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Three-dimensional networks in 5-methylimidazolium 3-carboxy-4-hydroxybenzenesulfonate and bis(5-methylimidazolium) 3-carboxylato-4-hydroxybenzenesulfonate

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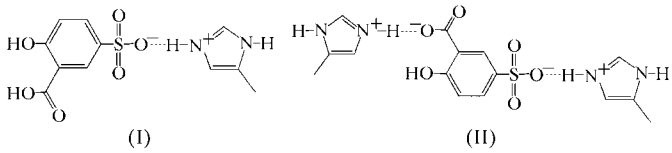
The two title proton-transfer compounds, 5-methylimidazolium 3-carboxy-4-hydroxybenzenesulfonate, $C_4H_7N_2^+\cdot C_7H_5O_6S^-$, (I), and bis(5-methylimidazolium) 3-carboxylato-4-hydroxybenzenesulfonate, $2C_4H_7N_2^+\cdot C_7H_5O_6S^{2-}$, (II), are each organized into a three-dimensional network by a combination of X—H$\cdots$O (X = O, N or C) hydrogen bonds, and π–π and C—H$\cdots\pi$ interactions.

Comment

5-Sulfosalicylic acid (5-H_2SSA) and its organic complexes or salts can develop well defined noncovalent supramolecular architectures because of their ability to form multiple hydrogen bonds containing components of complementary arrays of hydrogen-bonding sites (Smith *et al.*, 2004, 2006; Smith, Wermuth & White, 2005*a*,*b*; Smith, Wermuth & Healy, 2005; Muthiah *et al.*, 2003; Raj *et al.*, 2003; Fan *et al.*, 2005; Wang *et al.*, 2007). Our interest in these materials arises from their potential to display three-dimensional structural diversity. In continuation of our studies of hydrogen-bonding networks formed with 5-H_2SSA and Lewis bases (Meng *et al.*, 2007), we report here our findings on another two organic salts, both composed of 5-H_2SSA and 5-methylimidazole (5-MeIm), 5-$MeIm^+\cdot$5-$HSSA^-$, (I), and $(5\text{-MeIm}^+)_2\cdot$5-SSA^{2-}, (II).

Both anhydrous compounds crystallize in the space group $P2_1/c$, with Z' = 2 in (I), but Z' = 1 in (II) (Fig. 1). These different values may result from the experimental conditions (Das *et al.*, 2006; Anderson *et al.*, 2007). The powder X-ray diffraction patterns of bulk (I) and (II) are in good agreement with the calculated patterns based on the results from single-crystal X-ray diffraction (Fig. 2). Like most analogues containing the 5-$HSSA^-$ anion, the sulfonic acid H atoms transfer to the Lewis base N atoms in preference to the carboxyl group



in these two compounds, and the hydroxyl O atom forms a common intramolecular $S(6)$ ring with the carboxyl group [for hydrogen-bonding motifs, see Bernstein *et al.* (1995)]. With the aim of investigating the probable molar ratio of 5-H_2SSA with other Lewis bases in crystallized products, a search of the Cambridge Structural Database [*ConQuest*, Version 1.9, September 2006 release; Allen (2002); Bruno *et al.* (2002)] for organic compounds containing at least one of the 5-H_2SSA, 5-$HSSA^-$ and 5-SSA^{2-} moieties was conducted to determine the numbers of such organic adducts. As a result, three, 26 and four crystal structures with three-dimensional coordinates were found for the neutral, monoanionic or dianionic moieties, respectively, from which we can see that in most cases only the sulfonic acid H atoms transfer to the Lewis base atoms, forming 1:1 molecular adducts.

