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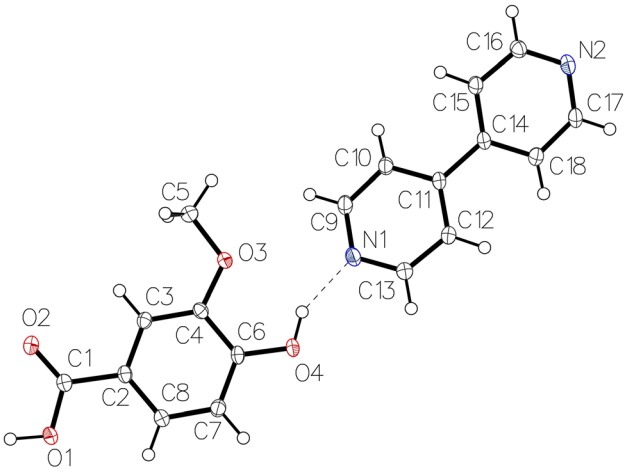
The co-crystal structure of 4-hydroxy-3-methoxybenzoic acid – 4,4′-bipyridine, $C_8H_8O_4 \cdot C_{10}H_8N_2$



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Abstract

$C_8H_8O_4 \cdot C_{10}H_8N_2$, monoclinic, $P2_1/c$ (no. 14), a = 13.427(4) Å, b = 10.069(3) Å, c = 12.751(4) Å, β = 116.124(7)°, V = 1547.7(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0426, $wR_{ref}(F^2)$ = 0.1152, T = 90 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

4,4′–Bipyridine (156.2 mg, 1.0 mmol) and *p*-vanillic acid (168.1 mg, 1.0 mmol) were dissolved in methanol in a 200 mL beaker. The beaker was left open to allow for crystal formation upon slow evaporation. Coformers were sourced from Combi–Blocks (*p*-vanillic acid, 98% and 4,4′-bipyridine, 97%). Methanol was purchased from Fischer Chemical (99.9%). No further material refinement was necessary.

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.35 × 0.12 × 0.02 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	29.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24407, 4098, 0.060
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3215
$N(param)_{refined}$:	226
Programs:	Bruker [1], Olex2 [2], SHELX [3]

Experimental details

X-ray diffraction data was collected using a Bruker APEX2 diffractometer installed at a rotating anode source (MoKα radiation, λ = 0.71073 Å) and equipped with an Oxford Cryosystems (Cryostream700) nitrogen gas-flow apparatus at 90 K. Five sets of data (290 frames each) were collected by the rotation method with 0.5° frame-width (ω scan). Using Olex2, the structure was solved with intrinsic phasing *via* the ShelXT structure solution program and refined with the ShelXL software suite using least squares minimization [2, 3]. The atomic coordinates and isotropic thermal parameters of H atoms attached to heteroatoms were freely refined. H atoms connected to carbon atoms were placed geometrically (C–H = 0.95 Å) and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C).

Comment

4-Hydroxy-3-methoxybenzoic acid, known commonly as *p*-vanillic acid, is found in great abundance in many fruits and vegetables that we consume [4]. *p*-Vanillic acid is

