Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Utilizing proton transfer to produce molecular salts in bromanilic acid substituted-pyridine molecular complexes – predictable synthons?

Lynne H. Thomas,[a]* Martin S. Adam,[b] Andrew O'Neill[b] and Chick C. Wilson[a]

[a]Department of Chemistry, University of Bath, Bath BA2 7AY, England, and [b]School of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland
Correspondence e-mail: l.h.thomas@bath.ac.uk

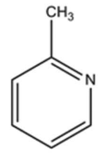
Received 3 October 2013
Accepted 26 October 2013

Controlled introduction of proton transfer into the design of a series of molecular complexes is described, delivering the systematic production of ionic molecular complexes (molecular salts). The controlled production of molecular salts has relevance as a potential strategy in the design of pharmaceutical materials. In nine molecular complexes consisting of bromanilic acid with the N-heterocyclic compounds 2-, 3- and 4-picoline [bis(2/3/4-methylpyridinium) 2,5-dibromo-3,6-dioxocyclohexa-1,4-diene-1,4-diolate, $2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$], 2,3-, 2,4-, 2,5- and 3,5-lutidine [2,3/2,4/2,5/3,5-dimethylpyridinium 2,5-dibromo-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate, $C_7H_{10}N^+\cdot C_6HBr_2O_4^-$], and 3-bromo-4-methylpyridine [3-bromo-4-methylpyridinium 2,5-dibromo-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate, $C_6H_7BrN^+\cdot C_6HBr_2O_4^-$] and 2-bromo-3-methylpyridine [2-bromo-3-methylpyridine–2,5-dibromo-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (1/1), $C_6H_6BrN\cdot C_6H_2Br_2O_4$], proton transfer occurs readily between the bromanilic acid molecule and the N heteroatom of the pyridine ring, in all cases producing a charge-assisted bifurcated N—H···O hydrogen bond. This reinforces the value of this motif as a design tool in the crystal engineering of such complexes. The protonation state (and stoichiometry) significantly affect the supramolecular synthons obtained, but 1:2 stoichiometries reliably give rise to PBP synthons and 1:1 stoichiometries to PBBP synthons (where P indicates a methylpyridine co-molecule and B a bromanilic acid molecule). The influence of halogen interactions on the wider crystal packing is also discussed, with C—H···Br and Br···O interactions the most prevalent; only one Br···Br interaction is found.

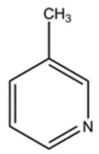
Keywords: crystal structure; crystal engineering; hydrogen bonding; proton transfer; lutidine salts; picoline salts; bromanilic acid.

1. Introduction

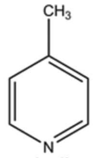
Hydrogen bonding is one of the key interactions in the field of crystal engineering; the directional and predictable nature of the formation of hydrogen bonds has allowed the controlled growth of supramolecular assemblies in a range of areas, including pharmaceuticals (Schultheiss & Newman, 2009), porosity (Bojdys *et al.*, 2011) and agrochemicals (Nauha *et al.*, 2011). While salt formation is a well-established route for developing new solid forms of, for example, pharmaceuticals, with modified physical properties (Childs *et al.*, 2007), the charge-assisted hydrogen bond is a much less studied interaction as a tool in crystal engineering (Ward, 2005). The use of proton transfer as a design tool in the creation of (ionic) molecular complexes is thus a potentially valuable element in the design of molecular complexes, and it is this aspect of crystal engineering that is investigated here.



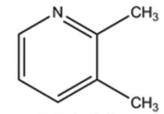
2-picoline



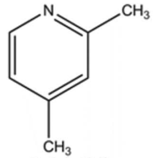
3-picoline



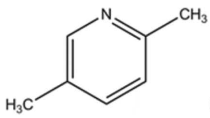
4-picoline



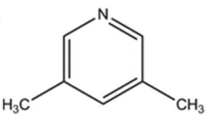
2,3-lutidine



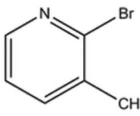
2,4-lutidine



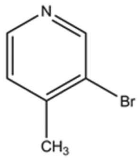
2,5-lutidine



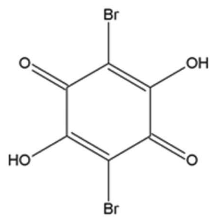
3,5-lutidine



2-bromo-3-methylpyridine



3-bromo-4-methylpyridine



bromanilic acid

Chloranilic acid (2,5-dichloro-3,6-dihydroxybenzoquinone) has been widely studied as a co-component in multicomponent solid forms. In contrast, bromanilic acid (2,5-dibromo-3,6-dihydroxybenzoquinone) is much less studied. Both have the capacity to form molecular complexes in their deprotonated

doi:10.1107/S0108270113029533

Table 1
Experimental details.

	Bis(2-picolinium) bromanilate	Bis(3-picolinium) bromanilate	Bis(4-picolinium) bromanilate
Crystal data			
Chemical formula	$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$	$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$	$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$
M_r	484.15	484.15	484.15
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100
a, b, c (Å)	16.3604 (13), 7.7452 (6), 14.3658 (9)	8.9526 (7), 9.6149 (8), 10.4275 (8)	8.1345 (8), 6.1517 (6), 17.7868 (17)
β (°)	100.911 (3)	103.935 (4)	96.177 (7)
V (Å^3)	1787.4 (2)	871.17 (12)	884.90 (15)
Z	4	2	2
μ (mm^{-1})	4.56	4.68	4.61
Crystal size (mm)	0.30 × 0.25 × 0.15	0.30 × 0.25 × 0.15	0.35 × 0.25 × 0.20
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)
$T_{\min}$, $T_{\max}$	0.567, 1.000	0.671, 1.000	0.576, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20956, 4883, 3506	9784, 2280, 2018	14105, 3234, 2464
$R_{\rm int}$	0.056	0.033	0.047
$\theta_{\max}$ (°)	29.4	28.9	32.8
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.690	0.679	0.763
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.080, 1.00	0.023, 0.061, 1.08	0.034, 0.087, 1.06
No. of reflections	4883	2280	3234
No. of parameters	245	123	123
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.64, −0.45	0.45, −0.63	0.82, −0.54

	2,4-Lutidinium bromanilate	2,5-Lutidinium bromanilate	3,5-Lutidinium bromanilate
Crystal data			
Chemical formula	$C_7H_{10}N^+\cdot C_6HBr_2O_4^-$	$C_7H_{10}N^+\cdot C_6HBr_2O_4^-$	$C_7H_{10}N^+\cdot C_6HBr_2O_4^-$
M_r	405.04	405.05	405.04
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100
a, b, c (Å)	8.2948 (2), 12.1560 (4), 13.9544 (5)	7.7357 (4), 11.1416 (6), 15.8011 (9)	11.6766 (5), 10.4926 (5), 11.5221 (5)
β (°)	102.966 (2)	94.269 (3)	98.834 (2)
V (Å^3)	1371.17 (8)	1358.09 (13)	1394.92 (11)
Z	4	4	4
μ (mm^{-1})	5.92	5.98	5.82
Crystal size (mm)	0.25 × 0.20 × 0.10	0.35 × 0.25 × 0.15	0.25 × 0.20 × 0.10
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)
$T_{\min}$, $T_{\max}$	0.631, 1.000	0.404, 1.000	0.684, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22482, 6064, 4537	38096, 9404, 6083	14020, 3817, 3131
$R_{\rm int}$	0.042	0.058	0.031
$\theta_{\max}$ (°)	36.0	42.1	31.5
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.826	0.943	0.736
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.081, 1.02	0.043, 0.101, 1.03	0.027, 0.067, 1.05
No. of reflections	6064	9404	3817
No. of parameters	191	184	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.85, −0.56	1.34, −1.29	0.58, −0.45

Table 1 (continued)

	3-Bromo-4-methylpyridinium bromanilate	2,3-Lutidinium bromanilate	2-Bromo-3-methylpyridine–bromanilic acid (1/1)
Crystal data			
Chemical formula	$C_6H_7BrN^+ \cdot C_6HBr_2O_4^-$	$C_7H_{10}N^+ \cdot C_6HBr_2O_4^-$	$C_6H_6BrN \cdot C_6H_2Br_2O_4$
M_r	469.91	405.04	469.91
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100
a, b, c (Å)	10.2229 (4), 5.5760 (2), 24.5300 (9)	4.9786 (4), 23.181 (3), 12.2811 (13)	5.2866 (3), 13.3814 (8), 20.3576 (13)
β (°)	95.802 (3)	100.794 (3)	91.556 (4)
V (Å^3)	1391.12 (9)	1392.3 (2)	1439.61 (15)
Z	4	4	4
μ (mm^{-1})	8.71	5.83	8.42
Crystal size (mm)	0.25 × 0.15 × 0.10	0.20 × 0.10 × 0.05	0.25 × 0.20 × 0.10
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)	Multi-scan (*SADABS*; Blessing, 1995)
T_{min}, T_{max}	0.499, 1.000	0.791, 1.000	0.465, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19916, 4796, 3311	9783, 2053, 1664	14350, 3202, 2267
R_{int}	0.057	0.046	0.071
θ_{max} (°)	32.2	23.6	27.2
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.749	0.563	0.644
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.101, 1.04	0.028, 0.065, 1.02	0.039, 0.086, 1.03
No. of reflections	4796	2053	3202
No. of parameters	190	182	188
No. of restraints	0	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.23, −1.13	0.45, −0.32	0.77, −0.67

Computer programs: *APEX2* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008) and *SHELXL97* (Sheldrick, 2008).

forms, through the loss of protons from one or both of the –OH groups. Bromanilic acid has been studied as a co-component in a number of multicomponent molecular complexes containing basic N heteroatoms to generate extended hydrogen-bonded architectures [pyrazines (Tomura & Yamashita, 2000), dipyridyls (Zaman *et al.*, 2001), 2,2′-bipyrimidine (Zaman *et al.*, 2004) and self-contained isolated supramolecular units such as 2-acetylpyridine (Thomas *et al.*, 2009)]. The ferroelectric properties of bromanilic complexes have also been probed [phenazine (Horiuchi *et al.*, 2005, 2009; Kumai *et al.*, 2007); 2,3,5,6-tetrakis(pyridin-2-yl)pyrazine (Horiuchi *et al.*, 2008)].

A previous study of the molecular complexes of chloranilic acid with picolines (methylpyridines) focused specifically on the use of proton transfer from chloranilic acid to the N atom of the pyridine ring to form bifurcated charge-assisted hydrogen bonds (Adam *et al.*, 2010). The systematic transfer of a proton within this hydrogen-bond motif was established as a reproducible factor in predictable supramolecular synthons; these synthons were not extended, with the primary hydrogen-bonding interactions saturated within the supramolecular unit. The synthons obtained were related to the stoichiometry (and therefore the protonation state of the chloranilic acid molecule), with PCP units (where P denotes picoline, or more generally in the present work the relevant methylpyridine, and C denotes chloranilic acid) formed for 2:1 stoichiometries (double deprotonation of the chloranilic acid) and PCCP units formed for 1:1 stoichiometries and single deprotonation of the chloranilic acid. This work is extended here to complexes of bromanilic acid with substituted pyridines [including picolines (methylpyridines), lutidines (dimethylpyridines) and bromo-substituted variants], allowing a comparison to be made with the complexes formed with chloranilic acid. While the primary hydrogen-bonding interactions are saturated within the synthons, the additional functionality of the halogen atoms gives them the potential to influence the wider crystal packing. Halogen interactions have been successfully utilized as additional directional interactions in the assembly of crystal structures (Priimagi *et al.*, 2013) and the effect of the Br atoms in these complexes can be assessed. The introduction of additional halogen substituents to the co-molecules also allows the effect of competing intermolecular interactions involving halogens to be assessed.

2. Experimental

2.1. Synthesis and crystallization

Bromanilic acid is a solid at room temperature. The co-molecules are all volatile liquids at room temperature. Crystals were therefore grown using an excess of the co-molecule.

Bis(2-picolinium) bromanilate crystals were grown by slow evaporation of a methanol solution containing bromanilic acid (12 mg) and 2-picoline (75 mg) at room temperature.

Bis(3-picolinium) bromaniliate crystals were grown by slow evaporation of a methanol–water solution (50:50 *v*/*v*) containing bromalinic acid (8 mg) and 3-picoline (50 mg) at 278 K.

Bis(4-picolinium) bromanilate crystals were grown by slow evaporation of a methanol–water solution (50:50 *v*/*v*) containing bromanilic (8 mg) acid and 4-picoline (50 mg) at 278 K.

2,3-Lutidinium bromanilate crystals were grown by slow evaporation of a propan-2-ol solution containing bromanilic acid (6 mg) and 2,3-lutidine (16 mg) at room temperature.

2,4-Lutidinium bromanilate crystals were grown by slow evaporation of a methanol–water solution (50:50 *v*/*v*) containing bromanilic acid (10 mg) and 2,4-lutidine (26 mg) at room temperature.

2,5-Lutidinium bromanilate crystals were grown by slow evaporation of a methanol–water solution (50:50 *v*/*v*) containing bromanilic acid (8 mg) and 2,5-lutidine (22 mg) at room temperature.

3,5-Lutidinium bromanilate crystals were grown by slow evaporation of a propan-2-ol solution containing bromanilic acid (10 mg) and 3,5-lutidine (26 mg) at room temperature.

2-Bromo-3-methylpyridine bromanilic acid crystals were grown by slow evaporation of a methanol solution containing bromanilic acid (10 mg) and 2-bromo-3-methylpyridine (14 mg) at 278 K.

3-Bromo-4-methylpyridinium bromanilate crystals were grown by slow evaporation of a methanol–water solution (50:50 *v*/*v*) containing bromanilic acid (10 mg) and 3-bromo-4-methylpyridine (14 mg) at room temperature.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. C-bound H atoms were positioned geometrically and treated as riding, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms, and C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) otherwise. Except as described below, N- and O-bound H atoms were located in difference Fourier maps and refined isotropically. For the 3,5- and 2,3-lutidinium salts, the N- and O-bound H atoms were positioned geometrically and treated as riding, with N—H = 0.86 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N), and with O—H = 0.82 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). In the case of the 2-bromo-3-methylpyridine complex, one hydroxy H atom (H1) was refined with an O—H distance restraint of 0.82 (2) Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O).

3. Results and discussion

Bromanilic acid is a strong acid and contains two protic –OH groups. In molecular complexes, a variety of supramolecular synthons can be formed, influenced by the multiple deprotonation states which bromanilic acid can adopt. It can exist as a neutral molecule (BAH_2), a singly deprotonated negatively charged anion (BAH^-) and a doubly deprotonated doubly negatively charged anion (BA^{2-}).

Nine molecular complexes of bromanilic acid with substituted pyridines have been synthesized with varying stoichiometries and protonation states. These substituted pyridines reflect a range of basicity and a range of steric bulk surrounding the N-heterocycle. In general, anilic acid molecules readily donate H atoms to basic N atoms in multicomponent molecular complexes, and stoichiometry and the consequent protonation state have a significant effect on the supramolecular synthons obtained. The nine molecular complexes presented here fit into three families: picoline isomers (methylpyridines), lutidine isomers (dimethylpyridines) and bromomethylpyridines. The picolines preferentially crystallize with bromanilic acid in 2:1 stoichiometries, whereas the lutidine isomers tend to crystallize in 1:1 stoichiometries and consequently tend to form different supramolecular synthons. The bromomethylpyridines introduce the additional possibility of further halogen bonding and form 1:1 complexes. However, one of the two complexes reported here shows no proton transfer and so different synthons might be expected.

3.1. Supramolecular synthons

3.1.1. PBP supramolecular synthons. Similar to chloranilic acid molecular complexes (Adam *et al.*, 2010; Molčanov & Kojić-Prodić, 2010), 2:1 picoline–bromanilic acid molecular complexes tend to give PBP (where P denotes the methylpyridine co-molecule and B the bromanilic acid) supramolecular synthons (Fig. 1). These units are comprised of a central doubly deprotonated bromanilic acid molecule sandwiched by two protonated (at the N heteroatom) picoline molecules (Fig. 1). Bifurcated hydrogen bonds are formed between the picoline NH^+ group and the two O atoms of the BA^{2-} anion. 2:1 molecular complexes of 3-picoline/4-picoline with bromanilic acid form centrosymmetric PBP units which are isostructural with the equivalent previously reported chloranilic acid–picoline molecular complexes {chloranilic acid–3-picoline form I [Cambridge Structural Database (CSD; Allen, 2002) refcode VURWAH] and chloranilic acid–4-picoline (VURSUX); Adam *et al.*, 2010}.

Figure 1

PBP supramolecular synthons formed in 2:1 picoline–bromanilic acid complexes. Right to left: 2-picoline, 3-picoline and 4-picoline. Displacement ellipsoids are drawn at the 50% probability level.

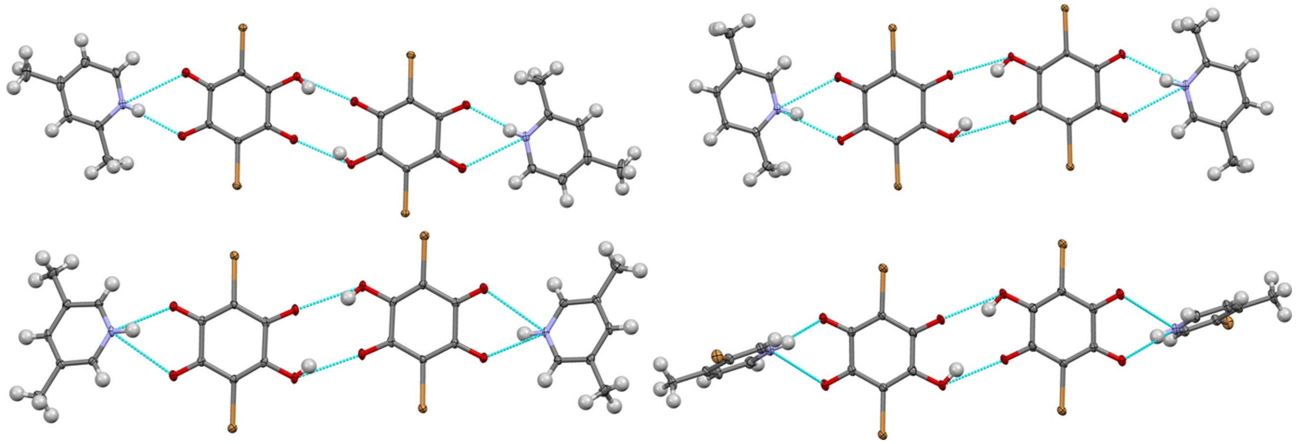


Figure 2
The PBBP supramolecular synthon where the bromanilic acid molecule has been singly deprotonated. Top left: 2,4-lutidine; top right: 2,5-lutidine; bottom left: 3,5-lutidine; bottom right: 3-bromo-4-methylpyridine. Displacement ellipsoids are drawn at the 50% probability level.