In the molecular structures of (I) and (II), the relative conformations between the sulfonate groups and their

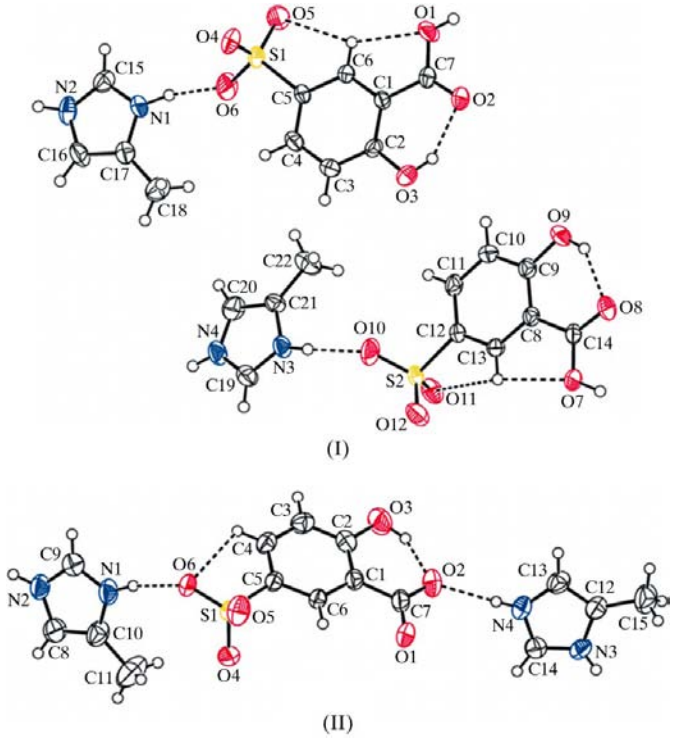


Figure 1
The molecular structures of (I) and (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

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attached benzene rings are slightly different. In (I), the plane consisting of atoms O4/O5/O6 makes a dihedral angle of 83.9 (1)° with the C1–C6 aryl ring, with the distances of each O atom from the benzene plane being *ca* 1.598 (1), 0.572 (1) and 0.367 (1) Å, respectively; the O10/O11/O12 plane makes a dihedral angle of 86.1 (1)° with its adjacent aryl ring, and the distances of each O atom from the benzene plane are *ca* 1.536 (1), 0.632 (1) and 0.462 (1) Å, respectively. However, the corresponding angles and distances in (II) are 85.3 (1)° and *ca* 1.379 (1), 1.025 (1) and 0.161 (1) Å, which are different from those in (I). The spatial difference between the sulfonate O-atom plane and the benzene rings may be the result of these hydrogen-bonding interactions involving the sulfonate O atoms.

In the packing structures of both title compounds, the components are linked into three-dimensional frameworks by combinations of X—H···O hydrogen bonds (X = O, N or C) and π–π and C—H···π noncovalent interactions. In (I), the supramolecular structure can be readily analyzed in terms of three simple substructures.

In the first of these substructures, imidazole atoms N1 and N2 at (x, y, z) act as hydrogen-bond donors to sulfonate atom O6 at (x, y, z) and carboxyl atom O2 at (x, $y-1$, z), respectively, forming a one-dimensional chain generated by translation running parallel to the [010] direction. Similarly, carboxyl atom O1 at (x, y, z) acts as hydrogen-bond donor to sulfonic atom O4 at ($-x, \frac{1}{2}+y, \frac{3}{2}-z$), producing another one-dimensional chain also running parallel to the [010] direction, but this time generated by 2_1 screw axis lying at (0, y, $\frac{3}{4}$). By a combination of these three hydrogen-bonding interactions, S1-containing anions and N1/N2-containing cations are interlinked into a one-dimensional tape (denoted tape *A*) built from $R_4^4(20)$ rings running along the [010] direction. Almost completely similar to the formation of tape *A*, S2-containing anions and N3/N4-containing cations are also linked by four hydrogen bonds into another one-dimensional tape (denoted tape *B*) also running parallel to the [010] direction, in which atoms N3, N4 and O7 act as hydrogen-bond donors to symmetry-related atoms O10, O8 and O11, respectively (Table 1 and Fig. 3).

