

Self-assembled supramolecular sheet- and channel-type frameworks in the *p*-phenetidinium hydrogen phthalate and cyclohexylaminium hydrogen phthalate hemihydrate salts

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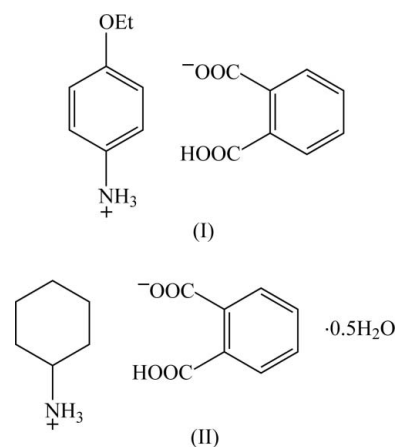
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The title compounds, *p*-phenetidinium hydrogen phthalate (or 4-ethoxyanilinium 2-carboxybenzoate), $C_8H_{12}NO^+ \cdot C_8H_5O_4^-$, (I), and cyclohexylaminium hydrogen phthalate hemihydrate (or cyclohexylaminium 2-carboxybenzoate hemihydrate), $C_6H_{14}N^+ \cdot C_8H_5O_4^- \cdot 0.5H_2O$, (II), form two- and one-dimensional supramolecular networks, respectively. In (I), the anionic–cationic network consists of $R_3^2(6)$ and $R_4^4(16)$ hydrogen-bonded rings forming a two-dimensional sheet along the (001) plane. In (II), O–H...O hydrogen bonds connect the glide-related anions, generating a supramolecular chain running parallel to [001] to which the cations are linked to form one-dimensional channels along [001]. The solvent water molecules, which reside on twofold axes, are trapped inside the molecular channels by N–H...O and O–H...O hydrogen bonds.

Comment

The physical and chemical properties of crystalline solids are characteristically dependant on the distribution or assembly of molecular components in the crystal structure (Ferrer *et al.*, 2001). The predictable supramolecular self-organization of molecular components can be developed by the use of N–H...O, O–H...O, C–H...O and other weak intermolecular interactions, creating one-, two- and three-dimensional networks in crystalline solids (Ranganathan *et al.*, 1999; Swift *et al.*, 1998). Supramolecular assemblies based on carboxylic acid groups (–COOH) have been given prime importance because of their ability to form robust hydrogen bonds on their own and with several aza compounds (anilines, pyridines, *etc.*; MacDonald *et al.*, 2000; Zhang & Chen, 2004). Phthalic acid is a good hydrogen-bond donor and acceptor and has been employed in constructing supramolecular architectures such as chains, sheets, ladders and ribbons (Ballabh *et al.*, 2005; Thanigaimani *et al.*, 2010; Dale *et al.*, 2004). Phthalic acid is

also important because hydrogen phthalate anions are versatile building blocks in organic and organometallic crystal engineering (Braga *et al.*, 1999), and the electro-optic properties of potassium hydrogen phthalate crystals reveal its use as a modulator (Kejalakshmy & Srinivasan 2003). As a continuation of our work in attempting to understand the hydrogen-bonded self-assembly of molecules in hydrogen phthalate salts (Jagan & Sivakumar, 2009), we present here the crystal structure and supramolecular self-assembly of two hydrogen phthalate salts, namely *p*-phenetidinium hydrogen phthalate, (I), and cyclohexylaminium hydrogen phthalate hemihydrate, (II).



The salts of (I) and (II) (Figs. 1 and 2) crystallize in the space groups $P\bar{1}$ and $Pbcn$, respectively. In (I), the asymmetric

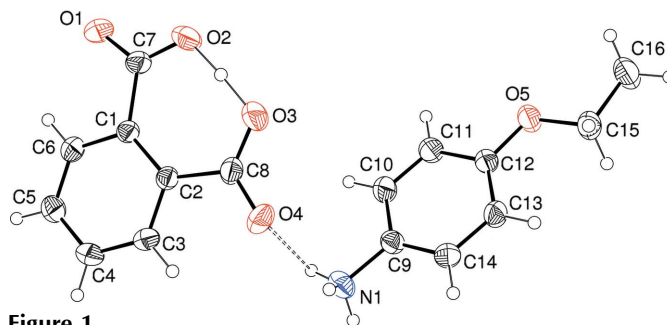


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. The dashed line indicates an intermolecular hydrogen bond.