The bromanilic acid–2-picoline 1:2 complex represents an anomaly in this series, where the PBP synthon is noncentrosymmetric; one 2-picoline molecule lies approximately in the plane of the bromanilic acid molecule and the second is significantly twisted from the plane. In the CSD (Version 5.34, with the November update), of 345 hits in which the chloranilic acid molecule is doubly deprotonated, only three PCP units are noncentrosymmetric [refcode EWOWUI (Ishida, 2004), pyrrolidinium; IZIHAA (Akhtaruzzaman *et al.*, 2004), 4,7-bis(pyridin-4-yl)-2,1,3-benzothiadiazole trihydrate; and TUQMAU (Hakim Al-arique *et al.*, 2010), lansoprazole]. There are no reported noncentrosymmetric bromanilic acid PBP units in the CSD, but there are considerably fewer bromanilic acid complexes reported of any sort. There is no obvious correlation between the co-molecules which give rise to noncentrosymmetric units.

The relative orientations of the picoline molecules compared with the bromanilic acid molecules are difficult to predict. It might be expected that a significant relative rotation of the rings would be found where the sterically bulky methyl group is adjacent to the N heteroatom in the 2-position. However, in this series of three complexes, the 2-picoline complex has one 2-picoline molecule which is in approximately the same plane as the bromanilic acid molecule. This results in a slightly longer bifurcated hydrogen bond on this side of the bromanilic acid molecule and an additional Br$\cdots$O interaction is formed to the O atom with the strongest hydrogen bond, in addition to a weak intra-synthon C—H$\cdots$O hydrogen bond from the methyl group of the 2-picoline molecule. This synthon is also unusual as the major hydrogen bonds comprising the bifurcated hydrogen bond are directed towards two O atoms adjacent to the same Br atom; the inversion centre dictates that this cannot be the case for the other molecular complexes.

3.1.2. PBBP supramolecular synthons. Where the bromanilic acid is in its singly deprotonated state, a PBBP supramolecular synthon tends to be formed, with a centrosymmetric bromanilic acid dimer flanked by two co-molecules on either side (Fig. 2). The relative orientations of the lutidine molecules on either side of the bromanilic acid dimer again do not appear to be influenced by the steric bulk of a methyl group adjacent to the N heteroatom, as all three of the lutidine isomers (2,4-, 2,5- and 3,5-lutidine) lie in approximately the same plane as the bromanilic acid dimer. In fact, the least sterically influenced 3,5-lutidine shows the most significant shift from coplanarity and this may suggest that the weak hydrogen bond formed between the methyl group and one of the O atoms of the bromanilic acid molecule is a favourable interaction and can only be formed where the methyl group is adjacent to the N heteroatom, forcing the molecules to be approximately coplanar.

Molecular complexes of chloranilic acid with 2,4-lutidine and 2,5-lutidine have been reported previously (Ishida & Kashino, 2002); the molecular complex of chloranilic acid with

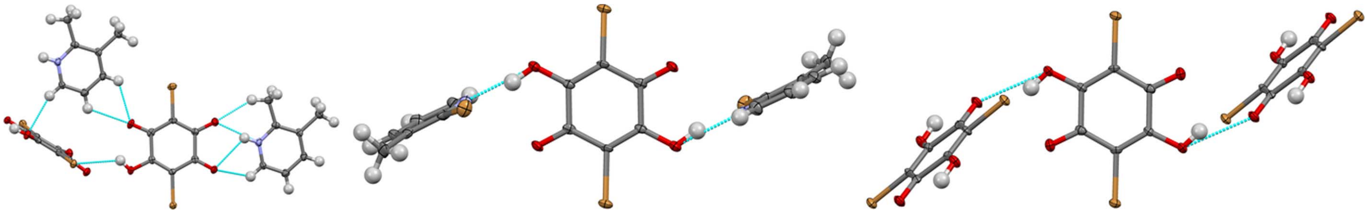


Figure 3
Exceptions to the 1:1 or 2:1 patterns. Left: 2,3-lutidine 1:1; middle and right: 2-bromo-3-methylpyridine 1:1. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Bond lengths (Å) for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (CSD refcode VAGTUS; Robl, 1987) with the doubly deprotonated bromanilic acid in 1:2 complexes with the picoline isomers.

The numbering scheme is as in Fig. 4 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry. Entries marked with an asterisk (*) are related by inversion symmetry to the other half of the bromanilic acid molecule.

	VAGTUS BAH_2	2-Picoline BA^{2-}	3-Picoline BA^{2-}	4-Picoline BA^{2-}
C1—Br1	1.868 (4)	1.905 (2)	1.9025 (18)	1.902 (2)
C1—C2	1.347 (6)	1.394 (4)	1.387 (2)	1.399 (3)
C2—O1	1.323 (5)	1.260 (3)	1.262 (2)	1.246 (2)
C2—C3	1.504 (5)	1.547 (4)	1.548 (3)	1.554 (3)
C3—O2	1.225 (5)	1.251 (3)	1.238 (2)	1.246 (3)
C3—C4	1.449 (5)	1.402 (4)	1.414 (2)	1.405 (3)
C4—Br2	1.868 (4)*	1.905 (3)	1.9025 (18)*	1.902 (2)*
C4—C5	1.347 (6)*	1.400 (4)	1.387 (2)*	1.399 (3)*
C5—O3	1.323 (5)*	1.249 (3)	1.262 (2)*	1.246 (2)*
C5—C6	1.504 (5)*	1.559 (4)	1.548 (3)*	1.554 (3)*
C6—O4	1.225 (5)*	1.249 (3)	1.238 (2)*	1.246 (3)*
C1—C6	1.449 (5)*	1.407 (4)	1.414 (2)*	1.405 (3)*

2,5-lutidine is isostructural with the equivalent bromanilic acid complex. However, whilst the same supramolecular unit (PCCP) is formed in the 2,4-lutidine–chloranilic acid complex, the molecules are not coplanar and the bifurcated hydrogen bond is significantly more asymmetric [N···O = 2.698 (3) and 3.263 (3) Å, *cf.* 2.847 (2) and 2.975 (2) Å].

The 3-bromo-4-methylpyridine bromanilic acid molecular complex does not form a coplanar PBBP supramolecular unit, with the two molecules twisted by ~80° relative to each other.

3.1.3. Exceptions to the predictable supramolecular synthons. The 1:1 molecular complex of 2,3-lutidine with bromanilic acid is an exception to the 1:1 supramolecular synthons: while a bifurcated hydrogen bond is still formed on the deprotonated side of the bromanilic acid molecule, the bromanilic acid homodimer does not form (Fig. 3, left). Instead, the hydroxy group forms a stronger intramolecular hydrogen bond (C—O···H angle ~105° *versus* ~112° in a PBBP complex) and forms weak interactions to a neighbouring Br atom [O···Br = 3.422 (2) Å]. The C═O double bond forms a bifurcated hydrogen bond with two C—H groups on a neighbouring lutidine molecule.

The 1:1 complex of 2-bromo-3-methylpyridine is the exception in all of the complexes studied. In this case, there is no proton transfer and this has a significant impact on the supramolecular synthons obtained. A PBP-type supramolecular unit is formed, similar to those complexes in which there is a 2:1 stoichiometry, with a hydrogen bond formed between the hydroxy groups on the bromanilic acid molecule and the N heteroatom of the 2-bromo-3-methylpyridine molecule (Fig. 3, middle). This unit is centrosymmetric and the H atom is pulled away from the intramolecular hydrogen bond with the other O atom of the bromanilic acid molecule. A second independent bromanilic acid molecule forms hydrogen bonds to the bromanilic acid molecule in the PBP unit and this forms chains of bromanilic acid molecules along the *b* axis (Fig. 3, right).

3.2. The effect of deprotonation on the conjugation of the bromanilic acid molecule

Regardless of whether the bromanilic acid molecule is singly or doubly deprotonated, the delocalization of charge is not located between two O atoms on the same side of the molecule, but rather passes across, through the O1—C2—C1—C6—O4 (and/or O2—C3—C4—C5—O3) linkage (Fig. 4, left), as evidenced by variations in the bond lengths (Tables 2–4). In all cases, a clear C—C single bond is indicated by the C2—C3 and C5—C6 bond lengths. In fact, these bond lengths are elongated relative to the neutral molecule found in pure bromanilic acid (CSD refcode VAGTUS; Robl, 1987), despite the discrepancies between the structure determination temperatures (100 K for the structures reported here, room temperature for VAGTUS). For singly deprotonated bromanilic acid molecules (Table 3), one of the C—O distances remains consistent with a single bond and can thus be defined as the remaining –OH group. Where deprotonation has occurred, the C—O single-bond length shortens considerably to somewhere intermediate between those expected for a single or a double bond. In addition, at least one of the C═O double bonds increases (only one increases where there is only a single deprotonation), and in some cases where there is double deprotonation it is approximately equal in length to the other C—O bond. When the molecule is neutral, C1—C2

Table 3
Bond lengths (Å) for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (CSD refcode VAGTUS; Robl, 1987) with the singly deprotonated bromanilic acid in 1:1 complexes with the lutidine isomers.

The numbering scheme is as in Fig. 4 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry. Entries marked with an asterisk (*) are related by inversion symmetry to the other half of the bromanilic acid molecule.

	VAGTUS BAH_2	2,3-Lutidine BAH^-	2,4-Lutidine BAH^-	2,5-Lutidine BAH^-	3,5-Lutidine BAH^-
C1—Br1	1.868 (4)	1.889 (4)	1.8753 (18)	1.8792 (17)	1.881 (2)
C1—C2	1.347 (6)	1.338 (5)	1.353 (2)	1.352 (2)	1.349 (3)
C2—O1	1.323 (5)	1.332 (4)	1.3204 (19)	1.3235 (19)	1.329 (3)
C2—C3	1.504 (5)	1.522 (6)	1.511 (2)	1.519 (2)	1.522 (3)
C3—O2	1.225 (5)	1.242 (4)	1.248 (2)	1.2495 (19)	1.240 (3)
C3—C4	1.449 (5)	1.409 (6)	1.405 (2)	1.398 (2)	1.412 (3)
C4—Br2	1.868 (4)*	1.897 (4)	1.8907 (17)	1.8868 (17)	1.888 (2)
C4—C5	1.347 (6)*	1.397 (5)	1.405 (2)	1.403 (2)	1.395 (3)
C5—O3	1.323 (5)*	1.255 (5)	1.2499 (19)	1.238 (2)	1.245 (2)
C5—C6	1.504 (5)*	1.542 (6)	1.545 (2)	1.554 (2)	1.554 (3)
C6—O4	1.225 (5)*	1.220 (5)	1.217 (2)	1.2224 (19)	1.219 (3)
C1—C6	1.449 (5)*	1.455 (6)	1.455 (2)	1.447 (2)	1.447 (3)

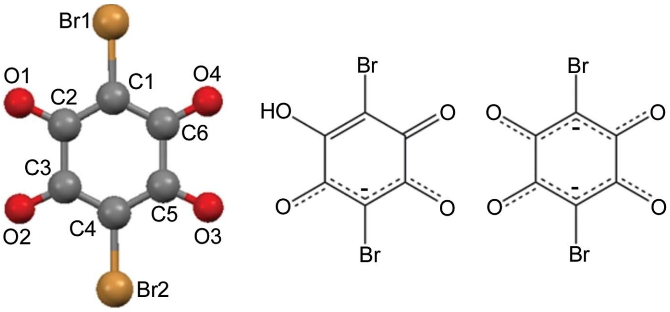


Figure 4
Left: labelling scheme used in Tables 2–4. Atom O1 is protonated when the bromanilic acid molecule is singly deprotonated, and atoms O1 and O3 are protonated when the bromanilic acid molecule is neutral. Middle: charge delocalization for a singly deprotonated bromanilic acid molecule. Right: charge delocalization for a doubly deprotonated bromanilic acid molecule.

and C4—C5 are shorter, reflecting their double-bond character. On single deprotonation of O3, C3—C4 and C4—C5 equalize in length and C4—Br2 lengthens slightly, reflecting the delocalization of charge across O2—C3—C4—C5—O3. Where double deprotonation occurs, C1—C2 and C1—C6 also equalize, reflecting the presence of two regions of negative charge.

3.3. Hydrogen bonding within the supramolecular synthons

While there is some predictability in the supramolecular synthons obtained in bromanilic acid complexes, the relative orientation of the two co-molecules and the directionality of the bifurcated hydrogen bonds is less easy to predict. Where the molecules are far from coplanar, the N—H group of the pyridine is able to approach closer to the bromanilic acid molecule and the resulting bifurcated hydrogen bond is more asymmetric (Table 5). This is well illustrated in the 2-picoline complex, where an approximately coplanar and a twisted conformation of the co-molecule are adopted within the same supramolecular unit. However, there is no simple correlation between the relative orientations of the two molecules and the degree of asymmetry in the bifurcated hydrogen bond.

In the cases where the bromanilic acid molecule is only singly deprotonated, the major component of the bifurcated N—H···O hydrogen bond is directed towards the charged side of the bromanilic acid molecule (indicated with the bond angle closest to 180°), with one exception, the complex with 2,5-lutidine. In this case, the most linear of the two hydrogen bonds is towards the neutral half of the molecule and the C═O double-bonded O atom. However, the shorter of the two bond lengths is between the N—H group and the charged side of the bromanilic acid molecule.

These singly deprotonated bromanilic acid molecules all form a PBBP synthon, except the complex with 2,3-lutidine, where two bromanilic acid molecules form a dimer connected by two O—H···O hydrogen bonds. There is some competition between this intermolecular hydrogen bond and an intramolecular O—H···O hydrogen bond within the bromanilic acid molecule. The intermolecular hydrogen bond is the most linear in all cases and the longest of the two interactions, with one exception, the 2,4-lutidine complex, where the intra- and intermolecular hydrogen bonds are approximately the same. Again, there is no obvious relationship between the strengths of these hydrogen bonds and the co-molecules.

The 2,3-lutidine bromanilic acid complex is the exception, in which an N—H···O bifurcated hydrogen bond is formed to one side of the molecule but the bromanilic acid homodimer is not formed. Instead, a shorter intramolecular O—H···O hydrogen bond is formed, along with a weak O—H···Br intermolecular hydrogen bond to a second bromanilic acid molecule.

The 2-bromo-3-methylpyridine–bromanilic acid molecular complex is the only one which does not show any proton transfer and the bromanilic acid molecule is present in its neutral state. One-dimensional hydrogen-bonded chains of bromanilic acid molecules are formed, similar in both orientation and strength to those found in pure bromanilic acid (VAGTUS; Robl, 1987). There are two independent neutral molecules. The first has a shorter intramolecular O—H···O

Table 4
Bond lengths (Å) for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (CSD refcode VAGTUS; Robl, 1987) with the doubly deprotonated bromanilic acid in 1:1 complexes with the bromomethylpyridine isomers.

The numbering scheme is as in Fig. 4 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry. Entries marked with an asterisk (*) are related by inversion symmetry to the other half of the bromanilic acid molecule. (i) and (ii) represent the two independent bromanilic acid molecules in the 2-bromo-3-methylpyridine molecular complex.

	VAGTUS BAH_2	2-Bromo-3-methylpyridine (i) BAH_2	2-Bromo-3-methylpyridine (ii) BAH_2	3-Bromo-4-methylpyridine BAH^-
C1—Br1	1.868 (4)	1.882 (4)	1.886 (4)	1.894 (4)
C1—C2	1.347 (6)	1.346 (6)	1.353 (6)	1.347 (5)
C2—O1	1.323 (5)	1.322 (5)	1.308 (5)	1.327 (4)
C2—C3	1.504 (5)	1.517 (6)	1.527 (6)	1.517 (5)
C3—O2	1.225 (5)	1.223 (5)	1.230 (5)	1.243 (4)
C3—C4	1.449 (5)	1.453 (6)	1.437 (6)	1.420 (5)
C4—Br2	1.868 (4)*	1.882 (4)*	1.886 (4)*	1.894 (4)
C4—C5	1.347 (6)*	1.346 (6)*	1.353 (6)*	1.390 (4)
C5—O3	1.323 (5)*	1.322 (5)*	1.308 (5)*	1.266 (4)
C5—C6	1.504 (5)*	1.517 (6)*	1.527 (6)*	1.531 (5)
C6—O4	1.225 (5)*	1.223 (5)*	1.231 (5)*	1.234 (4)
C1—C6	1.449 (5)*	1.453 (6)*	1.437 (6)*	1.442 (5)

hydrogen bond, and in addition this O—H group forms an intermolecular O—H···O hydrogen bond to the second bromanilic acid molecule. The second bromanilic acid molecule forms a PBP unit similar to those found in the 2:1 molecular complexes, but with the H atom clearly located on the O atom and with the N atom of the 2-bromo-3-methylpyridine molecule acting as the hydrogen-bond acceptor. This is the strongest hydrogen bond in the complex and the H atom is pulled out of the intramolecular hydrogen bond, weakening the latter.

