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The crystal structure of 4,4'-bipyridinium bis-(2-hydroxy-3-methoxybenzoate), $2(\text{C}_8\text{H}_7.68\text{O}_4) \cdot \text{C}_{10}\text{H}_{8.64}\text{N}_2$

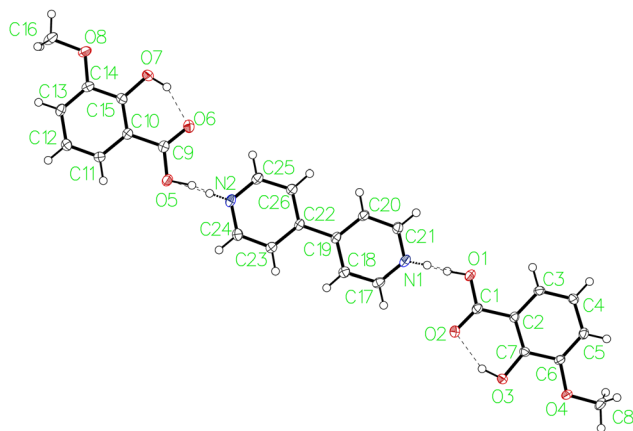


Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	$0.45 \times 0.13 \times 0.02$ mm
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	0.11 mm^{-1}
Diffractometer, scan mode:	BRUKER APEX-II, φ and ω
θ_{max} , completeness:	29.6° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	25,125, 6412, 0.071
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 4674
$N(\text{param})_{\text{refined}}$:	346
Programs:	BRUKER [1], OLEX2 [2], SHELX [3]

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Abstract

$\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_8$, monoclinic, $P2_1/c$ (no. 14), $a = 6.9170(9) \text{ \AA}$, $b = 26.012(3) \text{ \AA}$, $c = 12.7449(17) \text{ \AA}$, $\beta = 91.896(4)^\circ$, $V = 2291.9(5) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0471$, $wR_{\text{ref}}(F^2) = 0.1320$, $T = 90 \text{ K}$.

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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 *o*-vanillic acid (168.1 mg, 1.0 mmol) were dissolved using excess 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 (*o*-vanillic acid, 97% and 4,4'-bipyridine, 97%). Methanol was purchased from Fischer Chemical (HPLC grade; 99.9%). No further material refinement was necessary.

Experimental details

X-ray diffraction data was collected using a BRUKER SMART APEX-II CCD diffractometer installed at a rotating anode source (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems (CRYOSTREAM700) nitrogen gas-flow apparatus. Five sets of data (290 frames each) were collected by the rotation method with 0.5° frame-width (ω scan). The sample was run at 90 K. Using OLEX2, the structure was solved with intrinsic phasing *via* the SHELXT structure solution program and refined with the SHELXL software suite [2, 3]. The atomic coordinates of H atoms attached to heteroatoms were freely refined with thermal parameters constrained to be $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. H atoms connected to carbon atoms were placed geometrically ($\text{C-H} = 0.95 \text{ \AA}$) and refined with thermal parameters constrained to be $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The disordered protons were initially refined independently, however given the similar refined occupancies the disorder was ultimately modeled as correlated using a single occupancy parameter (Table 2).