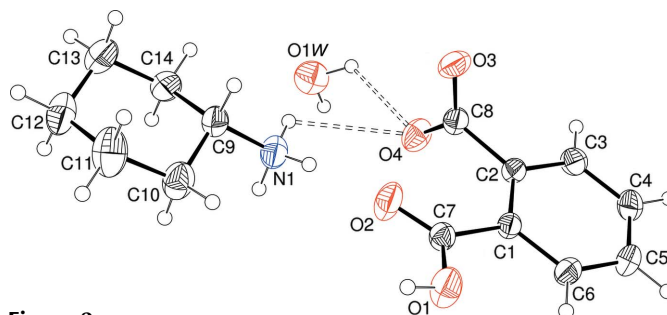


Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Dashed lines indicate intermolecular hydrogen bonds.

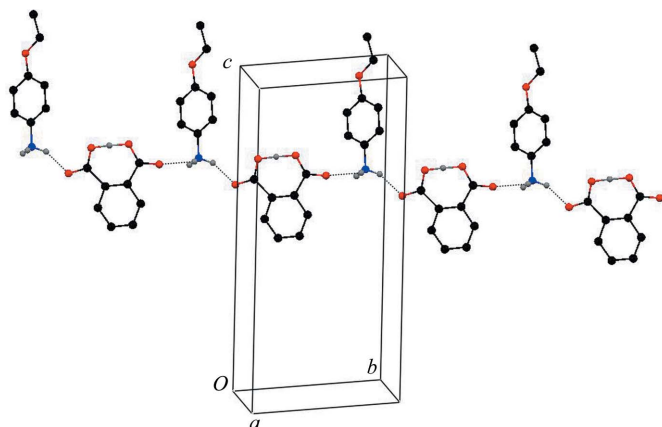


Figure 3

The extended supramolecular hydrogen-bonded one-dimensional chain in (I), viewed approximately down the a axis, showing the $N1-H1C \cdots O4$ and $N1-H1A \cdots O1$ linkages. H atoms not involved in these interactions have been omitted for clarity.

unit contains one hydrogen phthalate anion and one p -phenetidinium cation [this is the first crystal structure reported for a p -phenetidine (4-ethoxyaniline) salt], whereas in (II) the asymmetric unit contains a hydrogen phthalate anion, a cyclohexylaminium cation and half a water molecule. The water molecule of (II) is positioned on the twofold axis passing through $(0, y, \frac{1}{2})$. In the hydrogen phthalate anion of (I), the COOH and COO⁻ groups are approximately coplanar with the benzene ring and form an asymmetric intramolecular hydrogen bond (Küppers *et al.*, 1985). The centred H atom in (I) (H2A) is 1.16 (3) and 1.22 (3) Å from O2 and O3 atoms, respectively. This short intramolecular hydrogen-bond formation is responsible for the lengthening of the C1–C2 bond [C1–C2 = 1.4147 (18) Å; Janczak & Perpétuo, 2001]. The intramolecular hydrogen bond exerts a strain within the anion, causing some displacement of the inner O2 and O3 atoms (Adiwidjaja & Küppers, 1978). This is evident from the dihedral angles between the least-squares plane of the benzene ring and the carboxy or carboxylate groups, *viz.* 3.84 (11)° for O1/C7/O2 and 4.09 (11)° for O3/C8/O4. In (II), unlike (I), the COO⁻ and COOH groups are twisted from the benzene plane, making the COO⁻ group perpendicular at a dihedral angle of 89.76 (6)°, while the COOH group is slightly inclined at an angle of 7.64 (9)° (Kanai *et al.*, 2005). The geometric parameters of the p -phenetidinium and cyclohexylaminium cations of (I) and (II) are consistent with the reported literature, although since (I) is the first salt reported for p -phenetidine, it was compared with the 4-methoxyanilinium cation (Ben Amor *et al.*, 1995; Shahwar *et al.*, 2009).

