**SHORT PAPER**

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# Self-assembly of novel supramolecular networks formed by 1-[(1-propyl)iminomethyl]-2,4-dihydroxybenzene[†]

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The condensation of propylamine and 2,4-dihydroxybenzaldehyde in absolute ethanol leads to the formation of a unique supramolecular structure, whose crystal structure is reported here. The material displays an unusual synergistic combination of intra- and intermolecular hydrogen bonding.

Self-assembly is the interaction of several species via hydrogen bond interactions to form a supramolecular structure[1–3]. The literature contains many examples of self-assembled cages,[4] ribbons,[5] and chains, most of which are bound by an ordered system of hydrogen bonds. The order within many such ensembles is governed by the availability of sites which are hydrogen bonding active.

In previous work it has been shown that 1,3-dihydroxybenzene and its derivatives can hydrogen bond to form supramolecular structures with a range of host molecules including poly(vinylpyrrolidone)[6] and hexamethylenetetramine.[7] In the case of poly(vinylpyrrolidone), the two hydroxyl groups allow binding of every first and third pyrrolidone unit. This recognition causes the complex to self-assemble and precipitate from a variety of polar solvents.

We now report the structure of 1-[(1-propyl)iminomethyl]-2,4-dihydroxybenzene, and its unique self-assembly into long ribbons in an extremely polar and competitive hydrogen bonding environment.

While investigating the structures and properties of Schiff's base complexes formed between primary alkyl amines and phenolic aldehydes, it was noticed that the condensation of propylamine and 2,4-dihydroxybenzaldehyde in absolute ethanol was unique in that it yielded a solid product **(1)** which precipitated from solution.

The $^{1}$H NMR of **(1)** in dimethyl sulphoxide showed that on condensation, one of the hydroxyl protons was shifted from 10 to 14 ppm. Condensation of salicylaldehyde (*o*-hydroxybenzaldehyde) with propylamine also gives a product which shows this shift in the $^{1}$H NMR, though the compound is a liquid. The solid phase infra-red of **(1)** is consistent with that of a system containing very strong hydrogen bonding units. An intense, broad structural band covering the region *ca* 3500–1700 cm$^{-1}$, (Fig. 1) and typical of an easily polarisable hydrogen bond is observed. This infrared spectrum is only observed when propylamine is used and not when analagous molecules are synthesised using methylamine or phenylamine.

The interesting properties of **(1)** are consistent with both hydroxyl groups being involved in strong hydrogen bonding. It is not observed in the case of the products obtained using *o*-hydroxybenzaldehyde (salicylaldehyde) and *p*-hydroxybenzaldehyde, again indicating that the exsistence and position of both hydroxyls is vital for self assembly, as previously observed in other systems.[6,7]

The NMR data suggests the presence of an intramolecular hydrogen bond (highly deshielded proton) although one of the hydroxyl protons remains unshifted. It is likely that the strongly hydrogen bonding solvent, dimethyl sulphoxide, has disrupted the intermolecular hydrogen bonding in the compound.

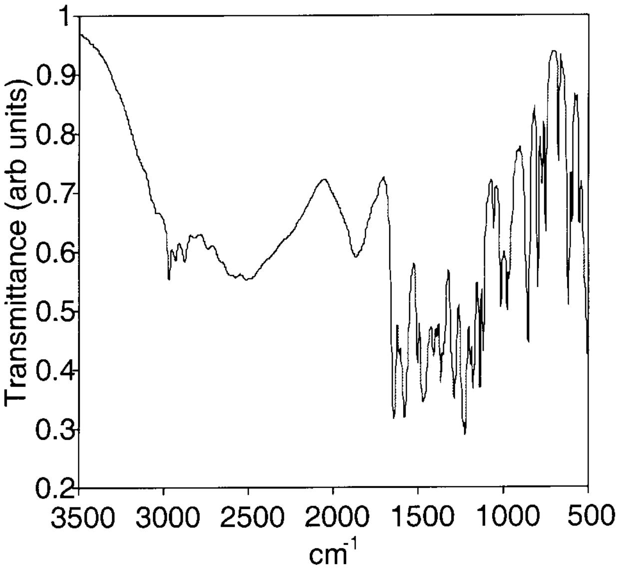

**Fig. 1** Diffuse reflectance FTIR showing the highly intense broad bands between 350–1700cm$^{-1}$ characteristic of strong hydrogen bonding

The crystal structure clearly shows the existence of a self-assembled supramolecular chain. An intramolecular hydrogen bond is established between the nitrogen and the ortho-hydroxyl, which is also part of a hydrogen bond involving the para-hydroxyl from a neighbouring molecule. The intra- and intermolecular hydrogen bonds will act synergistically, with the former increasing the electron density on the (electron acceptor) oxygen of the ortho hydroxyl group which makes it a more powerful electron donor in the intermolecular hydrogen bond. This repeating interaction leads to the formation of adjacent sheets (Fig. 2).

