Dicyclohexylaminium 4-nitroanthranilate

The crystal structure of dicyclohexylaminium 4-nitroanthranilate, $\text{C}_{12}\text{H}_{24}\text{N}^+\cdot\text{C}_7\text{H}_5\text{N}_2\text{O}_4^-\cdot\cdot\cdot$, shows a three-dimensional hydrogen-bonded network polymer in which the protonated amine groups of both the independent molecules of dicyclohexylamine give similar hydrogen-bonding interactions with oxygen acceptors of four separate anthranilate carboxylate groups \([\text{N} \cdot \cdot \cdot \text{O} = 2.730 (3)-2.782 (2) \text{ Å}]\). 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 N–H–O(carboxylate) associations [2.663 (3) and 2.679 (3) Å].

Comment

Nitro-substituted benzoic acids such as 3,5-dinitrosalicylic acid (DNSA) ($p_{K_a} = 2.2$) 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; $p_{K_a} = 3.9$) 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 [(EN)$_2^+$-2(4-NAA)-2H$_2$O] (Smith et al., 2002), in which both amine functional groups of the EN molecule ($p_{K_{a1}} = 6.9$ and $p_{K_{a2}} = 9.9$) 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; $p_{K_a} = 11.4$), (I).

![Structure of Dicyclohexylaminium 4-nitroanthranilate](image-url)
The protonated amine group in each DCHA molecule gives two direct hydrogen-bonding associations with carboxylate O atoms \( \text{N2} - \text{H}21\cdot\cdot\cdot\text{O71A} = 3.166 (3) \text{ Å} \). 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**

\( \text{C}_{12}\text{H}_{23}\text{N}^+\cdot\text{C}_{6}\text{H}_{4}\text{N}_{2}\text{O}_{4}^- \)

\[ Z = 4 \]

\[ D_r = 1.244 \text{ Mg m}^{-3} \]

Mo Kα radiation

Cell parameters from 25 reflections

\[ \alpha = 12.6–16.9^\circ \]

\[ \mu = 0.09 \text{ mm}^{-1} \]

\[ T = 295 (2) \text{ K} \]

Block, orange

**Data collection**

Rigaku AFC-7R diffractometer

\( \omega \cdot 20 \) scans

Absorption correction: none

7699 measured reflections

6830 independent reflections

4384 reflections with \( I > 2 \sigma(I) \)

\[ R_{	ext{int}} = 0.016 \]

H atoms treated by a mixture of independent and constrained refinement

**Refinement**

Refinement on \( F^2 \)

\[ R(F^2) = 0.151 \]

\[ wR(F^2) = 0.042 \]

\[ S = 0.89 \]

6830 reflections

502 parameters

H atoms treated by a mixture of independent and constrained refinement

**Table 1**

| Hydrogen-bonding geometry (Å, °) |
|----------------------------------|
| \( \text{D} - \text{H} \cdot \cdot \cdot \text{A} \) | \( \text{D} - \text{H} \) | \( \text{H} \cdot \cdot \cdot \text{A} \) | \( \text{D} - \cdot \cdot \cdot \text{A} \) | \( \text{D} - \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{A} \) |
|----------------------------------|
| N2A⋅H21A⋅O72A | 0.87 (3) | 1.97 (3) | 2.663 (3) | 135 (2) |
| N2B⋅H21B⋅O72B | 0.90 (2) | 1.95 (3) | 2.679 (3) | 136 (2) |
| N1C⋅H11C⋅O72B | 0.80 (2) | 1.85 (2) | 2.461 (3) | 152 (2) |
| N1D⋅H11D⋅O71A | 0.92 (2) | 1.87 (2) | 2.756 (2) | 160 (2) |
| N1D⋅H11D⋅O71A | 0.89 (2) | 1.86 (2) | 2.730 (2) | 160 (2) |
| N1D⋅H11D⋅O71A | 0.89 (2) | 1.86 (2) | 2.730 (2) | 160 (2) |
| N2B⋅H22B⋅O42B | 0.83 (3) | 2.33 (3) | 3.058 (3) | 147 (2) |
| C6A⋅H6A⋅O71A | 0.95 | 2.44 | 2.774 (3) | 100 |
| C8B⋅H8B⋅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 \( \text{H21} \) and \( \text{H22} \) (anions \( \text{A} \) and \( \text{B} \)), and \( \text{H11} \) and \( \text{H12} \) (cations \( \text{C} \) and \( \text{D} \)) 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 (\( \text{C} - \text{H} = 0.95 \text{ Å} \)), with \( U_{	ext{iso}} = 1.2U_{	ext{eq}} \) of the parent atom. For refined H atoms, the N–H range is 0.83 (3)–0.96 (3) Å.

**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 \( \alpha \), showing hydrogen-bonding associations as broken lines.
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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