The second substructure is formed by means of three intermolecular C—H···O hydrogen bonds, and adjacent tapes *A* and *B* are joined together into a two-dimensional layer (Fig. 4) running parallel to the (001) direction lying in the domain $0.532 < z < 0.958$. This layer is consolidated by two inner C—H···π interactions (C18—H18*A*···*Cg*4^{vii} and C22—H22*C*···*Cg*3^{viii}; full details and symmetry codes are given in Table 1) and two π–π stacking interactions (*Cg*1···*Cg*2^{ix} and *Cg*3···*Cg*3^{v}; full details and symmetry codes are given in

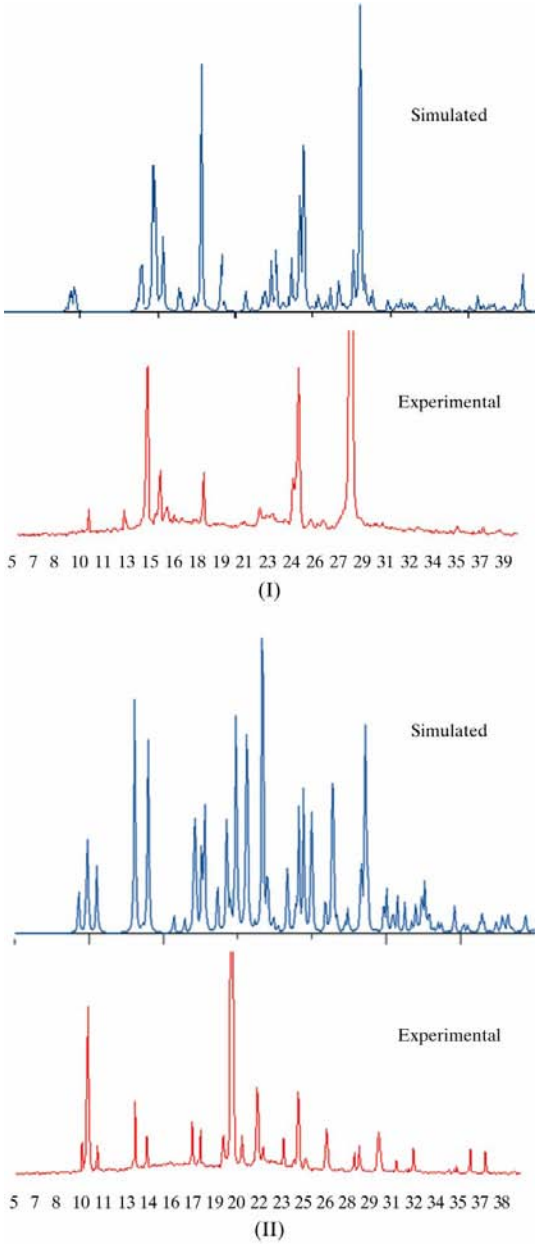

Figure 2
Experimental and simulated power diffraction patterns for (I) and (II).

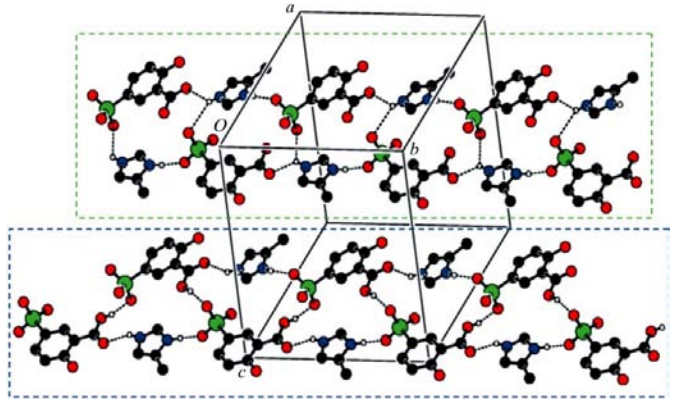

Figure 3
Part of the crystal structure of (I), showing the formation of tapes *A* and *B*, the one-dimensional chains running parallel to the [010] direction. Hydrogen bonds are shown as dashed lines. The top and bottom outlined areas show the tape *A* and tape *B* chains, respectively.