The extensive supramolecular architectures exhibited by (I) and (II) are primarily formed by N–H \cdots O and O–H \cdots O hydrogen bonds and by the presence of C–H \cdots O interactions (Tables 1 and 2). In (I), the $N1-H1C \cdots O4$ and $N1-H1A \cdots O1^i$ hydrogen bonds [symmetry code: (i) $x - 1, y + 1, z$] link the hydrogen phthalate anions and p -phenetidinium cations to form a one-dimensional supramolecular chain extending infinitely along the $[1\bar{1}0]$ direction (Fig. 3). Similar

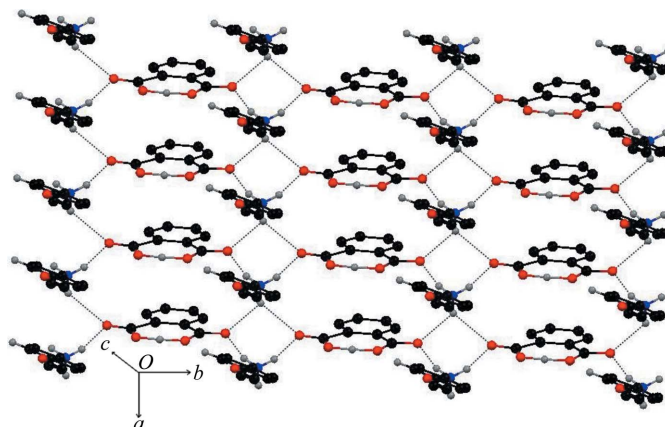


Figure 4

The two-dimensional sheet of anions and cations in (I), interlinked through $N1-H1C \cdots O4$, $N1-H1A \cdots O1^i$, $N1-H1B \cdots O4^{ii}$ and $N1-H1C \cdots O1^{iii}$ hydrogen bonds extending parallel to the (001) plane. H atoms not involved in these interactions have been omitted for clarity. Symmetry codes are as in Table 1.

one-dimensional chains are observed in the crystal structure of 1,4-phenylenediammonium bis(hydrogen phthalate) (Wang *et al.*, 2007). Two N–H \cdots O hydrogen bonds, $N1-H1B \cdots O4^{ii}$ and $N1-H1C \cdots O1^{iii}$ [symmetry codes: (ii) $x - 1, y, z$; (iii) $x, y + 1, z$] connect the one-dimensional chains to form a two-dimensional supramolecular sheet extending parallel to the (001) plane. The (001) sheet shown in Fig. 4 is built from the infinite repetition of graph-set motifs of type $R_3^2(6)$ and $R_4^4(16)$ (Bernstein *et al.*, 1995). The benzene rings of both the anions and the cations make angles of 61.93 and 76.71°, respectively, with the (001) plane. Inversion-related supramolecular sheets of anions and cations are further linked by $C11-H11 \cdots O5^{iv}$ [symmetry code: (iv) $-x, -y + 1, -z + 2$] interactions,

