organic compounds

A hydrogen-bonded heterodimer of 1-(4-hexyloxyphenyl)pyridin-4(1H)-one with 4-cyanobenzoic acid

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The two components of the title heterodimer, $C_{17}H_{21}NO_2 \cdot C_8H_5NO_2$, are linked end-to-end via O—H···O(=C) and C—H···O(=C) hydrogen-bond interactions. Additional lateral C—H···O interactions link the dimers in a side-by-side fashion to produce wide infinite molecular ribbons. Adjacent ribbons are interconnected via π–π stacking and C—H···π(arene) interactions. This structure represents the first evidence of robust hydrogen-bond formation between the moieties of pyridin-4(1H)-one and benzoic acid.

Comment

Our interest in the pyridin-4(1H)-one moiety (hereinafter 4-pyridone) stems from its potential for incorporation into liquid crystal units (Dyer et al., 1997), due to its inherent large birefringence and polarizability (Dirk et al., 1986). Such liquid crystals have the potential to be integrated into electro-optic devices, including a number of different flat-panel display configurations (Kuo & Suzuki, 2002). In fact, the 1-phenyl-4-pyridone aromatic core is reminiscent of the counterpart in the classical nCB and nOCB liquid crystals (Davey et al., 2005). Furthermore, the C=O group of 4-pyridone could be a better hydrogen-bond acceptor compared with the nitrile group of nCB and nOCB (Chen & Dannenberg, 2006). Thus, the 4-pyridone moiety may prove useful as a robust hydrogen-

bond unit in creating thin organic films with a macroscopic non-centrosymmetric architecture (Dyer et al., 2003; Facchetti, Annoni et al., 2004; Facchetti, Letizia et al., 2004). We have demonstrated previously that molecules containing the 4-pyridone moiety can crystallize either as a neat crystal (Li et al., 2005) or as a monohydrate (Robinson et al., 2005). This report details the structure of the hydrogen-bonded heterodimer, (I), of 1-(4-hexyloxyphenyl)pyridin-4(1H)-one (hereinafter C6-pyridone) with 4-cyanobenzoic acid (hereinafter NBA), which represents the first evidence of robust hydrogen-bond formation between the 4-pyridone moiety and the benzoic acid moiety.

(I)
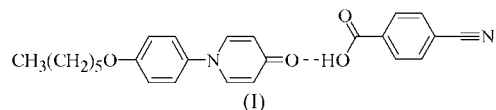
As can be seen in Fig. 1, the asymmetric heterodimer, (I), is made up of molecules of C6-pyridone and NBA in a 1:1 ratio. The dihedral angle between the 4-pyridone and the benzene ring of the C6-pyridone molecule is 40.61 (8)°, as opposed to the value of 46.19 (19)° found for C6-pyridone monohydrate (Robinson et al., 2005). The torsion angle C14—C15—C16—C17 of 62.7 (2)° shows that the terminal methyl group of the alkoxy chain is twisted significantly out of the 'all-trans' conformation (Hori & Wu, 1999). Atom O2 is essentially in the 4-pyridone plane, its deviation being only 0.057 (1) Å. Atoms C25 and N2 (C≡N group) are out of the NBA benzene ring by only 0.041 (2) and 0.095 (2) Å, respectively. The carboxyl group (O4/C18/O3) forms a dihedral angle of 9.2 (1)° with the NBA benzene ring plane, compared with the equivalent angle of 7.7 (7)° in the NBA homodimer [Higashi & Osaki, 1981; Cambridge Structural Database (November 2005 release; Allen, 2002) refcode TAGNAR]. While bond distances and angles are generally unremarkable, the C1=O2 double bond of 1.268 (2) Å is slightly longer than the value of 1.247 (2) Å in 1-(4-decylphenyl)-1H-pyridin-4-one (Li et al., 2005), a possible consequence of the stronger hydrogen-bond interaction effect in the heterodimer.

The two molecular components of (I) are linked end-to-end via O3—H3···O2 and C2—H2···O4 hydrogen-bond interactions [graph set $R_2^2(8)$; Bernstein et al., 1995], as shown in Figs. 1 and 2. Noticeably, O3—H3···O2 is a homonuclear hydrogen bond (Table 1), which can be classified as a strong hydrogen-bond interaction (Gilli et al., 1994), while the C—H···O bond is rather weak, even for a non-traditional inter-
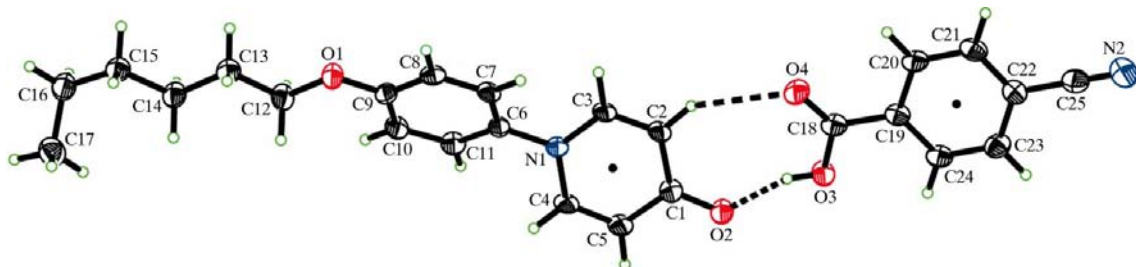
Figure 1

The molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds. Small black circles denote the centroids of rings involved in π–π stacking.

action. Considering the 14.8 (3)° dihedral angle between O2/C1/C2 and O4/C18/O3, the $R_2^2(8)$ ring is not planar. Nevertheless, the hydrogen-bond interactions seem robust enough to make the ring rigid and induce liquid crystallinity (Collings & Hird, 1997). Thus, the 4-pyridone moiety may prove to be a useful building block in self-assembled materials and liquid crystals.

