Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The 1:1 proton-transfer compounds of 4-(phenyldiazenyl)aniline (aniline yellow) with 3-nitrophthalic, 4-nitrophthalic and 5-nitroisophthalic acids

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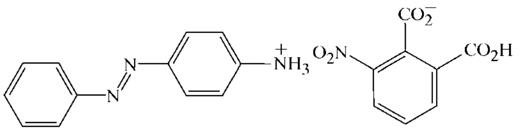
Received 19 September 2007
Accepted 15 January 2008
Online 9 February 2008

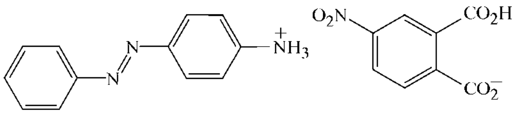
The structures of the anhydrous 1:1 proton-transfer compounds of the dye precursor aniline yellow [4-(phenyldiazenyl)aniline], namely isomeric 4-(phenyldiazenyl)anilinium 2-carboxy-6-nitrobenzoate, $C_{12}H_{12}N_3^+\cdot C_8H_4NO_6^-$, (I), and 4-(phenyldiazenyl)anilinium 2-carboxy-4-nitrobenzoate, $C_{12}H_{12}N_3^+\cdot C_8H_4NO_6^-$, (II), and 4-(phenyldiazenyl)anilinium 3-carboxy-5-nitrobenzoate monohydrate, $C_{12}H_{12}N_3^+\cdot C_8H_4NO_6^-\cdot H_2O$, (III), have been determined at 130 K. In (I) the cation has longitudinal rotational disorder. All three compounds have substructures comprising backbones formed through strong head-to-tail carboxyl–carboxylate hydrogen-bond interactions [graph set *C*(7) in (I) and (II), and *C*(8) in (III)]. Two-dimensional sheet structures are formed in all three compounds by the incorporation of the 4-(phenyldiazenyl)anilinium cations into the substructures, including, in the cases of (I) and (II), infinite H—N—H to carboxylate O—C—O group interactions [graph set *C*(6)], and in the case of (III), bridging through the water molecule of solvation. The peripheral alternating aromatic ring residues of both cations and anions give only weakly π-interactive step features which lie between the sheets.

Comment

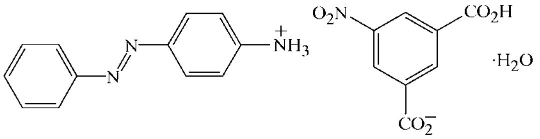
Aniline yellow [4-(phenyldiazenyl)aniline or *p*-aminodiazenylbenzene] is used as an intermediate in the manufacture of acid yellow and diazo dyes and its salts are used in dyeing (O'Neil, 2001). The structures of proton-transfer compounds of aniline yellow are not common in the literature, being limited to 1:1 salts with oxalic acid (Mahmoudkhani & Langer, 2001*b*), phenylphosphonic acid (Mahmoudkhani & Langer, 2002*a*) and butane-1,4-diphosphonic acid (Mahmoudkhani & Langer, 2002*b*), and the hydrochloride (Mahmoudkhani & Langer, 2001*a*). The structure of the hydrochloride has previously been determined from powder diffraction data (Yatsenko *et al.*, 2000), demonstrating an application of this method for structural elucidation in compounds such as dyes which generally have poor crystallinity. In this compound, the diazenyl group is protonated, whereas in the oxalate, the phenylphosphonate and the butane-1,4-diphosphonate, the aniline group is protonated. We have also confirmed the presence of the azonium group rather than the anilinium group in the intense red–black crystalline salts of aniline yellow with the strong organic acids 5-sulfosalicylic acid and picric acid (Smith *et al.*, 2008). With the hydrochloride, the absorption maximum is shifted bathochromically by 850 cm^{-1} from that of the ethanolic solution of the salt (Yatsenko *et al.*, 2000).