Table 5
Selected hydrogen-bond parameters (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
2-Picoline				
N2—H2···O4	0.86 (3)	2.02 (3)	2.838 (3)	159 (3)
N2—H2···O3	0.86 (3)	2.36 (3)	2.946 (3)	126 (2)
N1—H1···O1	0.77 (4)	1.96 (4)	2.693 (3)	160 (4)
N1—H1···O2	0.77 (4)	2.36 (4)	2.828 (3)	121 (4)
3-Picoline				
N1—H5···O1	0.84 (3)	1.78 (3)	2.598 (2)	165 (3)
N1—H5···O2^{i}	0.84 (3)	2.54 (3)	3.039 (2)	119 (3)
C4—H4···Br1^{ii}	0.93	2.96	3.7977 (18)	151
4-Picoline				
N1—H3···O1	0.74 (3)	2.12 (3)	2.760 (3)	145 (4)
N1—H3···O2	0.74 (3)	2.31 (3)	2.859 (3)	131 (3)
2,4-Lutidine				
O1—H1···O2^{iii}	0.68 (3)	2.03 (3)	2.6509 (18)	151 (3)
O1—H1···O2	0.68 (3)	2.26 (3)	2.6559 (19)	119 (3)
N1—H2···O3^{iv}	0.72 (2)	2.14 (2)	2.849 (2)	168 (3)
N1—H2···O4^{iv}	0.72 (2)	2.56 (2)	2.9807 (18)	119 (2)
2,5-Lutidine				
O1—H1···O2^{v}	0.82	2.01	2.6994 (17)	141
O1—H1···O2	0.82	2.16	2.6403 (19)	117
N1—H1*A*···O4	0.86	2.17	2.9794 (19)	158
N1—H1*A*···O3	0.86	2.34	2.883 (2)	122
3,5-Lutidine				
N1—H2···O3^{vi}	0.93 (3)	1.84 (3)	2.677 (3)	148 (3)
N1—H2···O4^{vi}	0.93 (3)	2.37 (3)	3.008 (3)	125 (3)
O1—H1···O2^{iii}	0.72 (3)	2.11 (3)	2.768 (3)	152 (3)
O1—H1···O2	0.72 (3)	2.23 (3)	2.631 (2)	116 (3)
3-Bromo-4-methylpyridine				
O1—H1···O2^{vii}	0.87 (5)	1.97 (5)	2.717 (3)	144 (4)
O1—H1···O2	0.87 (5)	2.12 (4)	2.637 (4)	118 (4)
N1—H5···O3^{viii}	0.79 (5)	1.91 (5)	2.675 (4)	161 (5)
N1—H5···O4^{viii}	0.79 (5)	2.53 (5)	2.915 (4)	112 (4)
2,3-Lutidine				
O1—H1···O2	0.82	2.13	2.611 (4)	117
O1—H1···Br1^{ix}	0.82	2.82	3.423 (3)	132
N1—H1*A*···O3^{x}	0.86	1.93	2.777 (4)	168
N1—H1*A*···O4^{x}	0.86	2.54	3.043 (4)	119
2-Bromo-3-methylpyridine				
O1—H1···O4	0.857 (19)	2.01 (3)	2.794 (4)	151 (5)
O1—H1···O2^{xi}	0.857 (19)	2.15 (5)	2.638 (5)	115 (4)
O3—H2···N1	0.92 (5)	1.73 (5)	2.619 (5)	163 (5)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$; (iv) $x - 1, y, z$; (v) $-x, -y, -z$; (vi) $-x, -y + 1, -z + 1$; (vii) $-x, -y, -z + 2$; (viii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ix) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (x) $x + 1, y, z$; (xi) $-x + 1, -y + 1, -z + 1$.

Table 6
A summary of the Br interactions in the molecular complexes with bromanilic acid.

	Br···Br	Br···O	C—H···Br	Br···π	O—H···Br
VAGTUS (Robl, 1987)	Yes	×	×	Yes	×
2-Picoline	×	Yes	×	×	×
3-Picoline	×	×	Yes	Yes	×
4-Picoline	×	×	Yes (×2)	×	×
2,3-Lutidine	×	Yes	Yes (×2)	Yes	Yes
2,4-Lutidine	Yes	Yes	×	×	×
2,5-Lutidine	×	×	Yes (×4)	×	×
3,5-Lutidine	×	Yes	Yes (×2)	×	×
2-Bromo-3-methylpyridine	×	Yes	×	×	×
3-Bromo-4-methylpyridine	×	Yes (×2)	Yes	×	×

3.4. Halogen interactions

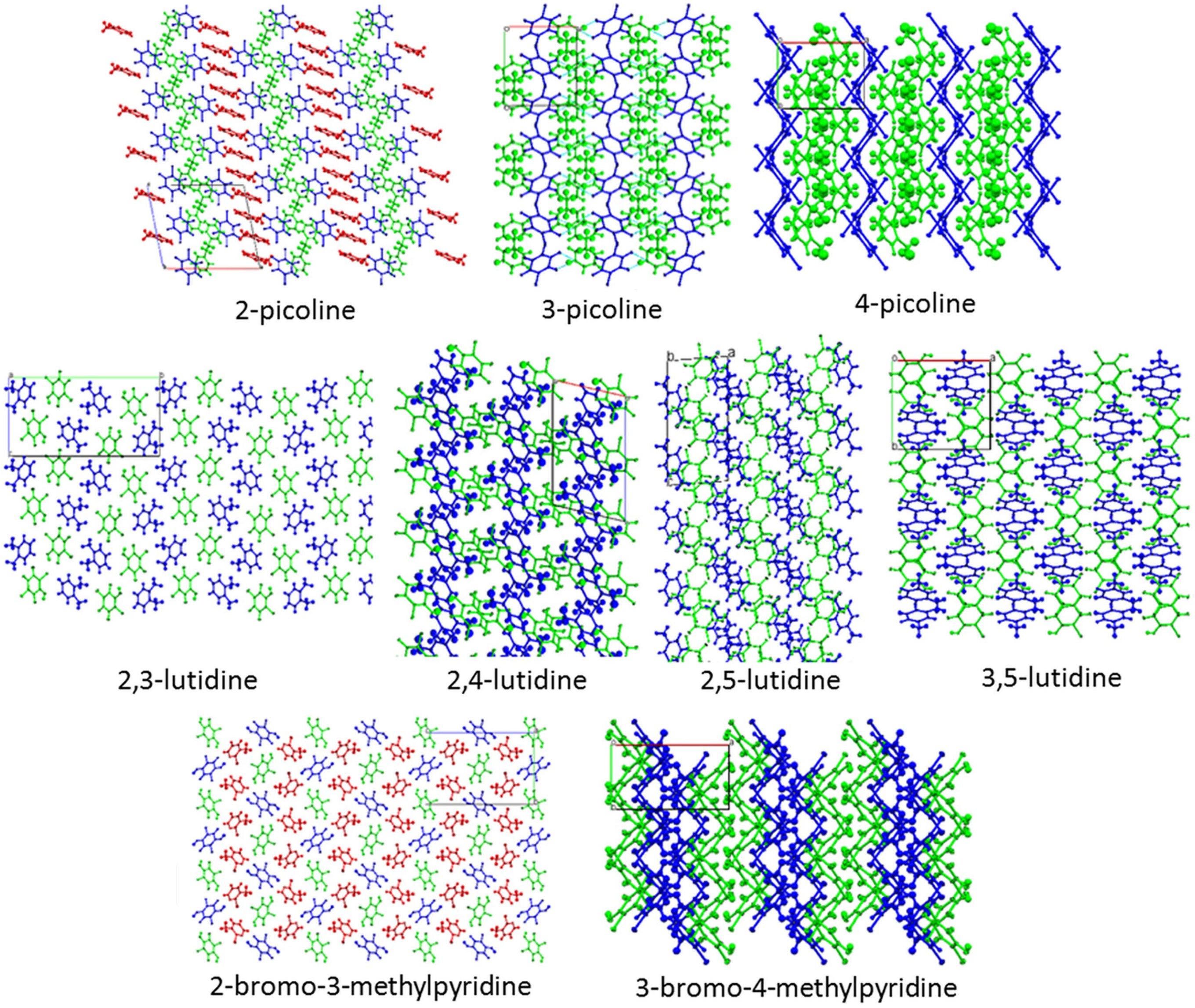
A range of halogen interactions are observed in these complexes (Table 6), the most prevalent being weak C—H···Br hydrogen bonds and Br···O halogen interactions, which occur at similar frequencies. The Br···O contacts also show an almost equal preference for halogen bonds to the neutral or charge-delocalized O atoms of the bromanilic acid molecules. The shortest Br···O contact does not involve charge and is found in the complex with 2-bromo-3-methylpyridine [2.851 (3) Å, *cf.* the sum of the van der Waals radii of 3.3 Å; Bondi, 1964]. There is only one complex which shows Br···Br contacts, that with 2,4-lutidine; the observed Br···Br distance of 3.6195 (4) Å is at the weak end of these interactions but is still significantly less than the sum of the van der Waals radii of two Br atoms (3.7 Å).

Bromomethylpyridines were chosen as co-molecules with the expectation that increasing the number of Br atoms might increase the number of halogen interactions, specifically favouring halogen–halogen interactions. However, in the two complexes reported here, no Br···Br interactions are found and the 2-bromo-3-methylpyridine complex only shows one Br interaction with an O atom, with two of the three Br atoms not participating in any interactions. The 3-bromo-4-methylpyridine complex contains three independent Br atoms and each one participates in one Br interaction, one very weak C—H···Br hydrogen bond [C···Br = 3.940 (4) Å] and two Br···O contacts.

3.5. Crystal packing

While the functional groups differ and are in different relative positions on the co-molecule, there are some similarities in the global packing of these nine molecular complexes. All of them show layers of alternating bromanilic acid and co-molecule, the thickness of which varies depending on the stoichiometries and the relative orientations of the molecules (Fig. 5). Some of the layers are interwoven (*e.g.* 2,4-lutidine and 3,5-lutidine) and some take a wave-like form (4-picoline, 2,3-lutidine, 3,5-lutidine and 3-bromo-4-methylpyridine).

The primary hydrogen-bonding interactions are contained within the supramolecular units (PBP or PBBP), with the exception of the 2-bromo-3-methylpyridine complex which features extended bromanilic hydrogen-bonded chains. The interactions within the extended structures are therefore primarily weak in nature and, in addition to the halogen


2-picoline 3-picoline 4-picoline

2,3-lutidine 2,4-lutidine 2,5-lutidine 3,5-lutidine

2-bromo-3-methylpyridine 3-bromo-4-methylpyridine

Figure 5
The crystal packing in the nine title bromanilic acid molecular complexes, coloured by symmetry-equivalent molecules. All molecular complexes show a layered structure, with some showing more interweaving of the layers than others. 2-Picoline is viewed along the *b* axis, with bromanilic acid blue, and 2-picoline molecules red (twisted) and green (coplanar). 3-Picoline and 4-picoline are viewed along the *c* axis, with bromanilic acid blue and picoline green. For the lutidines, bromanilic acid is shown in green, and lutidine blue. 2,3-Lutidine and 2,4-lutidine are viewed along the *a* axis, 2,5-lutidine along the *b* axis and 3,5-lutidine along the *c* axis. 2-Bromo-3-methylpyridine is viewed along the *a* axis, with bromanilic acid green and blue, and 2-bromo-3-methylpyridine red. 3-Bromo-4-methylpyridine is viewed along the *c* axis, with bromanilic acid green and 3-bromo-4-methylpyridine blue. (All colours refer to the electronic version of the paper.)

interactions (discussed in §3.4), feature C—H$\cdots$O, C—H$\cdots\pi$ and π–π interactions.

The methyl groups play both a steric and a connectivity role in the crystal packing through weak hydrogen bonds. The primary interactions formed by the methyl groups are weak C—H$\cdots$O hydrogen bonds, with five of the nine complexes showing a weak C—H$\cdots$Br hydrogen bond and three showing C—H$\cdots\pi$ hydrogen bonds. None of the complexes shows a saturation of hydrogen bonding involving the methyl group, rather showing one or two weak hydrogen bonds per methyl group.

In general, C—H$\cdots$O interactions are found in all nine complexes, except the 2,5- and 3,5-lutidine complexes where only C—H$\cdots\pi$ and O$\cdots\pi$ interactions are found. There are also no π–π interactions in the 3-picoline complex, but they are found in all six remaining complexes, reflecting a range of interactions between the same type of molecule (*e.g.* bromanilic acid to bromanilic acid) or between bromanilic acid and the co-molecule (2-picoline, 2,5-lutidine or 3-bromo-4-methylpyridine). The bromanilic acid–2-picoline complex stacks in pairs of hydrogen-bonded 2-picoline–bromanilic acid coplanar units in a head-to-tail manner. 2,5-Lutidine–bromanilic acid forms stacks of four molecules within the PBBP synthon and the π-stacking in the 4-picoline complex is limited to pairs of bromanilic acid molecules.

4. Conclusions

Nine new bromanilic acid methylpyridine molecular complexes have been reported. Proton transfer from the bromanilic acid molecule to the N heteroatom of the pyridine molecule is a common feature, occurring in all but one of the molecular complexes. The different possible protonation states of the bromanilic acid molecule (the two acidic OH groups) allow the formation of different supramolecular synthons. 2:1 stoichiometries (*i.e.* double deprotonation) give rise to a PBP unit and 1:1 stoichiometries (*i.e.* single deprotonation) give a PBBP unit, including a hydrogen-bonded dimer of bromanilic acid molecules. All complexes where proton transfer has occurred form charge-assisted bifurcated hydrogen bonds between the deprotonated bromanilic acid molecule and the protonated N heteroatom of the pyridine ring. This shows the predictability of this interaction in these systems and demonstrates that such a synthon can be reliably designed into a crystal structure.

While it is possible to predict the formation of this synthon, it does not appear to be possible to predict the relative orientations of the bromanilic acid molecule and the co-molecule. The presence of a methyl group on the 2-position does tend to result in a coplanar arrangement of the molecules, due to the formation of a weak intra-synthon C—H···O hydrogen bond between the methyl group and one of the O atoms of the bromanilic acid molecule. The 2-picoline complex is unusual as a PBP synthon, as the unit is not centrosymmetric and only one weak intra-synthon C—H···O hydrogen bond is formed on one side of the bromanilic acid molecule. Where the molecules of the supramolecular synthon are not coplanar, the bifurcated hydrogen bond tends to be asymmetric, with one hydrogen bond dominating over the other. Where they are approximately coplanar, the two hydrogen-bond lengths are more similar.

There are two exceptions to the PBP and PBBP synthons. The 2,3-lutidine molecular complex does show the bifurcated charge-assisted hydrogen bond between the N heteroatom of the pyridine ring and the O atoms of the singly deprotonated bromanilic acid molecule, but the bromanilic acid dimer does not form. In contrast, there is no proton transfer in the 2-bromo-3-methylpyridine molecular complex and therefore the bifurcated N—H···O hydrogen bonds do not form. Despite this, a PBP unit is formed, with an intramolecular O—H···N hydrogen bond to the 2-bromo-3-methylpyrdine molecule which competes with an intramolecular O—H···O hydrogen bond. However, the stoichiometry of the complex is 1:1, not 2:1, and the second bromanilic acid molecule connects the PBP units into an extended structure through O—H···O hydrogen bonds, creating a bromanilic acid chain.

Introducing additional Br atoms into the complexes by using brominated co-molecules does not, in the two cases reported here, induce the introduction of Br···Br interactions. In fact, the frequency of formation of halogen interactions of any kind does not appear to be increased. The prevalent bromine interactions in this series of complexes are weak C—H···Br hydrogen bonds and O···Br halogen interactions. Only one Br···Br interaction is found, in the 2,4-lutidine molecular complex.

Despite the significantly different interactions and the overall packing of the supramolecular synthons into the crystal structures, there is a clear recurrence of layers of bromanilic acid and co-molecules. These take different forms, with some linear and some wave-like, and some show interpenetration.

Proton transfer to generate charge-assisted hydrogen bonding can clearly be used as a tool in crystal engineering for reliably producing predictable supramolecular synthons, and reinforces the utility of controlled introduction of proton transfer into this design, allowing the production of ionic molecular complexes or molecular salts. The use of molecules which have multiple protonation or deprotonation states can also lead to a more diverse range of synthons with potentially different physical properties.

MSA and AON were funded by the University of Glasgow.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FM3015). Services for accessing these data are described at the back of the journal.

References

Adam, M. S., Parkin, A., Thomas, L. H. & Wilson, C. C. (2010). *CrystEngComm*, **12**, 917–924.

Akhtaruzzaman, M., Tomura, M., Nishida, J. & Yamashita, Y. (2004). *J. Org. Chem.* **69**, 2953–2958.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bojdys, M. J., Briggs, M. E., Jones, J. T. A., Adams, D. J., Chong, S. Y., Schmidtmann, M. & Cooper, A. I. (2011). *J. Am. Chem. Soc.* **133**, 16566–16571.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bruker (2009). *APEX*. Bruker AXS Inc., Madison, Wisconsin, USA.

Childs, S. L., Stahly, G. P. & Park, A. (2007). *Mol. Pharm.* **4**, 323–338.

Hakim Al-arique, Q. N. M., Jasinski, J. P., Butcher, R. J., Yathirajan, H. S. & Narayana, B. (2010). *Acta Cryst.* E**66**, o1507–o1508.

Horiuchi, S., Kumai, R., Tokunaga, Y. & Tokura, Y. (2008). *J. Am. Chem. Soc.* **130**, 13382–13391.

Horiuchi, S., Kumai, R. & Tokura, Y. (2005). *J. Am. Chem. Soc.* **127**, 5010–5011.

Horiuchi, S., Kumai, R. & Tokura, Y. (2009). *J. Mater. Chem.* **19**, 4421–4434.

Ishida, H. (2004). *Acta Cryst.* E**60**, o974–o976.

Ishida, H. & Kashino, S. (2002). *Z. Naturforsch. Teil A*, **57**, 829–836.

Kumai, R., Horiuchi, S., Sagayama, H., Arima, T.-H., Watanabe, M., Noda, Y. & Tokura, Y. (2007). *J. Am. Chem. Soc.* **129**, 12920–12921.

Molčanov, K. & Kojić-Prodić, B. (2010). *CrystEngComm*, **12**, 925–939.

Nauha, E., Kolehmainen, E. & Nissinen, M. (2011). *CrystEngComm*, **13**, 6531–6537.

Priimagi, A., Cavallo, G., Metrangolo, P. & Resnati, G. (2013). *Acc. Chem. Res.* **30**, doi:10.1021/ar400103r.

Robl, C. (1987). *Z. Kristallogr.* **180**, 249–253.

Schultheiss, N. & Newman, A. (2009). *Cryst. Growth Des.* **9**, 2950–2967.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Thomas, L. H. *et al.* (2009). *Acta Cryst.* E**65**, o1218.

Tomura, M. & Yamashita, Y. (2000). *CrystEngComm*, **2**, 92–95.

Ward, M. D. (2005). *Chem. Commun.* pp. 5838–5842.

Zaman, M. B., Tomura, M. & Yamashita, Y. (2001). *J. Org. Chem.* **66**, 5987–5995.

Zaman, M. B., Udachin, K. A. & Ripmeester, J. A. (2004). *Cryst. Growth Des.* **4**, 585–589.

supplementary materials

Acta Cryst. (2013). C**69**, 1279-1288 [doi:10.1107/S0108270113029533]

Utilizing proton transfer to produce molecular salts in bromanilic acid substituted-pyridine molecular complexes – predictable synthons?

Lynne H. Thomas, Martin S. Adam, Andrew O'Neill and Chick C. Wilson

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* (Bruker, 2009); data reduction: *APEX2* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008) for ba2pic_100k_1-1, ba24lut, ba_3br4mepyr; *SHELXL97* (Sheldrick, 2008) for ba3pic100k1121apr_0m, br3p14jan_0m, ba25lut_100k_11aug_0m, ba_35lut, ba23lut, ba_2br3mepyr.

