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Mixed dicationic and monocationic benzidine species in the proton-transfer compound of benzidine with 3,5-dinitrosalicylic acid

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The crystal structure of the proton-transfer compound of 1,1'-biphenyl-4,4'-diamine (benzidine) with 3,5-dinitrosalicylic acid, *viz.* 1,1'-biphenyl-4,4'-diaminium bis(4'-amino-1,1'-biphenyl-4-aminium) tetrakis(2-carboxy-4,6-dinitrophenolate) ethanol disolvate, $C_{12}H_{14}N_2^{2+} \cdot 2C_{12}H_{13}N_2^+ \cdot 4C_7H_3N_2O_7^- \cdot 2C_2H_6O$, shows the presence of both diprotonated and monoprotonated benzidine cations. The diprotonated species lie across crystallographic inversion centres in the unit cell, while the monoprotonated species occupy general sites. All amine H atoms participate in hydrogen bonding with carboxyl, phenolate and nitro O-atom acceptors of the salicylate anions, which also participate in hydrogen bonding with the disordered ethanol solvent molecules. Significant inter-ring anion–anion and anion–monocation π–π interactions are also present, giving a three-dimensional framework structure.

Comment

3,5-Dinitrosalicylic acid (DNSA) has proved to be a particularly useful compound for the promotion of the crystallization

(I)
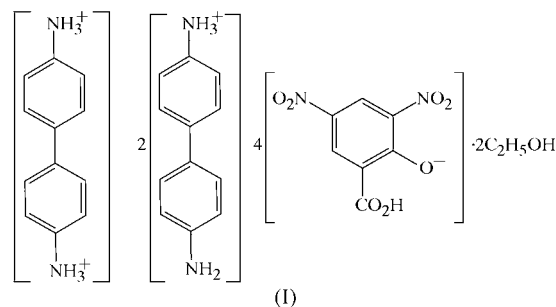
of Lewis bases as chemically stable proton-transfer compounds. We have previously determined the crystal structures of more than 40 of these compounds (Smith *et al.*, 1995, 2002, 2003, 2006), while adduct formation has been found with molecules such as urea (Smith *et al.*, 1997), 1,1-diethylurea (Smith *et al.*, 2000) and phenazine (Kumar *et al.*, 2002). These are analogous to the set of pseudopolymorphic solvates formed with DNSA, namely two monohydrates (Smith *et al.*, 1995; Kumar *et al.*, 1999), four dioxine solvates and a *tert*-butanol solvate (Kumar *et al.*, 1999). However, among the proton-transfer compounds of DNSA for which the crystal structures are known, only rarely are solvates formed, although most compounds are obtained from ethanol or
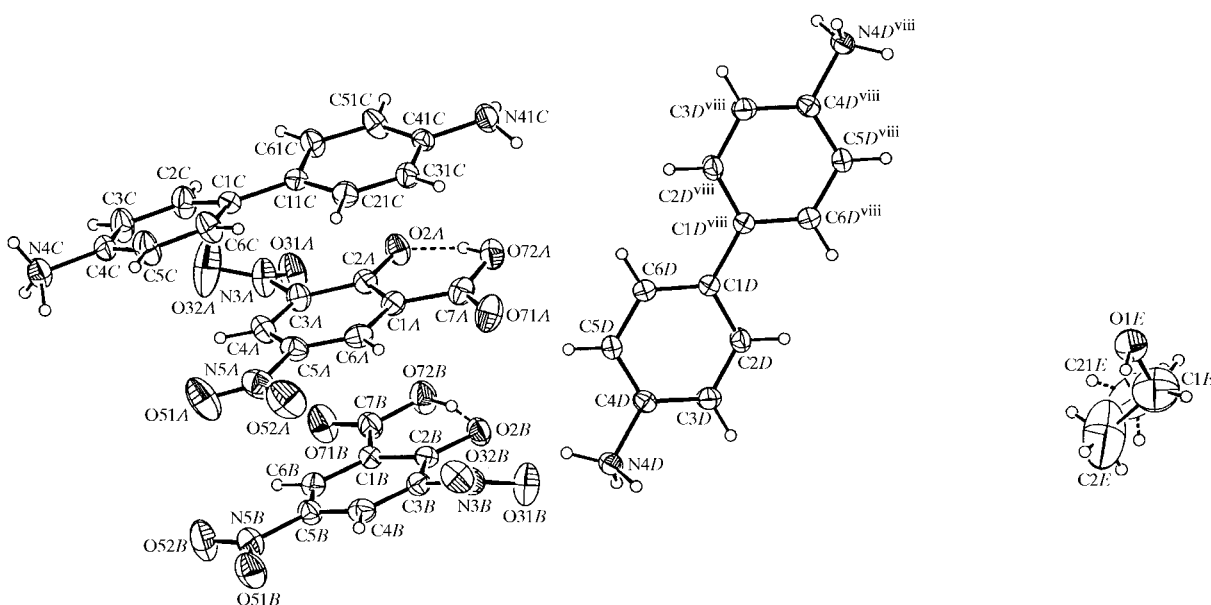

