4,4′-(Ethene-1,2-diyl)dipyridinium bis(2-hydroxy-3-methoxybenzoate)

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In the title double proton-transfer salt, C_{12}H_{12}N_{2}^{2+}\cdot2\text{C}_{8}H_{7}O_{4}^{−}, consisting of a 1:2 ratio of 4,4′-(ethene-1,2-diyl)dipyridinium cations (trans bipyridinium ethylene) to 2-hydroxy-3-methoxybenzoate anions (o-vanillate), the complete cation is generated by crystallographic inversion symmetry and it is linked to adjacent o-vanillate anions by N—H⋯O hydrogen bonds, forming trimolecular assemblies. The trimers are linked by C—H⋯O hydrogen bonds as well as aromatic π⋯π stacking interactions into a three-dimensional network. The anion features an intramolecular O—H⋯O hydrogen bond.

Structure description

2-Hydroxy-3-methoxybenzoic acid (o-vanillic acid, C_{7}H_{8}O_{4}) is similar in nature to its isomeric counterpart 4-hydroxy-3-methoxybenzoic acid (p-vanillic acid), with the exception of the hydroxyl-group positioning. Much like its counterpart, o-vanillic acid is being investigated for its medicinal benefits, such as its anti-allergic inflammatory effects (Kim et al., 2017). Despite its potential usage for medicinal purposes, there is a significant lack of structural data on this compound and its salts. As such it is beneficial to study the solid-state forms of o-vanillic acid and its salts to better understand its interactions. To achieve this, bipyridine ethylene (C_{12}H_{10}N_{2}) was selected due to its demonstrated ability to form both simple and complex hydrogen-bonded networks (MacGillivray et al., 2000; Wang et al., 2007). In addition, as the ΔpK_a value between o-vanillic acid (pK_a = 2.5) and bipyridine ethylene (pK_a = 5.5) is approximately 3, the observed salt formation can reasonably be expected due to the acid–base crystalline complexes ΔpK_a rule (Cruz-Cabeza, 2012).

The structure of the resulting bipyridinium ethylene bis-o-vanillate molecular salt, C_{12}H_{12}N_{2}^{2+}\cdot2\text{C}_{8}H_{7}O_{4}^{−}, exhibits monoclinic (P2_1/c) symmetry at 90 K: the complete cation is generated by crystallographic inversion symmetry. A trimolecular unit consisting...
of one bipyridinium ethylene cation (BPyE) with two o-vanillate anions, each of which accepts an N1·H1···O4 hydrogen bond from the pyridinium N atoms of the cation is observed, in which the H1···O4 distance of 1.45 (2) Å and the N1···O4 separation of 2.5402 (15) Å are notably short. The cation–anion bonding is consolidated by a C13—H13···O2 link and within the anion, an S(6) intramolecular O2—H2···O3 hydrogen bond is observed between the hydroxyl group and the O atom of the carboxyl group (Fig. 1, Table 1). These trimolecular units (Fig. 2) then stack through aromatic π–π interactions [shortest centroid–centroid separation =

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1···O4i | 1.09 (2) | 1.45 (2) | 2.5402 (15) | 178 (2) |
| O2···O3i | 0.96 (2) | 1.64 (2) | 2.5270 (14) | 150 (2) |
| C13···O2ii | 0.95 | 2.52 | 3.1831 (16) | 127 |
| C13···O3ii | 0.95 | 2.57 | 3.2092 (14) | 125 |
| C12···O1ii | 0.95 | 2.46 | 3.591 (17) | 159 |

Symmetry codes: (i) x−1, y, z−1; (ii) −x, −y+1, −z.

Figure 1
The asymmetric unit of the title molecular salt showing 50% displacement ellipsoids.

Figure 2
A trimolecular unit of the synthesized salt consisting of two o-vanillate anions and one bipyridinium ethylene cation. Hydrogen-bonding interactions are shown as red dashed lines with distances displayed between interacting heteroatoms.

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

A 1:2 molar ratio of bipyridine ethylene (182.2 mg, 1 mmol) and o-vanillic acid (336.2 mg, 2 mmol) were dissolved into a vial of excess methanol. The resulting solution was vortexed for 30 s at 3,000 rpm on a VWR Mini Vortexer MV I. The solution was then stored in the dark uncapped to allow for crystal formation while the solvent slowly evaporated.

