Structural and IR-spectroscopic evidence of S–H···Ph hydrogen bonding in the solid state

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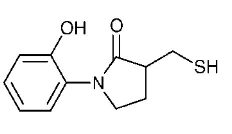
Structural and IR spetroscopic evidence is given for S–H···Ph hydrogen bonding in the solid state, an effect previously only known in solution. In the crystalline thiol *N*-(*o*-hydroxyphenyl)-3-sulfanylmethylpyrrolidin-2-one, hydrogen bond energies based on red shifts of the infrared S–H stretching marks are estimated as slightly below 0.5 (in benzene) and 1.0 (solid state) kcal mol^{-1}.

It was originally recognized over 60 years ago that the π-electron cloud of phenyl rings and of other π-bonded moieties can act as an acceptor of hydrogen bonds.[1] However, greater interest in hydrogen bonds of this type has developed only recently.[2] Today, it is well known that hydrogen bonds to π-acceptors play important roles in a wide variety of systems, ranging from organometallic[3] to organic[4] and biological[5] compounds. As donors of these hydrogen bonds, O–H, N–H, Cl–H and acidic C–H groups have been identified in the solid state.[2] For the donor S–H, there is some early solution IR-spectroscopic indication of very weak S–H···Ph hydrogen bonding,[6,7] but this finding has attracted little attention and has, to our knowledge, never been substantiated in a solid state investigation. In the present study, we first give combined structural and IR-spectroscopic evidence for S–H···Ph hydrogen bonding in crystals, allowing us to describe the geometry and energetics of this interaction.

As a suitable model system to study the anticipated hydrogen bond effect, compound **1** [*N*-(*o*-hydroxyphenyl)-3-sulfanylmethylpyrrolidin-2-one] was selected, the synthesis and structure of which one of us has reported previously.[8] In the crystal, this compound forms a conventional intermolecular O–H···O=C hydrogen bond, Fig. 1 and Table 1. The thiol group is not oriented towards one of the O- or S-atoms of the neighboring molecules, but points at the centre of an aromatic ring. This interaction links pairs of adjacent molecules into centrosymmetric dimers. The distance of the H-atom to the aromatic midpoint is only 2.57 Å, which is a typical value for X–H···Ph hydrogen bonding with O–H, N–H and polar C–H groups.[2–5] Notably, for the weak donor C≡C–H, the hydrogen bond nature could be shown by solid state IR spectroscopy for C–H···Ph contacts in terminal alkynes with very similar distances.[9]

This contact is a promising candidate to show S–H···Ph hydrogen bonding with the technique that is best suited for this purpose, that is vibrational spectroscopy. Unlike crystallography, vibrational spectroscopy can *directly* infer the hydrogen bond nature of a given intermolecular interaction. This is done by measuring the S–H stretching frequency ν_{SH} of **1**, in the solid state and in an inert solvent. If the S–H···Ph contact in the solid is in fact of the hydrogen bond type, the absorption maximum of ν_{SH} will shift to a lower frequency relative to a free molecule in inert solution.



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Ideally, ν_{SH} of the undisturbed S–H group should be measured in a solvent as apolar as possible. Because **1** is insoluble in CCl_4, absorption spectra of dilute solutions in chloroform were recorded. The weak ν_{SH} band was revealed by measure-

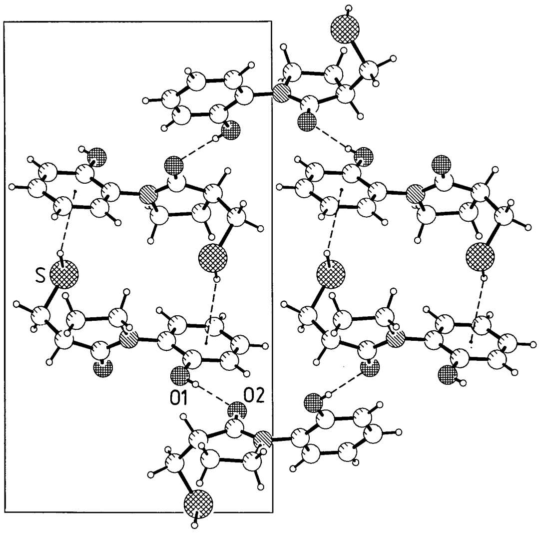

Fig. 1 Crystal structure of **1**, drawn using data from ref. 8.