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.1488 (2)	0.33321 (5)	0.39798 (10)	0.0164 (3)
C2	0.32354 (19)	0.30060 (5)	0.39479 (10)	0.0147 (3)
C3	0.3691 (2)	0.27359 (5)	0.30307 (10)	0.0171 (3)
H3A	0.287959	0.275990	0.243602	0.021*
C4	0.5326 (2)	0.24373 (6)	0.30102 (11)	0.0187 (3)
H4	0.561497	0.225917	0.240237	0.022*
C5	0.6562 (2)	0.23995 (6)	0.39011 (11)	0.0181 (3)
H5A	0.767171	0.219828	0.388024	0.022*
C6	0.6139 (2)	0.26601 (5)	0.48102 (10)	0.0160 (3)
C7	0.4465 (2)	0.29675 (5)	0.48407 (10)	0.0154 (3)
C8	0.8782 (2)	0.22887 (6)	0.57887 (12)	0.0268 (3)
H8A	0.976734	0.238913	0.531699	0.040*
H8B	0.830637	0.195357	0.559851	0.040*
H8C	0.931471	0.228037	0.649353	0.040*
C9	0.5586 (2)	0.07387 (5)	0.31047 (11)	0.0170 (3)
C10	0.74424 (19)	0.10248 (5)	0.31791 (10)	0.0152 (3)
C11	0.8053 (2)	0.13242 (5)	0.23358 (10)	0.0159 (3)
H11	0.727475	0.135376	0.172947	0.019*
C12	0.9801 (2)	0.15734 (5)	0.24090 (11)	0.0177 (3)
H12	1.021426	0.176585	0.184377	0.021*
C13	1.0969 (2)	0.15412 (5)	0.33233 (11)	0.0183 (3)
H13	1.215866	0.170805	0.335830	0.022*
C14	1.0361 (2)	0.12618 (5)	0.41775 (11)	0.0170 (3)
C15	0.8597 (2)	0.09921 (5)	0.41040 (10)	0.0161 (3)
C16	1.3035 (2)	0.15430 (6)	0.52587 (13)	0.0253 (3)
H16A	1.347720	0.153616	0.598051	0.038*
H16B	1.272224	0.188975	0.505895	0.038*
H16C	1.403527	0.141496	0.482426	0.038*
C17	0.6459 (2)	0.40244 (5)	0.40800 (11)	0.0187 (3)
H17	0.700538	0.393133	0.472909	0.022*
C18	0.4767 (2)	0.43064 (6)	0.40500 (11)	0.0177 (3)
H18	0.418900	0.439987	0.467034	0.021*
C19	0.39245 (19)	0.44510 (5)	0.30780 (11)	0.0154 (3)
C20	0.4869 (2)	0.43039 (5)	0.21812 (11)	0.0176 (3)
H20	0.437275	0.439659	0.152091	0.021*
C21	0.6554 (2)	0.40184 (6)	0.22774 (11)	0.0192 (3)
H21	0.716340	0.391837	0.167081	0.023*
C22	0.20895 (19)	0.47480 (5)	0.29949 (11)	0.0151 (3)
C23	0.1542 (2)	0.50732 (5)	0.38053 (10)	0.0172 (3)
H23	0.232326	0.510615	0.440958	0.021*
C24	−0.0170 (2)	0.53456 (6)	0.37018 (11)	0.0183 (3)
H24	−0.052492	0.556019	0.424652	0.022*
C25	−0.0809 (2)	0.50091 (5)	0.20513 (11)	0.0189 (3)
H25	−0.160049	0.499230	0.144807	0.023*
C26	0.0876 (2)	0.47206 (5)	0.20979 (11)	0.0173 (3)
H26	0.119525	0.451094	0.153844	0.021*
H1A ^a	0.844 (12)	0.373 (3)	0.314 (5)	0.040*
H1B ^b	−0.064 (6)	0.3530 (15)	0.318 (2)	0.040*
H2B ^b	0.342 (6)	0.0588 (12)	0.227 (2)	0.031*
H2A ^a	−0.232 (13)	0.551 (3)	0.278 (5)	0.040*
N1	0.73415 (18)	0.38805 (5)	0.32100 (10)	0.0186 (3)
N2	−0.13397 (18)	0.53112 (5)	0.28421 (10)	0.0180 (2)
O1	0.04370 (16)	0.33450 (4)	0.31118 (8)	0.0234 (2)
O2	0.10698 (15)	0.35762 (4)	0.47794 (8)	0.0223 (2)
O3	0.41371 (16)	0.32155 (4)	0.57534 (8)	0.0228 (2)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H3	0.307 (3)	0.3391 (8)	0.5615 (14)	0.034*
O4	0.72337 (15)	0.26493 (4)	0.57248 (8)	0.0231 (2)
O5	0.46117 (15)	0.07778 (4)	0.22146 (8)	0.0205 (2)
O6	0.50174 (15)	0.04783 (4)	0.38533 (8)	0.0228 (2)
O7	0.80804 (16)	0.07094 (4)	0.49432 (8)	0.0222 (2)
H7	0.699 (3)	0.0567 (8)	0.4768 (15)	0.033*
O8	1.13486 (15)	0.12267 (4)	0.51279 (8)	0.0227 (2)

^aOccupancy: 0.32 (4), ^bOccupancy: 0.68 (4).

Comment

2-Hydroxy-3-methoxybenzoic acid, known commonly as o-vanillic acid, has been under investigation for its medicinal benefits such as its anti-allergenic inflammatory response [4]. Despite the rise in interest and utility of this molecule, only a handful of crystal structures containing o-vanillic acid have been reported [5–7]. As such additional co-crystals and/or salts of o-vanillic acid may aid in further understanding its solid-state interactions. In this report the coformer 4,4'-bipyridine (4,4'-BIPY) was selected due to its ability to form a variety of crystalline systems including metal-organic frameworks, co-crystals, and salts [8–10].

o-Vanillic acid co-crystallizes with 4,4'-BIPY in a 2:1 ratio in the monoclinic spacegroup (*P*2₁/*c*). Subsequent refinements revealed the presence of disorder involving the acidic protons of the carboxylic acid groups of the vanillic acid and the pyridyl groups of the 4,4'-BIPY. For each of the two crystallographically unique acid groups, the proton was disordered over two positions. In one case, the proton was located near the oxygen, and in the second case the proton was located near the nitrogen of the pyridyl group. The ratio of the occupancies (HO:HN) of the disordered protons when refined independently were determined to be 0.68225:0.31775 and 0.68721:0.31279. Given the similar values, the occupancies were treated with a single parameter in the final model and determined to be 0.68(4):0.32(4).

These values may be interpreted as a partial charge transfer with the proton being transferred to the nitrogen resulting in a salt 32(4)% of the time. The other 68(4)% of the time, the protons reside on the acid oxygen resulting in charge neutral carboxylic acid and pyridyl groups. The two acids and the 4,4'-BIPY together form discrete hydrogen bonded trimolecular assemblies. These assemblies form slipped stacks through π - π interactions approximately along [100]. Lateral Van der Waals interactions

approximately along [001] give rise to 2-D sheets. These sheets form alternating layers along [010] in which each layer is rotated by 180° .

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