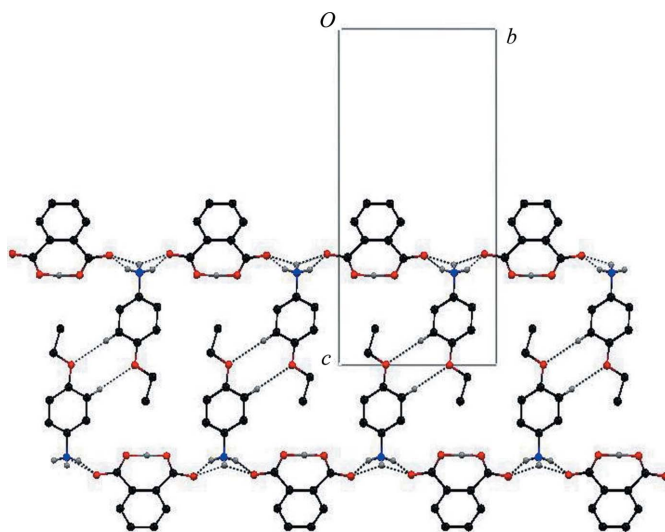


Figure 5

Part of the crystal structure of (I), viewed along the a axis, showing the formation of the $R_2^2(8)$ rings of the C–H \cdots O hydrogen-bonded dimers, which connect inversion-related (001) sheets. H atoms not involved in these interactions have been omitted for clarity.

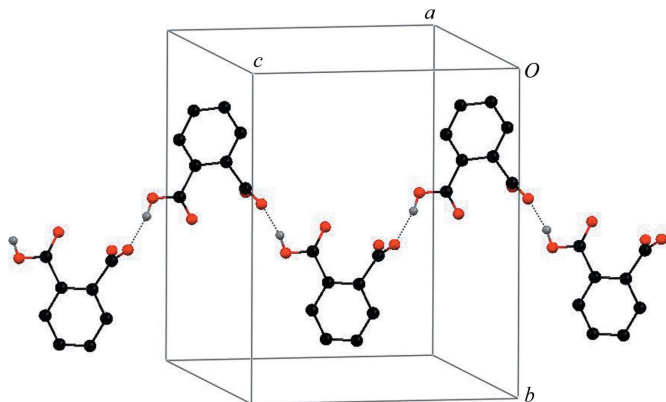


Figure 6
Part of the crystal structure of (II), showing the $O1-H1A \cdots O3^i$ hydrogen-bond linkage between the $[010]$ glide-related anions, forming an extended one-dimensional chain along the $[001]$ direction. Symmetry codes are as in Table 2. H atoms not involved in these interactions have been omitted for clarity.

resulting in the formation of an $R_2^2(8)$ ring dimer, the centroid of which occupies the crystallographic inversion centre. The combination of $N-H \cdots O$ hydrogen bonds and $C-H \cdots O$ interactions generates a supramolecular sheet of thickness equal to the length of the c axis extending along the ab plane, as shown in Fig. 5.

In (II), the hydrogen phthalate anions alone form a one-dimensional hydrogen-bonded chain running parallel to the $[001]$ direction. The $O1-H1A \cdots O3^i$ hydrogen bond [symmetry code: (i) $x, -y + 1, z + \frac{1}{2}$] links the anions, forming a $C(7)$ chain generated by the glide plane perpendicular to $[010]$, whose glide component is $(0, 0, \frac{1}{2})$, ending with an anionic substructure as shown in Fig. 6. The two antiparallel $[001]$ chains are bridged by the cyclohexylammonium cation through $N1-H1C \cdots O2$ and $N1-H1E \cdots O4^{ii}$ hydrogen bonds [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$]. Inter-

estingly, the bridging of the cations between the chains forms saddle-like cavities in which the solvent water molecules are located. The anions and cations form an extended self-assembled molecular channel along the $[001]$ direction in which the trapped water molecules are located, separated by a distance of 5.97 \AA (Fig. 7). The water molecules are bound to the molecular channel through $O1W-H1W \cdots O4$, $O1W-H1W \cdots O2^{iii}$ [symmetry code: (iii) $x + 1, -y + 1, z - \frac{1}{2}$] and $N1-H1D \cdots O1W$ hydrogen bonds, as illustrated. These water interactions, along with the bridging hydrogen bonds, form a variety of ring motifs [including $R_4^4(8)$, $R_2^2(8)$ and $R_3^3(10)$], giving a self-assembled hydrogen-bonded network.