(ba2pic_100k_1-1) Bis(2-picolinium) bromanilate

Crystal data

$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$	$Z = 4$
$M_r = 484.15$	$F(000) = 960$
Monoclinic, $P2_1/c$	$D_x = 1.799$ Mg m^{-3}
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.3604$ (13) Å	$\mu = 4.56$ mm^{-1}
$b = 7.7452$ (6) Å	$T = 100$ K
$c = 14.3658$ (9) Å	Block, purple
$\beta = 100.911$ (3)°	0.3 × 0.25 × 0.15 mm
$V = 1787.4$ (2) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	4883 independent reflections
CCD; rotation images scans	3506 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$R_{int} = 0.056$
$T_{min} = 0.567$, $T_{max} = 1.000$	$\theta_{max} = 29.4°$, $\theta_{min} = 1.3°$
20956 measured reflections	$h = -22 \rightarrow 22$
	$k = -10 \rightarrow 10$
	$l = -19 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
4883 reflections	$\Delta\rho_{min} = -0.45$ e Å^{-3}
245 parameters	
0 restraints	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
C14	0.37734 (17)	0.6533 (4)	0.6404 (2)	0.0225 (6)
H14	0.3549	0.6463	0.6951	0.027*
N2	0.47738 (15)	0.7632 (3)	0.55824 (16)	0.0154 (5)
H2	0.5221 (18)	0.819 (3)	0.555 (2)	0.014 (8)*
C13	0.44575 (17)	0.7605 (3)	0.6381 (2)	0.0182 (6)
C16	0.37626 (17)	0.5683 (3)	0.4798 (2)	0.0198 (6)
H16	0.353	0.5058	0.426	0.024*
C17	0.44378 (18)	0.6720 (3)	0.4803 (2)	0.0190 (6)
H17	0.467	0.6799	0.4261	0.023*
C15	0.34340 (18)	0.5586 (4)	0.5619 (2)	0.0228 (6)
H15	0.298	0.4873	0.5637	0.027*
C18	0.48453 (18)	0.8700 (4)	0.7190 (2)	0.0233 (6)
H18A	0.518	0.7995	0.7665	0.035*
H18B	0.4418	0.9256	0.7457	0.035*
H18C	0.5189	0.956	0.6974	0.035*
Br1	0.77406 (2)	1.20048 (3)	0.68748 (2)	0.01821 (8)
Br2	0.69958 (2)	0.79178 (3)	0.26985 (2)	0.01666 (8)
O3	0.59107 (12)	0.8222 (2)	0.42497 (13)	0.0183 (4)
O1	0.87359 (12)	1.1929 (2)	0.52699 (13)	0.0204 (4)
O2	0.84955 (12)	1.0180 (3)	0.36536 (13)	0.0235 (5)
O4	0.62485 (11)	0.9647 (2)	0.59632 (13)	0.0184 (4)
C5	0.65969 (16)	0.8970 (3)	0.44594 (18)	0.0136 (5)
C6	0.67803 (17)	0.9850 (3)	0.54532 (18)	0.0143 (5)
C4	0.71999 (16)	0.9081 (3)	0.38883 (18)	0.0147 (5)
C2	0.80862 (16)	1.1020 (3)	0.50893 (18)	0.0154 (5)
C1	0.75152 (17)	1.0828 (3)	0.56894 (18)	0.0151 (5)
C3	0.79362 (16)	1.0039 (3)	0.41342 (18)	0.0151 (5)
N1	0.96988 (16)	1.2838 (3)	0.40231 (18)	0.0191 (5)
H1	0.934 (3)	1.254 (5)	0.426 (3)	0.058 (14)*
C10	1.09443 (19)	1.2292 (4)	0.3478 (2)	0.0225 (6)
H10	1.1357	1.1531	0.3371	0.027*
C9	1.09745 (17)	1.4029 (4)	0.32392 (18)	0.0206 (6)
H9	1.1408	1.4444	0.2966	0.025*
C8	1.03543 (17)	1.5140 (3)	0.34108 (18)	0.0191 (6)
H8	1.0379	1.6305	0.3262	0.023*
C7	0.97025 (17)	1.4529 (3)	0.37997 (18)	0.0166 (5)
C11	1.02907 (18)	1.1726 (3)	0.3874 (2)	0.0202 (6)
H11	1.0258	1.057	0.4039	0.024*
C12	0.89918 (18)	1.5601 (4)	0.3976 (2)	0.0241 (6)
H12A	0.8514	1.5385	0.3489	0.036*

H12B	0.9139	1.6801	0.397	0.036*
H12C	0.8865	1.531	0.4582	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C14	0.0175 (15)	0.0271 (15)	0.0244 (16)	0.0084 (12)	0.0076 (12)	0.0078 (13)
N2	0.0142 (12)	0.0156 (11)	0.0167 (12)	0.0021 (9)	0.0037 (9)	0.0031 (9)
C13	0.0193 (15)	0.0181 (13)	0.0176 (14)	0.0080 (10)	0.0046 (11)	0.0043 (11)
C16	0.0147 (14)	0.0196 (13)	0.0248 (15)	0.0022 (11)	0.0028 (11)	0.0003 (11)
C17	0.0188 (15)	0.0183 (13)	0.0201 (15)	0.0065 (11)	0.0038 (11)	0.0032 (11)
C15	0.0176 (15)	0.0217 (14)	0.0305 (17)	0.0022 (11)	0.0081 (12)	0.0073 (12)
C18	0.0213 (16)	0.0280 (15)	0.0206 (15)	0.0060 (12)	0.0036 (11)	0.0019 (13)
Br1	0.02134 (16)	0.02129 (14)	0.01274 (14)	−0.00143 (11)	0.00508 (10)	−0.00220 (11)
Br2	0.01661 (15)	0.01926 (13)	0.01452 (14)	−0.00167 (11)	0.00401 (10)	−0.00316 (11)
O3	0.0170 (10)	0.0197 (10)	0.0187 (10)	−0.0032 (8)	0.0046 (8)	−0.0016 (8)
O1	0.0224 (11)	0.0223 (10)	0.0176 (10)	−0.0088 (8)	0.0069 (8)	−0.0054 (8)
O2	0.0206 (11)	0.0298 (11)	0.0226 (11)	−0.0077 (9)	0.0103 (8)	−0.0060 (9)
O4	0.0168 (10)	0.0237 (10)	0.0166 (10)	−0.0008 (8)	0.0078 (8)	0.0018 (8)
C5	0.0127 (13)	0.0112 (11)	0.0170 (13)	0.0037 (10)	0.0028 (10)	0.0028 (10)
C6	0.0184 (15)	0.0126 (11)	0.0127 (13)	0.0040 (10)	0.0043 (10)	0.0039 (10)
C4	0.0160 (14)	0.0172 (12)	0.0108 (13)	−0.0002 (10)	0.0024 (10)	−0.0006 (10)
C2	0.0169 (14)	0.0139 (12)	0.0155 (13)	0.0023 (10)	0.0030 (10)	0.0011 (10)
C1	0.0206 (15)	0.0148 (12)	0.0111 (13)	0.0009 (10)	0.0057 (10)	−0.0010 (10)
C3	0.0159 (14)	0.0157 (12)	0.0145 (13)	−0.0005 (10)	0.0046 (10)	0.0004 (10)
N1	0.0160 (13)	0.0221 (12)	0.0198 (13)	−0.0042 (10)	0.0050 (10)	0.0015 (10)
C10	0.0236 (16)	0.0272 (15)	0.0156 (14)	0.0044 (12)	0.0011 (11)	−0.0013 (12)
C9	0.0181 (15)	0.0298 (15)	0.0141 (14)	−0.0074 (12)	0.0036 (10)	0.0014 (12)
C8	0.0224 (15)	0.0179 (13)	0.0152 (14)	−0.0029 (11)	−0.0005 (11)	−0.0002 (11)
C7	0.0177 (14)	0.0198 (13)	0.0109 (13)	−0.0004 (11)	−0.0010 (10)	−0.0002 (10)
C11	0.0210 (15)	0.0169 (13)	0.0217 (15)	−0.0009 (11)	0.0021 (11)	0.0015 (11)
C12	0.0243 (16)	0.0285 (15)	0.0177 (15)	0.0033 (12)	−0.0005 (12)	−0.0033 (12)

Geometric parameters (Å, º)

C14—C15	1.371 (4)	C5—C4	1.400 (4)
C14—C13	1.399 (4)	C5—C6	1.559 (4)
C14—H14	0.93	C6—C1	1.407 (4)
N2—C13	1.346 (3)	C4—C3	1.402 (4)
N2—C17	1.350 (4)	C2—C1	1.394 (4)
N2—H2	0.86 (3)	C2—C3	1.547 (4)
C13—C18	1.481 (4)	N1—C11	1.343 (4)
C16—C17	1.365 (4)	N1—C7	1.349 (3)
C16—C15	1.388 (4)	N1—H1	0.77 (4)
C16—H16	0.93	C10—C11	1.375 (4)
C17—H17	0.93	C10—C9	1.392 (4)
C15—H15	0.93	C10—H10	0.93
C18—H18A	0.96	C9—C8	1.387 (4)
C18—H18B	0.96	C9—H9	0.93
C18—H18C	0.96	C8—C7	1.378 (4)

Br1—C1	1.905 (2)	C8—H8	0.93
Br2—C4	1.905 (3)	C7—C12	1.489 (4)
O3—C5	1.249 (3)	C11—H11	0.93
O1—C2	1.260 (3)	C12—H12A	0.96
O2—C3	1.251 (3)	C12—H12B	0.96
O4—C6	1.249 (3)	C12—H12C	0.96
C15—C14—C13	120.0 (3)	O1—C2—C1	124.8 (2)
C15—C14—H14	120	O1—C2—C3	116.3 (2)
C13—C14—H14	120	C1—C2—C3	118.9 (2)
C13—N2—C17	122.5 (3)	C2—C1—C6	123.4 (2)
C13—N2—H2	121.9 (19)	C2—C1—Br1	117.56 (19)
C17—N2—H2	115.5 (19)	C6—C1—Br1	119.02 (19)
N2—C13—C14	117.9 (3)	O2—C3—C4	126.2 (2)
N2—C13—C18	118.9 (3)	O2—C3—C2	115.9 (2)
C14—C13—C18	123.2 (3)	C4—C3—C2	117.9 (2)
C17—C16—C15	118.1 (3)	C11—N1—C7	123.3 (3)
C17—C16—H16	121	C11—N1—H1	121 (3)
C15—C16—H16	121	C7—N1—H1	116 (3)
N2—C17—C16	121.0 (3)	C11—C10—C9	118.5 (3)
N2—C17—H17	119.5	C11—C10—H10	120.8
C16—C17—H17	119.5	C9—C10—H10	120.8
C14—C15—C16	120.6 (3)	C8—C9—C10	119.6 (3)
C14—C15—H15	119.7	C8—C9—H9	120.2
C16—C15—H15	119.7	C10—C9—H9	120.2
C13—C18—H18A	109.5	C7—C8—C9	120.5 (3)
C13—C18—H18B	109.5	C7—C8—H8	119.7
H18A—C18—H18B	109.5	C9—C8—H8	119.7
C13—C18—H18C	109.5	N1—C7—C8	117.9 (3)
H18A—C18—H18C	109.5	N1—C7—C12	117.5 (3)
H18B—C18—H18C	109.5	C8—C7—C12	124.5 (3)
O3—C5—C4	126.0 (2)	N1—C11—C10	120.2 (3)
O3—C5—C6	115.6 (2)	N1—C11—H11	119.9
C4—C5—C6	118.4 (2)	C10—C11—H11	119.9
O4—C6—C1	125.8 (2)	C7—C12—H12A	109.5
O4—C6—C5	116.6 (2)	C7—C12—H12B	109.5
C1—C6—C5	117.6 (2)	H12A—C12—H12B	109.5
C5—C4—C3	123.5 (2)	C7—C12—H12C	109.5
C5—C4—Br2	118.27 (19)	H12A—C12—H12C	109.5
C3—C4—Br2	118.22 (19)	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O4	0.86 (3)	2.02 (3)	2.838 (3)	159 (3)
N2—H2···O3	0.86 (3)	2.36 (3)	2.946 (3)	126 (2)
N1—H1···O1	0.77 (4)	1.96 (4)	2.693 (3)	160 (4)
N1—H1···O2	0.77 (4)	2.36 (4)	2.828 (3)	121 (4)

(ba3pic100k1121apr_0m) Bis(3-picolinium) bromanilate

Crystal data

$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$	$Z = 2$
$M_r = 484.15$	$F(000) = 480$
Monoclinic, $P2_1/c$	$D_x = 1.846$ Mg m^{-3}
$a = 8.9526$ (7) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.6149$ (8) Å	$\mu = 4.68$ mm^{-1}
$c = 10.4275$ (8) Å	$T = 100$ K
$\beta = 103.935$ (4)°	Block, purple
$V = 871.17$ (12) Å^3	0.3 × 0.25 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	2280 independent reflections
Graphite monochromator	2018 reflections with $I > 2\sigma(I)$
CCD; rotation images scans	$R_{\text{int}} = 0.033$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$\theta_{\text{max}} = 28.9°$, $\theta_{\text{min}} = 2.3°$
$T_{\text{min}} = 0.671$, $T_{\text{max}} = 1.000$	$h = -12\rightarrow12$
9784 measured reflections	$k = -13\rightarrow11$
	$l = -11\rightarrow14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.023$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.5432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2280 reflections	$\Delta\rho_{\text{max}} = 0.45$ e Å^{-3}
123 parameters	$\Delta\rho_{\text{min}} = -0.63$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
H5	0.893 (4)	0.515 (3)	0.285 (3)	0.057 (10)*
Br1	0.43444 (2)	0.23608 (2)	0.18610 (2)	0.01678 (7)
O1	0.71755 (15)	0.42622 (14)	0.21943 (13)	0.0185 (3)
O2	0.23321 (14)	0.35789 (14)	−0.07254 (14)	0.0182 (3)
C1	0.4732 (2)	0.38635 (18)	0.07990 (18)	0.0137 (3)
C3	0.3575 (2)	0.41949 (18)	−0.03428 (18)	0.0136 (3)

C6	1.2623 (2)	0.61801 (19)	0.47325 (18)	0.0158 (4)
H6	1.3581	0.6454	0.5237	0.019*
C2	0.6123 (2)	0.45631 (18)	0.11904 (18)	0.0135 (3)
N1	0.98369 (19)	0.53679 (17)	0.32431 (16)	0.0179 (3)
C4	0.9917 (2)	0.64850 (19)	0.40243 (19)	0.0160 (4)
H4	0.9021	0.6963	0.4047	0.019*
C5	1.1315 (2)	0.69418 (19)	0.47996 (18)	0.0141 (3)
C7	1.2510 (2)	0.5025 (2)	0.39267 (19)	0.0181 (4)
H7	1.3384	0.4521	0.3886	0.022*
C9	1.1387 (2)	0.8178 (2)	0.5686 (2)	0.0210 (4)
H9A	1.1519	0.9007	0.5213	0.031*
H9B	1.2239	0.8077	0.6441	0.031*
H9C	1.0448	0.8242	0.5974	0.031*
C8	1.1086 (2)	0.4633 (2)	0.31852 (19)	0.0195 (4)
H8	1.0992	0.3854	0.2642	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01435 (10)	0.01840 (11)	0.01676 (11)	−0.00363 (7)	0.00212 (7)	0.00366 (7)
O1	0.0149 (6)	0.0217 (7)	0.0159 (7)	−0.0044 (5)	−0.0021 (5)	0.0023 (5)
O2	0.0133 (6)	0.0184 (7)	0.0207 (7)	−0.0043 (5)	−0.0004 (5)	0.0005 (5)
C1	0.0145 (8)	0.0134 (8)	0.0136 (9)	−0.0027 (6)	0.0042 (7)	0.0001 (7)
C3	0.0129 (8)	0.0138 (8)	0.0138 (9)	−0.0005 (6)	0.0027 (6)	−0.0032 (7)
C6	0.0113 (8)	0.0192 (9)	0.0159 (9)	−0.0013 (7)	0.0011 (7)	0.0013 (7)
C2	0.0136 (8)	0.0142 (8)	0.0127 (8)	−0.0006 (6)	0.0034 (7)	−0.0025 (7)
N1	0.0150 (8)	0.0223 (8)	0.0138 (8)	−0.0055 (6)	−0.0016 (6)	0.0051 (6)
C4	0.0127 (8)	0.0177 (9)	0.0168 (9)	0.0015 (7)	0.0023 (7)	0.0072 (7)
C5	0.0151 (8)	0.0138 (8)	0.0140 (9)	−0.0009 (7)	0.0044 (7)	0.0035 (7)
C7	0.0175 (9)	0.0182 (9)	0.0190 (9)	0.0034 (7)	0.0055 (7)	0.0016 (7)
C9	0.0212 (9)	0.0177 (9)	0.0259 (11)	0.0002 (7)	0.0091 (8)	−0.0029 (8)
C8	0.0258 (10)	0.0172 (9)	0.0151 (9)	−0.0035 (7)	0.0044 (8)	−0.0009 (7)

Geometric parameters (Å, º)

Br1—C1	1.9025 (18)	N1—C4	1.339 (3)
O1—C2	1.262 (2)	N1—H5	0.85 (3)
O2—C3	1.238 (2)	C4—C5	1.387 (3)
C1—C2	1.387 (2)	C4—H4	0.9300
C1—C3	1.414 (2)	C5—C9	1.498 (3)
C3—C2^{i}	1.548 (3)	C7—C8	1.375 (3)
C6—C7	1.381 (3)	C7—H7	0.9300
C6—C5	1.397 (3)	C9—H9A	0.9600
C6—H6	0.9300	C9—H9B	0.9600
C2—C3^{i}	1.548 (3)	C9—H9C	0.9600
N1—C8	1.336 (3)	C8—H8	0.9300

C2—C1—C3	124.22 (16)	C5—C4—H4	119.4
C2—C1—Br1	118.27 (13)	C4—C5—C6	117.00 (17)
C3—C1—Br1	117.51 (13)	C4—C5—C9	120.62 (17)

O2—C3—C1	125.66 (17)	C6—C5—C9	122.36 (16)
O2—C3—C2$^{\rm i}$	116.88 (16)	C8—C7—C6	118.99 (18)
C1—C3—C2$^{\rm i}$	117.47 (15)	C8—C7—H7	120.5
C7—C6—C5	120.83 (17)	C6—C7—H7	120.5
C7—C6—H6	119.6	C5—C9—H9A	109.5
C5—C6—H6	119.6	C5—C9—H9B	109.5
O1—C2—C1	124.82 (17)	H9A—C9—H9B	109.5
O1—C2—C3$^{\rm i}$	116.88 (15)	C5—C9—H9C	109.5
C1—C2—C3$^{\rm i}$	118.30 (15)	H9A—C9—H9C	109.5
C8—N1—C4	121.90 (16)	H9B—C9—H9C	109.5
C8—N1—H5	124 (2)	N1—C8—C7	120.14 (18)
C4—N1—H5	114 (2)	N1—C8—H8	119.9
N1—C4—C5	121.13 (17)	C7—C8—H8	119.9
N1—C4—H4	119.4		

C2—C1—C3—O2	179.04 (18)	C8—N1—C4—C5	0.9 (3)
Br1—C1—C3—O2	−1.0 (3)	N1—C4—C5—C6	−0.4 (3)
C2—C1—C3—C2$^{\rm i}$	−1.2 (3)	N1—C4—C5—C9	−178.95 (17)
Br1—C1—C3—C2$^{\rm i}$	178.77 (12)	C7—C6—C5—C4	−0.1 (3)
C3—C1—C2—O1	−178.72 (18)	C7—C6—C5—C9	178.45 (18)
Br1—C1—C2—O1	1.4 (3)	C5—C6—C7—C8	0.1 (3)
C3—C1—C2—C3$^{\rm i}$	1.2 (3)	C4—N1—C8—C7	−0.9 (3)
Br1—C1—C2—C3$^{\rm i}$	−178.76 (12)	C6—C7—C8—N1	0.4 (3)

Symmetry code: (i) $-x+1, -y+1, -z$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H5···O1	0.84 (3)	1.78 (3)	2.598 (2)	165 (3)
N1—H5···O2$^{\rm i}$	0.84 (3)	2.54 (3)	3.039 (2)	119 (3)
C4—H4···Br1$^{\rm ii}$	0.93	2.96	3.7977 (18)	151

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, y+1/2, -z+1/2$.