Figure 1
The molecular conformation and atom-labelling scheme for the two DNSA⁻ anions (*A* and *B*), the benzidine monocation (*C*) and dication (*D*), and the disordered ethanol molecule of solvation (*E*) in (I). The dication lies across a crystallographic inversion centre [symmetry code: (viii) $-x + 1$, $-y + 1$, $-z$]. The intramolecular hydrogen bonds in anions *A* and *B* are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

ethanol–water mixtures. The only known examples of solvates are 2-aminopyridinium–3,5-dinitrosalicylate–ethanol (4/4/1) (Smith *et al.*, 2002) and brucinium 3,5-dinitrosalicylate monohydrate (Smith *et al.*, 2006). Generally, reaction of DNSA with aniline-type Lewis bases results in the formation of 1:1 anilinium cations, which usually enhance molecular self-assembly through extensive hydrogen-bonding interactions. Seldom are π–π interactions significant in this process, occurring only among polycyclic heteroaromatic Lewis base–DNSA compounds (Smith *et al.*, 2006).

To extend the investigation of the systematics of the hydrogen bonding in proton-transfer compounds of DNSA with Lewis bases, we decided to prepare and crystallographically characterize the compounds with certain aromatic polyamines. The 1:1 and 2:1 compounds of DNSA with 1,1′-biphenyl-4,4′-diamine (benzidine, BD) were synthesized and investigated spectroscopically by Issa *et al.* (1981). However, our attempted preparation of the 1:1 compound in 80% ethanol–water solvent surprisingly gave instead the compound reported here, *viz.* the ethanol solvate of the proton-transfer compound, (I), which contains both dicationic and monocationic benzidine cation species, and corresponds to neither of the compounds reported by Issa *et al.* (1981)

Compound (I) is best described in terms of the centrosymmetric molecular unit, [BD^{2+}·2(BD^{+})·4(DNSA^{-})·2(EtOH)] (Fig. 1). The crystallographic asymmetric unit of (I) comprises two DNSA^{-} anions (anions A and B), a BD^{+} monocation (cation C), a BD^{2+} dication (cation D) lying across an inversion centre in the cell and a disordered ethanol

molecule of solvation (molecule E). The methyl group of the ethanol molecule occupies two partial sites, C2E [0.806 (17) occupancy] and C21E [0.194 (17) occupancy]. The monoprotonated C cations differ conformationally from the essentially planar doubly protonated D cations [C2C—C1C—C11C—C61C = 15.7 (3)°, *cf.* 0.2 (4)° for the equivalent angle in D]. The six aminium H atoms on cation D are involved in eight hydrogen-bonding interactions, *viz.* six to DNSA^{-} anions (carboxyl, phenol and nitro groups) and two to the unprotonated N-atom acceptors of benzidine cations C (Table 1). Included in this set is the primary linear H(aminium)$\cdots$O(carboxyl) interaction [N4D—H43$D\cdots$O71A^{vi}; symmetry code: (vi) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$], whereas the carboxyl group of the second DNSA^{-} anion is not involved in any such interaction. Instead, it forms a three-centred asymmetric $R_1^2(4)$ interaction with the hydroxy H atom of the ethanol molecule of solvation [O1E—H1$E\cdots$O71B^i/O72B^i; symmetry code: (i) $x + 1$, y, z]. Anion C participates in four interactions *via* the protonated amine group (N4C), including two to ethanol (E) molecules. The unprotonated amine group (N41C) forms only weak interactions with O atoms of the nitro groups but acts as an acceptor to a C-cation aminium H atom.