The dimers are linked in a side-by-side fashion by three additional C—H···O interactions (Table 1 and Fig. 2), which produces graph-set motifs $R_3^2(7)$ and $R_3^2(13)$. The result is a wide infinite molecular ribbon, which propagates in the [010] direction (vertically in Fig. 2) within the $(20\bar{1})$ plane. The ribbon is roughly 29 Å wide, and the edges of the ribbon (on the left and right of Fig. 2) are composed of terminal methyl groups of the alkoxy 'tail'. The dimers shown in Fig. 2 are essentially in the plane of the paper and the ribbon repeats every other link and has only a minor zigzag character. It should be noted that the ribbon is held together entirely by non-traditional hydrogen bonds and is thus quite loosely knit. Full details of the hydrogen-bond geometry are given in Table 1.

The ribbons are interconnected via π–π stacking and C—H···π(arene) interactions. Fig. 3 shows an end-on view of

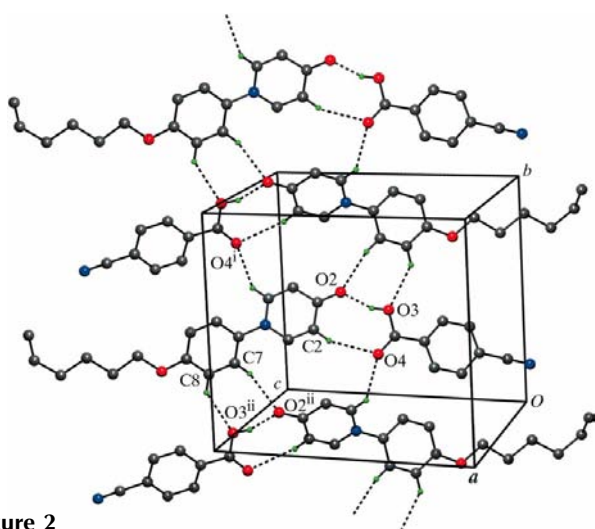**Figure 2**
The hydrogen bonding in (I). Infinite molecular ribbons propagate along [010] as a result of O—H···O and C—H···O interactions coupled with unit translations (see Table 1). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.]
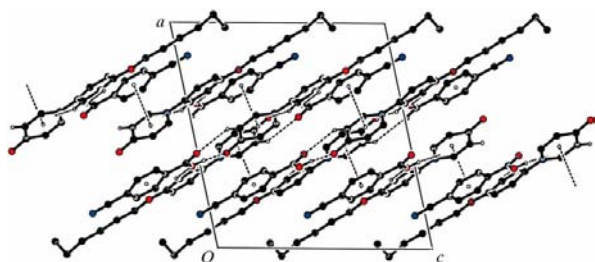

Figure 3
The packing of (I) via molecular π–π stacking interactions (dashed lines). Portions of six molecular ribbons, which emerge from the plane of the paper along [010], are shown.

parallel ribbons emerging from the paper along [010]. The π–π stacking interactions are between Cg1 and Cg2, where Cg1 is the centroid of the origin 4-pyridone ring and Cg2 is the centroid of the NBA benzene ring at $(1 - x, 1 - y, 1 - z)$. The centroid-to-centroid distance is 3.6891 (10) Å, the dihedral angle is 7.90 (8)° and the average perpendicular distance is 3.515 Å, with a 1.05 Å offset, and this geometry is in good agreement with similar interactions (Wheatley et al., 1999). In addition, C—H···π(arene) interactions interconnect the parallel ribbons (entry 6 in Table 1, not shown in Fig. 3). This interaction is in reasonably good agreement with the most frequently observed values (Braga et al., 1998).

Experimental

Crystal data

$C_{17}H_{21}NO_2 \cdot C_8H_5NO_2$	$Z = 4$
$M_r = 418.48$	$D_x = 1.285$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.4115$ (6) Å	$\mu = 0.09$ mm^{-1}
$b = 11.4432$ (4) Å	$T = 100$ (2) K
$c = 13.4320$ (5) Å	Block, colorless
$\beta = 102.434$ (2)°	$0.30 \times 0.22 \times 0.16$ mm
$V = 2163.16$ (14) Å^3	

Data collection

Bruker Kappa-APEX-II CCD area-detector diffractometer	53973 measured reflections
φ and ω scans	4460 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	3365 reflections with $I > 2\sigma(I)$
$T_{min} = 0.773$, $T_{max} = 0.986$	$R_{int} = 0.077$
	$\theta_{max} = 26.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.5135P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
4460 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
283 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.0027 (6)

Table 1
Hydrogen-bond geometry (Å, °).

Cg3 is the centroid of the C6-pyridone ring.

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2	0.84	1.72	2.5244 (17)	159
C2—H2···O4	0.95	2.60	3.438 (2)	147
C4—H4···O4^i	0.95	2.37	3.148 (2)	139
C7—H7···O2^{ii}	0.95	2.41	3.303 (2)	156
C8—H8···O3^{ii}	0.95	2.48	3.273 (2)	140
C13—H13B···Cg3^{iii}	0.99	2.91	3.856 (2)	161

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.

The rotational orientation of the methyl group was refined by the circular Fourier method available in SHELXL97 (Sheldrick, 1997).

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The position of the hydroxyl H atom was determined in a similar manner. All H atoms were treated as riding, with C—H = 0.99 Å and O—H = 0.84 Å, and with $U_{iso}(H) = 1.5U_{eq}$(parent) for hydroxyl and methyl H atoms or $1.2U_{eq}$(parent) for all other H atoms.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SADABS* (Bruker, 2005); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3021). Services for accessing these data are described at the back of the journal.

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