structure of **1** should provide enough driving force for 'compressing' the molecules close enough together so that proton transfer actually takes place. We estimate [Gaussian03, 6-311G(2d,2p)] a total herringbone stabilisation of −29.67 kcal mol^{-1} for a reference molecule in the β–As structure of **1**,[11] (see also ESI†). This means that the upper limit for the barrier to proton transfer is roughly half this value (there are two proton transfers per molecule). Proton transfer from the S–H···N geometry is easy although the S–H group is a weak acid because the smaller bond dissociation energy of S–H compensates for this. For example, studies on proton transfer in the HCl–NH_3 and H_2S–NH_3 systems show that the enthalpy changes for heterolytic dissociation of the Cl–H and S–H bonds are virtually identical.[12] We conclude that a pure S–H···N hydrogen bond may be rather difficult to find. The β-As network may well provide the impetus for the appearance of this novel $\mathrm{N^{(+)}}$–H···$\mathrm{S^{(-)}}$ hydrogen bond.

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Notes and references

‡ The grease is soft at −30 °C but hard at −70 °C.

§ *Crystal data* for **1**: (C_6H_7NS), M = 125.19, monoclinic, space group Pc, a = 7.230(12), b = 5.8513(10), c = 7.7552(13) Å, β = 107.364(3), V = 313.15(9) Å^3, T = 203(2) K, Z' = 1, μ = 0.399 mm^{-1}, λ(Mo-Kα) = 0.71073 Å, size 0.24 × 0.18 × 0.05 mm. Siemens SMART CCD area detector, 3386 total reflections of which 1518 were independent, 1474 observed [$I > 2\sigma(I)$]. Structure solution and refinement with SHELXTL Vers. 6.12, final refinement against F^2 with 86 parameters, R_1 [$I > 2\sigma(I)$] = 0.0277, wR_2 = 0.0767. H-atoms bound to the phenyl group were generated by a riding model on idealized geometries and refined isotropically with thermal parameters based upon the corresponding carbon atoms [U(H) = 1.2U_{eq}(C)], while the H-atoms of the anilinium ion were located in difference Fourier maps and these H-atoms were refined isotropically without any constraints. CCDC 238927. See http://www.rsc.org/suppdata/cc/b4/b407319c/ for crystallographic data in .cif or other electronic format.

¶ We estimate that there is around 10% of the thiol form at 33 °C.

1 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999, pp. 253–266; G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565.
2 C. H. Görbitz and B. Dalhus, *Acta Crystallogr., Sect. C*, 1996, **52**, 1756; T. Steiner, *Acta Crystallogr., Sect. C*, 2000, **56**, 876; V. R. Vangala, G. R. Desiraju, R. K. R. Jetti, D. Bläser and R. Boese, *Acta Crystallogr., Sect. C*, 2002, **58**, 635.
3 V. R. Vangala, B. R. Bhogala, A. Dey, G. R. Desiraju, C. K. Broder, P. S. Smith, R. Mondal, J. A. K. Howard and C. C. Wilson, *J. Am. Chem. Soc.*, 2003, **125**, 14495.
4 O. Ermer and A. Eling, *J. Chem. Soc., Perkin Trans. 2*, 1994, 925.
5 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189; J. L. Atwood and L. J. Barbour, *Cryst. Growth Des.*, 2003, **3**, 3.
6 B. Becker, K. Baranowska, J. Chojnacki and W. Wojnowski, *Chem. Commun.*, 2004, 620.
7 J. W. Bats, *Acta Crystallogr., Sect. B*, 1976, **32**, 2866.
8 Q. Zhu-Ohlback, R. Gleiter, F. Rominger, H.-L. Schmidt and T. Reda, *Eur. J. Org. Chem.*, 1998, 2409.
9 A. K. Saxena, S. K. Sinha and T. P. Singh, *Acta Crystallogr., Sect. C.*, 1991, **47**, 2374.
10 J. G. David and H. E. Hallam, *Trans. Faraday Soc.*, 1964, **60**, 2013.
11 R. L. Jaffe and G. D. Smith, *J. Chem. Phys.*, 1996, **105**(7), 2780.
12 P. Herbine, T. A. Hu, G. Johnson and T. R. Dyke, *J. Chem. Phys.*, 1990, **93**, 5485.