## Experimental

A 100 ml reaction flask with charged with 2,4-dihydroxybenzaldehyde (0.01 mol) in 20 ml absolute ethanol. To this propylamine (0.01 mol) was added and the solution instantly became yellow. After stirring at room temperature for a few minutes, a yellow solid precipitated and was recovered by filtration. The product

**Table 1** Hydrogen bonding data

| D–H...A | d(D–H) | d(D...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)–H(1N)...O(2) | 0.86Å | 1.97Å | 2.637(7)Å | 134.0· |
| O(1)–H(10)...O(2)#1 | 0.82Å | 1.75Å | 2.559(5)Å | 168.6· |

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

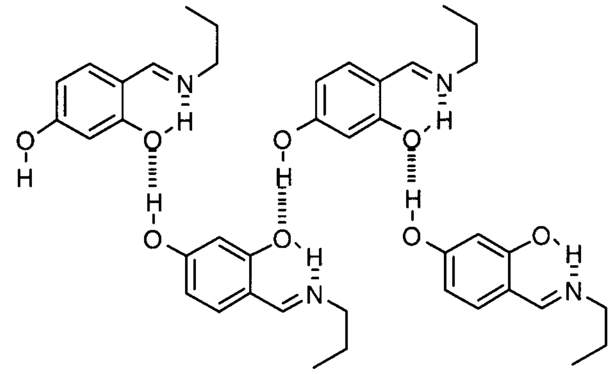

**Fig. 2** Complex [**1**]: Self-assembled ribbons of 1-[(1-propyl)iminomethyl]-2,4-dihydroxybenzene

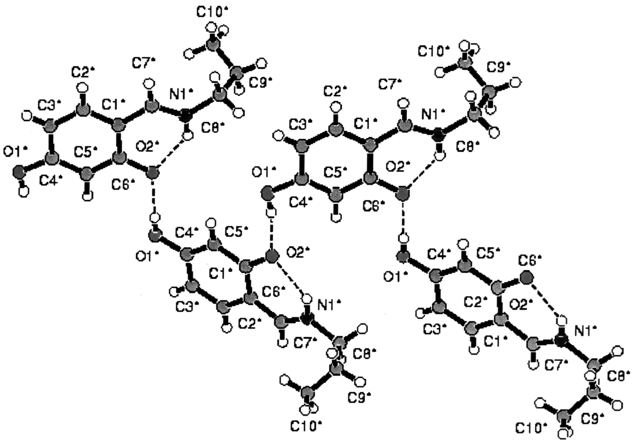

**Fig. 3** Crystal structure showing hydrogen bonding network

1-[(1-propyl)iminomethyl]-2,4-dihydroxybenzene (97% yield by NMR) was allowed to dry under suction and was recrystallised from a 50/50 mix of dimethyl sulphoxide and absolute ethanol to give a bright yellow crystalline solid (m.p. 118°C; mass spectrum: *m/z* = 179 (M+, 100), 150 (96), 123 (53), 164 (46), 136 (31), 28 (29), 39 (12), 65 (10); crystal structure shown in Fig. 3).

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## Crystal Data[8]

*Crystal data for* $C_{10}H_{13}NO_2$, Mr = 179.21, orthorhombic, space group Pna21, $a$ = 10.749(3), $b$ = 9.828(2), $c$ = 9.165(4) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, V = 968.2(5) $Å^3$, Z = 4, $D_c$ = 1.229Mg / $m^3$, $\mu$ (Mo-K$\alpha$) = 0.7107Å, $F(000)$ = 384, crystal size = 0.7 × 0.4 × 0.3 mm. Data were collected at 293(2)K on a Rigaku AFC6S diffractometer and Mo-K$\alpha$ radiation ($\lambda$ = 0.7107 Å), Unit cell indexed by least squares refinement on diffractometer angles for 20 automatically centred reflections. The structure was solved using direct methods and expanded using Fourier techniques with DRIDIF.[9] Full matrix least squares refinement on $F^2$ with SHELXL97[10] with all non-hydrogen atoms anisotropic and hydrogens refined using a rigid model. H1N was located in the difference Fourier map and refined using a rigid model. $\omega$ scan width = 1.05 + 0.3 tan$\theta$, $\omega$ scan speed $4°min^{-1}$, 1020 reflections measured (2.81 $\le \theta \le$ 24.99°) ($h,k+1$), 911 unique. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0856P)^2]$, $P = [\max(I_o, 0) + 2F_c^2]/3$ gave satisfactory agreement analysis. Final $R_F$, $wR_I$ values on all data were 0.1276, 0.1614 and $R_F$, $wR_I$ values on $[I_o > 2\sigma(I_o)]$ data were 0.0562, 0.1327, goodness of fit on $F^2$ = 1.003

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## References

1 J.M. Lehn, *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 89.
2 J.M. Lehn, *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 1304.
3 F. Vogtle, *Supramolecular Chemistry*, Wiley, 1993.
4 C.M. Drain, R. Fischeer, E.G. Nolen, J.M. Lehn, *Chem. Commun.*, 1993, 243..
5 J.M. Lehn, M. Mascal, A. Decian, J. Fischer, *J.Chem.Soc. Perkin Trans. 2*, 1992, 461.
6 J.H. Clark, C.J. Locke, D.J. Nightingale, *Supramolecular Science*, 1995, **2**, 41.
7 M.M Mahmoud, S.C. Wallwork, *Acta Cryst.*, 1979, **B35**, 2370.
8 Molecular Structure Corporation (1992). TEXSAN. TEXRAY Structure Analysis Package. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
9 P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M Smits, C. Smykalla, (1992). *The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.*
10 G.M. Sheldrick, (1997). SHELXL97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.