Dicyclohexylaminium 4-nitroanthranilate

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.042

wR factor = 0.150

Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of dicyclohexylaminium 4-nitroanthranilate, $\text{C}_{12}\text{H}_{24}\text{N}^+\cdot\text{C}_7\text{H}_5\text{N}_2\text{O}_4^-$, shows a three-dimensional hydrogen-bonded network polymer in which the protonated amine groups of both of the independent molecules of dicyclohexylamine give similar hydrogen-bonding interactions with oxygen acceptors of four separate anthranilate carboxylate groups [$\text{N}\cdots\text{O} = 2.730(3)\text{--}2.782(2) \text{ \AA}$]. Secondary centrosymmetric peripheral hydrogen-bonding linkages involve the amine groups of the anthranilate anions with nitro and carboxylate O-atom acceptors, while these groups are also involved in intramolecular $\text{N}-\text{H}\cdots\text{O}(\text{carboxylate})$ associations [$2.663(3)$ and $2.679(3) \text{ \AA}$].

Comment

Nitro-substituted benzoic acids such as 3,5-dinitrosalicylic acid (DNSA) ($\text{p}K_a = 2.2$) readily protonate the nitrogen functional groups of most Lewis bases, giving compounds which have moderately to extensively hydrogen-bonded structures (Smith, Wermuth *et al.*, 2002; Smith *et al.*, 2003). 4-Nitroanthranilic acid (4-NAA; $\text{p}K_a = 3.9$) is slightly weaker than DNSA but similar protonation of Lewis bases might be expected. However, structures of proton-transfer compounds with 4-NAA are not common. We have previously prepared and reported the structure of only one such compound, that of ethylenediaminium 4-nitroanthranilate dihydrate [$(\text{EN})^{2+}\cdot 2(4\text{-NAA})^-\cdot 2\text{H}_2\text{O}$] (Smith *et al.*, 2002), in which both amine functional groups of the EN molecule ($\text{p}K_{a1} = 6.9$ and $\text{p}K_{a2} = 9.9$) are protonated and are involved in an extensive hydrogen-bonded array, giving a three-dimensional network polymer structure. We report here the crystal structure of the proton-transfer compound of 4-NAA with the secondary amine dicyclohexylamine (DCHA; $\text{p}K_a = 11.4$), (I).

The structure determination of (I) shows the presence of two independent but similar 4-nitroanthranilate anions (A and B) and two dicyclohexylaminium cations (C and D) in the asymmetric unit. Fig. 1 shows an associated pair (cation C and anion B). Each of the anion and cation pairs is conformationally and associatively similar. The 4-NAA anions are essentially planar, with both the carboxylate group and the nitro group $<10^\circ$ away from coplanarity with the benzene ring.

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Figure 1
The molecular configuration and atom-naming scheme for one of the independent associated 4-NAA anion (*B*) and DCHA cation (*C*) pairs in (I). Atoms are shown as 30% probability ellipsoids

Figure 2
Packing in the unit cell, viewed down *a*, showing hydrogen-bonding associations as broken lines.

In the case of the carboxyl group, this is due to the presence of an intramolecular hydrogen bond between an amino H and a carboxyl O atom [N2—H21...O72: 2.663 (3) Å (anion *A*) and 2.679 (3) Å (anion *B*)]. This is similar to that found in the EN compound [2.694 (2) Å; Smith Wermuth & Healy, 2002]. The inter-ring torsion angles in the DCHA cations (C2—C1—N1—C7 and C8—C7—N1—C1) are also similar [173.1 (2)/60.0 (3) and 172.3 (2)/51.4 (2)° for cations *C* and *D*, respectively].

The protonated amine group in each DCHA molecule gives two direct hydrogen-bonding associations with carboxylate O-atom acceptors of independent 4-NAA anions [N1C—H11C···O72B = 2.744 (3) Å, N1C—H12C···O71Bⁱ = 2.730 (3) Å, N1D—H12D···O72Aⁱⁱ = 2.765 (2) Å and N1D—H11D···O71Aⁱⁱⁱ = 2.782 (2) Å; symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) x, 1 + y, z; (iii) 2 - x, 1 - y, -z]. The second proton of the 4-NAA amine group is involved in peripheral hydrogen-bonding interactions, with anion A to a nitro O atom [N2A—H22A···O42B^{iv} = 3.058 (3) Å; symmetry code: (iv) 1 - x, 1 - y, -z], with anion B to a carboxylate O atom

[N2B—H22B...O71Aⁱⁱⁱ = 3.166 (3) Å]. This results in a three-dimensional network polymer (Fig. 2).

Experimental

The synthesis of the title compound, (I), was carried out by heating under reflux for 10 min 1 mmol quantities of 2-amino-4-nitrobenzoic acid (4-nitroanthranilic acid, 4-NAA) and *N*-cyclohexylcyclohexanamine (dicyclohexylamine, DCHA) in 50 ml of 80% ethanol–water. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave orange crystal masses (m.p. 394.2–395.1 K).

Crystal data

$\text{C}_{12}\text{H}_{24}\text{N}^+\cdot\text{C}_7\text{H}_5\text{N}_2\text{O}_4^-$
 $M_r = 363.45$
 Triclinic, $P\bar{1}$
 $a = 12.486(2) \text{ \AA}$
 $b = 13.1960(19) \text{ \AA}$
 $c = 12.068(2) \text{ \AA}$
 $\alpha = 98.775(14)^\circ$
 $\beta = 90.839(14)^\circ$
 $\gamma = 98.860(12)^\circ$
 $V = 1940.2(5) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.244 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.6\text{--}16.9^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 295 (2) \text{ K}$
 Block, orange
 $0.34 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction: none
 7699 measured reflections
 6830 independent reflections
 4384 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25.0^\circ$
 $h = -14 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -6 \rightarrow 14$
 3 standard reflections
 every 150 reflections
 intensity decay: 2.7%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.151$
 $S = 0.89$

6830 reflections
502 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5711P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.013$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0054 (12)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2A-H21A\cdots O72A$	0.87 (3)	1.97 (3)	2.663 (3)	135 (2)
$N2B-H21B\cdots O72B$	0.90 (2)	1.95 (3)	2.679 (3)	136 (2)
$N1C-H11C\cdots O72B$	0.90 (2)	1.84 (2)	2.744 (3)	179 (2)
$N1C-H12C\cdots O71B^i$	0.89 (2)	1.86 (2)	2.730 (3)	165 (2)
$N1D-H12D\cdots O72A^{ii}$	0.92 (2)	1.88 (2)	2.765 (2)	160 (2)
$N1D-H11D\cdots O71A^{iii}$	0.96 (3)	1.84 (3)	2.782 (2)	166 (2)
$N2B-H22B\cdots O71A^{iii}$	0.91 (3)	2.30 (2)	3.166 (3)	161 (2)
$N2A-H22A\cdots O42B^{iv}$	0.83 (3)	2.33 (3)	3.058 (3)	147 (2)
$C6A-H6A\cdots O71A$	0.95	2.44	2.774 (3)	100
$C6B-H6B\cdots O71B$	0.95	2.40	2.742 (3)	101

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

H atoms involved in hydrogen-bonding interactions [H21 and H22 (anions *A* and *B*), and H11 and H12 (cations *C* and *D*)] were located by difference methods and their positional and isotropic displacement parameters were refined. Others were included in the refinement at calculated positions as riding models (C–H = 0.95 Å), with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom. For refined H atoms, the N–H range is 0.83 (3)–0.96 (3) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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