Table 2
Experimental details.

| Crystal data | Chemical formula | C₁₂H₁₂N₂²⁺·2C₈H₇O₄⁻ |
|--------------|------------------|-----------------------|
| M₀           | 518.51           |
| Crystal system, space group | Monoclinic, P2₁/c |
| Temperature (K) | 90 |
| a, b, c (Å) | 8.543 (2), 20.729 (5), 7.7061 (17) |
| β (°) | 114.898 (4) |
| V (Å³) | 1237.8 (5) |
| Z | 2 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.10 |
| Crystal size (mm) | 0.58 × 0.25 × 0.02 |

| Data collection | Diffractometer | Bruker APEX2 CCD |
|-----------------|----------------|------------------|
| Absorption correction | Multi-scan (SADABS; Bruker, 2016) | |
| Tmin, Tmax | 0.552, 0.746 | |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 20958, 3650, 2905 |
| R(int) | 0.066 |
| (sin θ/λ)max (Å⁻¹) | 0.708 |

| Refinement | R[F² > 2σ(F²)], wR(F²), S | 0.047, 0.132, 1.03 |
| No. of reflections | 3650 |
| No. of parameters | 181 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.53, −0.22 |

Computer programs: APEX2 and SAINT (Bruker, 2016), olex2.solve (Bourhis et al., 2015), SHELXL (Sheldrick, 2008), and OLEX2 (Dolomanov et al., 2009).

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References

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A71, 59–75.

Figure 6
View down [101] showing slipped stacks running along [101] with alternating domains parallel to [010] being highlighted in pink and blue. Hydrogen-bonding interactions are shown as blue dashed lines.
full crystallographic data

IUCrData (2022). 7, x220510  [https://doi.org/10.1107/S2414314622005107]

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Crystal data
C12H12N22+·2C8H7O4−  F(000) = 544
Mr = 518.51  Dα = 1.391 Mg m−3
Monoclinic, P21/c  Mo Kα radiation, λ = 0.71073 Å
a = 8.543 (2) Å  Cell parameters from 4917 reflections
b = 20.729 (5) Å  θ = 2.6–30.2°
c = 7.7061 (17) Å  μ = 0.10 mm−1
β = 114.898 (4)°  T = 90 K
V = 1237.8 (5) Å³  Plate, clear colourless
Z = 2  0.58 × 0.25 × 0.02 mm

Data collection
Bruker APEXII CCD
φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2016)
Tmin = 0.552, Tmax = 0.746
20958 measured reflections
3650 independent reflections
2905 reflections with I > 2σ(I)
Rint = 0.066
θmax = 30.2°, θmin = 2.0°
h = −11→12
k = −29→29
l = −10→10

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.047
wR(F²) = 0.132
S = 1.03
3650 reflections
181 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
w = 1/[σ²(Fo²) + (0.0606P)² + 0.4983P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max < 0.001
Δρ max = 0.53 e Å⁻³
Δρ min = −0.22 e Å⁻³

Special details
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms attached to heteroatoms were freely refined isotropically. H atoms connected to carbon atoms were placed geometrically (C—H = 0.95 Å) and refined as riding atoms with Uiso(H) = 1.2Ueq(C).
### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x               | y               | z               | \(U_{\text{iso}}^{\#1}/U_{\text{eq}}^{\#1}\) |
|-----|-----------------|-----------------|-----------------|---------------------------------------------|
| O2  | 0.24089 (12)    | 0.42238 (4)     | 0.25115 (13)    | 0.0198 (2)                                  |
| O3  | 0.56630 (12)    | 0.41986 (5)     | 0.42339 (13)    | 0.0225 (2)                                  |
| O1  | −0.04982 (12)   | 0.36590 (4)     | 0.01841 (14)    | 0.0217 (2)                                  |
| O4  | 0.71834 (12)    | 0.35219 (5)     | 0.32767 (15)    | 0.0254 (2)                                  |
| N1  | −0.02080 (14)   | 0.41143 (5)     | −0.43034 (15)   | 0.0171 (2)                                  |
| C6  | 0.41360 (15)    | 0.34659 (6)     | 0.17054 (16)    | 0.0147 (2)                                  |
| C7  | 0.25353 (15)    | 0.37113 (5)     | 0.14897 (16)    | 0.0145 (2)                                  |
| C2  | 0.09975 (15)    | 0.34088 (6)     | 0.02102 (17)    | 0.0158 (2)                                  |
| C11 | 0.26852 (16)    | 0.47304 (6)     | −0.16647 (17)   | 0.0173 (2)                                  |
| C8  | 0.57618 (16)    | 0.37522 (6)     | 0.31710 (17)    | 0.0175 (2)                                  |
| C5  | 0.41996 (16)    | 0.29391 (6)     | 0.06001 (18)    | 0.0185 (2)                                  |
| H5  | 0.528263        | 0.277301        | 0.073926        | 0.022*                                      |
| C13 | −0.03901 (16)   | 0.45885 (6)     | −0.32230 (18)   | 0.0179 (2)                                  |
| H13 | −0.151365       | 0.470811        | −0.337355       | 0.022*                                      |
| C9  | 0.13651 (17)    | 0.39427 (6)     | −0.41449 (18)   | 0.0194 (2)                                  |
| H9  | 0.146696        | 0.360930        | −0.493684       | 0.023*                                      |
| C3  | 0.10839 (16)    | 0.28915 (6)     | −0.08333 (18)   | 0.0190 (2)                                  |
| H3  | 0.005280        | 0.269293        | −0.176397       | 0.023*                                      |
| C14 | 0.41779 (16)    | 0.50517 (6)     | −0.01775 (18)   | 0.0198 (2)                                  |
| H14 | 0.395078        | 0.536024        | 0.059892        | 0.024*                                      |
| C12 | 0.10275 (16)    | 0.49066 (6)     | −0.18939 (18)   | 0.0188 (2)                                  |
| H12 | 0.087893        | 0.524298        | −0.113955       | 0.023*                                      |
| C10 | 0.28331 (16)    | 0.42435 (6)     | −0.28499 (18)   | 0.0194 (2)                                  |
| C11 | 0.393602        | 0.412167        | −0.276192       | 0.023*                                      |
| C4  | 0.26890 (17)    | 0.26605 (6)     | −0.06931 (18)   | 0.0207 (3)                                  |
| H4  | 0.273946        | 0.230930        | −0.145981       | 0.025*                                      |
| C1  | −0.20613 (18)   | 0.33220 (7)     | −0.0933 (2)     | 0.0270 (3)                                  |
| H1A | −0.233819       | 0.337474        | −0.229464       | 0.041*                                      |
| H1B | −0.300275       | 0.349769        | −0.066656       | 0.041*                                      |
| H1C | −0.191431       | 0.286266        | −0.060228       | 0.041*                                      |
| H2  | 0.357 (3)       | 0.4327 (11)     | 0.340 (3)       | 0.055 (6)*                                  |
| H1  | −0.131 (3)      | 0.3851 (10)     | −0.532 (3)      | 0.056 (6)*                                  |