The result is a stable three-dimensional cage structure (Fig. 2), which has, in addition, significant π–π interactions between adjacent DNSA^{-} anion species [$A\cdots B$; the ring centroid separation ($Cg_A\cdots Cg_B$) is 3.605 (3) Å; the dihedral angle (α) is 4.7 (1)°] and A-anion–unprotonated C-cation species [$Cg_A\cdots Cg_C$ = 3.753 (3) Å and α = 6.2 (1)°]. Similar

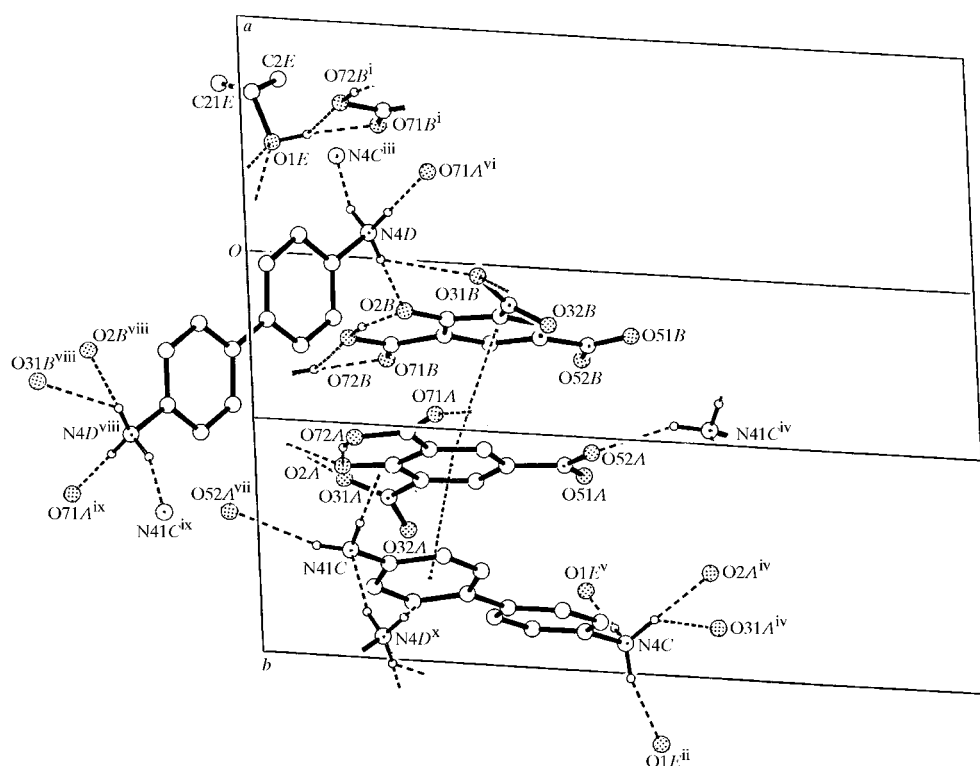**Figure 2**
A perspective view of the partial packing in the unit cell, showing hydrogen-bonding associations as dashed lines. In addition, π–π interactions are present between DNSA^{-} anions A and B, as well as between anions A and unprotonated benzidine rings C. [Symmetry codes: (ix) $-x + 1$, $-y + 2$, $-z$; (x) x, $y + 1$, z; for other symmetry codes, see Table 1 and Fig. 1.]

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interactions have been found in the structures of a number of benzidine compounds (Herbstein, 1971), where it was observed that in the formation of ternary complexes, involvement of the third species in π-bonding did not occur. This is apparent in the series of pseudopolymorphic 1:1 benzidene complexes with 7,7,8,8-tetracyano-p-quinodimethane, the solvent-free complex (Yakushi *et al.*, 1974*a*), the benzene solvate (Yakushi *et al.*, 1974*b*) and the dichloromethane solvate (Ikemoto *et al.*, 1972). These structures are somewhat analogous to the structure of (I), where, in addition, it would appear that the lack of flexibility of the protonated benzidine molecule together with the enforced π–π interactions place constraints on the availability of suitable O-atom acceptor sites on DNSA, resulting in the incorporation of the unusual molecule of ethanol in the structure. As indicated previously, ethanol or water solvent molecules are rare in DNSA proton-transfer compounds and it can only be speculated that ethanol incorporation in (I) (rather than water) has to do with a space-filling requirement.