(I)



(II)



(III)

Our attempted 1:1 stoichiometric reaction of 4-(phenyldiazenyl)aniline with a number of carboxylic acids in aqueous ethanol generally gave no new products, but with the isomeric

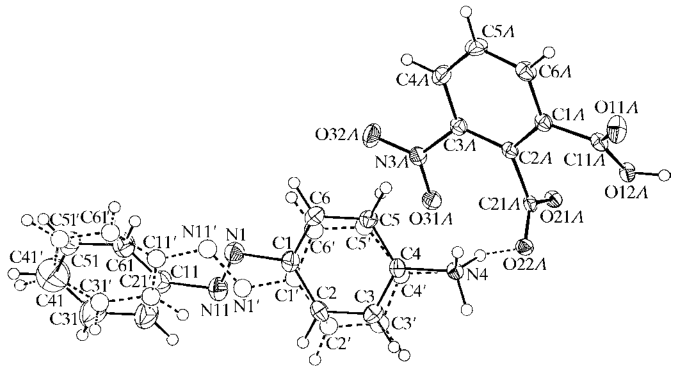


Figure 1
The molecular configuration and atom-numbering scheme for the 4-(phenyldiazenyl)anilinium cation and 2-carboxy-6-nitrobenzoate anion in (I). Displacement ellipsoids of the major-occupancy atoms are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The inter-ion hydrogen bond is shown as a dashed line. The longitudinal rotationally disordered isotropic atoms of the cation [N1′, N11′, C1′–C6′, C11′–C61′ and their attached H atoms; site-occupancy factor = 0.225 (8)] are also joined by dashed lines.

DOI: 10.1107/S0108270108001595

3- and 4-nitrophthalic acids, good crystals of the anhydrous proton-transfer compounds 4-(phenyldiazenyl)anilinium 2-carboxy-6-nitrobenzoate, (I), and 4-(phenyldiazenyl)anilinium 2-carboxy-4-nitrobenzoate, (II), were obtained. With the third isomeric acid, 5-nitroisophthalic acid, the hydrated salt 4-(phenyldiazenyl)anilinium 3-carboxy-5-nitrobenzoate monohydrate, (III), was obtained. The crystals of (I) and (II) are orange–yellow, while (III) is red, suggesting that all were anilinium rather than azonium salts (which are typically dark red–black). The aim of this investigation was to confirm the presence of the anilinium species in each compound and to look for a common structural feature which favours the hydrogen phthalates for the formation of stable crystalline proton-transfer products with aniline yellow.

Although the aniline group is protonated in all three compounds, in (I) it is the 2-carboxylic acid group of 3-nitrophthalic acid which is deprotonated (Fig. 1). This is also the case in other acid 3-nitrophthalate salts (Glidewell *et al.*, 2003, 2005; Smith *et al.*, 2007). With (II) it is the 1-carboxylic acid group that is deprotonated (Fig. 2). The hydrated cation and anion species in (III) are shown in Fig. 3. It should also be noted that the 4-(phenyldiazenyl)anilinium cation in (I) shows a 0.799 (7):0.201 (7) longitudinal rotational disorder, similar to that which has been observed in an investigation of the structure of the parent aniline yellow (Smith *et al.*, 2008).

In each of compounds (I)–(III), the anilinium group displays inter-species hydrogen bonding (Tables 1–3), resulting in two-dimensional sheet structures (Figs. 4–7). Similar two-dimensional structures are also found in the other aminium salts of aniline yellow (Mahmoudkhani & Langer, 2001*b*, 2002*a*,*b*). A feature of the hydrogen bonding in all three compounds is the presence of a substructure formed through strong head-to-tail carboxyl–carboxylate O—H⋯O interactions [graph set *C*(7) in (I) and (II), and *C*(8) in (III); Etter *et al.*, 1990], with O⋯O separations of 2.5794 (15), 2.480 (3), 2.536 (4) Å for (I)–(III), respectively. These substructures (best seen in Fig. 6) incorporate the anilinium cations and, in the case of (III), additionally the water molecule of solvation, giving the sheet structures. With (I) and (II), the heteromeric interactions include similar *C*(6) infinite linear extensions involving both O-atom acceptors of the carboxylate group of the anion [atoms O21 and O22 in (I), and atoms O11 and O12 in (II)] linked through two anilinium H atoms of the cation. These extend down the *c*-axial direction in (I) and the *a*-axial direction in (II) (see Figs. 4 and 5). With (III), the water molecule is central in the extension, acting in a bridging capacity as a dual donor linking separate anion carboxyl groups *via* atom O12*A*, and as a dual acceptor linking separate cation anilinium groups (see Fig. 7). The peripheral alternating cation and the anion aromatic ring residues form step features which lie between the sheets (see Figs. 4, 5 and 7). There are no hydrogen-bonding or π–π interactions between these residues; both the nitro O and the diazenyl N

