

## Dicyclohexylammonium 4-nitroanthranilate

Graham Smith,<sup>a\*</sup> Urs D. Wermuth<sup>b</sup> and Peter C. Healy<sup>c</sup><sup>a</sup>School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, <sup>b</sup>Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and <sup>c</sup>School of Science, Griffith University, Nathan 4111, Australia

Correspondence e-mail: g.smith@qut.edu.au

## 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

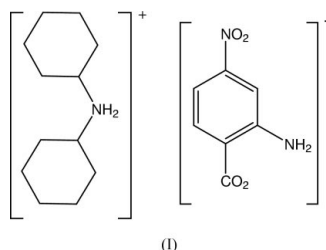
Data-to-parameter ratio = 13.6

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

The crystal structure of dicyclohexylammonium 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).

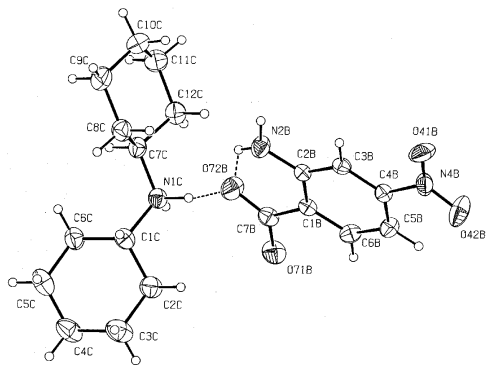


The structure determination of (I) shows the presence of two independent but similar 4-nitroanthranilate anions (A and B) and two dicyclohexylammonium cations (C and D) in the asymmetric unit. Fig. 1 shows an associated pair (cation C and anion B). Each of the anion and cation pairs is conformationally 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.

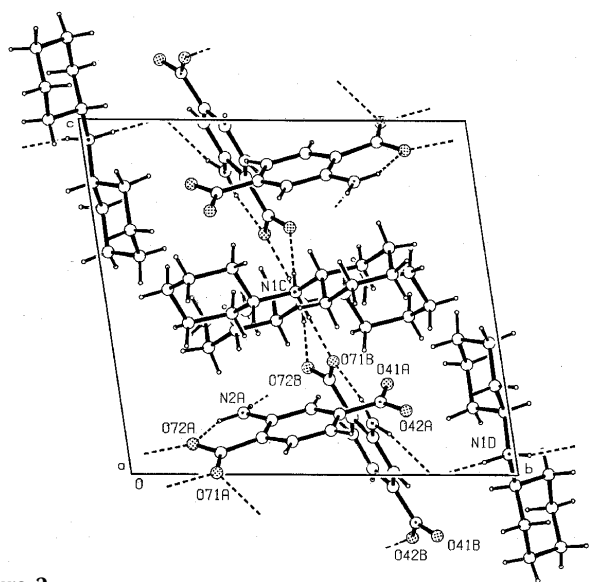
Received 18 March 2004

Accepted 24 March 2004

Online 31 March 2004



**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...O71B<sup>i</sup> = 2.730 (3) Å, N1D—H12D...O72A<sup>ii</sup> = 2.765 (2) Å and N1D—H11D...O71A<sup>iii</sup> = 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<sup>iv</sup> = 3.058 (3) Å; symmetry code: (iv) 1 - *x*, 1 - *y*, -*z*], with anion *B* to a carboxylate O atom

[N2B—H22B...O71A<sup>iii</sup> = 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

C<sub>12</sub>H<sub>24</sub>N<sup>+</sup>·C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>O<sub>4</sub><sup>-</sup>  
M<sub>r</sub> = 363.45  
Triclinic, P $\bar{1}$   
*a* = 12.486 (2) Å  
*b* = 13.1960 (19) Å  
*c* = 12.068 (2) Å  
 $\alpha$  = 98.775 (14)°  
 $\beta$  = 90.839 (14)°  
 $\gamma$  = 98.860 (12)°  
*V* = 1940.2 (5) Å<sup>3</sup>

*Z* = 4  
*D*<sub>x</sub> = 1.244 Mg m<sup>-3</sup>  
Mo K $\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta$  = 12.6–16.9°  
 $\mu$  = 0.09 mm<sup>-1</sup>  
*T* = 295 (2) K  
Block, orange  
0.34 × 0.30 × 0.20 mm

## Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ -2 $\theta$  scans  
Absorption correction: none  
7699 measured reflections  
6830 independent reflections  
4384 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.016

$\theta_{\max}$  = 25.0°  
*h* = -14 → 14  
*k* = -15 → 15  
*l* = -6 → 14  
3 standard reflections every 150 reflections  
intensity decay: 2.7%

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.042  
*wR*(*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.013$   
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$   
Extinction correction: SHELXL97  
Extinction coefficient: 0.0054 (12)

**Table 1**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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	0.90 (2)	1.84 (2)	2.744 (3)	179 (2)
N1C—H12C...O71B <sup>i</sup>	0.89 (2)	1.86 (2)	2.730 (3)	165 (2)
N1D—H12D...O72A <sup>ii</sup>	0.92 (2)	1.88 (2)	2.765 (2)	160 (2)
N1D—H11D...O71A <sup>iii</sup>	0.96 (3)	1.84 (3)	2.782 (2)	166 (2)
N2B—H22B...O71A <sup>iii</sup>	0.91 (3)	2.30 (2)	3.166 (3)	161 (2)
N2A—H22A...O42B <sup>iv</sup>	0.83 (3)	2.33 (3)	3.058 (3)	147 (2)
C6A—H6A...O71A	0.95	2.44	2.774 (3)	100
C6B—H6B...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*<sub>iso</sub> = 1.2*U*<sub>eq</sub> 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*.

The authors acknowledge financial support from the School of Physical and Chemical Sciences (Queensland University of Technology) and Griffith University.

### References

- Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN for Windows* (Version 1.06). MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Smith, G., Wermuth, U. D., Bott, R. C., Healy, P. C. & White, J. M. (2002). *Aust. J. Chem.* **55**, 349–356.
- Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2003). *Aust. J. Chem.* **56**, 707–713.
- Smith, G., Wermuth, U. D. & Healy, P. C. (2002). *Acta Cryst.* **E58**, o1088–o1090.
- Spek, A. L. (1999). *PLATON for Windows*. September 1999 Version. University of Utrecht, The Netherlands.