(br3p14jan_0m) Bis(4-picolinium) bromanilate

Crystal data

$2C_6H_8N^+\cdot C_6Br_2O_4^{2-}$
$M_r = 484.15$
Monoclinic, $P2_1/c$
$a = 8.1345$ (8) Å
$b = 6.1517$ (6) Å
$c = 17.7868$ (17) Å
$\beta = 96.177$ (7)°
$V = 884.90$ (15) Å^3

$Z = 2$
$F(000) = 480$
$D_x = 1.817$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 4.61$ mm^{-1}
$T = 100$ K
Block, purple
0.35 × 0.25 × 0.2 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Graphite monochromator
CCD; rotation images scans

Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.576$, $T_{\max} = 1.000$
14105 measured reflections
3234 independent reflections

2464 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.047$
$\theta_{\text{max}} = 32.8°$, $\theta_{\text{min}} = 2.3°$

$h = -11 \rightarrow 12$
$k = -9 \rightarrow 8$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.06$
3234 reflections
123 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.2356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.82$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.54$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
H3	−0.105 (4)	0.310 (6)	−0.2171 (19)	0.047 (10)*
Br1	0.25110 (3)	0.07121 (3)	0.02493 (2)	0.01863 (8)
O1	0.07011 (19)	0.2668 (2)	−0.12123 (8)	0.0186 (3)
O2	−0.1218 (2)	0.6144 (3)	−0.14197 (9)	0.0189 (3)
C3	−0.0715 (3)	0.5690 (3)	−0.07520 (12)	0.0154 (4)
C5	−0.3229 (3)	−0.0633 (3)	−0.26829 (13)	0.0196 (4)
H5	−0.3546	−0.2000	−0.2528	0.024*
C6	−0.2127 (3)	0.0570 (4)	−0.22235 (13)	0.0215 (5)
H6	−0.1685	0.0014	−0.1759	0.026*
C2	0.0452 (2)	0.3690 (3)	−0.06305 (12)	0.0146 (4)
N1	−0.1680 (3)	0.2553 (3)	−0.24406 (11)	0.0214 (4)
C4	−0.3880 (3)	0.0175 (4)	−0.33817 (13)	0.0176 (4)
C1	0.1120 (3)	0.3196 (3)	0.01073 (12)	0.0157 (4)
C7	−0.2265 (3)	0.3409 (4)	−0.31087 (13)	0.0213 (4)
H7	−0.1925	0.4781	−0.3247	0.026*
C8	−0.3370 (3)	0.2240 (4)	−0.35860 (12)	0.0195 (4)
H8	−0.3783	0.2827	−0.4050	0.023*
C9	−0.5047 (3)	−0.1147 (4)	−0.39065 (15)	0.0275 (5)
H9A	−0.4464	−0.1745	−0.4300	0.041*
H9B	−0.5930	−0.0237	−0.4126	0.041*
H9C	−0.5494	−0.2306	−0.3630	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02148 (12)	0.01545 (11)	0.01885 (12)	0.00438 (8)	0.00160 (8)	0.00058 (8)
O1	0.0216 (8)	0.0192 (7)	0.0148 (7)	0.0018 (6)	0.0013 (6)	−0.0037 (6)
O2	0.0247 (8)	0.0181 (7)	0.0134 (7)	0.0011 (6)	−0.0003 (6)	0.0014 (6)
C3	0.0152 (10)	0.0133 (9)	0.0176 (10)	−0.0028 (7)	0.0019 (8)	0.0003 (8)
C5	0.0230 (11)	0.0147 (10)	0.0222 (11)	0.0006 (8)	0.0080 (9)	0.0022 (8)
C6	0.0255 (12)	0.0250 (12)	0.0141 (10)	0.0041 (9)	0.0021 (9)	0.0035 (8)
C2	0.0130 (9)	0.0139 (9)	0.0168 (9)	−0.0020 (7)	0.0015 (8)	−0.0001 (8)
N1	0.0219 (10)	0.0261 (11)	0.0165 (9)	−0.0058 (8)	0.0030 (8)	−0.0047 (8)
C4	0.0155 (10)	0.0185 (10)	0.0196 (10)	0.0018 (8)	0.0048 (8)	−0.0046 (8)
C1	0.0151 (10)	0.0125 (9)	0.0193 (10)	0.0015 (7)	0.0001 (8)	0.0000 (8)
C7	0.0251 (11)	0.0171 (11)	0.0221 (11)	−0.0041 (9)	0.0045 (9)	0.0014 (9)
C8	0.0212 (11)	0.0211 (11)	0.0160 (10)	0.0010 (8)	0.0016 (8)	0.0039 (8)
C9	0.0214 (12)	0.0289 (12)	0.0319 (13)	−0.0045 (9)	0.0015 (10)	−0.0092 (10)

Geometric parameters (Å, º)

Br1—C1	1.902 (2)	N1—C7	1.339 (3)
O1—C2	1.246 (2)	N1—H3	0.74 (3)
O2—C3	1.246 (3)	C4—C8	1.396 (3)
C3—C1^{i}	1.405 (3)	C4—C9	1.498 (3)
C3—C2	1.554 (3)	C1—C3^{i}	1.405 (3)
C5—C6	1.364 (3)	C7—C8	1.372 (3)
C5—C4	1.390 (3)	C7—H7	0.9300
C5—H5	0.9300	C8—H8	0.9300
C6—N1	1.341 (3)	C9—H9A	0.9600
C6—H6	0.9300	C9—H9B	0.9600
C2—C1	1.399 (3)	C9—H9C	0.9600

O2—C3—C1^{i}	125.9 (2)	C8—C4—C9	121.2 (2)
O2—C3—C2	116.31 (18)	C2—C1—C3^{i}	123.93 (19)
C1^{i}—C3—C2	117.75 (18)	C2—C1—Br1	117.69 (15)
C6—C5—C4	120.3 (2)	C3^{i}—C1—Br1	118.15 (15)
C6—C5—H5	119.9	N1—C7—C8	119.3 (2)
C4—C5—H5	119.9	N1—C7—H7	120.3
N1—C6—C5	120.1 (2)	C8—C7—H7	120.3
N1—C6—H6	119.9	C7—C8—C4	120.6 (2)
C5—C6—H6	119.9	C7—C8—H8	119.7
O1—C2—C1	126.0 (2)	C4—C8—H8	119.7
O1—C2—C3	115.80 (18)	C4—C9—H9A	109.5
C1—C2—C3	118.17 (18)	C4—C9—H9B	109.5
C7—N1—C6	122.1 (2)	H9A—C9—H9B	109.5
C7—N1—H3	123 (3)	C4—C9—H9C	109.5
C6—N1—H3	115 (3)	H9A—C9—H9C	109.5
C5—C4—C8	117.6 (2)	H9B—C9—H9C	109.5
C5—C4—C9	121.2 (2)		

C4—C5—C6—N1	0.8 (3)	O1—C2—C1—C3^{i}	−175.6 (2)

O2—C3—C2—O1	−3.6 (3)	C3—C2—C1—C3^{i}	4.4 (3)
C1^{i}—C3—C2—O1	175.83 (19)	O1—C2—C1—Br1	−1.1 (3)
O2—C3—C2—C1	176.4 (2)	C3—C2—C1—Br1	178.82 (14)
C1^{i}—C3—C2—C1	−4.1 (3)	C6—N1—C7—C8	0.7 (3)
C5—C6—N1—C7	−1.0 (3)	N1—C7—C8—C4	−0.2 (3)
C6—C5—C4—C8	−0.3 (3)	C5—C4—C8—C7	0.0 (3)
C6—C5—C4—C9	177.9 (2)	C9—C4—C8—C7	−178.2 (2)

Symmetry code: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H3···O1	0.74 (3)	2.12 (3)	2.760 (3)	145 (4)
N1—H3···O2	0.74 (3)	2.31 (3)	2.859 (3)	131 (3)

(ba24lut) 2,4-Dimethylpyridinium bromanilate

Crystal data

$C_7H_{10}N^+·C_6HBr_2O_4^-$	$Z = 4$
$M_r = 405.04$	$F(000) = 792$
Monoclinic, $P2_1/c$	$D_x = 1.962$ Mg m^{-3}
Hall symbol: -P 2ybc	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$a = 8.2948$ (2) Å	$\mu = 5.92$ mm^{-1}
$b = 12.1560$ (4) Å	$T = 100$ K
$c = 13.9544$ (5) Å	Block, purple
$\beta = 102.966$ (2)°	0.25 × 0.2 × 0.1 mm
$V = 1371.17$ (8) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	6064 independent reflections
CCD; rotation images scans	4537 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$R_{int} = 0.042$
$T_{min} = 0.631$, $T_{max} = 1.000$	$\theta_{max} = 36.0°$, $\theta_{min} = 2.3°$
22482 measured reflections	$h = -13 \rightarrow 12$
	$k = -20 \rightarrow 19$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.02$	$\Delta\rho_{max} = 0.85$ e Å^{-3}
6064 reflections	$\Delta\rho_{min} = -0.56$ e Å^{-3}
191 parameters	
0 restraints	

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.9045 (2)	0.19237 (15)	0.55371 (13)	0.0139 (3)
C6	1.0303 (2)	0.18822 (15)	0.49598 (13)	0.0143 (3)
C5	1.00553 (19)	0.10938 (15)	0.40704 (12)	0.0128 (3)
C4	0.8566 (2)	0.05013 (15)	0.38346 (12)	0.0128 (3)
C3	0.73806 (19)	0.05285 (15)	0.44130 (12)	0.0124 (3)
C2	0.77015 (19)	0.12614 (15)	0.53102 (12)	0.0122 (3)
O1	0.65618 (16)	0.12722 (12)	0.58359 (10)	0.0172 (3)
O2	0.60467 (15)	0.00124 (12)	0.42410 (9)	0.0180 (3)
Br2	0.81175 (2)	−0.03915 (2)	0.26962 (2)	0.01608 (5)
O3	1.12026 (14)	0.10678 (11)	0.36234 (9)	0.0160 (3)
O4	1.15299 (15)	0.24626 (13)	0.51291 (10)	0.0211 (3)
Br1	0.93387 (2)	0.29327 (2)	0.65786 (2)	0.01894 (5)
C7	0.4727 (2)	0.23284 (18)	0.31075 (13)	0.0184 (4)
C8	0.6120 (2)	0.29544 (18)	0.30788 (15)	0.0226 (4)
H8	0.6627	0.2868	0.2553	0.027*
C9	0.6772 (2)	0.37030 (18)	0.38125 (17)	0.0246 (4)
C10	0.5959 (2)	0.38279 (17)	0.45817 (17)	0.0233 (4)
H10	0.6353	0.4328	0.5084	0.028*
C11	0.4577 (2)	0.32110 (17)	0.45937 (15)	0.0195 (4)
H11	0.4038	0.3295	0.5106	0.023*
N1	0.39987 (18)	0.24877 (15)	0.38719 (12)	0.0157 (3)
C13	0.8327 (3)	0.4343 (2)	0.3811 (2)	0.0379 (6)
H13A	0.9259	0.3972	0.4213	0.057*
H13B	0.8235	0.5067	0.4068	0.057*
H13C	0.8478	0.4397	0.315	0.057*
C12	0.4002 (2)	0.1503 (2)	0.23501 (14)	0.0271 (5)
H12A	0.352	0.0916	0.2651	0.041*
H12B	0.4854	0.1214	0.2056	0.041*
H12C	0.3164	0.1846	0.1853	0.041*
H1	0.595 (4)	0.091 (3)	0.565 (2)	0.050 (10)*
H2	0.332 (3)	0.211 (2)	0.3888 (18)	0.023 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0158 (7)	0.0135 (9)	0.0136 (7)	−0.0006 (6)	0.0059 (6)	−0.0020 (6)
C6	0.0143 (7)	0.0151 (9)	0.0141 (7)	−0.0005 (6)	0.0046 (6)	−0.0010 (6)
C5	0.0135 (6)	0.0135 (9)	0.0117 (7)	0.0013 (6)	0.0030 (5)	0.0020 (6)
C4	0.0152 (6)	0.0128 (9)	0.0107 (7)	−0.0010 (6)	0.0034 (5)	−0.0008 (6)
C3	0.0147 (7)	0.0115 (8)	0.0113 (7)	−0.0002 (6)	0.0032 (5)	0.0006 (6)
C2	0.0130 (6)	0.0113 (8)	0.0134 (7)	−0.0007 (6)	0.0055 (5)	0.0000 (6)
O1	0.0162 (5)	0.0178 (7)	0.0205 (6)	−0.0055 (5)	0.0100 (5)	−0.0057 (6)
O2	0.0168 (5)	0.0204 (7)	0.0178 (6)	−0.0071 (5)	0.0060 (5)	−0.0027 (5)
Br2	0.01998 (8)	0.01664 (10)	0.01232 (8)	−0.00307 (6)	0.00512 (6)	−0.00285 (6)
O3	0.0151 (5)	0.0199 (7)	0.0146 (6)	−0.0007 (5)	0.0065 (4)	−0.0012 (5)
O4	0.0179 (6)	0.0250 (8)	0.0229 (7)	−0.0080 (5)	0.0097 (5)	−0.0073 (6)
Br1	0.02109 (9)	0.01842 (10)	0.02018 (9)	−0.00729 (7)	0.01073 (7)	−0.00876 (7)

C7	0.0149 (7)	0.0253 (11)	0.0158 (8)	0.0077 (7)	0.0052 (6)	0.0057 (7)
C8	0.0162 (7)	0.0307 (12)	0.0236 (9)	0.0079 (7)	0.0103 (7)	0.0126 (8)
C9	0.0157 (7)	0.0214 (11)	0.0390 (11)	0.0032 (7)	0.0109 (7)	0.0132 (9)
C10	0.0179 (8)	0.0169 (10)	0.0365 (11)	−0.0020 (7)	0.0091 (7)	−0.0020 (9)
C11	0.0191 (7)	0.0170 (10)	0.0251 (9)	0.0001 (7)	0.0107 (7)	−0.0008 (8)
N1	0.0138 (6)	0.0166 (8)	0.0181 (7)	−0.0002 (6)	0.0065 (5)	0.0023 (6)
C13	0.0202 (9)	0.0312 (14)	0.0657 (18)	0.0011 (9)	0.0168 (10)	0.0192 (13)
C12	0.0233 (9)	0.0417 (14)	0.0159 (8)	0.0069 (9)	0.0037 (7)	−0.0048 (9)

Geometric parameters (Å, º)

C1—C2	1.353 (2)	C3—C2	1.511 (2)
C1—C6	1.455 (2)	C2—O1	1.3204 (19)
C1—Br1	1.8753 (18)	C7—N1	1.352 (2)
C6—O4	1.217 (2)	C7—C8	1.392 (3)
C6—C5	1.545 (2)	C7—C12	1.483 (3)
C5—O3	1.2499 (19)	C8—C9	1.386 (3)
C5—C4	1.404 (2)	C9—C10	1.398 (3)
C4—C3	1.405 (2)	C9—C13	1.506 (3)
C4—Br2	1.8907 (17)	C10—C11	1.373 (3)
C3—O2	1.248 (2)	C11—N1	1.342 (3)
C2—C1—C6	120.32 (16)	C4—C3—C2	118.29 (14)
C2—C1—Br1	121.83 (12)	O1—C2—C1	121.24 (16)
C6—C1—Br1	117.85 (12)	O1—C2—C3	116.83 (14)
O4—C6—C1	123.00 (16)	C1—C2—C3	121.83 (14)
O4—C6—C5	118.05 (14)	N1—C7—C8	117.71 (19)
C1—C6—C5	118.92 (14)	N1—C7—C12	118.54 (17)
O3—C5—C4	126.77 (16)	C8—C7—C12	123.75 (17)
O3—C5—C6	115.96 (14)	C9—C8—C7	121.78 (17)
C4—C5—C6	117.26 (14)	C8—C9—C10	117.57 (17)
C5—C4—C3	123.06 (15)	C8—C9—C13	122.0 (2)
C5—C4—Br2	119.22 (12)	C10—C9—C13	120.4 (2)
C3—C4—Br2	117.72 (12)	C11—C10—C9	119.9 (2)
O2—C3—C4	125.60 (16)	N1—C11—C10	120.51 (18)
O2—C3—C2	116.09 (14)	C11—N1—C7	122.55 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.68 (3)	2.03 (3)	2.6509 (18)	151 (3)
O1—H1···O2	0.68 (3)	2.26 (3)	2.6559 (19)	119 (3)
N1—H2···O3^{ii}	0.72 (2)	2.14 (2)	2.849 (2)	168 (3)
N1—H2···O4^{ii}	0.72 (2)	2.56 (2)	2.9807 (18)	119 (2)

