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Phenyl-ring rotational disorder in the two-dimensional hydrogen-bonded structure of the 1:1 proton-transfer salt of the diazo-dye precursor 4-(phenyldiazenyl)aniline (aniline yellow) with L-tartaric acid

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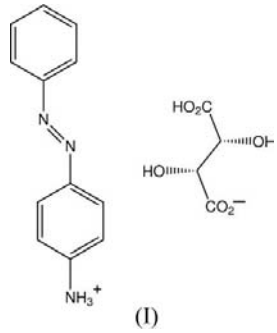
In the structure of the 1:1 proton-transfer compound from the reaction of L-tartaric acid with the azo-dye precursor aniline yellow [4-(phenyldiazenyl)aniline], namely 4-(phenyldiazenyl)anilinium (2*R*,3*R*)-3-carboxy-2,3-dihydroxypropanoate, $C_{12}H_{12}N_3^+\cdot C_4H_5O_6^-$, the asymmetric unit contains two independent 4-(phenyldiazenyl)anilinium cations and two hydrogen L-tartrate anions. The structure is unusual in that all four phenyl rings of the two cations have identical rotational disorder with equal occupancy of the conformations. The two hydrogen L-tartrate anions form independent but similar chains through head-to-tail carboxyl–carboxylate O—H···O hydrogen bonds [graph set $C(7)$], which are then extended into a two-dimensional hydrogen-bonded sheet structure through hydroxy O—H···O hydrogen-bonded links. The anilinium groups of the 4-(phenyldiazenyl)anilinium cations are incorporated into the sheets and also provide internal hydrogen-bonded extensions, while their aromatic tails are layered in the structure without significant association except for weak π–π interactions [minimum ring centroid separation = 3.844 (3) Å]. The hydrogen L-tartrate residues of both anions exhibit the common short intramolecular hydroxy–carboxylate O—H···O hydogen bonds. This work provides a solution to the unusual disorder problem inherent in the structure of this salt, as well as giving another example of the utility of the hydrogen tartrate anion in the generation of sheet substructures in molecular assembly processes.

Comment

The diazo-dye precursor aniline yellow [4-(phenyldiazenyl)-aniline or *p*-aminoazobenzene, PAZAN] has provided a number of structure types among its compounds with carboxylic acids, the majority of these being proton-transfer salts with aromatic acids (Smith *et al.*, 2009), particularly the stronger nitro-substituted analogues. With most of these the aniline group of the PAZAN molecule is protonated, giving orange–red crystalline compounds, examples being the 1:1 salts with the isomeric 3- and 4-nitrophthalic and 5-nitroisophthalic acids (Smith *et al.*, 2008). However, with 3,5-dinitrobenzoic acid (DNBA), no proton transfer occurs, giving instead a PAZAN–bis(DNBA) dimer adduct (Smith *et al.*, 2009). Only with the stronger aromatic sulfonic acids does diazenyl-group protonation occur, giving red–black crystalline products, *e.g.* the 5-sulfosalicylate salt, while in the structure of the unusual dichroic red to red–black salt with benzenesulfonic acid (Smith *et al.*, 2009) both aniline- and diazenyl-protonated species co-exist. The distinctive colour allows qualitative recognition of the nature of the salt which, in the case of the hydrochloride, is purple–black with a metallic sheen (Yatsenko *et al.*, 2000; Mahmoudkhani & Langer, 2001*a*).



(I)

Our general observation through experimentation has been that crystalline proton-transfer salts of either type from the reaction of PAZAN with most aliphatic carboxylic acids are rare, with the only reported structure of a PAZAN salt with an aliphatic acid being the oxalate (Mahmoudkhani & Langer, 2001*b*). A requirement is that the acid itself be capable of forming a stable hydrogen-bonded substructure with which the protonated anilinium group of the cation may interact, such as is the case with the nitrophthalates. An acid which has such properties is the diprotic L-tartaric acid, which as the hydrogen tartrate has proven utility in the formation of crystalline salts of Lewis bases. Much of the research on this acid has been directed towards the synthesis of stable Lewis base salts, mainly hydrogen L-tartrates having inherent chirality and hence potential for nonlinear optical applications (Aakeröy *et al.*, 1992, 2004; Kadirvelraj *et al.*, 1995). The reported structures of such salts include a number of anilinium hydrogen L-tartrates, *e.g.* with 4-carboxyaniline (*p*-aminobenzoic acid) (Athimoolam & Natarajan, 2007), both 3- and 4-methoxyaniline (*m*- and *p*-anisidine) (Kadirvelraj *et al.*, 1998), and 4-chloroaniline (Smith *et al.*, 2007). We therefore carried out the 1:1 stoichiometric reaction of L-tartaric acid with aniline yellow in an ethanol–water solvent mixture, providing minor orange–red crystals of 4-(phenyldiazenyl)anilinium hydrogen (2*R*,3*R*)-tartrate, (I), the structure of which is reported here.