Table 1 Geometry of the hydrogen bonds X–H···A in **1** (for normalized H-atom positions: O–H = 0.983, S–H = 1.33 Å). M denotes the center of the aromatic ring

Contact	H···A/Å	X···A/Å	X–H···A/°
O1–H···O2	1.70	2.67	172
S–H···C1	2.94	3.82	122
S–H···C2	2.85	4.00	144
S–H···C3	2.82	4.14	171
S–H···C4	2.88	4.11	153
S–H···C5	2.98	3.95	129
S–H···C6	3.02	3.81	117
S–H···M	2.57	3.73	144

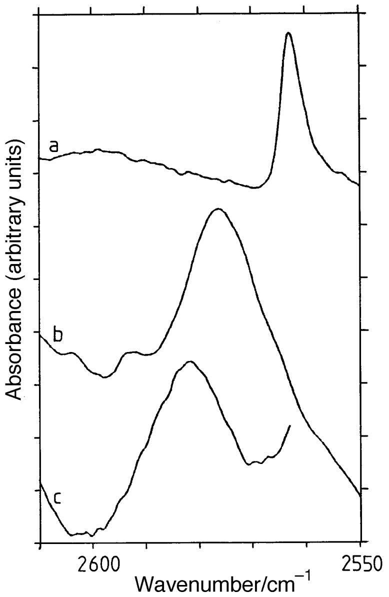

Fig. 2 Infrared absorption spectrum of (a) microcrystalline **1** between KBr plates, (b) a dilute solution of **1** in benzene, and (c) a solution of **1** in $CHCl_3$ (concentration 10^{-2} M, 1 cm infrasil cell). Only the relevant section with the S–H absorption band is shown. The curves peak at 2562.9 cm^{-1} for a, 2576.2 cm^{-1} for b and 2581.7 cm^{-1} for c. The spectra were measured at room temperature on a Bruker 113v FTIR spectrometer and processed using the Bruker OPUS program.

ments at several concentrations in the range 10^{-2}–10^{-3} M. In $CHCl_3$, ν_{SH} peaks at 2581.7 cm^{-1} (Fig. 2, trace *c*, technical details in the figure legend), which is in the range typical for undisturbed R–CH_2–SH molecules in CCl_4.[7] The half-width $\Delta\nu_{1/2} = 15$ cm^{-1} and the molar integral intensity coefficient of 0.027×10^4 cm mmol^{-1} are also typical for ν_{SH} bands of molecules in inert solution.[10] In the crystal, the S–H oscillator of **1** absorbs at 2562.9 cm^{-1} (Fig. 2, trace *a*). This is a reduction of 18.8 cm^{-1} compared to the solution in $CHCl_3$, well within what is accepted as an indication of hydrogen bonding. For comparison, typical values are around 20 cm^{-1} for S–H···S hydrogen bonding involving thiols, sulfanes and thiophenols, and around 50 cm^{-1} for normal S–H···O hydrogen bonds (all values at room temperature).[2] This indicates at least qualitatively that the S–H···Ph interaction in crystalline **1** compares in strength with a typical S–H···S hydrogen bond.

When **1** is dissolved in benzene, the ν_{SH} band peaks at 2576.2 cm^{-1} (Fig. 2, trace *b*). The reduction of 5.5 cm^{-1} compared to the $CHCl_3$ solution is most likely due to an S–H···π interaction with the solvent. Obviously, this interaction is even weaker than the S–H···Ph hydrogen bond in the crystalline state.

It is of interest to estimate the bond energy of the S–H···Ph interaction in **1**. Systematic studies of ν_{SH} band shifts and intensity enhancement upon hydrogen bond formation have earlier been performed for several mercaptanes and hydrogen sulfide in various solvents (from CCl_4 to pyridine),[10] and bond energies were determined with the 'rue of intensity'[11] of Iogansen (which states proportionality of hydrogen bond energy and intensification of the ν_{XH} band). For hydrogen sulfide, these results were later confirmed by gas chromatography measurements.[12] By application of the published correlations[10] to the ν_{SH} shifts in the present experiments, approximate estimations are obtained as 0.3–0.5 kcal mol^{-1} for the S–H···Ph interaction with benzene solvent molecules, and 0.9–1.0 kcal mol^{-1} for the S–H···Ph interaction in the crystalline state. For comparison, energies of typical O/N–H···Ph hydrogen bonds are in the range 2–4 kcal mol^{-1}, but can fall below this range in the case of geometrical distortions.[2] Energies of typical C≡C–H···Ph hydrogen bonds are around 1–1.5 kcal mol^{-1}.[9]

The structural and spectroscopic data shown here indicate the presence of unambiguous S–H···Ph hydrogen bonds in crystalline **1**. With a magnitude of 1 kcal mol^{-1}, the interaction is quite weak, but it is directional, and the view in Fig. 1 suggests that it does play an organizing role in the solid. This finding is of importance for the structural chemist who, when interpreting the architecture of supramolecular assemblies, has to take into account an ever growing number of different intermolecular interactions. In the present case, the structure of **1** would be difficult to rationalize without considering the S–H···Ph hydrogen bond, because this would mean an S–H group that is 'free' in the solid state despite several hydrogen bond acceptors being present. When taking the S–H···Ph interaction into account, the structure becomes much easier to undestand.

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