

# Neutron diffraction study of a very short O–H···N hydrogen bond: crystalline adduct of 2-methylpyridine and pentachlorophenol

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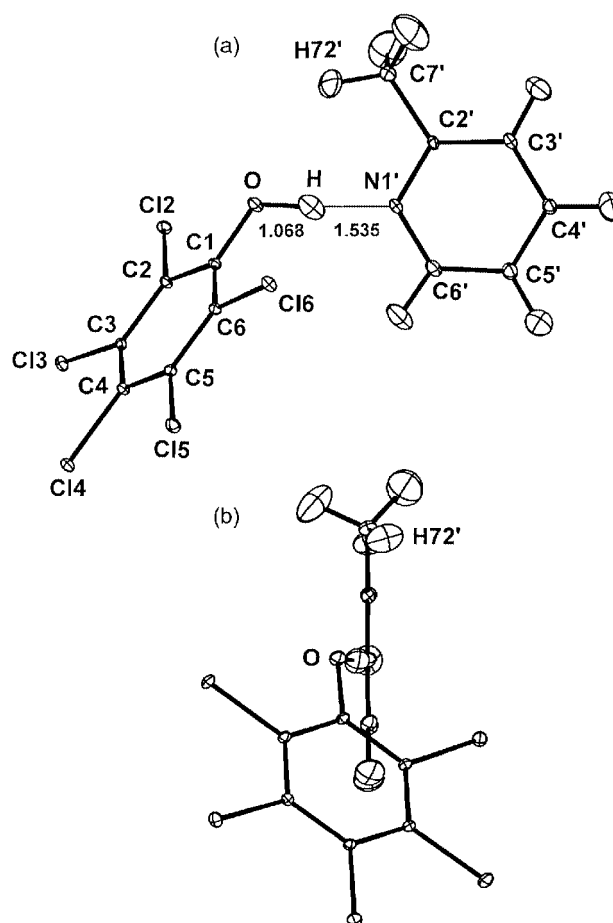
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In the neutron diffraction study of the 1:1 adduct 2-methylpyridine–pentachlorophenol, a very short O–H···N hydrogen bond is found with a sharply defined proton position, and distances of O–H = 1.068(7), H···N = 1.535(7) and O···N = 2.588(3) Å; the bond order of H···N is about 0.24 valence units.

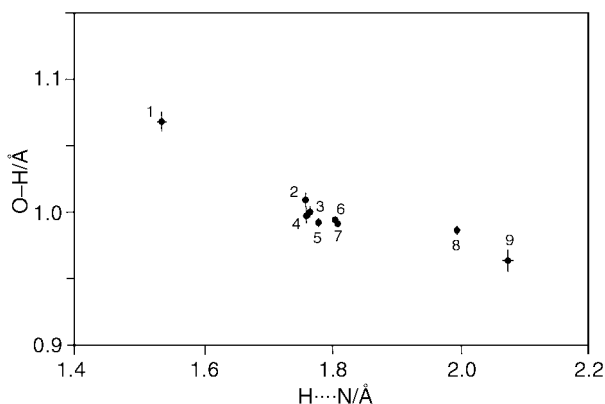
There is great current interest in the strongest types of hydrogen bonds, in particular in the context of chemical reactivity.<sup>1</sup> Whereas strong homonuclear hydrogen bonds O–H···O are today quite well investigated,<sup>2</sup> the experimental material on the very important heteronuclear N–H···O and O–H···N hydrogen bonds is still far from satisfactory. N–H···O and O–H···N hydrogen bonds are in most cases only of moderate strength, but can in some situations also become very strong. An interesting example are adducts of amines and phenols with suitably small values of  $\Delta pK_a$  [ $\Delta pK_a = pK_a(\text{NH}^+) - pK_a(\text{OH})$ ].<sup>3</sup> In a certain ‘critical’ range of  $\Delta pK_a$ , the systems can be found in crystals as molecular adducts linked by hydrogen bonds O–H···N, as ionic adducts linked by  $\text{N}^+ \cdots \text{H} \cdots \text{O}^-$  interactions, or even as an equilibrium between the two.<sup>4</sup> In all these situations, hydrogen bond distances  $\text{N} \cdots \text{O}$  can be  $< 2.6$  Å. Strong intramolecular N–H···O and O–H···N hydrogen bonds have been described for resonance-assisted cases,<sup>5</sup> but they suffer from steric restrictions and have longer H···O separations than the more linear interactions in molecular adducts. Some of the most poorly described properties of strong heteronuclear hydrogen bonds are the distance characteristics at the H-atom, which cannot be deduced from X-ray diffraction data, but require neutron diffraction experiments. For strong O/N–H···N/O hydrogen bonds, not even one neutron diffraction study has been published as yet (for a survey, see ref. 6).