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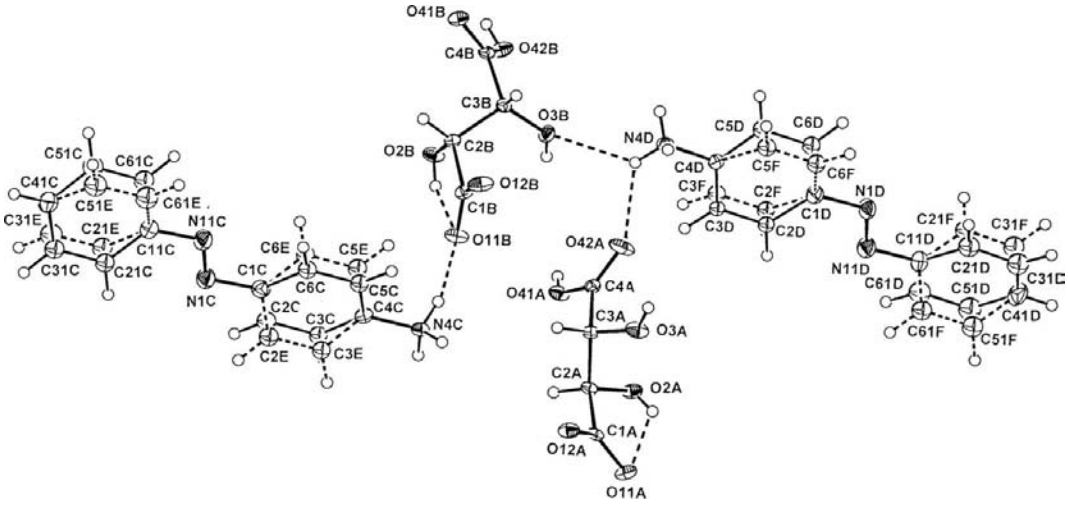

Figure 1
The molecular configurations and atom-numbering schemes for the two hydrogen L-tartrate anions (*A* and *B*) and the two 4-(phenyldiazenyl)anilinium cations in the asymmetric unit of (I). Within the four equally occupied rotationally disordered components of the two cations (rings *C*/*E* and *D*/*F*), atoms C2/C3/C5/C6 and C21/C31/C51/C61 are isotropic, while all other non-H atoms are shown as 40% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Inter-species dashed lines indicate hydrogen bonds.

In (I), as qualitatively expected from the colour of the crystal, the aniline group is protonated rather than the diazenyl group (Fig. 1). The structure obtained from diffraction data acquired at room temperature showed a generally ordered structure, except for exceptionally large unidirectional U_{22} displacement parameters for all non-axially located C atoms of all four phenyl rings of the two PAZAN molecules in the asymmetric unit of the triclinic unit cell. The diffraction data were therefore re-collected at 200 K, but the same disorder problem was evident although marginally reduced.

All four phenyl rings of the two cations (*A* and *B*) in the asymmetric unit show almost identical rotational disorder about the C1···C4 ring axial lines with equal occupancy of the conformations (Fig. 1). The presence of identical axial rotational disorder in the phenyl rings was readily recognized from residual difference electron-density analyses, in which the U_{22} components of all four peripheral ring C atoms (C2/C3/C5/C6) were up to eight times greater than the typical values for the other two axial atoms (C1 and C4) (maximum value = 0.227 Å^2 for atom C6*C*, *cf.* 0.031 Å^2 for C1*C*). This rotational disorder was modelled as two equivalent 0.50 occupancy rings, *viz*. *C* and *E* [C1*C*–C6*C* and C1*C*/C2*E*/C3*E*/C4*C*/C5*E*/C6*E*], and *D* and *F* [C1*D*–C6*D* and C1*D*/C2*F*/C3*F*/C4*D*/C5*F*/C6*F*]. The peripheral C atoms of the *E* and *F* components were subsequently refined isotropically, with U_{iso} values ranging from 0.0186 (11) to 0.0384 (15) Å^2 (C51*D*).