Table 3). The three-dimensional network in (I) is ultimately shaped through linking of adjacent up and down (001) layers by a combination of another three π–π stacking interactions, *i.e.* $Cg1\cdots Cg1^{v}$, $Cg2\cdots Cg4^{vi}$ and $Cg4\cdots Cg2^{vi}$ (Table 3).

By comparison, components in (II) are also linked into a three-dimensional network by a combination of X—H$\cdots$O hydrogen bonds (X = N, O or C) and π–π stacking interactions, which can be analysed more easily than those in (I). Firstly, 5-SSA^{2-} and 5-MeIm^{+} ions are linked together into a one-dimensional column structure (Fig. 5) by a combination of four intermolecular N—H$\cdots$O and C14—H14*A*$\cdots$O1($-x+1, -y, z-2$) hydrogen bonds. Atoms N3, N4 and C14 act as hydrogen-bond donors, *via* atoms H3*A*, H14*A* and H4*A*, respectively, to each symmetry-related sulfonate atom O4 or O2 and carboxyl atom O1, forming a centrosymmetric $R_4^4(14)$ ring centred at ($\frac{1}{2}$, 0, 1) and two asymmetric $R_2^2(11)$ rings. Adjacent discrete edge-fused $R_4^4(14)$ and $R_2^2(11)$ rings are joined together by intermolecular N1—H1*A*$\cdots$O6 and N2—H2*A*$\cdots$O1^{i} hydrogen bonds, forming a one-dimensional column structure running parallel to the [101] direction, which is further strengthened by a π–π stacking interaction between two adjacent imidazole rings ($Cg1\cdots Cg2^{i}$; Table 3).

Next, adjacent [101] columns are linked by the π–π stacking interaction (*i.e.* $Cg2\cdots Cg2^{v}$) formed between two N3/N4-containing imidazole rings, producing a two-dimensional layer (Fig. 5) running parallel to the (010) plane. The reference two-dimensional layer lies in the domain $-0.226 < y < 0.226$ and two such two-dimensional layers pass through each unit cell. Finally, neighbouring (010) two-dimensional layers are linked into a three-dimensional network by two C—H$\cdots$O interactions (Table 2), each of which produces a $C(11)$ chain running parallel to the [201] direction and generated by the *c*-glide plane at $y = \frac{1}{4}$.

In comparison with the stacking pattern of sulfonic aryl and Lewis base heterocyclic rings (Meng *et al.*, 2007), in (I) both the sulfonic aryl and imidazole rings form an up and down homogeneous arrangement, *i.e.* 5-HSSA^{-} anions stack only on top of 5-HSSA^{-} anions and 5-MeIm^{+} cations stack only on top of 5-MeIm^{+} cations. In (II), the imidazole rings also stack homogeneously, but the 5-SSA^{2-} dianions adopt an almost linear arrangement, which is completely different to that in (I) and the analogues previously reported by us.

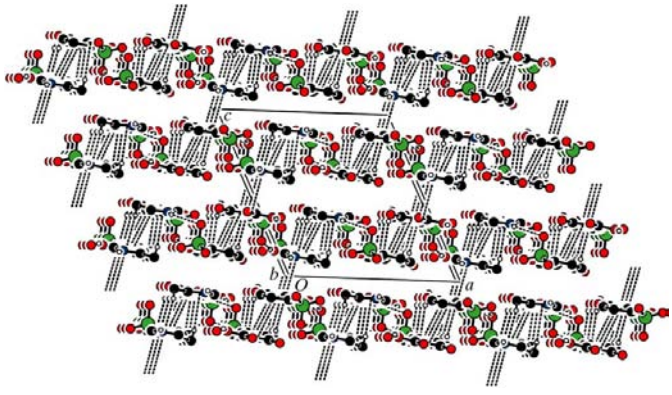

Figure 4
Part of the crystal structure of (I), showing the formation of the two-dimensional network built from hydrogen bonds and C—H$\cdots\pi$ and π–π interactions, shown as dashed lines.