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

(ba25lut_100k_11aug_0m) 2,5-Dimethylpyridinium bromanilate

Crystal data

$C_7H_{10}N^+ \cdot C_6HBr_2O_4^-$	$Z = 4$
$M_r = 405.05$	$F(000) = 792$
Monoclinic, $P2_1/c$	$D_x = 1.981$ Mg m^{-3}
$a = 7.7357$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.1416$ (6) Å	$\mu = 5.98$ mm^{-1}
$c = 15.8011$ (9) Å	$T = 100$ K
$\beta = 94.269$ (3)°	Block, purple
$V = 1358.09$ (13) Å^3	0.35 × 0.25 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	9404 independent reflections
Graphite monochromator	6083 reflections with $I > 2\sigma(I)$
CCD; rotation images scans	$R_{int} = 0.058$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$\theta_{max} = 42.1°$, $\theta_{min} = 2.2°$
$T_{min} = 0.404$, $T_{max} = 1.000$	$h = -14 \rightarrow 14$
38096 measured reflections	$k = -20 \rightarrow 20$
	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.0632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
9404 reflections	$\Delta\rho_{max} = 1.34$ e Å^{-3}
184 parameters	$\Delta\rho_{min} = -1.29$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.47843 (2)	0.233106 (16)	0.109383 (11)	0.01484 (4)
Br2	0.31634 (2)	−0.007081 (16)	−0.274211 (11)	0.01501 (4)
C3	0.2818 (2)	0.10008 (15)	−0.01690 (11)	0.0119 (3)
C6	0.5275 (2)	0.11978 (14)	−0.14671 (11)	0.0123 (3)
O1	0.09913 (16)	−0.00774 (12)	−0.12129 (9)	0.0173 (3)
H1	0.0473	−0.01	−0.0779	0.026*

C4	0.4370 (2)	0.16251 (15)	0.00124 (11)	0.0122 (3)
N1	0.96656 (18)	0.26704 (13)	−0.16218 (11)	0.0155 (3)
H1A	0.8804	0.2191	−0.1584	0.019*
O3	0.70419 (18)	0.22877 (14)	−0.04465 (10)	0.0258 (3)
O2	0.16434 (16)	0.08351 (13)	0.03197 (9)	0.0195 (3)
C1	0.3631 (2)	0.05998 (14)	−0.16580 (10)	0.0117 (3)
C2	0.24886 (19)	0.04840 (14)	−0.10558 (11)	0.0117 (3)
C5	0.5638 (2)	0.17603 (16)	−0.05714 (11)	0.0141 (3)
O4	0.63921 (16)	0.12894 (12)	−0.19711 (9)	0.0187 (3)
C7	1.0291 (2)	0.28251 (16)	−0.23903 (12)	0.0156 (3)
C8	1.1653 (2)	0.36261 (16)	−0.24409 (13)	0.0177 (3)
H8	1.2113	0.3762	−0.296	0.021*
C10	1.1676 (2)	0.40233 (16)	−0.09342 (12)	0.0165 (3)
C11	1.0320 (2)	0.32284 (16)	−0.09082 (12)	0.0162 (3)
H11	0.9849	0.3073	−0.0395	0.019*
C12	0.9487 (3)	0.21602 (18)	−0.31284 (13)	0.0212 (4)
H12A	0.9596	0.1313	−0.3026	0.032*
H12B	1.0061	0.2367	−0.3626	0.032*
H12C	0.8282	0.2369	−0.3212	0.032*
C13	1.2407 (3)	0.46639 (19)	−0.01483 (14)	0.0233 (4)
H13A	1.1682	0.4516	0.0308	0.035*
H13B	1.245	0.5511	−0.0258	0.035*
H13C	1.3556	0.4373	0.0006	0.035*
C9	1.2329 (2)	0.42230 (17)	−0.17244 (12)	0.0173 (3)
H9	1.3231	0.4766	−0.1768	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01520 (7)	0.01706 (8)	0.01267 (8)	−0.00345 (6)	0.00383 (5)	−0.00279 (6)
Br2	0.01336 (7)	0.02117 (9)	0.01085 (8)	−0.00387 (6)	0.00315 (5)	−0.00109 (6)
C3	0.0101 (6)	0.0137 (7)	0.0126 (7)	−0.0014 (5)	0.0046 (5)	−0.0004 (5)
C6	0.0107 (6)	0.0128 (7)	0.0139 (7)	−0.0009 (5)	0.0047 (5)	−0.0004 (5)
O1	0.0122 (5)	0.0264 (7)	0.0141 (6)	−0.0088 (5)	0.0056 (4)	−0.0027 (5)
C4	0.0106 (6)	0.0134 (7)	0.0130 (7)	−0.0015 (5)	0.0033 (5)	−0.0013 (5)
N1	0.0104 (5)	0.0156 (6)	0.0206 (7)	−0.0011 (5)	0.0030 (5)	0.0043 (5)
O3	0.0161 (6)	0.0394 (8)	0.0232 (7)	−0.0155 (6)	0.0089 (5)	−0.0115 (6)
O2	0.0149 (5)	0.0284 (7)	0.0164 (6)	−0.0087 (5)	0.0086 (4)	−0.0036 (5)
C1	0.0102 (6)	0.0125 (7)	0.0126 (7)	−0.0016 (5)	0.0034 (5)	−0.0008 (5)
C2	0.0089 (6)	0.0122 (7)	0.0144 (7)	−0.0015 (5)	0.0037 (5)	0.0007 (5)
C5	0.0112 (6)	0.0163 (7)	0.0154 (8)	−0.0030 (5)	0.0049 (5)	−0.0018 (6)
O4	0.0137 (5)	0.0258 (7)	0.0179 (6)	−0.0056 (5)	0.0098 (4)	−0.0045 (5)
C7	0.0117 (6)	0.0160 (7)	0.0195 (8)	0.0045 (5)	0.0048 (6)	0.0026 (6)
C8	0.0133 (7)	0.0199 (8)	0.0211 (9)	0.0024 (6)	0.0094 (6)	0.0057 (7)
C10	0.0098 (6)	0.0179 (8)	0.0220 (9)	0.0013 (6)	0.0013 (6)	0.0051 (6)
C11	0.0118 (6)	0.0193 (8)	0.0178 (8)	−0.0002 (6)	0.0033 (6)	0.0051 (6)
C12	0.0208 (8)	0.0214 (9)	0.0216 (9)	0.0021 (7)	0.0040 (7)	−0.0025 (7)
C13	0.0202 (8)	0.0280 (10)	0.0214 (9)	−0.0036 (7)	−0.0010 (7)	0.0036 (8)
C9	0.0111 (6)	0.0178 (8)	0.0236 (9)	−0.0003 (6)	0.0043 (6)	0.0054 (6)

Geometric parameters (Å, º)

Br1—C4	1.8868 (17)	C7—C8	1.387 (2)
Br2—C1	1.8792 (17)	C7—C12	1.479 (3)
C3—O2	1.2495 (19)	C8—C9	1.382 (3)
C3—C4	1.398 (2)	C8—H8	0.93
C3—C2	1.519 (2)	C10—C11	1.376 (2)
C6—O4	1.2224 (19)	C10—C9	1.399 (3)
C6—C1	1.447 (2)	C10—C13	1.506 (3)
C6—C5	1.554 (2)	C11—H11	0.93
O1—C2	1.3235 (19)	C12—H12A	0.96
O1—H1	0.82	C12—H12B	0.96
C4—C5	1.403 (2)	C12—H12C	0.96
N1—C7	1.351 (2)	C13—H13A	0.96
N1—C11	1.352 (2)	C13—H13B	0.96
N1—H1A	0.86	C13—H13C	0.96
O3—C5	1.238 (2)	C9—H9	0.93
C1—C2	1.352 (2)		
O2—C3—C4	126.84 (16)	C9—C8—C7	120.33 (17)
O2—C3—C2	115.73 (14)	C9—C8—H8	119.8
C4—C3—C2	117.41 (14)	C7—C8—H8	119.8
O4—C6—C1	123.74 (16)	C11—C10—C9	117.11 (17)
O4—C6—C5	118.11 (14)	C11—C10—C13	121.42 (17)
C1—C6—C5	118.15 (13)	C9—C10—C13	121.47 (16)
C2—O1—H1	109.5	N1—C11—C10	120.66 (16)
C3—C4—C5	123.35 (15)	N1—C11—H11	119.7
C3—C4—Br1	118.58 (12)	C10—C11—H11	119.7
C5—C4—Br1	118.07 (12)	C7—C12—H12A	109.5
C7—N1—C11	123.63 (15)	C7—C12—H12B	109.5
C7—N1—H1A	118.2	H12A—C12—H12B	109.5
C11—N1—H1A	118.2	C7—C12—H12C	109.5
C2—C1—C6	120.49 (15)	H12A—C12—H12C	109.5
C2—C1—Br2	120.78 (12)	H12B—C12—H12C	109.5
C6—C1—Br2	118.67 (11)	C10—C13—H13A	109.5
O1—C2—C1	121.46 (15)	C10—C13—H13B	109.5
O1—C2—C3	115.90 (13)	H13A—C13—H13B	109.5
C1—C2—C3	122.63 (14)	C10—C13—H13C	109.5
O3—C5—C4	126.44 (16)	H13A—C13—H13C	109.5
O3—C5—C6	115.69 (14)	H13B—C13—H13C	109.5
C4—C5—C6	117.88 (14)	C8—C9—C10	120.99 (16)
N1—C7—C8	117.26 (17)	C8—C9—H9	119.5
N1—C7—C12	119.15 (16)	C10—C9—H9	119.5
C8—C7—C12	123.59 (17)		
O2—C3—C4—C5	179.27 (17)	Br1—C4—C5—O3	1.3 (3)
C2—C3—C4—C5	−2.0 (2)	C3—C4—C5—C6	0.8 (3)
O2—C3—C4—Br1	−1.1 (2)	Br1—C4—C5—C6	−178.86 (12)
C2—C3—C4—Br1	177.66 (11)	O4—C6—C5—O3	1.5 (3)
O4—C6—C1—C2	176.91 (17)	C1—C6—C5—O3	−178.24 (16)

C5—C6—C1—C2	−3.3 (2)	O4—C6—C5—C4	−178.34 (16)
O4—C6—C1—Br2	−0.4 (2)	C1—C6—C5—C4	1.9 (2)
C5—C6—C1—Br2	179.37 (12)	C11—N1—C7—C8	−1.6 (2)
C6—C1—C2—O1	−178.85 (15)	C11—N1—C7—C12	179.42 (16)
Br2—C1—C2—O1	−1.6 (2)	N1—C7—C8—C9	0.5 (2)
C6—C1—C2—C3	2.2 (2)	C12—C7—C8—C9	179.45 (17)
Br2—C1—C2—C3	179.44 (12)	C7—N1—C11—C10	1.3 (3)
O2—C3—C2—O1	0.4 (2)	C9—C10—C11—N1	0.1 (3)
C4—C3—C2—O1	−178.49 (15)	C13—C10—C11—N1	179.28 (16)
O2—C3—C2—C1	179.37 (16)	C7—C8—C9—C10	0.8 (3)
C4—C3—C2—C1	0.5 (2)	C11—C10—C9—C8	−1.2 (3)
C3—C4—C5—O3	−179.05 (18)	C13—C10—C9—C8	179.70 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2[i]	0.82	2.01	2.6994 (17)	141
O1—H1···O2	0.82	2.16	2.6403 (19)	117
N1—H1*A*···O4	0.86	2.17	2.9794 (19)	158
N1—H1*A*···O3	0.86	2.34	2.883 (2)	122

Symmetry code: (i) −*x*, −*y*, −*z*.

(ba_35lut) 3,5-Dimethylpyridinium bromanilate

Crystal data

$C_7H_{10}N^+\cdot C_6HBr_2O_4^-$
M_r = 405.04
Monoclinic, $P2_1/c$
a = 11.6766 (5) Å
b = 10.4926 (5) Å
c = 11.5221 (5) Å
β = 98.834 (2)°
V = 1394.92 (11) Å^3

Z = 4
F(000) = 792
D_x = 1.929 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
μ = 5.82 mm^{-1}
T = 100 K
Block, purple
0.25 × 0.2 × 0.1 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Graphite monochromator
CCD; rotation images scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
T_{min} = 0.684, T_{max} = 1.000
14020 measured reflections

3817 independent reflections
3131 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 31.5°, θ_{min} = 1.8°
h = −13→12
k = −14→15
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.067
S = 1.05
3817 reflections
191 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.6408P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
H atoms were placed on calculated positions modelled as riding on the atoms to which they were bonded except those involved in hydrogen bonding H1 and H2 (bonded to O1 and N1, respectively) which were identified in a Fourier difference map and the position and isotropic thermal parameters allowed to freely refine.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.1510 (2)	0.0322 (2)	0.38903 (18)	0.0123 (5)
C6	0.0825 (2)	0.1413 (2)	0.41310 (18)	0.0123 (4)
C5	0.1428 (2)	0.2483 (2)	0.49363 (18)	0.0123 (4)
C4	0.2597 (2)	0.2332 (2)	0.53947 (18)	0.0112 (4)
C3	0.3269 (2)	0.1288 (2)	0.51195 (18)	0.0120 (5)
C2	0.2658 (2)	0.0288 (2)	0.42894 (18)	0.0122 (5)
O1	0.33345 (18)	−0.06415 (16)	0.40007 (15)	0.0165 (4)
O2	0.43032 (15)	0.10769 (16)	0.55024 (13)	0.0158 (3)
Br2	0.32803 (2)	0.35454 (2)	0.649891 (18)	0.01431 (7)
O3	0.08053 (15)	0.33992 (15)	0.51253 (15)	0.0173 (4)
O4	−0.01960 (15)	0.15499 (16)	0.37320 (14)	0.0183 (4)
Br1	0.07565 (2)	−0.09875 (2)	0.295328 (19)	0.01606 (7)
C10	0.3537 (2)	0.6732 (2)	0.55142 (19)	0.0144 (5)
C9	0.3628 (2)	0.6104 (2)	0.44682 (19)	0.0155 (5)
H9	0.4359	0.5971	0.4263	0.019*
C8	0.2654 (2)	0.5670 (2)	0.37211 (18)	0.0151 (5)
C7	0.1590 (2)	0.5907 (2)	0.40512 (19)	0.0144 (5)
H7	0.092	0.5631	0.3574	0.017*
N1	0.15066 (19)	0.65280 (18)	0.50482 (16)	0.0137 (4)
C11	0.2440 (2)	0.6936 (2)	0.57811 (19)	0.0142 (5)
H11	0.2347	0.7358	0.647	0.017*
C12	0.2730 (2)	0.4943 (3)	0.2616 (2)	0.0239 (6)
H12A	0.2701	0.4045	0.277	0.036*
H12B	0.3446	0.5144	0.2344	0.036*
H12C	0.2092	0.5174	0.2025	0.036*
C13	0.4582 (2)	0.7162 (3)	0.6358 (2)	0.0230 (6)
H13A	0.4606	0.8076	0.6379	0.034*
H13B	0.5273	0.6842	0.6104	0.034*
H13C	0.4531	0.684	0.7129	0.034*
H2	0.078 (3)	0.664 (3)	0.528 (3)	0.037 (9)*
H1	0.393 (3)	−0.058 (3)	0.428 (3)	0.026 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0128 (14)	0.0138 (10)	0.0105 (9)	0.0014 (8)	0.0030 (8)	0.0005 (7)
C6	0.0116 (14)	0.0143 (10)	0.0115 (9)	0.0005 (9)	0.0030 (8)	0.0019 (8)
C5	0.0120 (13)	0.0126 (10)	0.0132 (9)	0.0006 (8)	0.0045 (8)	0.0022 (8)
C4	0.0086 (13)	0.0133 (10)	0.0120 (9)	0.0000 (8)	0.0023 (8)	−0.0001 (7)
C3	0.0101 (14)	0.0153 (10)	0.0114 (9)	0.0018 (8)	0.0044 (8)	0.0050 (8)
C2	0.0143 (14)	0.0112 (10)	0.0118 (9)	0.0040 (8)	0.0046 (8)	0.0035 (7)
O1	0.0109 (11)	0.0174 (8)	0.0212 (8)	0.0056 (7)	0.0021 (7)	−0.0023 (6)
O2	0.0097 (10)	0.0202 (8)	0.0177 (7)	0.0050 (7)	0.0024 (6)	0.0006 (6)
Br2	0.01108 (15)	0.01456 (11)	0.01695 (11)	0.00013 (8)	0.00107 (8)	−0.00140 (8)
O3	0.0115 (10)	0.0145 (8)	0.0259 (8)	0.0028 (6)	0.0028 (7)	−0.0038 (6)
O4	0.0117 (10)	0.0202 (8)	0.0220 (8)	0.0041 (7)	−0.0012 (7)	−0.0033 (7)
Br1	0.01622 (16)	0.01440 (11)	0.01679 (11)	0.00185 (9)	0.00011 (9)	−0.00278 (8)
C10	0.0115 (14)	0.0145 (10)	0.0165 (10)	−0.0007 (9)	−0.0003 (9)	0.0033 (8)
C9	0.0094 (14)	0.0203 (11)	0.0175 (10)	0.0042 (9)	0.0043 (9)	0.0052 (9)
C8	0.0182 (15)	0.0146 (10)	0.0126 (9)	0.0049 (9)	0.0028 (9)	0.0020 (8)
C7	0.0138 (14)	0.0128 (10)	0.0156 (10)	0.0014 (9)	−0.0012 (9)	−0.0005 (8)
N1	0.0077 (12)	0.0167 (9)	0.0171 (9)	0.0023 (8)	0.0034 (8)	0.0004 (7)
C11	0.0149 (14)	0.0132 (10)	0.0149 (9)	0.0002 (9)	0.0037 (9)	−0.0010 (8)
C12	0.0264 (16)	0.0267 (13)	0.0187 (11)	0.0071 (11)	0.0036 (10)	−0.0055 (10)
C13	0.0160 (15)	0.0315 (14)	0.0204 (11)	−0.0066 (11)	−0.0008 (10)	0.0020 (10)

Geometric parameters (Å, º)

C1—C2	1.349 (3)	C3—C2	1.522 (3)
C1—C6	1.447 (3)	C2—O1	1.329 (3)
C1—Br1	1.881 (2)	C10—C11	1.379 (3)
C6—O4	1.219 (3)	C10—C9	1.392 (3)
C6—C5	1.554 (3)	C10—C13	1.507 (3)
C5—O3	1.245 (3)	C9—C8	1.394 (3)
C5—C4	1.395 (3)	C8—C7	1.376 (4)
C4—C3	1.412 (3)	C8—C12	1.499 (3)
C4—Br2	1.888 (2)	C7—N1	1.337 (3)
C3—O2	1.240 (3)	N1—C11	1.343 (3)

C2—C1—C6	120.4 (2)	C4—C3—C2	116.9 (2)
C2—C1—Br1	121.94 (17)	O1—C2—C1	122.1 (2)
C6—C1—Br1	117.65 (17)	O1—C2—C3	115.1 (2)
O4—C6—C1	124.0 (2)	C1—C2—C3	122.8 (2)
O4—C6—C5	117.8 (2)	C11—C10—C9	117.6 (2)
C1—C6—C5	118.2 (2)	C11—C10—C13	119.8 (2)
O3—C5—C4	125.8 (2)	C9—C10—C13	122.6 (2)
O3—C5—C6	116.0 (2)	C10—C9—C8	121.7 (2)
C4—C5—C6	118.1 (2)	C7—C8—C9	117.1 (2)
C5—C4—C3	123.3 (2)	C7—C8—C12	120.0 (2)
C5—C4—Br2	117.77 (16)	C9—C8—C12	122.8 (2)
C3—C4—Br2	118.86 (17)	N1—C7—C8	120.9 (2)
O2—C3—C4	127.1 (2)	C7—N1—C11	122.5 (2)