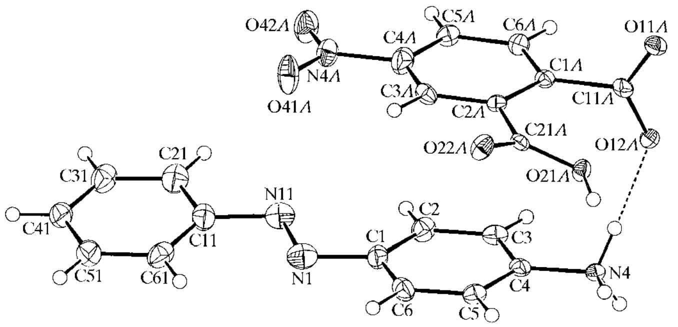


Figure 2
The molecular configuration and atom-numbering scheme for the 4-(phenyldiazenyl)anilinium cation and 2-carboxy-4-nitrobenzoate anion in (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates an inter-ion hydrogen bond.

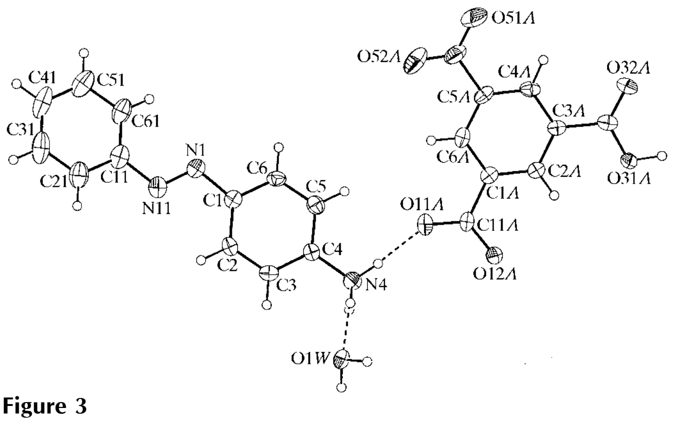


Figure 3
The molecular configuration and atom-numbering scheme for the 4-(phenyldiazenyl)anilinium cation, the 3-carboxy-5-nitrobenzoate anion and the water molecule of solvation in (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the inter-species hydrogen bonds.

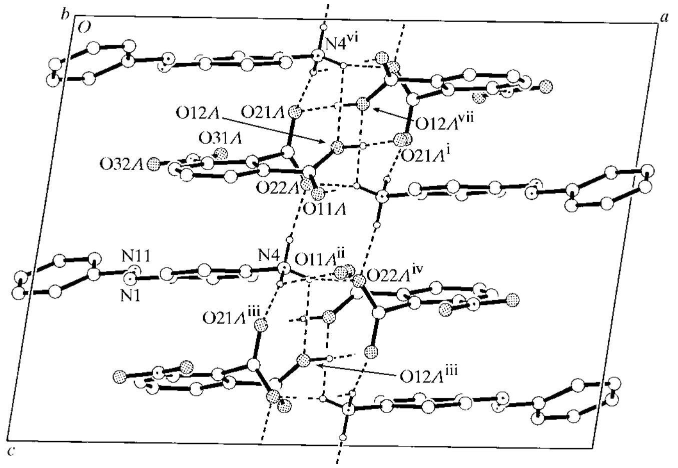


Figure 4
The *C*(6) hydrogen-bonded cation–anion extension in (I), viewed down the *b*-axial direction. The disordered portion of the cation has been omitted, as have H atoms not involved in these interactions. Hydrogen bonding is indicated by dashed lines. [Symmetry codes: (vi) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $x, y - \frac{1}{2}, -z + \frac{1}{2}$; for other symmetry codes, see Table 1.]

atoms are unassociated, with a minimal number of aromatic C—H···O associations, but with weak π–π aromatic ring interactions. In all three compounds, these take the form of partial ring overlap, in (I) and (II) between cation ring 1 (C1–C6) and anion ring 2 (C1*A*–C6*A*) [$Cg1\cdots Cg2$ = 3.7310 (13) and 3.7701 (19) Å, respectively; *Cg* are the ring centroids], while in (III) the interactions are cation–cation [$Cg1\cdots Cg1$ = 3.796 (3) Å] and anion–anion [$Cg2\cdots Cg2$ = 3.883 (3) Å].