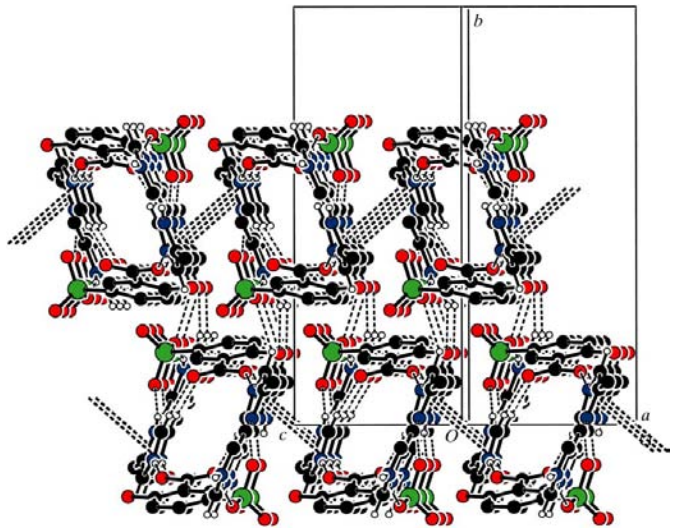

Figure 5
Part of the crystal structure of (II), showing the formation of the three-dimensional network. Hydrogen bonds and π–π interactions are shown as dashed lines.

In conclusion, the formation of these two three-dimensional networks in (I) and (II) may be largely attributed to the different directional outspread of the sulfonate O atoms acting as hydrogen-bond acceptors. The different arrangement of the aryl and heterocyclic rings in the crystalline state may be mainly related to the crystallization temperature. Further research on how temperature and other related factors effect the crystallization behaviour is currently underway.

Experimental

All reagents and solvents were used as obtained without further purification. Equivalent molar quantities of 2-methylimidazole (0.2 mmol, 16.2 mg) and 5-sulfosalicylic acid dihydrate (0.2 mmol, 50.8 g) were dissolved in 95% methanol (10 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The resulting colourless solution was kept in air for two weeks. Block-shaped colourless crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 56%, 38 mg, based on the 1:1 organic salt).

Crystals of (II) were obtained by mixing 2:1 molar quantities of 2-methylimidazole (0.2 mmol, 16.2 mg) and 5-sulfosalicylic acid dihydrate (0.1 mmol, 25.4 mg) in 95% methanol (10 ml). The mixture was stirred for 30 min at 330 K and then filtered. The resulting colourless solution was kept in air for 3 d. Block-shaped colourless crystals of (II) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 40%, 17.0 mg, based on the 2:1 organic salt).

Compound (I)

Crystal data

$C_4H_7N_2^+\cdot C_7H_5O_6S^-$
M_r = 300.29
Monoclinic, $P2_1/c$
a = 13.2702 (6) Å
b = 14.9930 (7) Å
c = 14.0947 (7) Å
β = 115.471 (1)°
V = 2531.7 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 294 (2) K
0.10 × 0.10 × 0.06 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*b*)
T_{min} = 0.951, T_{max} = 0.983
25930 measured reflections
4971 independent reflections
2829 reflections with $I > 2\sigma(I)$
R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.158
S = 1.01
4971 reflections
387 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