Since the above-described work is the continuation of our previously reported structures, a comparison of (I) and (II) with our previous structures of the 4-chloroanilinium, (III), 2-hydroxyanilinium, (IV), and 3-hydroxyanilinium, (V), hydrogen phthalates (Jagan & Sivakumar, 2009) is appropriate. In (II), the one-dimensional anionic supramolecular chain built from a $C(7)$ motif is similar to the network observed in (III). The anionic chains in (II) are generated by a c -glide, whereas in (III) they are generated by a 2_1 screw parallel to the b axis. The formation of this type of symmetry-related anionic network in hydrogen phthalate salts was investigated previously and studied by Langkilde *et al.* (2004). In the case of (I), (IV) and (V), the formation of short intramolecular $O-H \cdots O$ hydrogen bonds restricts the generation of the anionic one-dimensional chains observed in (II) and (III), and instead it forms one-dimensional chains built from alternating anions and cations linked through $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds, which further self-assemble into higher-dimensional supramolecular networks. In the closely related salt 1,4-phenylenediammonium bis(-hydrogen phthalate) [Cambridge Structural Database (Version 5.3.1; Allen 2002; Macrae *et al.*, 2008) refcode NEVKUV (Wang *et al.*, 2007)], the formation of a one-dimensional supramolecular chain is observed, as in (I).

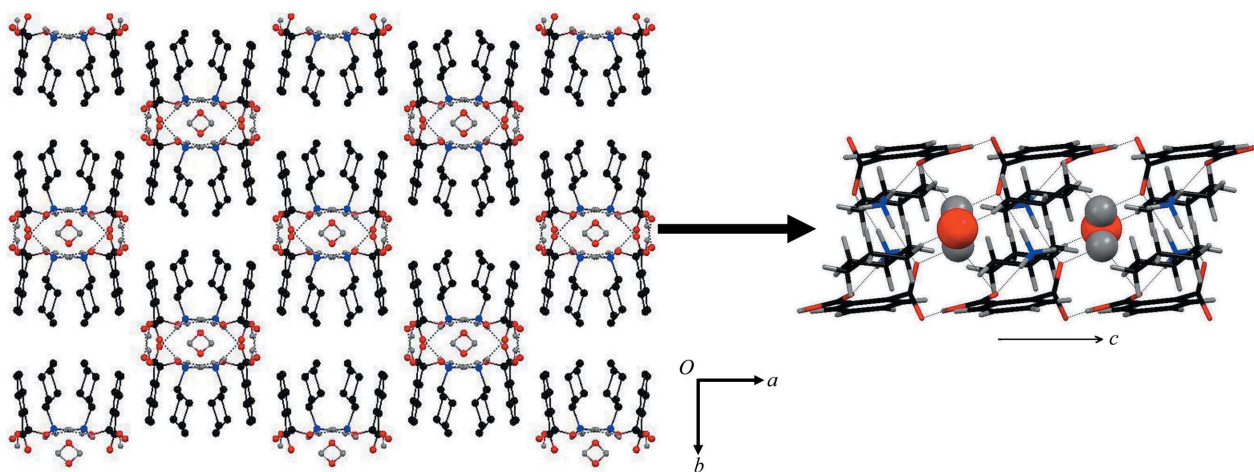


Figure 7
The molecular packing in (II), showing the formation of channels along the $[001]$ direction holding the water molecules inside. Also shown is the trapping of water molecules through hydrogen bonds between the cavities, viewed along the b axis. H atoms not involved in these interactions have been omitted for clarity.

However, the presence of an NH₃ group instead of an ethoxy group in the *para* position results in the formation of an infinite three-dimensional network instead of the two-dimensional sheets seen in (I). Comparing the structures closely related to (II), the supramolecular architecture observed in the crystal structure of hexamethylenediamminium hydrogen phthalate dihydrate (CSD refcode CIZZIU; Jagannathan *et al.*, 1984) shows the self-assembly of ions forming molecular channels in which the water molecules are trapped through hydrogen bonds, as in (II), whereas in piperazine-1,4-dium bis(orthohydrogen phthalate) dihydrate (CSD refcode VAJWUZ; Jin *et al.*, 2003), the water molecules act as a bridge between the anionic–cationic one-dimensional networks and do not lie in channels. It is to be concluded that phthalates can form interesting tunable supramolecular self-assembled architectures like other organic salts, and the presence of weak C–H···O interactions demonstrates their importance in the molecular packing of phthalates.

