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The 1:1 complex of 4-nitrophenol and 4-methylpyridine

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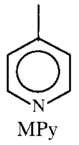
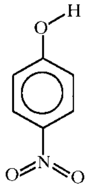
4-Nitrophenol and 4-methylpyridine form a 1:1 hydrogen-bonded dimer, $C_6H_5NO_3.C_6H_7N$, with the molecules linked by an O—H···N hydrogen bond [O···N 2.668 (2) Å]. The dihedral angle between the phenyl and pyridine ring is 57.8 (4)°. The dimers pack in a herring-bone structure in the crystal lattice.

Comment

The phenol–pyridine solution systems have been intensively studied by various means (Emsley, 1968; Moreau Descoings *et al.*, 1985), focusing on the tautomerization (Ratajczak & Sobszyk, 1965; Nouwen & Huyskens, 1973) between hydrogen bonds of O—H···N and N^+—H···O^-. Of equivalently interesting is to reveal the hydrogen-bond patterns and their nature in solid state. As part of the investigation on the complex of pyridine with phenol in solid state, the crystal structure of the complex of 4-nitrophenol (NP) and 4-methylpyridine (MPy) has been determined, and reported herein.


MPy


NP

In the crystallographic structure, the entities of NP and MPy are linked by an O1—HO1···N2 hydrogen bond [O1—N2 2.668 (2) Å, HO1···N2 1.74 (2) Å and O1—HO1···N2 174 (2)°]. The base of MPy does not appear to be protonated by the NP. In comparison with the original pyridine, while the angle of C—N—C in the ring of pyridinium is expanded, both of N—C—C are reduced. These feature are obviously showed in the 1:1 crystalline complexes (Malarski *et al.*, 1987, 1996) of MPy and pentachlorophenol (MPy—PCP) respectively at 80 and 295 K. The bond angle values of C—N—C, N—C—C in the 4-methylpyridinium of MPy—PCP at 80 K have been revealed to be 119.9 (2), 121.3 (2) and 121.4 (2)°, respectively, and in the MPy of MPy—PCP at 295 K to be 118.0 (4), 122.3 (4) and 122.5 (4)°, respectively. The 4-methylpyridinium in it's trifluoroacetate (Dega-Szafran *et al.*, 1992) displays itself with angles of C—N—C [120.5 (3)°] and N—C—C [119.9 (4) and 120.4 (4)°]. The MPy in the title complex with angles of C11—N2—C7 [116.1 (2)°], N2—C7—C8 [123.6 (2)°] and N2—C11—C10 [123.7 (2)°] demonstrate obviously unprotonated features. The O1—C1 length value of 1.344 (2) %Å, with a minute deviation from 1.351 Å for crystal NP (Coppens & Schmidt (1965), is closed to the average C—O length value of 1.36 Å for phenol (Sakurai, 1962), and deviated obviously from average C—O value of 1.255 Å for phenolate (Sawka-Dobrowolska *et al.*, 1995). Such a value for the C1—O1 bond length with the angle C1—O1—H (116.8°) point to some contribution of sp^2 hybridization of the O atom and the double-bond character of the C1—O1 bond in the title complex. The N1—C4 bond length [1.449 (2) Å] with the angle sum around N1 (360°) indicate also some double-bond character (Kawai *et al.*, 1976).

The geometrical arrangement in the crystal structure is characterized by the formation of herring-bone structure of MPy and NP. The nitro group is coplanar with the phenyl ring. The dihedral angle between phenol phenyl ring and pyridine ring is 57.8°. While, one molecule pair of NP and MPy are connected by hydrogen bond of O1—N2 to form such a structure with an orientation, another pair are arranged in the same fashion except for an inverse orientation to the former pair.

Experimental

NP (0.01 mol) was dissolved in MPy (0.02 mol) by heating to a temperature where a clear solution resulted. Single crystals of the title complex was formed by standing of the resulting solution overnight at 293 K.

Crystal data

$C_6H_5NO_3 \cdot C_6H_7N$
$M_r = 232.24$
Orthorhombic, *Pbca*
$a = 7.199$ (1) Å
$b = 12.896$ (1) Å
$c = 25.077$ (3) Å
$V = 2328.1$ (5) Å^3
$Z = 8$
$D_x = 1.325$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 29 reflections
$\theta = 3.34$–17.27°
$\mu = 0.097$ mm^{-1}
$T = 296$ (2) K
Prism, pale yellow
0.44 × 0.36 × 0.28 mm

Data collection

Bruker *P*4 diffractometer
ω scans
3576 measured reflections
2280 independent reflections
893 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0242$
$\theta_{\max} = 26°$

$h = -1 \rightarrow 8$
$k = -1 \rightarrow 15$
$l = -1 \rightarrow 30$
3 standard reflections
every 97 reflections
intensity decay: 3.93%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.077$	$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$S = 0.810$	$\Delta\rho_{\min} = -0.13$ e Å^{-3}
2280 reflections	Extinction correction: *SHELXL*97
160 parameters	Extinction coefficient: 0.0071 (5)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.344 (2)	N1—C4	1.449 (2)
O2—N1	1.230 (2)	N2—C11	1.327 (2)
O3—N1	1.220 (2)	N2—C7	1.328 (2)
O3—N1—O2	122.1 (2)	C11—N2—C7	116.1 (2)
O3—N1—C4	119.4 (2)	N2—C7—C8	123.6 (2)
O2—N1—C4	118.5 (2)	N2—C11—C10	123.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H···N2	0.93 (2)	1.74 (2)	2.668 (2)	174 (2)

The carboxyl H-atom coordinates were refined isotropically; all other H atoms were treated as riding atoms.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS* (Siemens, 1991); data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL-Plus* (Sheldrick, 1990).

References

Coppens, P. & Schmidt, G. M. J. (1965). *Acta Cryst.* **18**, 62–67.

Dega-Szafran, Z., Gdaniec, M., Grundwald-Wyspianska, M., Kosturkiewicz, Z., Koput, J., Kryzanowsky, P. & Szafran, M. (1992). *J. Mol. Struct.* **270**, 99–124.

Emsley, J. W. (1968). *J. Chem. Soc. A*, pp. 1387–1393.

Kawai, R., Kashino, S. & Haisa, M. (1976). *Acta Cryst.* B**32**, 1972–1975.

Malarski, Z., Majerz, I. & Lis, T. (1987). *J. Mol. Struct.* **158**, 369–377.

Malarski, Z., Majerz, I. & Lis, T. (1996). *J. Mol. Struct.* **380**, 249–256.

Moreau Descoings, M. C., Guillaume Vilport, F., Seguin, J. P., Uzan, R. & Doucet, J. P. (1985). *J. Mol. Struct.* **127**, 297–303.

Nouwen, R., & Huyskens, P. (1973). *J. Mol. Struct.* **16**, 459–471.

Ratajczak, H.& Sobszyk, L. (1965). *Zh. Struckt. Khim.* **6**, 262–270.

Sakurai, T. (1962). *Acta Cryst.* **15**, 1164–1168.

Sawka-Dobrowolska, W., Grech, E., Brzezinski, B., Malarski, Z. & Sobczyk, L. (1995). *J. Mol. Struct.* **356**, 117–124.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.