In the crystal structure of (I), the two independent hydrogen L-tartrate anions (*A* and *B*) form separate head-to-tail hydrogen-bonded chains through carboxyl–carboxylate acid O—H···O interactions of graph set *C*(7) (Etter *et al.*, 1990), which are characteristic of many hydrogen tartrate structures (Aakeröy *et al.*, 2004; Smith & Wermuth, 2010). These duplex chains lie mutually parallel and extend along the *b* axial direction, and interact through hydroxy–carboxyl O—H···O hydrogen bonds (Table 1) to give sheet substructures (Fig. 2). It has previously been noted (Athimoolam & Natarajan, 2007) that these duplex chains are often present in structures having two independent hydrogen tartrate anions in the asymmetric unit, such as is found in (I). The anilinium groups of the cations are incorporated peripherally into the substructure of (I), giving hydrogen-bonding associations with carboxyl and hydroxyl O-atom acceptors. The sheets extend down the *a* direction in the unit cell (Fig. 3), giving a two-dimensional structure. The diazo aromatic ring residues of the cations are layered in the structure, with no associations other than weak π–π interactions [minimum ring centroid separation = 3.844 (3) Å for rings C1*C*–C6*C* and C1*D*–C6*D*].

The anions in (I) have conformational features similar to those found in other 1:1 proton-transfer compounds of L-tartaric acid. These include the presence of the common intramolecular hydroxy–carboxylate O—H···O hydrogen bond [O···O = 2.601 (3) (*A*) and 2.599 (3) Å (*B*)], and the

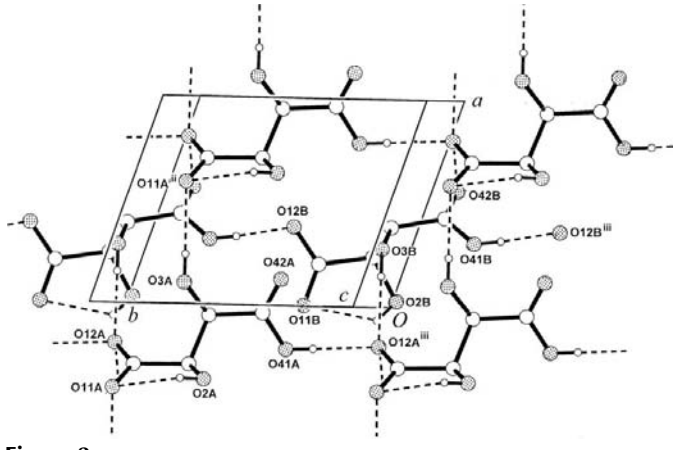

Figure 2
Part of the hydrogen-bonded sheet substructure in (I), showing the interlinked duplex *C*(7) *A* and *B* hydrogen tartrate chains, and extensions along the *a* cell direction in the two-dimensional sheet substructure of (I). The 4-(phenyldiazenyl)anilinium cations have been omitted. For symmetry codes, see Table 1.

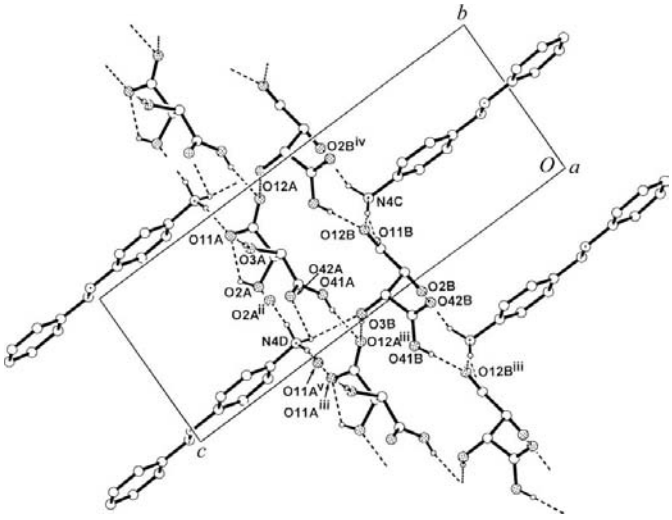

Figure 3
The structure of (I), viewed down the sheets, with the 4-(phenyldiazenyl)anilinium cations inserted into the hydrogen tartrate substructure. Only the *C* and *D* ring components are shown. H atoms not involved in these interactions have been omitted. For symmetry codes, see Table 1.

inter-hydroxy group O2—C2—C3—O3 torsion angles [−72.1 (2) (*A*) and −62.1 (2)° (*B*)], which compare with values of −61.7 (7) and −69.5 (6)° found for the two independent hydrogen L-tartrate anions in the structure of the 4-chloroanilinium salt (Smith *et al.*, 2007).