### Atomic displacement parameters (Å²)

|     | \(U_{11}^{\#1}\) | \(U_{22}^{\#1}\) | \(U_{33}^{\#1}\) | \(U_{12}^{\#1}\) | \(U_{13}^{\#1}\) | \(U_{23}^{\#1}\) |
|-----|------------------|------------------|------------------|------------------|------------------|------------------|
| O2  | 0.0201 (5)       | 0.0218 (4)       | 0.0187 (4)       | −0.0005 (3)      | 0.0094 (4)       | −0.0056 (3)      |
| O3  | 0.0197 (5)       | 0.0270 (5)       | 0.0186 (4)       | −0.0036 (4)      | 0.0060 (4)       | −0.0076 (4)      |
| O1  | 0.0138 (4)       | 0.0248 (5)       | 0.0271 (5)       | −0.0010 (3)      | 0.0092 (4)       | −0.0032 (4)      |
| O4  | 0.0142 (4)       | 0.0300 (5)       | 0.0291 (5)       | −0.0030 (4)      | 0.0063 (4)       | −0.0096 (4)      |
| N1  | 0.0155 (5)       | 0.0192 (5)       | 0.0148 (5)       | −0.0025 (4)      | 0.0047 (4)       | 0.0013 (4)       |
| C6  | 0.0138 (5)       | 0.0171 (5)       | 0.0130 (5)       | −0.0019 (4)      | 0.0055 (4)       | 0.0002 (4)       |
| C7  | 0.0163 (5)       | 0.0115 (5)       | 0.0123 (5)       | −0.0012 (4)      | 0.0068 (4)       | 0.0005 (4)       |
| C2  | 0.0144 (5)       | 0.0185 (5)       | 0.0150 (5)       | 0.0002 (4)       | 0.0067 (4)       | 0.0022 (4)       |
| C11 | 0.0168 (6)       | 0.0190 (5)       | 0.0144 (5)       | −0.0017 (4)      | 0.0049 (4)       | 0.0029 (4)       |

\(U_{\text{iso}}^{\#1}/U_{\text{eq}}^{\#1}\) is the isotropic or equivalent isotropic displacement parameter, and \(U_{11}^{\#1}, U_{22}^{\#1}, U_{33}^{\#1}, U_{12}^{\#1}, U_{13}^{\#1}, U_{23}^{\#1}\) are the components of the atomic displacement parameter tensor.