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C1	1.09607 (10)	0.45834 (13)	0.80850 (11)	0.0167 (3)
C2	0.99142 (10)	0.46545 (12)	0.82183 (11)	0.0154 (2)
C3	0.97455 (10)	0.37150 (12)	0.89381 (11)	0.0159 (2)
H3	1.029132	0.305530	0.932321	0.019*
C4	0.87823 (10)	0.37483 (12)	0.90882 (11)	0.0153 (2)
C5	0.92922 (11)	0.18543 (13)	1.03420 (12)	0.0205 (3)
H5A	0.946260	0.136130	0.977827	0.031*
H5B	0.897505	0.124807	1.071614	0.031*
H5C	0.997416	0.224875	1.093751	0.031*
C6	0.79791 (10)	0.47377 (12)	0.85243 (11)	0.0158 (2)
C7	0.81397 (11)	0.56382 (12)	0.77869 (11)	0.0176 (3)
H7	0.758598	0.628350	0.738390	0.021*
C8	0.91054 (11)	0.56047 (12)	0.76321 (11)	0.0169 (3)
H8	0.921056	0.622671	0.712961	0.020*
C9	0.66153 (11)	0.25859 (13)	0.57113 (12)	0.0201 (3)
H9	0.738985	0.275912	0.608242	0.024*
C10	0.59381 (10)	0.32881 (13)	0.60809 (11)	0.0182 (3)
H10	0.624593	0.393448	0.668170	0.022*
C11	0.47967 (10)	0.30336 (12)	0.55590 (11)	0.0155 (2)
C12	0.43914 (11)	0.20780 (13)	0.46776 (12)	0.0193 (3)
H12	0.362390	0.186513	0.430581	0.023*
C13	0.51320 (11)	0.14449 (13)	0.43552 (12)	0.0208 (3)
H13	0.484632	0.080936	0.374279	0.025*
C14	0.40541 (10)	0.37396 (12)	0.59617 (11)	0.0157 (2)
C15	0.42670 (11)	0.50417 (13)	0.63812 (11)	0.0180 (3)
H15	0.488739	0.551079	0.639722	0.022*
C16	0.35639 (11)	0.56438 (13)	0.67743 (12)	0.0193 (3)
H16	0.371066	0.653584	0.704153	0.023*
C17	0.24845 (11)	0.37797 (14)	0.63836 (13)	0.0224 (3)
H17	0.186313	0.333192	0.638701	0.027*
C18	0.31262 (11)	0.31054 (13)	0.59541 (13)	0.0213 (3)
H18	0.293845	0.222744	0.565984	0.026*
N1	0.62331 (9)	0.16781 (11)	0.48594 (10)	0.0201 (2)
N2	0.26870 (9)	0.50268 (11)	0.67950 (10)	0.0198 (2)
O1	1.10629 (8)	0.55635 (9)	0.74365 (9)	0.0222 (2)
H1	1.172 (2)	0.541 (2)	0.730 (2)	0.061 (7)*
O2	1.16489 (8)	0.37046 (10)	0.85106 (9)	0.0224 (2)
O3	0.85112 (7)	0.28829 (9)	0.97499 (8)	0.0195 (2)
O4	0.70308 (7)	0.48247 (9)	0.86544 (8)	0.0189 (2)
H4	0.6996 (18)	0.421 (2)	0.917 (2)	0.053 (6)*

also being investigated for medicinal properties such as its anti-inflammatory response [5]. Despite the wide consumption of the molecule and its growing potential for pharmaceutical use, solid-state structures of the compound and its interactions remain scant. As such its beneficial to synthesize co-crystals and/or salts of *p*-vanillic acid so as to study its interactions in the solid-state. For this purpose (4,4′-BIPY) was selected due to its dynamic composite structure making capabilities [6, 7].

p-Vanillic acid co-crystallizes with 4,4′-BIPY in a 1:1 ratio with the resulting co-crystal possessing monoclinic ($P2_1/c$) symmetry at 90 K. As observed in the figure, within the resulting co-crystal the *p*-vanillic acid has two distinct O–H···N type hydrogen bonding interactions; with one of these interactions being between a 4,4′-BIPY and the para-position hydroxyl group resulting in a 2.6919(15) Å distance between heteroatoms. The other O–H···N type hydrogen bonding interaction occurs between the hydroxyl group of the carboxyl group and the nearest pyridine of a 4,4′-BIPY molecule resulting in a 2.6996(15) Å distance between heteroatoms. Dimolecular assemblies consisting of one acid molecule and one 4,4′-BIPY bind together to form C_2^2 (17) chain motifs. These chains form twisting wires that run approximately orthognal to (–403). The wires stack along (–403) through a series of weak C–H···O interactions to form sheets. These sheets stack along [010] with every other sheet being rotated 180° about [010].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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