*Cg*3 is the centroid of the N1/N2/C15–C17 ring and *Cg*4 is the centroid of the N3/N4/C19–C21 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···O4^{i}	0.84 (4)	1.76 (4)	2.588 (3)	166 (4)
N2—H2A···O2^{ii}	0.90 (4)	2.10 (4)	2.916 (4)	152 (3)
N4—H4A···O8^{ii}	0.89 (4)	2.20 (4)	2.913 (4)	136 (3)
N4—H4A···O11^{iii}	0.89 (4)	2.55 (4)	3.186 (4)	129 (3)
O7—H7A···O11^{iv}	0.86 (4)	1.74 (4)	2.596 (3)	173 (4)
C15—H15···O9^{v}	0.93	2.52	3.378 (5)	154
C22—H22C···O1^{v}	0.96	2.55	3.445 (5)	156
C19—H19···O3^{vi}	0.93	2.33	3.241 (5)	167
N1—H1A···O6	0.91 (4)	1.87 (4)	2.740 (4)	158 (3)
N3—H3A···O10	0.90 (3)	1.89 (4)	2.763 (4)	164 (3)
O3—H3B···O2	0.86 (4)	1.87 (4)	2.646 (3)	149 (4)
O9—H9A···O8	0.82 (4)	1.96 (4)	2.658 (3)	142 (4)
C18—H18A···$Cg4^{vii}$	0.96	2.89	3.758 (4)	151
C22—H22A···$Cg3^{viii}$	0.96	2.76	3.582 (4)	143

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

Compound (II)

Crystal data

$2C_4H_7N_2^+\cdot C_7H_4O_6S^{2-}$
M_r = 382.39
Monoclinic, $P2_1/c$
a = 9.5394 (5) Å
b = 17.8475 (9) Å
c = 10.4174 (5) Å
β = 94.136 (1)°
V = 1768.99 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 297 (2) K
0.20 × 0.20 × 0.13 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*b*)
T_{min} = 0.947, T_{max} = 0.972
19241 measured reflections
3840 independent reflections
3138 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.155
S = 0.82
3840 reflections
252 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O6	0.84 (3)	1.94 (3)	2.767 (2)	168 (3)
O3—H3B···O2	0.93 (4)	1.70 (4)	2.542 (3)	150 (3)
N4—H4A···O2	0.79 (3)	1.95 (3)	2.737 (2)	174 (3)
N2—H2A···O1^{i}	0.90 (3)	1.80 (3)	2.685 (2)	166 (2)
N3—H3A···O4^{ii}	0.83 (3)	1.91 (3)	2.725 (2)	167 (2)
C14—H14A···O1^{ii}	0.93	2.36	3.287 (3)	175
C9—H9A···O3^{iii}	0.93	2.55	3.333 (3)	142
C13—H13A···O6^{iv}	0.93	2.43	3.230 (2)	144

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

Table 3
Geometry of π–π stacking interactions for (I) and (II) (°, Å).

For (I), *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of rings C1–C6, C8–C13, N1/N2/C15–C17 and N3/N4/C19–C21, respectively, and for (II), *Cg*1 is the centroid of the N1/N2/C8–C10 ring and *Cg*2 is the centroid of the N3/N4/C12–C14 ring.

CgI	*CgJ*	Dihedral angle	Centroid distance	Interplanar spacing
(I)				
*Cg*1	*Cg*1^{v}	0.00	4.200 (2)	3.667 (2)
*Cg*1	*Cg*2^{ix}	3.5 (1)	4.187 (2)	3.478 (2)
*Cg*2	*Cg*4^{vi}	7.2 (1)	3.864 (2)	3.485 (2)
*Cg*3	*Cg*3^{v}	0.02 (1)	3.618 (2)	3.372 (2)
*Cg*4	*Cg*2^{vi}	2.30 (1)	3.864 (2)	3.485 (2)
(II)				
*Cg*1	*Cg*2^{i}	16.3 (1)	3.582 (2)	3.490 (2)
*Cg*2	*Cg*2^{v}	0.03 (1)	3.523 (2)	3.231 (2)

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

For both compounds, H atoms bonded to C atoms were positioned geometrically, with C—H = 0.93 (aromatic) or 0.96 Å (methyl), and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(aromatic C) or 1.5U_{eq}(methyl C). H atoms bonded to N and O atoms were found in Fourier difference maps. N—H and O—H distances were refined freely [N—H = 0.79 (3)–0.89 (4) Å and O—H = 0.82 (4)–0.93 (4) Å] and U_{iso}(H) values were set at 1.2U_{eq}(N) or 1.5U_{eq}(O).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3124). Services for accessing these data are described at the back of the journal.

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