O2—C3—C2	115.96 (19)	N1—C11—C10	120.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O3^{i}	0.93 (3)	1.84 (3)	2.677 (3)	148 (3)
N1—H2···O4^{i}	0.93 (3)	2.37 (3)	3.008 (3)	125 (3)
O1—H1···O2^{ii}	0.72 (3)	2.11 (3)	2.768 (3)	152 (3)
O1—H1···O2	0.72 (3)	2.23 (3)	2.631 (2)	116 (3)

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

(ba_3br4mepyr) 3-Bromo-4-methylpyridinium bromanilate

Crystal data

$C_6H_7BrN^+\cdot C_6HBr_2O_4^-$	$Z = 4$
$M_r = 469.91$	$F(000) = 896$
Monoclinic, $P2_1/c$	$D_x = 2.244$ Mg m^{-3}
Hall symbol: -P 2ybc	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$a = 10.2229$ (4) Å	$\mu = 8.71$ mm^{-1}
$b = 5.5760$ (2) Å	$T = 100$ K
$c = 24.5300$ (9) Å	Block, purple
$\beta = 95.802$ (3)°	0.25 × 0.15 × 0.1 mm
$V = 1391.12$ (9) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	4796 independent reflections
CCD; rotation images scans	3311 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$R_{int} = 0.057$
$T_{min} = 0.499$, $T_{max} = 1.000$	$\theta_{max} = 32.2°$, $\theta_{min} = 1.7°$
19916 measured reflections	$h = -15\rightarrow15$
	$k = -8\rightarrow6$
	$l = -36\rightarrow36$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.04$	$\Delta\rho_{max} = 1.23$ e Å^{-3}
4796 reflections	$\Delta\rho_{min} = -1.13$ e Å^{-3}
190 parameters	
0 restraints	

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.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C4	0.2394 (3)	0.2669 (7)	0.91013 (13)	0.0159 (7)

C3	0.1456 (3)	0.1217 (7)	0.93350 (13)	0.0167 (7)
C2	0.0747 (3)	−0.0693 (7)	0.89770 (13)	0.0168 (7)
C1	0.1034 (3)	−0.1083 (7)	0.84602 (13)	0.0157 (7)
C6	0.2048 (3)	0.0288 (7)	0.82360 (13)	0.0158 (7)
C5	0.2691 (3)	0.2388 (7)	0.85643 (13)	0.0158 (7)
O3	0.3444 (3)	0.3718 (5)	0.83178 (9)	0.0205 (6)
O4	0.2426 (3)	−0.0150 (5)	0.77843 (9)	0.0200 (6)
Br1	0.01728 (3)	−0.34997 (7)	0.80172 (2)	0.01880 (10)
O1	−0.0141 (3)	−0.1955 (5)	0.92133 (10)	0.0217 (6)
O2	0.1142 (2)	0.1390 (5)	0.98099 (9)	0.0203 (6)
Br2	0.31926 (4)	0.51666 (7)	0.95403 (2)	0.01953 (10)
C8	0.7096 (3)	0.1138 (7)	0.86016 (14)	0.0171 (7)
C9	0.6171 (3)	−0.0257 (7)	0.88470 (13)	0.0174 (7)
C10	0.5522 (4)	−0.2030 (7)	0.85268 (14)	0.0201 (8)
H10	0.49	−0.2991	0.8673	0.024*
C11	0.5796 (4)	−0.2372 (7)	0.79908 (14)	0.0211 (8)
H11	0.538	−0.3595	0.7782	0.025*
N1	0.6657 (3)	−0.0950 (6)	0.77734 (13)	0.0208 (7)
C7	0.7321 (4)	0.0788 (7)	0.80625 (14)	0.0194 (8)
H7	0.7924	0.1739	0.7902	0.023*
C12	0.5888 (4)	0.0144 (8)	0.94276 (14)	0.0240 (9)
H12A	0.5601	0.1767	0.947	0.036*
H12B	0.6671	−0.0138	0.9669	0.036*
H12C	0.521	−0.0939	0.9516	0.036*
Br3	0.80539 (4)	0.35718 (7)	0.89969 (2)	0.02332 (10)
H1	−0.027 (4)	−0.120 (8)	0.9513 (18)	0.031 (13)*
H5	0.681 (5)	−0.102 (9)	0.746 (2)	0.039 (14)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C4	0.0167 (16)	0.020 (2)	0.0113 (15)	−0.0020 (14)	0.0024 (11)	−0.0030 (13)
C3	0.0160 (16)	0.024 (2)	0.0099 (14)	0.0002 (14)	0.0005 (11)	0.0011 (13)
C2	0.0186 (17)	0.017 (2)	0.0146 (16)	0.0008 (14)	0.0012 (12)	0.0012 (13)
C1	0.0190 (17)	0.015 (2)	0.0127 (15)	−0.0025 (14)	0.0012 (12)	−0.0008 (13)
C6	0.0162 (16)	0.020 (2)	0.0117 (15)	0.0027 (14)	0.0027 (12)	0.0014 (13)
C5	0.0174 (16)	0.017 (2)	0.0130 (15)	−0.0007 (14)	0.0032 (12)	0.0012 (13)
O3	0.0263 (14)	0.0234 (16)	0.0124 (11)	−0.0063 (11)	0.0055 (9)	0.0011 (10)
O4	0.0253 (13)	0.0241 (16)	0.0116 (11)	−0.0030 (11)	0.0069 (9)	−0.0005 (10)
Br1	0.02324 (18)	0.0218 (2)	0.01161 (15)	−0.00572 (15)	0.00313 (12)	−0.00253 (13)
O1	0.0270 (14)	0.0285 (17)	0.0109 (11)	−0.0101 (12)	0.0085 (10)	−0.0047 (11)
O2	0.0224 (13)	0.0304 (17)	0.0088 (11)	−0.0073 (11)	0.0052 (9)	−0.0036 (10)
Br2	0.02441 (18)	0.0226 (2)	0.01180 (15)	−0.00683 (15)	0.00318 (12)	−0.00302 (14)
C8	0.0183 (17)	0.019 (2)	0.0146 (15)	−0.0029 (14)	0.0028 (12)	0.0006 (13)
C9	0.0184 (17)	0.020 (2)	0.0132 (15)	−0.0006 (14)	0.0009 (12)	0.0007 (14)
C10	0.0229 (18)	0.023 (2)	0.0154 (16)	−0.0045 (15)	0.0065 (13)	−0.0004 (14)
C11	0.0223 (18)	0.023 (2)	0.0178 (17)	0.0000 (16)	0.0008 (13)	−0.0060 (15)
N1	0.0246 (16)	0.025 (2)	0.0134 (14)	0.0067 (14)	0.0058 (12)	0.0001 (13)
C7	0.0212 (18)	0.021 (2)	0.0162 (16)	0.0007 (15)	0.0044 (13)	0.0009 (14)
C12	0.029 (2)	0.033 (3)	0.0117 (15)	−0.0061 (17)	0.0074 (13)	−0.0020 (15)

Br3	0.0249 (2)	0.0231 (2)	0.02254 (19)	−0.00646 (16)	0.00484 (14)	−0.00396 (15)

Geometric parameters (Å, º)

C4—C5	1.390 (4)	C6—C5	1.531 (5)
C4—C3	1.420 (5)	C5—O3	1.266 (4)
C4—Br2	1.894 (4)	C8—C7	1.379 (5)
C3—O2	1.243 (4)	C8—C9	1.406 (5)
C3—C2	1.517 (5)	C8—Br3	1.884 (4)
C2—O1	1.327 (4)	C9—C10	1.389 (5)
C2—C1	1.347 (5)	C9—C12	1.499 (5)
C1—C6	1.442 (5)	C10—C11	1.385 (5)
C1—Br1	1.892 (3)	C11—N1	1.335 (5)
C6—O4	1.234 (4)	N1—C7	1.344 (5)
C5—C4—C3	122.7 (3)	C1—C6—C5	119.5 (3)
C5—C4—Br2	119.9 (3)	O3—C5—C4	126.0 (3)
C3—C4—Br2	117.4 (2)	O3—C5—C6	116.5 (3)
O2—C3—C4	125.7 (3)	C4—C5—C6	117.5 (3)
O2—C3—C2	116.3 (3)	C7—C8—C9	121.2 (3)
C4—C3—C2	118.0 (3)	C7—C8—Br3	117.8 (3)
O1—C2—C1	123.3 (3)	C9—C8—Br3	121.0 (3)
O1—C2—C3	115.3 (3)	C10—C9—C8	117.1 (3)
C1—C2—C3	121.4 (3)	C10—C9—C12	121.1 (3)
C2—C1—C6	120.4 (3)	C8—C9—C12	121.8 (3)
C2—C1—Br1	121.5 (3)	C11—C10—C9	120.3 (3)
C6—C1—Br1	118.0 (2)	N1—C11—C10	120.2 (4)
O4—C6—C1	122.7 (3)	C11—N1—C7	122.4 (3)
O4—C6—C5	117.9 (3)	N1—C7—C8	118.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.87 (5)	1.97 (5)	2.717 (3)	144 (4)
O1—H1···O2	0.87 (5)	2.12 (4)	2.637 (4)	118 (4)
N1—H5···O3^{ii}	0.79 (5)	1.91 (5)	2.675 (4)	161 (5)
N1—H5···O4^{ii}	0.79 (5)	2.53 (5)	2.915 (4)	112 (4)

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $-x+1, y-1/2, -z+3/2$.

(ba23lut) 2,3-Dimethylpyridinium bromanilate

Crystal data

$C_7H_{10}N^+\cdot C_6HBr_2O_4^-$
M_r = 405.04
Monoclinic, $P2_1/n$
a = 4.9786 (4) Å
b = 23.181 (3) Å
c = 12.2811 (13) Å
β = 100.794 (3)°
V = 1392.3 (2) Å^3

Z = 4
F(000) = 792
D_x = 1.932 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
μ = 5.83 mm^{-1}
T = 100 K
Block, purple
0.2 × 0.1 × 0.05 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Graphite monochromator
CCD; rotation images scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.791$, $T_{\max} = 1.000$
9783 measured reflections

2053 independent reflections
1664 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.046$
$\theta_{\max} = 23.6°$, $\theta_{\min} = 1.8°$
$h = -5\rightarrow5$
$k = -26\rightarrow25$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.02$
2053 reflections
182 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.8134P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.
All H atoms were placed on calculated positions and refined as riding on the atom to which they were bonded with the exception of H1 where the position was allowed to freely refine but the thermal parameter was constrained to take a value of 1.2 times the U_{eq} of the atom to which it was bonded (O1).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6253 (8)	0.29473 (17)	0.0801 (3)	0.0161 (9)
C2	0.6786 (8)	0.29433 (17)	0.1910 (3)	0.0163 (9)
C3	0.5234 (8)	0.33215 (18)	0.2594 (3)	0.0182 (10)
C4	0.3191 (8)	0.36859 (17)	0.2012 (3)	0.0174 (10)
C5	0.2523 (8)	0.37123 (17)	0.0857 (3)	0.0173 (9)
C6	0.4239 (8)	0.33427 (17)	0.0198 (3)	0.0174 (10)
O4	0.3842 (6)	0.33949 (12)	−0.0808 (2)	0.0226 (7)
O3	0.0655 (6)	0.40095 (12)	0.0294 (2)	0.0232 (7)
Br2	0.11288 (8)	0.413330 (18)	0.28551 (3)	0.02328 (15)
O2	0.5924 (6)	0.32675 (12)	0.3614 (2)	0.0226 (7)
O1	0.8656 (6)	0.25996 (12)	0.2500 (2)	0.0222 (7)
H1	0.8817	0.2679	0.316	0.033*
Br1	0.81832 (8)	0.247086 (17)	−0.00350 (3)	0.01960 (14)
C7	0.6455 (8)	0.43225 (18)	−0.2235 (3)	0.0188 (10)

C8	0.5129 (8)	0.43486 (17)	−0.3345 (3)	0.0179 (9)
C9	0.5929 (9)	0.39720 (18)	−0.4105 (3)	0.0226 (10)
H9	0.5042	0.3981	−0.4842	0.027*
C10	0.8046 (8)	0.35822 (19)	−0.3772 (3)	0.0260 (11)
H10	0.8596	0.3333	−0.4281	0.031*
C11	0.9303 (8)	0.35721 (18)	−0.2685 (3)	0.0220 (10)
H11	1.0725	0.3315	−0.2447	0.026*
N1	0.8484 (7)	0.39346 (15)	−0.1956 (3)	0.0211 (8)
H1A	0.93	0.3918	−0.1274	0.025*
C13	0.2859 (9)	0.47821 (18)	−0.3707 (4)	0.0270 (11)
H13A	0.2121	0.473	−0.4481	0.041*
H13B	0.3577	0.5166	−0.3586	0.041*
H13C	0.1441	0.4725	−0.3285	0.041*
C12	0.5747 (9)	0.46959 (18)	−0.1333 (3)	0.0244 (10)
H12A	0.6972	0.4613	−0.0649	0.037*
H12B	0.3902	0.4619	−0.125	0.037*
H12C	0.5915	0.5094	−0.1522	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.017 (2)	0.016 (2)	0.016 (2)	−0.0026 (18)	0.0050 (18)	−0.0026 (18)
C2	0.015 (2)	0.015 (2)	0.019 (2)	−0.0042 (19)	0.0012 (18)	0.0037 (19)
C3	0.018 (2)	0.019 (2)	0.019 (3)	−0.0088 (19)	0.0044 (19)	−0.0001 (19)
C4	0.015 (2)	0.017 (2)	0.021 (2)	−0.0028 (18)	0.0053 (18)	−0.0057 (19)
C5	0.014 (2)	0.018 (2)	0.020 (2)	−0.0024 (19)	0.0030 (18)	−0.001 (2)
C6	0.018 (2)	0.013 (2)	0.020 (3)	−0.0045 (18)	0.0005 (19)	−0.0008 (19)
O4	0.0213 (17)	0.0315 (18)	0.0144 (17)	0.0028 (13)	0.0022 (12)	0.0009 (13)
O3	0.0213 (17)	0.0252 (17)	0.0208 (16)	0.0035 (14)	−0.0015 (13)	−0.0016 (14)
Br2	0.0204 (3)	0.0277 (3)	0.0230 (3)	−0.0018 (2)	0.00735 (18)	−0.0073 (2)
O2	0.0240 (17)	0.0306 (18)	0.0128 (16)	−0.0069 (14)	0.0021 (13)	0.0015 (13)
O1	0.0238 (17)	0.0273 (18)	0.0137 (15)	0.0049 (14)	−0.0008 (13)	0.0021 (14)
Br1	0.0197 (3)	0.0216 (3)	0.0173 (2)	0.00247 (19)	0.00311 (17)	−0.0020 (2)
C7	0.015 (2)	0.019 (2)	0.024 (2)	−0.0028 (19)	0.0073 (18)	−0.001 (2)
C8	0.014 (2)	0.016 (2)	0.022 (2)	−0.0031 (18)	−0.0009 (18)	−0.0011 (19)
C9	0.023 (3)	0.026 (3)	0.017 (2)	−0.001 (2)	−0.0019 (18)	−0.001 (2)
C10	0.024 (3)	0.031 (3)	0.022 (3)	0.001 (2)	0.003 (2)	−0.006 (2)
C11	0.021 (3)	0.023 (3)	0.020 (2)	0.006 (2)	−0.0002 (19)	0.001 (2)
N1	0.018 (2)	0.027 (2)	0.0167 (19)	−0.0008 (17)	−0.0005 (15)	−0.0006 (17)
C13	0.022 (3)	0.028 (3)	0.029 (3)	0.005 (2)	0.002 (2)	0.000 (2)
C12	0.026 (3)	0.023 (3)	0.026 (2)	0.002 (2)	0.009 (2)	−0.002 (2)

Geometric parameters (Å, º)

C1—C2	1.338 (5)	C5—C6	1.542 (6)
C1—C6	1.455 (6)	C6—O4	1.220 (5)
C1—Br1	1.889 (4)	C7—N1	1.348 (5)
C2—O1	1.332 (4)	C7—C8	1.399 (6)
C2—C3	1.522 (6)	C7—C12	1.499 (5)
C3—O2	1.242 (4)	C8—C9	1.390 (6)

C3—C4	1.409 (6)	C8—C13	1.515 (6)
C4—C5	1.397 (5)	C9—C10	1.391 (6)
C4—Br2	1.897 (4)	C10—C11	1.364 (5)
C5—O3	1.255 (5)	C11—N1	1.346 (5)

C2—C1—C6	120.6 (4)	C4—C5—C6	117.3 (4)
C2—C1—Br1	121.7 (3)	O4—C6—C1	122.9 (4)
C6—C1—Br1	117.7 (3)	O4—C6—C5	118.4 (4)
O1—C2—C1	122.9 (4)	C1—C6—C5	118.7 (3)
O1—C2—C3	114.8 (3)	N1—C7—C8	118.1 (4)
C1—C2—C3	122.3 (4)	N1—C7—C12	117.7 (4)
O2—C3—C4	127.5 (4)	C8—C7—C12	124.1 (4)
O2—C3—C2	115.2 (4)	C9—C8—C7	119.0 (4)
C4—C3—C2	117.3 (3)	C9—C8—C13	120.7 (4)
C5—C4—C3	123.6 (4)	C7—C8—C13	120.3 (4)
C5—C4—Br2	118.7 (3)	C8—C9—C10	120.5 (4)
C3—C4—Br2	117.6 (3)	C11—C10—C9	118.9 (4)
O3—C5—C4	126.4 (4)	N1—C11—C10	120.0 (4)
O3—C5—C6	116.2 (3)	C11—N1—C7	123.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	2.13	2.611 (4)	117
O1—H1···Br1^{i}	0.82	2.82	3.423 (3)	132
N1—H1*A*···O3^{ii}	0.86	1.93	2.777 (4)	168
N1—H1*A*···O4^{ii}	0.86	2.54	3.043 (4)	119

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x+1, y, z$.