To perform a neutron diffraction study of a strong O–H···N hydrogen bond, we have selected as a model system the adduct of 2-methylpyridine and pentachlorophenol, **1**, which grows crystals of the large size that is required. X-Ray diffraction crystal structures of several related compounds have been published, as found surveyed in ref. 4. Neutron diffraction data on a single crystal of **1** were collected at 30 K at the instrument SXD of the ISIS facility.<sup>7†</sup> In the crystal, a molecular (not an ionic) adduct is formed, as is shown in Fig. 1. The hydrogen bond connecting the molecules has a geometry of O–H = 1.068(7), H···N1' = 1.535(7), O···N1' = 2.588(3) Å, O–H···N1' = 167.5(6)°, and is directed almost ideally at the electron lone-pair of the pyridyl N-atom [ $\text{H} \cdots \text{N1}' \cdots \text{C4}' = 172.7(3)^\circ$ ]. This is by far the shortest O–H···N bond for which neutron diffraction data are available. The H(O) atom is a relatively short distance from one of the methyl H-atoms,  $\text{H} \cdots \text{H72}' = 2.33(1)$  Å; this probably repulsive interaction might be responsible for a significant rotation of the methyl group out of the minimum energy conformation [torsion angle  $\text{N1}'\text{--C2}'\text{--C7}'\text{--H72}' = 17.8(7)^\circ$ ; note that H and H72' are displaced in opposite directions from the pyridyl plane, Fig. 1(b)]. Some further parameters of the molecular geometries are given in the legend of Fig. 1.

With very short hydrogen bonds, an important question is how sharply the hydrogen atom is located, and if there possibly is proton disorder. A look at Fig. 1 shows that the mean square displacement of the proton in the hydrogen bond is small, even smaller than those of the protons of the hydrogen atoms bonded to C. Numerically, its mean square displacement  $U_{\text{eq}}$  is 0.021(1) Å<sup>2</sup> compared to an average  $U_{\text{eq}} = 0.025(1)$  Å<sup>2</sup> of the C(sp<sup>2</sup>)–H and 0.038(2) Å<sup>2</sup> of the methyl protons. This means that the proton in the hydrogen bond is very sharply located. To study the possibility of hydrogen atom disorder,  $\text{O} \cdots \text{H} \cdots \text{N}^+$ , a hypothetical and partially occupied proton position at the N-atom was included in test refinements (compare the related



**Fig. 1** Structure of **1** at 30 K, displacement ellipsoids are drawn at the 50% probability level. (a) View on the pyridine plane, (b) view perpendicular to the pyridine plane. Relevant geometrical parameters: O–H = 1.068(7), C1–O = 1.317(3) Å, C–O–H = 117.1(5), C2–C1–O–H =  $-140.3(6)^\circ$ , N1'–C2' = 1.338(3), N1'–C6' = 1.335(4) Å, C2'–N1'–C6' =  $119.2(2)^\circ$ , H···N1' = 1.535(7), O···N1' = 2.588(3) Å, O–H···N1' =  $167.5(6)^\circ$ , H···C16 = 2.728(6), O···C16 = 2.963(3) Å, O–H···C16 =  $91.9(4)^\circ$ .



**Fig. 2** Plot of O–H against H...N distances in O–H...N hydrogen bonds studied by neutron diffraction. Standard uncertainties are shown as bars, unless they are smaller than the central graphical symbol. **1**: this work. **2, 3**: 3-aminophenol and 2-aminophenol, respectively.<sup>12a</sup> **4**: 3-amino-1,6-anhydro-3-deoxy- $\beta$ -D-glucopyranose.<sup>12b</sup> **5, 8**: adenosine.<sup>12c</sup> **6**: ethanedial dioxime.<sup>12d</sup> **7**: formamide oxime.<sup>12e</sup> **9**: sodium 6-nitrosaccharin tetrahydrate.<sup>12f</sup>

refinement of a disordered hydrogen bond in benzoic acid, ref. 8). In free refinement, the occupancy of the proton at the O-atom remained at 1.0, whereas that of the hypothetical proton at N dropped to  $-0.02$ . This means that an ionic adduct, if present in the crystal, at 30 K can only be populated spuriously.

An important general feature of X–H...Y hydrogen bonds is an elongation of the X–H bond compared to free X–H groups. This points at the hydrogen bond being an incipient proton transfer reaction.<sup>9</sup> In Fig. 2, the dependence of the O–H from the H...N distance is shown for all published neutron diffraction data (substances and references given in the Figure legend). The elongation of the O–H bond in **1** exceeds by far that in all previous studies, following trends that are much better studied in homonuclear hydrogen bonds.<sup>9</sup> If bond orders  $s$  of the O–H and H...N bonds are calculated from the distances using the Pauling approximation with the most recent set of numerical parameters,<sup>6</sup> one obtains  $s_{\text{OH}} = 0.71$  and  $s_{\text{H...N}} = 0.24$ . The rule of bond order conservation ( $s_{\text{OH}} + s_{\text{H...N}} = 1.0$ ) is not ideally fulfilled, indicating that the parameters in ref. 6 are only roughly valid for very short hydrogen bonds. Nevertheless, it becomes clear that the bond order of H...N is about  $\frac{1}{4}$  of a valence unit, meaning that the ‘incipient proton transfer’ characterizing a hydrogen bond has reached already quite an advanced stage in **1**. This gives particular importance to the observation of a sharply located proton with a small vibration amplitude, and disfavors widespread concepts that in very short hydrogen bonds, the proton would oscillate in a potential that is deep but relatively flat at the bottom. Published views that heteronuclear hydrogen bonds cannot be very short (in H...X) by principle are disfavored too, and it may be assumed that O–H...N hydrogen

bonds can be made even shorter by suitably tuning the  $pK_a$  values of the donor and/or acceptor molecules.

