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The co-crystal structure of 4-hydroxy-3-methoxybenzoic acid – 4,4′-bipyridine, C$_8$H$_8$O$_4$·C$_{10}$H$_8$N$_2$

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Abstract

C$_8$H$_8$O$_4$·C$_{10}$H$_8$N$_2$, monoclinic, P2$_1$/c (no. 14), $a = 13.427(4)$ Å, $b = 10.069(3)$ Å, $c = 12.751(4)$ Å, $\beta = 116.124(7)$°, $V = 1547.7(8)$ Å$^3$, $Z = 4$, $R_{gt} = 0.0426$, $wR_{ref} = 0.1152$, $T = 90$ 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 atoms including atomic coordinates and displacement parameters.

Experimental details

X-ray diffraction data was collected using a Bruker APEX2 diffractometer installed at a rotating anode source (MoK$_\alpha$ radiation, $\lambda = 0.71073$ 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 ($\omega$ 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) = 1.2$U_{eq}$(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 1: Data collection and handling.

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

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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.
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 2.6991(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 $C_2$ (17) chain motifs. These chains form twisting wires that run approximately orthogonal 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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