Experimental

Salt (I) was prepared by dissolving equimolar quantities of phthalic acid and *p*-phenetidine in methanol. The resulting solution was stirred well for 15 mins and was then left undisturbed in a test tube with the lid partially covered, for slow evaporation. Good diffraction-quality crystals were obtained after a few days. Salt (II) was prepared by mixing equimolar quantities of water and methanol solutions of cyclohexylamine and phthalic acid, respectively. The solution thus prepared was allowed to evaporate slowly and crystals were obtained.

Compound (I)

Crystal data

C₈H₁₂NO⁺·C₈H₅O₄[−] $\gamma = 86.708 (1)^\circ$
M_r = 303.31 $V = 729.82 (3) \text{ \AA}^3$
 Triclinic, *P* $\bar{1}$ $Z = 2$
 $a = 3.9983 (1) \text{ \AA}$ Mo *K* α radiation
 $b = 9.2595 (2) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $c = 19.8227 (5) \text{ \AA}$ $T = 292 \text{ K}$
 $\alpha = 89.670 (1)^\circ$ $0.25 \times 0.20 \times 0.20 \text{ mm}$
 $\beta = 84.947 (1)^\circ$

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer 16579 measured reflections
 Absorption correction: multi-scan (SADABS; Bruker, 2004) 3350 independent reflections
 $T_{\min} = 0.905$, $T_{\max} = 0.980$ 2780 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Table 1

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···O1 ⁱ	0.89	1.95	2.7766 (18)	153
N1–H1B···O4 ⁱⁱⁱ	0.89	1.95	2.7996 (19)	160
N1–H1C···O1 ⁱⁱⁱ	0.89	2.39	3.0264 (19)	129
C11–H11···O5 ^{iv}	0.93	2.58	3.5110 (19)	178
N1–H1C···O4	0.89	2.26	2.9193 (19)	130

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

Table 2

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1A···O3 ⁱ	0.82	1.67	2.4696 (14)	166
N1–H1E···O4 ⁱⁱⁱ	0.89	1.92	2.7983 (19)	170
O1W–H1W···O2 ⁱⁱⁱ	0.92 (1)	2.45 (2)	3.0985 (13)	128 (2)
N1–H1C···O2	0.89	1.97	2.8531 (17)	175
O1W–H1W···O4	0.92 (1)	2.26 (3)	2.8726 (16)	124 (2)
N1–H1D···O1W	0.89	2.25	3.0963 (14)	159

Symmetry codes: (i) $x, -y + 1, z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, -y + 1, z - \frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.124$
 $S = 1.08$
 3350 reflections
 208 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

C₆H₁₄N⁺·C₈H₅O₄[−]·0.5H₂O $V = 2789.59 (10) \text{ \AA}^3$
M_r = 274.31 $Z = 8$
 Orthorhombic, *Pbcn* Mo *K* α radiation
 $a = 16.9402 (4) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $b = 14.1463 (3) \text{ \AA}$ $T = 292 \text{ K}$
 $c = 11.6407 (2) \text{ \AA}$ $0.30 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer 37264 measured reflections
 Absorption correction: multi-scan (SADABS; Bruker, 2004) 4565 independent reflections
 $T_{\min} = 0.911$, $T_{\max} = 0.981$ 2931 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.147$
 $S = 1.02$
 4565 reflections
 186 parameters
 1 restraint
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