## Notes and references

† *Crystal data*: Single crystals of **1** ( $\text{C}_6\text{H}_7\text{N}\cdot\text{C}_6\text{HCl}_5\text{O}$ ,  $M = 359.47$ ) were obtained by slow evaporation of a  $\text{CCl}_4$  solution of pentachlorophenol (Fluka) and an excess of 2-methylpyridine (Merck). A single crystal of dimensions  $2.5 \times 2 \times 1$  mm,  $V$  ca.  $5 \text{ mm}^3$ , was wrapped in aluminium foil and mounted on the time-of-flight Laue diffractometer SXD of the ISIS spallation neutron source.<sup>7a</sup> Crystals are sensitive to atmosphere of high humidity, requiring swift handling. Diffraction data were collected at 30(1) K, and reduced to 4303 independent structure factors<sup>7b</sup> (wavelength range 0.5–5.0 Å, total of 48 frames with a three weeks interruption after seven frames due to a failure of the source; because of continued cooling only 20% reduction in the scattering after this delay). Unit cell dimensions at 30 K are  $a = 9.227(5)$ ,  $b = 11.668(6)$ ,  $c = 6.849(4)$  Å,  $\alpha = 104.61(3)$ ,  $\beta = 105.06(3)$ ,  $\gamma = 99.87(3)^\circ$ ,  $U = 666.5(6)$  Å<sup>3</sup>, with space group  $P\bar{1}$  (no. 2). The structure was solved by molecular replacement methods,<sup>10a</sup> using the phenol and pyridine moieties in the related crystal structure of 4-methylpyridine–pentachlorophenol<sup>11</sup> as the search fragment. Anisotropic refinement with standard methods<sup>10b</sup> (245 parameters) proceeded smoothly, and converged at an  $R$  value of 0.0735 [ $wR(F^2) = 0.1830$ ].

CCDC 182/1663. See <http://www.rsc.org/suppdata/cc/b0/b001179g/> for crystallographic files in .cif format.

- 1 F. Hibbert and J. Emsley, *Adv. Phys. Org. Chem.*, 1990, **26**, 255; G. A. Jeffrey, *Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.
- 2 V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, *Chem. Eur. J.*, 1996, **2**, 925.
- 3 Z. Malarski, M. Rospenk, L. Sobczyk and E. Grech, *J. Phys. Chem.*, 1982, **86**, 401.
- 4 I. Majerz, Z. Malarski and L. Sobczyk, *Chem. Phys. Lett.*, 1997, **274**, 361.
- 5 V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli and K. Vaughan, *New J. Chem.*, 1999, **23**, 1261; A. Filarowski, A. Koll and T. Glowiak, *Monatsh. Chem.*, 1999, **130**, 1097.
- 6 T. Steiner, *J. Phys. Chem. A*, 1998, **102**, 7041.
- 7 (a) C. C. Wilson, in *Neutron Scattering Data Analysis*, ed. M. W. Johnson, Adam Hilger, Bristol, 1990, ch. 2; (b) C. C. Wilson, *J. Mol. Struct.*, 1997, **405**, 207.
- 8 C. C. Wilson, N. Shankland and A. J. Florence, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 5051.
- 9 H. B. Bürgi and J. D. Dunitz, *Acc. Chem. Res.*, 1983, **16**, 153.
- 10 (a) E. Egert and G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1985, **41**, 262; (b) G. M. Sheldrick, SHELXL97, University of Göttingen, 1997.
- 11 Z. Malarski, I. Majerz and T. Lis, *J. Mol. Struct.*, 1987, **158**, 369.
- 12 (a) F. H. Allen, V. J. Hoy, J. A. K. Howard, V. R. Thalladi, G. R. Desiraju, C. C. Wilson and G. J. McIntyre, *J. Am. Chem. Soc.*, 1997, **119**, 3477; (b) J. H. Noordik and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 1977, **33**, 403; (c) W. T. Klooster, J. R. Ruble, B. M. Craven and R. K. McMullan, *Acta Crystallogr., Sect. B*, 1991, **47**, 376; (d) G. A. Jeffrey, J. R. Ruble and J. A. Pople, *Acta Crystallogr., Sect. B*, 1982, **38**, 1975; (e) G. A. Jeffrey, J. R. Ruble, R. K. McMullan, D. J. DeFrees and J. A. Pople, *Acta Crystallogr., Sect. B*, 1981, **37**, 1381; (f) R. Rudert, J. Buschmann, P. Luger, D. Gregson and G. Trummelitz, *Acta Crystallogr., Sect. C*, 1989, **45**, 1013.