(ba_2br3mepyr) 2-Bromo-3-methylpyridine–bromanilic acid (1/1)

Crystal data

$C_6H_6BrN\cdot C_6H_2Br_2O_4$
$M_r = 469.91$
Monoclinic, $P2_1/c$
$a = 5.2866$ (3) Å
$b = 13.3814$ (8) Å
$c = 20.3576$ (13) Å
$\beta = 91.556$ (4)°
$V = 1439.61$ (15) Å^3

$Z = 4$
$F(000) = 896$
$D_x = 2.168$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 8.42$ mm^{-1}
$T = 100$ K
Block, red
0.25 × 0.2 × 0.1 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Graphite monochromator
CCD; rotation images scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.465$, $T_{max} = 1.000$
14350 measured reflections

3202 independent reflections
2267 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 27.2°$, $\theta_{min} = 1.8°$
$h = -6\rightarrow 5$
$k = -17\rightarrow 17$
$l = -26\rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.086$
$S = 1.03$
3202 reflections
188 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
All H atoms were placed on calculated positions and modelled as riding on the atoms to which they were bonded except H1 and H2. H1 was constrained to take a thermal parameter 1.2 times the $U_{\rm eq}$ of the atom to which it was bonded (O1) to ensure that a sensible thermal parameter was obtained. The methyl group positons were based on the electron density but with the bond lengths and angles constrained to take standard values for a methyl group.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.6951 (8)	0.5218 (3)	0.4532 (2)	0.0142 (10)
C3	0.6017 (8)	0.5990 (3)	0.4964 (2)	0.0153 (10)
C2	0.6005 (8)	0.4285 (3)	0.4553 (2)	0.0134 (10)
O1	0.6758 (6)	0.3552 (2)	0.41693 (17)	0.0226 (8)
O2	0.6701 (6)	0.6863 (2)	0.49613 (16)	0.0244 (8)
Br1	0.95526 (9)	0.55598 (3)	0.39596 (2)	0.01783 (14)
C4	0.6894 (8)	0.0737 (3)	0.5152 (2)	0.0149 (10)
C6	0.5333 (8)	0.0834 (3)	0.4566 (2)	0.0148 (10)
C5	0.3339 (8)	0.0032 (3)	0.4423 (2)	0.0141 (10)
O3	0.1920 (6)	0.0119 (2)	0.38894 (16)	0.0188 (8)
O4	0.5461 (6)	0.1528 (2)	0.41714 (16)	0.0190 (7)
Br2	0.93951 (9)	0.17269 (3)	0.52850 (2)	0.01781 (14)
C7	0.3385 (8)	0.1755 (3)	0.2548 (2)	0.0169 (11)
C8	0.3281 (9)	0.2589 (4)	0.2135 (2)	0.0205 (11)
C9	0.1496 (9)	0.3294 (4)	0.2290 (2)	0.0244 (12)
H9	0.1296	0.3858	0.2027	0.029*
C10	0.0000 (9)	0.3180 (3)	0.2830 (2)	0.0239 (12)
H10	−0.1194	0.3661	0.2933	0.029*
C11	0.0310 (9)	0.2333 (4)	0.3214 (2)	0.0233 (12)
H11	−0.0658	0.2259	0.3586	0.028*
N1	0.1966 (7)	0.1620 (3)	0.30642 (18)	0.0161 (9)
C12	0.4994 (9)	0.2719 (4)	0.1563 (2)	0.0308 (13)

H12A	0.4070	0.2577	0.1162	0.046*
H12B	0.6400	0.2268	0.1609	0.046*
H12C	0.5604	0.3394	0.1554	0.046*
Br3	0.56870 (10)	0.06825 (4)	0.23905 (3)	0.02778 (16)
H1	0.601 (8)	0.301 (2)	0.427 (2)	0.033*
H2	0.227 (10)	0.064 (4)	0.361 (3)	0.042 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.013 (3)	0.018 (2)	0.012 (2)	−0.0009 (19)	0.0048 (19)	0.0018 (19)
C3	0.014 (3)	0.015 (2)	0.018 (3)	0.0006 (19)	0.001 (2)	0.005 (2)
C2	0.012 (3)	0.013 (2)	0.015 (2)	−0.0030 (18)	0.0001 (19)	0.0026 (19)
O1	0.028 (2)	0.0113 (17)	0.029 (2)	−0.0051 (15)	0.0139 (16)	−0.0011 (15)
O2	0.029 (2)	0.0144 (19)	0.030 (2)	−0.0055 (15)	0.0083 (16)	−0.0055 (15)
Br1	0.0156 (3)	0.0173 (3)	0.0208 (3)	−0.00355 (18)	0.0055 (2)	0.0019 (2)
C4	0.015 (3)	0.013 (2)	0.017 (2)	−0.0071 (18)	0.004 (2)	−0.0015 (19)
C6	0.009 (3)	0.013 (2)	0.022 (3)	0.0018 (18)	0.005 (2)	−0.001 (2)
C5	0.015 (3)	0.011 (2)	0.017 (3)	−0.0012 (19)	0.005 (2)	−0.002 (2)
O3	0.021 (2)	0.0135 (18)	0.022 (2)	−0.0048 (14)	−0.0002 (16)	0.0040 (15)
O4	0.023 (2)	0.0131 (17)	0.0206 (18)	−0.0049 (14)	0.0025 (15)	0.0047 (14)
Br2	0.0172 (3)	0.0130 (2)	0.0234 (3)	−0.00624 (19)	0.0034 (2)	−0.0012 (2)
C7	0.011 (3)	0.018 (3)	0.022 (3)	−0.0001 (19)	−0.002 (2)	−0.002 (2)
C8	0.021 (3)	0.026 (3)	0.014 (3)	−0.007 (2)	−0.004 (2)	−0.003 (2)
C9	0.030 (3)	0.019 (3)	0.024 (3)	−0.008 (2)	−0.001 (2)	0.004 (2)
C10	0.025 (3)	0.017 (3)	0.029 (3)	0.003 (2)	0.003 (2)	−0.004 (2)
C11	0.025 (3)	0.025 (3)	0.020 (3)	−0.001 (2)	0.007 (2)	0.001 (2)
N1	0.019 (2)	0.013 (2)	0.017 (2)	−0.0002 (16)	−0.0008 (17)	−0.0014 (17)
C12	0.029 (3)	0.044 (3)	0.019 (3)	−0.008 (3)	0.001 (2)	0.014 (3)
Br3	0.0233 (3)	0.0317 (3)	0.0284 (3)	0.0097 (2)	0.0017 (2)	−0.0022 (2)

Geometric parameters (Å, º)

C1—C2	1.346 (6)	O3—H2	0.92 (5)
C1—C3	1.453 (6)	C7—N1	1.321 (6)
C1—Br1	1.882 (4)	C7—C8	1.397 (6)
C3—O2	1.223 (5)	C7—Br3	1.914 (4)
C3—C2^{i}	1.517 (6)	C8—C9	1.378 (7)
C2—O1	1.322 (5)	C8—C12	1.504 (7)
C2—C3^{i}	1.517 (6)	C9—C10	1.379 (7)
O1—H1	0.857 (19)	C9—H9	0.9300
C4—C5^{ii}	1.353 (6)	C10—C11	1.384 (6)
C4—C6	1.437 (6)	C10—H10	0.9300
C4—Br2	1.886 (4)	C11—N1	1.336 (6)
C6—O4	1.230 (5)	C11—H11	0.9300
C6—C5	1.527 (6)	C12—H12A	0.9600
C5—O3	1.308 (5)	C12—H12B	0.9600
C5—C4^{ii}	1.353 (6)	C12—H12C	0.9600
C2—C1—C3	120.5 (4)	N1—C7—Br3	114.1 (3)

C2—C1—Br1	121.6 (3)	C8—C7—Br3	120.9 (4)
C3—C1—Br1	117.9 (3)	C9—C8—C7	115.2 (4)
O2—C3—C1	124.9 (4)	C9—C8—C12	121.9 (4)
O2—C3—C2^{i}	116.6 (4)	C7—C8—C12	122.9 (4)
C1—C3—C2^{i}	118.5 (4)	C8—C9—C10	121.2 (5)
O1—C2—C1	123.4 (4)	C8—C9—H9	119.4
O1—C2—C3^{i}	115.6 (4)	C10—C9—H9	119.4
C1—C2—C3^{i}	121.0 (4)	C9—C10—C11	118.7 (5)
C2—O1—H1	110 (4)	C9—C10—H10	120.7
C5^{ii}—C4—C6	122.7 (4)	C11—C10—H10	120.7
C5^{ii}—C4—Br2	121.2 (3)	N1—C11—C10	121.6 (5)
C6—C4—Br2	116.1 (3)	N1—C11—H11	119.2
O4—C6—C4	124.7 (4)	C10—C11—H11	119.2
O4—C6—C5	117.1 (4)	C7—N1—C11	118.3 (4)
C4—C6—C5	118.2 (4)	C8—C12—H12A	109.5
O3—C5—C4^{ii}	122.6 (4)	C8—C12—H12B	109.5
O3—C5—C6	118.3 (4)	H12A—C12—H12B	109.5
C4^{ii}—C5—C6	119.1 (4)	C8—C12—H12C	109.5
C5—O3—H2	117 (3)	H12A—C12—H12C	109.5
N1—C7—C8	125.1 (4)	H12B—C12—H12C	109.5

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.86 (2)	2.01 (3)	2.794 (4)	151 (5)
O1—H1···O2^{i}	0.86 (2)	2.15 (5)	2.638 (5)	115 (4)
O3—H2···N1	0.92 (5)	1.73 (5)	2.619 (5)	163 (5)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Bond lengths for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (VAGTUS; Robl, 1987) with the doubly deprotonated bromanilic acid in 1:2 complex with the picoline isomers

The numbering scheme is as in Fig. 5 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry.

	VAGTUS BAH$_2$	2-picoline BA^{2-}	3-picoline BA^{2-}	4-picoline BA^{2-}
C1-Br1	1.868 (4)	1.905 (2)	1.902 (2)	1.902 (2)
C1-C2	1.347 (6)	1.394 (4)	1.387 (2)	1.399 (3)
C2-O1	1.323 (5)	1.260 (3)	1.262 (2)	1.246 (3)
C2-C3	1.504 (5)	1.547 (4)	1.548 (3)	1.555 (3)
C3-O2	1.225 (5)	1.251 (4)	1.239 (2)	1.246 (3)
C3-C4	1.449 (5)	1.402 (3)	1.414 (2)	1.405 (3)
C4-Br2	1.868 (4)*	1.905 (3)	1.902 (2)*	1.902 (2)*
C4-C5	1.347 (6)*	1.400 (4)	1.387 (2)*	1.399 (3)*
C5-O3	1.323 (5)*	1.249 (3)	1.262 (2)*	1.246 (3)*
C5-C6	1.504 (5)*	1.559 (4)	1.548 (3)*	1.555 (3)*
C6-O4	1.225 (5)*	1.249 (4)	1.239 (2)*	1.246 (3)*
C1-C6	1.449 (5)*	1.407 (4)	1.414 (2)*	1.405 (3)*

* Related by inversion symmetry to the other half of the bromanilic acid molecule

Bond lengths for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (VAGTUS; Robl, 1987) with the singly deprotonated bromanilic acid in 1:1 complex with the lutidine isomers

The numbering scheme is as in Fig. 5 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry.

	VAGTUS BAH_2	2,3-lutidine BAH^-	2,4-lutidine BAH^-	2,5-lutidine BAH^-	3,5-lutidine BAH^-
C1-Br1	1.868 (4)	1.889 (4)	1.875 (2)	1.879 (2)	1.879 (2)
C1-C2	1.347 (6)	1.338 (5)	1.354 (2)	1.352 (2)	1.352 (2)
C2-O1	1.323 (5)	1.332 (5)	1.320 (2)	1.323 (2)	1.323 (2)
C2-C3	1.504 (5)	1.521 (6)	1.511 (2)	1.519 (2)	1.519 (2)
C3-O2	1.225 (5)	1.242 (4)	1.247 (2)	1.249 (2)	1.249 (2)
C3-C4	1.449 (5)	1.409 (5)	1.406 (3)	1.399 (2)	1.399 (2)
C4-Br2	1.868 (4)*	1.897 (4)	1.891 (2)	1.887 (2)	1.887 (2)
C4-C5	1.347 (6)*	1.396 (5)	1.404 (2)	1.404 (2)	1.404 (2)
C5-O3	1.323 (5)*	1.256 (5)	1.250 (2)	1.238 (2)	1.238 (2)
C5-C6	1.504 (5)*	1.542 (6)	1.545 (2)	1.554 (2)	1.554 (2)
C6-O4	1.225 (5)*	1.220 (4)	1.217 (2)	1.222 (2)	1.222 (2)
C1-C6	1.449 (5)*	1.455 (5)	1.455 (3)	1.447 (2)	1.447 (2)

* Related by inversion symmetry to the other half of the bromanilic acid molecule.

Bond lengths for the bromanilic acid molecule contrasting bromanilic acid in its neutral form (VAGTUS; Robl, 1987) with the doubly deprotonated bromanilic acid in 1:1 complex with the bromomethylpyridine isomers

The numbering scheme is as in Fig. 5 and does not necessarily relate to the CIF entries as some molecules have internal inversion symmetry.

	VAGTUS BAH_2	2-bromo-3-methylpyridine (i) BAH_2	2-bromo-3-methylpyridine (ii) BAH_2	3-bromo-4-methylpyridine BAH^-
C1-Br1	1.868 (4)	1.883 (4)	1.886 (4)	1.892 (3)
C1-C2	1.347 (6)	1.346 (6)	1.352 (6)	1.347 (5)
C2-O1	1.323 (5)	1.322 (5)	1.308 (5)	1.327 (5)
C2-C3	1.504 (5)	1.517 (6)	1.527 (6)	1.517 (5)
C3-O2	1.225 (5)	1.223 (5)	1.231 (5)	1.243 (4)
C3-C4	1.449 (5)	1.452 (6)	1.438 (6)	1.419 (5)
C4-Br2	1.868 (4)*	1.883 (4)*	1.886 (4)*	1.894 (4)
C4-C5	1.347 (6)*	1.346 (6)*	1.352 (6)*	1.390 (5)
C5-O3	1.323 (5)*	1.322 (5)*	1.308 (5)*	1.266 (5)
C5-C6	1.504 (5)*	1.517 (6)*	1.527 (6)*	1.531 (5)
C6-O4	1.225 (5)*	1.223 (5)*	1.231 (5)*	1.234 (4)
C1-C6	1.449 (5)*	1.452 (6)*	1.438 (6)*	1.441 (5)

* Related by inversion symmetry to the other half of the bromanilic acid molecule. (i) and (ii) represent the two independent bromanilic acid molecules in the 2-bromo-3-methylpyridine molecular complex.

Selected hydrogen-bond parameters (Å, °)

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
2-picoline				
N2—H2···O4	0.86 (3)	2.02 (3)	2.838 (3)	159 (3)
N2—H2···O3	0.86 (3)	2.36 (3)	2.946 (3)	126 (2)
N1—H1···O1	0.77 (4)	1.96 (4)	2.693 (3)	160 (4)
N1—H1···O2	0.77 (4)	2.36 (4)	2.828 (3)	121 (4)
3-picoline				

N1—H5···O1	0.84 (3)	1.78 (3)	2.598 (2)	165 (3)
N1—H5···O2^{i}	0.84 (3)	2.54 (3)	3.039 (2)	119 (3)
C4—H4···Br1^{ii}	0.93	2.96	3.7977 (18)	151.0
4-picoline				
N1—H3···O1	0.74 (3)	2.12 (3)	2.760 (3)	145 (4)
N1—H3···O2	0.74 (3)	2.31 (3)	2.859 (3)	131 (3)
2,4-lutidine				
O1—H1···O2^{iii}	0.68 (3)	2.03 (3)	2.6509 (18)	151 (3)
O1—H1···O2	0.68 (3)	2.26 (3)	2.6559 (19)	119 (3)
N1—H2···O3^{iv}	0.72 (2)	2.14 (2)	2.849 (2)	168 (3)
N1—H2···O4^{iv}	0.72 (2)	2.56 (2)	2.9807 (18)	119 (2)
2,5-lutidine				
O1—H1···O2^{v}	0.82	2.01	2.6994 (17)	140.8
O1—H1···O2	0.82	2.16	2.6403 (19)	117
N1—H1A···O4	0.86	2.17	2.9794 (19)	157.6
N1—H1A···O3	0.86	2.34	2.883 (2)	121.6
3,5-lutidine				
N1—H2···O3^{vi}	0.93 (3)	1.84 (3)	2.677 (3)	148 (3)
N1—H2···O4^{vi}	0.93 (3)	2.37 (3)	3.008 (3)	125 (3)
O1—H1···O2^{iii}	0.72 (3)	2.11 (3)	2.768 (3)	152 (3)
O1—H1···O2	0.72 (3)	2.23 (3)	2.631 (2)	116 (3)
3-bromo-4-methylpyridine				
O1—H1···O2^{vii}	0.87 (5)	1.97 (5)	2.717 (3)	144 (4)
O1—H1···O2	0.87 (5)	2.12 (4)	2.637 (4)	118 (4)
N1—H5···O3^{viii}	0.79 (5)	1.91 (5)	2.675 (4)	161 (5)
N1—H5···O4^{viii}	0.79 (5)	2.53 (5)	2.915 (4)	112 (4)
2,3-lutidine				
O1—H1···O2	0.82	2.13	2.611 (4)	117.1
O1—H1···Br1^{ix}	0.82	2.82	3.423 (3)	131.9
N1—H1A···O3^{x}	0.86	1.93	2.777 (4)	168.4
N1—H1A···O4^{x}	0.86	2.54	3.043 (4)	118.7
2-bromo-3-methylpyridine				
O1—H1···O4	0.857 (19)	2.01 (3)	2.794 (4)	151 (5)
O1—H1···O2^{xi}	0.857 (19)	2.15 (5)	2.638 (5)	115 (4)
O3—H2···N1	0.92 (5)	1.73 (5)	2.619 (5)	163 (5)

Symmetry codes: (i) -x+1, -y+1, -z; (ii) -x+1, y+1/2, -z+1/2; (iii) -x+1, -y, -z+1; (iv) x-1, y, z; (v) -x, -y, -z; (vi) -x, -y+1, -z+1; (vii) -x, -y, -z+2; (viii) -x+1, y-1/2, -z+3/2; (ix) x+1/2, -y+1/2, z+1/2; (x) x+1, y, z; (xi) -x+1, -y+1, -z+1.

A summary of the Br interactions in the molecular complexes with bromanilic acid

No data available in manuscript - please supply missing values.

	Br···Br	Br···O	C-H···Br	Br···π	O-H···Br
VAGTUS (Robl, 1987)					
2-picoline					
3-picoline					
4-picoline			?(x2)		
2,3-lutidine			?(x2)		

2,4-lutidine		
2,5-lutidine		?(x4)
3,5-lutidine		?(x2)
2-bromo-3-methylpyridine		
3-bromo-4-methylpyridine	?(x2)	