In (I) and (II), the positions of the H atoms bound to N and O atoms were initially identified from difference electron-density maps. The hydroxy H atom in (I) was refined isotropically and the symmetry-unique water H atom in (II) was refined isotropically with an O–H distance restraint of 0.93 (1) Å. The H atoms bound to N atoms were subsequently geometrically optimized, with N–H = 0.89 Å, and allowed to ride on their parent atom, with $U_{\text{iso}}(\text{H})$ values freely refined. In (I), the orientation of the –NH₃ group was allowed to rotate to fit the observed electron density, while the best staggered positions were used in the case of (II). The hydroxy H atom in (II) was also geometrically optimized with O–H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, and the O–H vector allowed to rotate around the C–O bond. H atoms bound to C atoms were treated as riding atoms, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H, and C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups.

For both compounds, data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TP3002). Services for accessing these data are described at the back of the journal.

References

- Adiwidjaja, G. & Küppers, H. (1978). *Acta Cryst.* **B34**, 2003–2005.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Ballabh, A., Trivedi, D. R. & Dastidar, P. (2005). *Cryst. Growth Des.* **5**, 1545–1553.
- Ben Amor, F., Soumhi, E. H., Ould Abdellahi, M. & Jouini, T. (1995). *Acta Cryst.* **C51**, 933–935.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Braga, D., Angeloni, A., Maini, L., Götz, A. W. & Grepioni, F. (1999). *New J. Chem.* pp. 17–24.
- Bruker (2004). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dale, S. H., Elsegood, M. R. J., Hemmings, M. & Wilkinson, A. L. (2004). *CrystEngComm*, **6**, 207–214.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Ferrer, J. R., Lahti, P. M., George, C., Oliete, P., Julier, M. & Palacio, F. (2001). *Chem. Mater.* **13**, 2447–2454.
- Jagan, R. & Sivakumar, K. (2009). *Acta Cryst.* **C65**, o414–o418.
- Jagannathan, N. R., Subramanian, E., Srinivasan, R. & Trotter, J. (1984). *Acta Cryst.* **C40**, 1743–1744.
- Janczak, J. & Perpétuo, G. J. (2001). *Acta Cryst.* **C57**, 123–125.
- Jin, Z. M., Pan, Y. J., Xu, D. J., He, L., Li, Z. G. & Yu, K. B. (2003). *Anal. Sci.* **19**, 333–334.
- Kanai, M., Ueda, K., Yasumoto, M., Kuriyama, Y., Inomiya, K., Ootsuka, T., Katsuhara, Y., Higashiyama, K. & Ishii, A. (2005). *J. Fluorine Chem.* **126**, 377–383.
- Kejalakshmy, N. & Srinivasan, K. (2003). *J. Phys. D Appl. Phys.* **36**, 1778–1782.
- Küppers, H., Ttakusagawa, F. & Koetzle, T. F. (1985). *J. Chem. Phys.* **82**, 5636–5647.
- Langkilde, A., Madsen, D. & Larsen, S. (2004). *Acta Cryst.* **B60**, 502–511.
- MacDonald, J. C., Dorrestein, P. C. & Pilley, M. M. (2000). *Cryst. Growth Des.* **1**, 29–38.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Ranganathan, A., Pedireddi, V. R. & Rao, C. N. R. (1999). *J. Am. Chem. Soc.* **121**, 1752–1753.
- Shahwar, D., Tahir, M. N., Ahmad, N., Khan, M. A. & Saeed, A. (2009). *Acta Cryst.* **E65**, o1313.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Swift, J. A., Pirovar, A. N., Reynolds, A. M. & Ward, M. D. (1998). *J. Am. Chem. Soc.* **120**, 5887–5894.
- Thanigaimani, K., Devi, P., Muthiah, P. T., Lynch, D. E. & Butcher, R. J. (2010). *Acta Cryst.* **C66**, o324–o328.
- Wang, K.-W., Zhang, H. & Shen, L.-Q. (2007). *Acta Cryst.* **E63**, o126–o128.
- Zhang, X. L. & Chen, X. (2004). *Cryst. Growth Des.* **5**, 617–622.