The expected intramolecular hydrogen bond is found between the phenol and carboxylate substituent groups of the DNSA$^-$ anions (O72—H72···O2), with the H atoms located on the carboxylate O atoms. The carboxyl group is therefore essentially coplanar with the benzene ring [C6—C1—C7—O72 = 177.9 (2) (*A*) and −178.9 (3)° (*B*)], as are the nitro groups at C5 [C4—C5—N5—O52 = −177.8 (2) (*A*) and −175.7 (2)° (*B*)]. However, in both anion species, the nitro group at C3 is rotated out of the plane [C2—C3—N3—O32 = −149.5 (3) (*A*) and 147.7 (2)° (*B*)].

Experimental

The title compound was synthesized by heating 1 mmol quantities of DNSA and benzidine in 80% ethanol/water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave yellow–brown prismatic crystals of (I) (m.p. 480–483 K).

Crystal data

$C_{12}H_{14}N_2{}^{2+}\cdot 2C_{12}H_{13}N_2{}^+\cdot$	$V = 3574.6$ (7) Å^3
$4C_7H_3N_2O_7{}^-\cdot 2C_2H_6O$	$Z = 2$
$M_r = 1557.34$	$D_x = 1.447$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 18.862$ (2) Å	$\mu = 0.12$ mm^{-1}
$b = 10.5138$ (11) Å	$T = 295$ (2) K
$c = 19.081$ (2) Å	Prism, yellow–brown
$\beta = 109.154$ (2)°	$0.45 \times 0.15 \times 0.08$ mm

Data collection

Bruker SMART CCD diffractometer	8165 independent reflections
	3072 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.063$
22178 measured reflections	$\theta_{max} = 27.6°$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.049$	independent and constrained
$wR(F^2) = 0.098$	refinement
$S = 0.87$	$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$
8165 reflections	where $P = (F_o^2 + 2F_c^2)/3$
549 parameters	$(\Delta/\sigma)_{max} = 0.002$
	$\Delta\rho_{max} = 0.19$ e Å^{-3}
	$\Delta\rho_{min} = -0.15$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O72A—H72A···O2A	0.89 (3)	1.62 (3)	2.479 (3)	161 (3)
O72B—H72B···O2B	0.92 (3)	1.61 (3)	2.487 (3)	160 (3)
O1E—H1E···O71B^i	0.92 (3)	1.79 (3)	2.706 (3)	175 (3)
O1E—H1E···O72B^i	0.92 (3)	2.53 (3)	3.165 (3)	126 (3)
N4C—H41C···O1E^{ii}	0.89 (3)	2.12 (3)	2.903 (4)	147 (3)
N4C—H42C···O2A^{iii}	0.95 (4)	1.81 (4)	2.761 (3)	180 (4)
N4C—H42C···O31A^{iii}	0.95 (4)	2.50 (4)	2.870 (3)	103 (3)
N4C—H43C···O1E^{iv}	0.94 (3)	1.85 (3)	2.794 (3)	176 (2)
N4D—H41D···N41C^v	0.87 (2)	1.99 (2)	2.835 (3)	162 (2)
N4D—H42D···O2B	0.95 (3)	1.89 (3)	2.838 (3)	180 (3)
N4D—H42D···O31B	0.95 (3)	2.51 (3)	2.906 (3)	105 (2)
N4D—H43D···O71A^{vi}	0.96 (3)	1.82 (3)	2.781 (3)	180 (3)
N41C—H44C···O52A^{vii}	0.92 (3)	2.33 (3)	3.133 (4)	146 (3)
N41C—H45C···O31B^{iv}	0.87 (3)	2.49 (3)	3.356 (4)	176 (3)

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

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions (C—H = 0.93–0.96 Å), using the riding-model approximation, with U_{iso}(H) fixed at 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003).

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