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C8  0.0160 (6)  0.0205 (6)  0.0150 (5)  −0.0035 (4)  0.0056 (4)  0.0002 (4)
C5  0.0162 (6)  0.0202 (6)  0.0195 (6)  0.0001 (4)  0.0080 (5)  −0.0016 (4)
C13 0.0163 (6)  0.0192 (5)  0.0177 (6)  0.0010 (4)  0.0066 (5)  0.0026 (4)
C9  0.0193 (6)  0.0223 (6)  0.0176 (6)  −0.0007 (5)  0.0088 (5)  −0.0008 (4)
C3  0.0163 (6)  0.0214 (6)  0.0170 (6)  −0.0031 (4)  0.0046 (5)  −0.0021 (4)
C14 0.0189 (6)  0.0209 (6)  0.0190 (6)  −0.0017 (4)  0.0074 (5)  −0.0016 (5)
C12 0.0183 (6)  0.0186 (5)  0.0186 (6)  −0.0010 (4)  0.0070 (5)  0.0010 (5)
C10 0.0153 (6)  0.0242 (6)  0.0194 (6)  −0.0002 (4)  0.0079 (5)  0.0010 (5)
C4  0.0213 (6)  0.0204 (6)  0.0207 (6)  −0.0021 (5)  0.0092 (5)  −0.0063 (5)
C1  0.0159 (6)  0.0304 (7)  0.0335 (7)  −0.0028 (5)  0.0090 (6)  −0.0009 (6)

Geometric parameters (Å, °)

O2—C7 1.3535 (14)  C5—H5 0.9500
O2—H2 0.96 (2)  C5—C4 1.3818 (18)
O3—C8 1.2618 (15) C13—H13 0.9500
O1—C2 1.3713 (15) C13—C12 1.3806 (17)
O1—C1 1.4297 (16) C9—H9 0.9500
O4—C8 1.2753 (16) C9—C10 1.3797 (18)
N1—C13 1.3389 (16) C3—H3 0.9500
N1—C9 1.3451 (17) C3—C4 1.4005 (18)
N1—H1 1.09 (2)  C14—C14i 1.330 (3)
C6—C7 1.4018 (16) C14—H14 0.9500
C6—C8 1.4954 (16) C12—H12 0.9500
C6—C5 1.3999 (16) C10—H10 0.9500
C7—C2 1.4144 (17) C4—H4 0.9500
C2—C3 1.3849 (17) C1—H1A 0.9800
C11—C14 1.4672 (17) C1—H1B 0.9800
C11—C12 1.3998 (18) C1—H1C 0.9800
C11—C10 1.4020 (17)

C7—O2—H2 105.9 (13)  C12—C13—H13 119.4
C2—O1—C1 116.90 (10) N1—C9—H9 119.5
C13—N1—C9 120.72 (11) N1—C9—C10 121.02 (11)
C13—N1—H1 121.6 (12) C10—C9—C10 119.52 (11)
C9—N1—H1 117.7 (12) C5—C4—C3 120.11 (11)
C7—C6—C8 119.67 (10) C2—C3—C4 119.9
C7—C6—C5 120.79 (11) C4—C3—C4 120.11 (11)
C5—C6—C8 120.50 (11) C11—C14—C11 117.2
O2—C7—C6 119.93 (10) C14—C14—H14 125.64 (15)
O2—C7—C2 118.38 (10) C14—C14—H14 117.2
C6—C7—C2 119.68 (11) C11—C12—C11 120.2
C1—C2—C7 115.39 (10) C13—C12—C11 119.60 (12)
C1—C2—C3 124.89 (11) C13—C12—H12 120.2
C3—C2—C7 119.71 (11) C11—C10—H10 120.2
C12—C11—C14 118.72 (11) C9—C10—C11 119.52 (11)
C12—C11—C10 118.00 (11) C9—C10—H10 120.2
C10—C11—C14 123.27 (11) C5—C4—C3 120.57 (12)
O3—C8—O4 123.73 (11) C5—C4—H4 119.7
O3—C8—C6 119.12 (11) C3—C4—H4 119.7
O4—C8—C6 117.15 (11) O1—C1—H1A 109.5
C6—C5—H5 120.0 O1—C1—H1B 109.5
C4—C5—C6 120.07 (11) O1—C1—H1C 109.5
C4—C5—H5 120.0 H1A—C1—H1B 109.5
N1—C13—H13 119.4 H1A—C1—H1C 109.5
N1—C13—C12 121.11 (11) H1B—C1—H1C 109.5

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···O4ii | 1.09 (2) | 1.45 (2) | 2.5402 (15) | 178 (2) |
| O2—H2···O3 | 0.96 (2) | 1.64 (2) | 2.5270 (14) | 150 (2) |
| C13—H13···O2iii | 0.95 | 2.52 | 3.1831 (16) | 127 |
| C13—H13···O3iv | 0.95 | 2.57 | 3.2092 (17) | 125 |
| C12—H12···O1iii | 0.95 | 2.46 | 3.3591 (17) | 159 |

Symmetry codes: (ii) x−1, y, z−1; (iii) −x, −y+1, −z; (iv) −x+1, −y, −z.

Hydrogen-bond geometry (Å, °)

Symmetry code: (i) −x, −y, −z.