In summary, this work provides a further example of the utility of the hydrogen tartrate anion in molecular assembly, as well as solving the problem of rotational disorder inherent in this particular 4-(phenyldiazenyl)anilinium cation. Ring disorder of a different type was observed in the structure of the salt 4-(phenyldiazenyl)anilinium 2-carboxy-6-nitrobenzoate (Smith *et al.*, 2008).

Experimental

The title compound was synthesized by heating together 4-(phenyldiazenyl)aniline (1 mmol) and L-tartaric acid (1 mmol) in ethanol–water (1:1 *v*/*v*, 50 ml) for 10 min under reflux. Orange–red crystals of (I) (m.p. 467 K with decomposition) were obtained as a minor product after partial room-temperature evaporation of the solvent.

Crystal data

$C_{12}H_{12}N_3^+\cdot C_4H_5O_6^-$
M_r = 347.33
Triclinic, *P*1
a = 6.1710 (3) Å
b = 7.4134 (3) Å
c = 18.2438 (6) Å
α = 91.754 (3)°
β = 91.308 (3)°
γ = 108.135 (4)°
V = 792.33 (6) Å^3
Z = 2
Mo *Kα* radiation
μ = 0.11 mm^{-1}
T = 200 K
0.30 × 0.20 × 0.15 mm

Data collection

Oxford Gemini-S CCD detector diffractometer
Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
T_{min} = 0.874, T_{max} = 0.980
16695 measured reflections
4174 independent reflections
3593 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Table 1
Hydrogen-bond and short contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H21*A*···O11*A*	0.77	2.11	2.601 (3)	122
O2*B*—H21*B*···O11*B*	0.77	2.09	2.599 (3)	124
O2*B*—H21*B*···O42*B*^{i}	0.77	2.21	2.754 (3)	129
O3*A*—H31*A*···O11*A*^{ii}	0.80	2.07	2.872 (3)	178
O3*B*—H31*B*···O12*A*^{iii}	0.80	2.08	2.881 (3)	180
O41*A*—H41*A*···O12*A*^{iii}	0.78	1.83	2.602 (3)	170
O41*B*—H41*B*···O12*B*^{iii}	0.80	1.73	2.531 (3)	176
N4*C*—H42*C*···O2*B*^{iv}	0.95	1.87	2.779 (3)	158
N4*C*—H43*C*···O11*B*	0.85	1.91	2.724 (3)	162
N4*C*—H44*C*···O12*B*^{i}	0.89	1.91	2.785 (3)	168
N4*D*—H42*D*···O2*A*^{ii}	0.88	1.95	2.814 (3)	169
N4*D*—H43*D*···O3*B*	0.92	2.30	2.898 (3)	122
N4*D*—H43*D*···O42*A*	0.92	2.39	2.847 (3)	111
N4*D*—H44*D*···O11*A*^{v}	0.82	1.98	2.781 (3)	167

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

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.118
S = 1.01
4174 reflections
432 parameters
3 restraints
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. However, in the final refinement cycles, these atoms were constrained; see Table 1 for dimensions. Other H atoms were included at calculated positions, with aromatic C—H = 0.95 Å and aliphatic C—H = 1.00 Å, and treated as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The axial rotational disorder in all four phenyl rings of the two 4-(phenyldiazenyl)anilinium cations was modelled as two equivalent 0.50 occupancy rings [average refined occupancy = 0.50 (1)], *C*/*E* (C1*C*–C6*C* and C1*C*/C2*E*/C3*E*/C4*C*/C5*E*/C6*E*) and *D*/*F* (C1*D*–C6*D* and C1*D*/C2*F*/C3*F*/C4*D*/C5*F*/C6*F*). The peripheral C atoms (*E* and *F*) were subsequently refined isotropically. Friedel pairs in the diffraction data for this light-atom structure were merged in the final cycles of refinement. The known absolute configuration for L-tartaric acid, *viz.* (2*R*,3*R*) (Bijvoet *et al.*, 1951; Lutz & Schreurs, 2008), was invoked.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); 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: FG3168). Services for accessing these data are described at the back of the journal.

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