With the cation species, the two aromatic rings are expected to be essentially coplanar, as has been found in the structures of the other aniline yellow compounds (Mahmoudkhani & Langer, 2001*a*,*b*, 2002*a*,*b*). The torsion angles C6—C1—N1—N11 and C21—C11—N11—N1 are 164.2 (2) and 169.1 (3)°, respectively, in (I), and −173.8 (4) and −167.4 (5)°, respectively, in (III), compared with 166.0 (3) and −173.7 (3)°, respectively, for the ordered molecular part of the cation in (I). With 3-nitrophthalate anions, it is more usual for the sterically encumbered 2-carboxylate group to be rotated significantly out of the plane of the benzene ring compared with the 1-carboxylic acid group. The associated torsion angles C1*A*—C2*A*—C21*A*—O22*A* [81.36 (17)°] and C2*A*—C1*A*—C11*A*—O11*A* [−152.97 (15)°] in (I) reflect this. With the absence of any hydrogen bonding associated with the nitro group in the structure, this group is almost coplanar with the benzene ring [torsion angle C2*A*—C3*A*—N3*A*—O32*A* = 175.40 (14)°]. The three equivalent torsion angles found in guanidinium 2-carboxy-6-nitrobenzoate monohydrate (Smith *et al.*, 2007) are 101.2 (2), 173.3 (2) and 151.2 (2)°, respectively. With (II), there are fewer steric constraints except those associated with the *ortho*-related carboxyl groups [corresponding torsion angles = 160.9 (3), −82.4 (3) and −176.4 (3)°], while in (III), the anion is essentially planar [torsion angles = −176.5 (4), −173.5 (4) and −174.1 (5)°]. This is also the case in 5-nitroisophthalic acid (Colapietro *et al.*, 1984) and its polymorphic monohydrate structures (Mahapatra *et al.*, 1999; Saleh *et al.*, 2006). With (III), there is also a short intramolecular aromatic C—H···O$_{\rm carboxyl}$ association [C2···O11*A* = 2.733 (5) Å].

It may be concluded that the hydrogen phthalate cations in the structures considered in this work have a strong influence on the molecular assembly process, with their inherent ability to form primary substructures through head-to-tail hydrogen-bonding associations. The presence of the anilinium group rather than the azonium group in the cation (confirmed in all cases) is essential in the secondary assembly process, while the aromatic ring systems of both the phenyldiazenylanilinium cations and the hydrogen phthalate anions act as peripheral and only weakly π-associated step features.

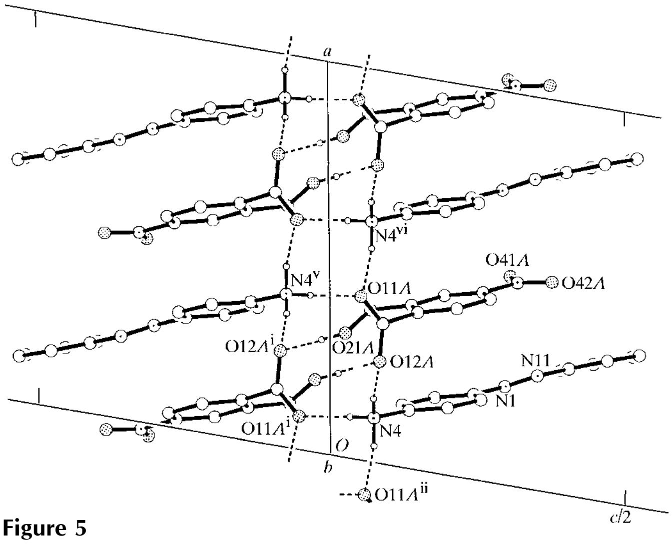


Figure 5
A view, down the *b* cell direction, of the *C*(6) chain extension in the two-dimensional hydrogen-bonded sheet structure of (II). H atoms not involved in these interactions have been omitted. [Symmetry codes: (v) *x*, *y* + 1, *z*; (vi) *x* + $\frac{1}{2}$, *y* + $\frac{1}{2}$, *z*; for other symmetry codes, see Table 2.]

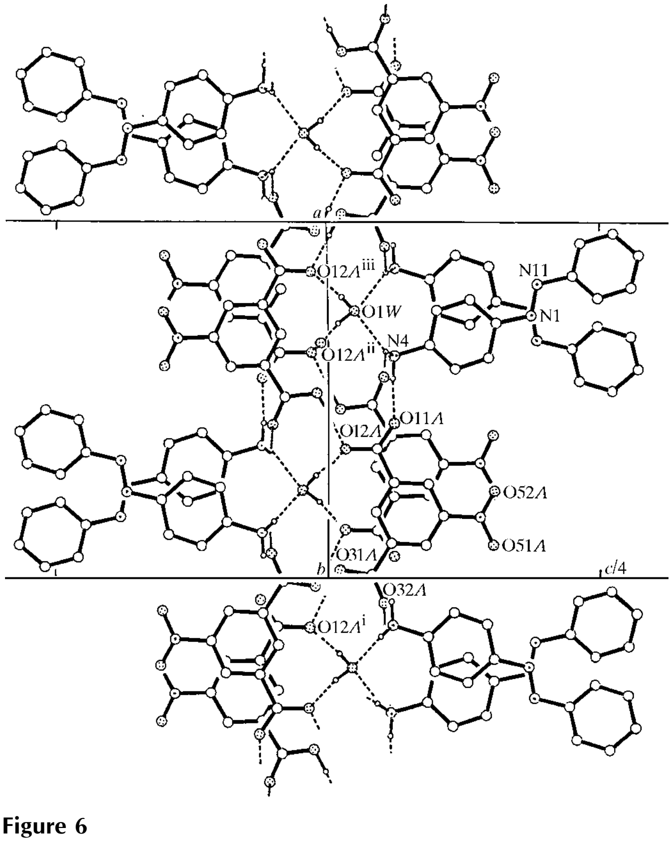


Figure 6
A view, down the *b*-axial direction of the cell, of the undulating hydrogen-bonded anion substructure and its extension in the two-dimensional hydrogen-bonded sheet structure of (III). H atoms not involved in these interactions have been omitted. For symmetry codes, see Table 3.

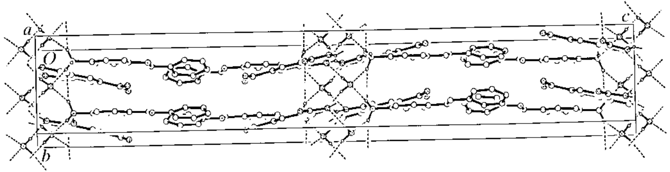


Figure 7
The unit cell of (III), viewed down the approximate *a* cell direction, showing the water bridges in the two-dimensional sheets at *z* = 0 and $\frac{1}{2}$, and the interstitial cation–anion aromatic ring step features.

Experimental

Compounds (I)–(III) were synthesized by heating together for 10 min under reflux 1 mmol quantities of 4-(phenyldiazenyl)aniline and, respectively, 3-nitrophthalic acid, 4-nitrophthalic acid and 5-nitroisophthalic acid in ethanol–water (80%, 50 ml). Compounds (I) (m.p. 441 K) and (II) (m.p. 512–513 K) were obtained as orange–yellow needles after partial room-temperature evaporation of the solvents, while (III) was obtained as red needle prisms (m.p. 393 K).

Compound (I)

Crystal data

$C_{12}H_{12}N_3^+ \cdot C_8H_4NO_6^-$
$M_r = 408.37$
Monoclinic, $P2_1/c$
$a = 17.873$ (2) Å
$b = 7.9729$ (10) Å
$c = 13.3054$ (16) Å
$\beta = 98.198$ (2)°

$V = 1876.6$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 130$ (2) K
0.55 × 0.30 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.88$, $T_{max} = 0.99$

9511 measured reflections
3306 independent reflections
2888 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.100$
$S = 1.04$
3306 reflections
320 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O12A—H12A···O21A^{i}	0.94 (2)	1.64 (2)	2.5794 (15)	175 (2)
N4—H42···O11A^{ii}	0.91 (2)	2.50 (2)	2.8399 (18)	102.8 (13)
N4—H42···O21A^{iii}	0.91 (2)	1.98 (2)	2.8768 (17)	167.7 (19)
N4—H43···O22A^{iv}	0.98 (2)	1.87 (2)	2.8194 (17)	162.3 (19)
N4—H43···O12A^{iii}	0.98 (2)	2.53 (2)	2.9164 (17)	103.7 (14)
N4—H44···O22A	0.94 (2)	1.81 (2)	2.7250 (16)	161.7 (15)
C6A—H6A···O31A^{v}	0.95	2.41	3.182 (2)	138

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

Compound (II)

Crystal data

$C_{12}H_{12}N_3^+ \cdot C_8H_4NO_6^-$
$M_r = 408.37$
Monoclinic, $C2$
$a = 12.950$ (3) Å
$b = 7.5571$ (18) Å
$c = 19.364$ (5) Å
$\beta = 100.371$ (5)°

$V = 1864.1$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 130$ (2) K
0.45 × 0.05 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.98$, $T_{max} = 0.99$

4865 measured reflections
1766 independent reflections
1564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.096$
$S = 1.04$
1766 reflections
270 parameters

1 restraint
H-atom parameters not refined
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O21A—H21A···O12A^{i}	0.90	1.58	2.480 (3)	179
N4—H42···O11A^{ii}	0.99	2.46	2.902 (3)	107
N4—H42···O22A^{iii}	0.99	1.93	2.885 (3)	162
N4—H43···O11A^{i}	0.92	1.92	2.835 (3)	179
N4—H44···O12A	0.92	1.90	2.809 (3)	172
C6—H6···O12A^{iv}	0.93	2.46	3.205 (4)	138

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

Compound (III)

Crystal data

$C_{12}H_{12}N_3^+ \cdot C_8H_4NO_6^- \cdot H_2O$
$M_r = 426.38$
Orthorhombic, $Pbca$
$a = 14.0965$ (15) Å
$b = 6.7602$ (7) Å
$c = 43.091$ (5) Å

$V = 4106.4$ (8) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 130$ (2) K
0.50 × 0.15 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
20144 measured reflections

3612 independent reflections
2720 reflections with $I > 2\sigma(I)$
$R_{int} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.085$
$wR(F^2) = 0.211$
$S = 1.22$
3612 reflections
304 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
O31A—H31A···O12A^{i}	0.98 (7)	1.58 (7)	2.536 (4)	164 (7)
O1W—H1W···O12A^{ii}	0.88 (5)	1.95 (5)	2.830 (5)	173 (4)
O1W—H2W···O12A^{iii}	0.97 (8)	1.98 (9)	2.939 (5)	170 (8)
N4—H42···O1W	0.84 (6)	1.98 (5)	2.821 (6)	173 (5)
N4—H43···O1W^{iv}	0.90 (5)	2.26 (6)	2.977 (6)	137 (5)
N4—H43···O32A^{v}	0.90 (5)	2.27 (6)	3.005 (6)	138 (6)
N4—H44···O11A	0.92 (6)	1.82 (6)	2.733 (6)	174 (4)
C3—H3···O32A^{vi}	0.93	2.38	3.278 (6)	163
C5—H5···O11A	0.93	2.59	3.279 (6)	131

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

The atoms of the disordered phenyldiazenylanilinium cation in (I) (indicated by primed atom labels) were generally located by difference methods and the ring atoms were refined as a fixed group with their common site occupancy determined by least-squares refinement [0.225 (8)]. These atoms were refined isotropically. H atoms potentially involved in hydrogen-bonding interactions in compounds (I)–

(III) were located by difference methods and their positional and isotropic displacement parameters were refined. However, because of the poor data-to-refined-parameter ratio in (II), these atoms were constrained in the final refinement cycles. Other H atoms for all three compounds were included in calculated positions (C—H = 0.93–0.95 Å) and treated as riding, with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(C).

For all three compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the School of Physical and Chemical Sciences, Queensland University of Technology, the School of Biomolecular and Physical Sciences, Griffith University, and the School of Chemistry, University of Melbourne.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3114). Services for accessing these data are described at the back of the journal.

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