

The hydrogen-bonding network in *rac*-ammonium  
*trans*-2-carboxycyclohexanecarboxylateRobert T. Stibrany, Harvey J.  
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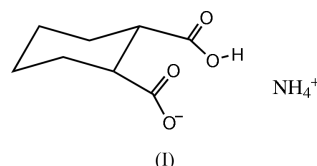
## Key indicators

Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.054  
 $wR$  factor = 0.154  
Data-to-parameter ratio = 9.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title salt,  $\text{NH}_4^+\cdot\text{C}_8\text{H}_{11}\text{O}_4^-$ , contains tetrahedrally coordinated ammonium ions and monodeprotonated anions of *rac-trans*-1,2-cyclohexanedicarboxylic acid. In the anions, carboxylic acid and carboxylate fragments are identified by their clearly differentiated C—O bond distances. The cations and anions form columns along the  $b$  axis, which are arranged in the crystal structure to give tilted, alternating hydrophobic (back-to-back cyclohexyl) and hydrophilic (ammonium, carboxylate and carboxylic acid) layers stacked along the  $a$  direction. The ammonium ion utilizes each of its four H atoms to form five hydrogen bonds with the negatively charged carboxylate O atoms. A hydrogen bond between a carboxylate O atom and the hydroxyl group of the carboxylic acid fragment completes an extensive interionic hydrogen-bonding network.

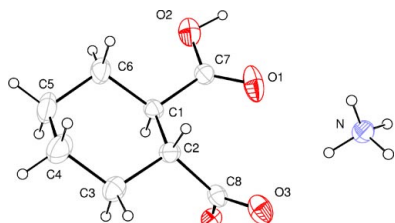
## Comment

We have been interested for some time in the synthesis of bis-chelating benzimidazoles for the purpose of binding metal ions. An important synthetic step in these studies is often the condensation of a dicarboxylic acid with two molar equivalents of a 1,2-phenylenediamine. Previously, we reported the synthesis of bisbenzimidazoles derived from a number of carboxylic acids, including malonic and tartronic (Stibrany *et al.*, 2003), diphenic (Stibrany *et al.*, 2003a, 2004), and tartaric (Stibrany *et al.*, 2003b). We report here the structure of (I), the monoammonium salt of the diacid precursor *rac-trans*-1,2-cyclohexanedicarboxylic acid, which was prepared by ammonia diffusion into an aqueous solution of the diacid.

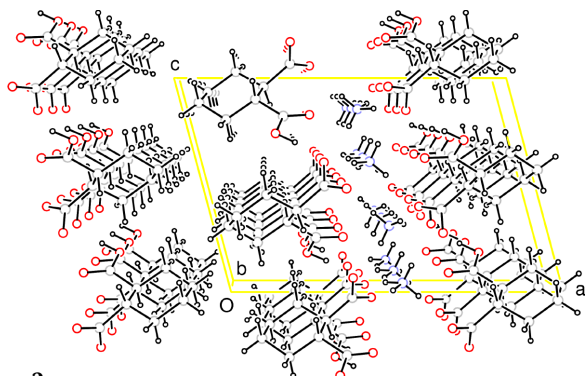


The structure of (I) contains ammonium ions and monodeprotonated anions of *rac-trans*-1,2-cyclohexanedicarboxylic acid (Fig. 1). Individual anions are chiral, while the centers of symmetry in the space group demand equal amounts of the  $R,R$  and  $S,S$  enantiomers, making the crystal a racemic mixture. In the anions, the cyclohexyl rings adopt the favored chair conformation as expected, and the carboxylic acid and carboxylate groups are clearly distinguishable. For the carboxylic acid group, double and single bonds (Table 1) are clearly delineated by their lengths, which compare favorably with those reported [1.209 (3) and 1.311 (3) Å, respectively (Kimura *et al.*, 1999), for the  $R,R$  enantiomer of the same anion]. C—O bond distances in the carboxylate group are

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**Figure 1**  
Contents of the asymmetric unit of the title salt, showing 25% probability displacement ellipsoids.



**Figure 2**  
View, along the *b* axis, of the crystal packing.

nearly equal and lie midway between the single and double C—O bond lengths in the carboxylic acid fragment, implying virtually complete electron delocalization. These lengths also compare favorably with those reported [1.231 (3) and 1.273 (3) Å] by Kimura *et al.* (1999). The ammonium N atom exhibits distorted tetrahedral coordination (Table 1) by four H atoms, as expected.

In the crystal structure, the cations and anions form columns along the *b* axis (Fig. 2), within which individual ions are related by translation; because of this, each anion column contains a given enantiomer exclusively. Anion columns related to each other by centers of symmetry and twofold screw axes in the *bc* ( $x = 0$ ) plane form zigzag bilayers with the carboxylic acid and carboxylate groups oriented towards the centers of adjacent unit cells along the *a* axis. In the *c* direction, adjacent columns exhibit alternating *R,R* and *S,S* stereochemistry. Cation columns related by the centers of symmetry and twofold screw axes in the  $x = \frac{1}{2}$  plane form a corresponding layer parallel to the *bc* plane. Viewed in this way, the structure appears as slanted, alternating hydrophobic (cyclohexyl) and hydrophilic (ammonium and carboxylic) slabs stacked along the *a* direction.

The ammonium ion and the carboxylate group are close to each other in the crystal structure, as might be expected for oppositely charged species. In addition, the ammonium ion utilizes each of its four H atoms to form a total of five hydrogen bonds (Table 2) with the O atoms (O3 and O4) of the carboxylate group. These bonds appear to complement the Coulombic interaction and help further to stabilize the structure. An additional hydrogen bond is formed between atom O4 of the carboxylate ion and the O2—H group of the carboxylic acid from a neighboring anion. The carbonyl atom O1 does not appear to participate in the hydrogen-bonding

network. Lastly, analysis suggests the possible presence of a weak intramolecular C—H···O hydrogen bond involving carboxylate atom O4 and atom C1. This interaction could provide some modest conformational stability to the carboxylate group.

## Experimental

*rac-trans*-1,2-Cyclohexanedicarboxylic acid was obtained from the Aldrich Chemical Company. The title salt was crystallized from an aqueous solution of the acid by vapor diffusion of ammonia and slow evaporation of the solution [m.p. 493 K (decomposition)], IR (KBr pellet,  $\text{cm}^{-1}$ ): 3157 (*s*), 2960 (*m*), 2853 (*m*), 1705 (*m*), 1557 (*s*), 1400 (*s*), 1309 (*m*), 1200 (*m*), 903 (*w*), 723 (*w*).

### Crystal data

$\text{NH}_4^+ \cdot \text{C}_8\text{H}_{11}\text{O}_4^-$	$D_x = 1.295 \text{ Mg m}^{-3}$
$M_r = 189.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 710 reflections
$a = 15.712 (7) \text{ \AA}$	$\theta = 2.7\text{--}21.4^\circ$
$b = 6.141 (3) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 10.464 (5) \text{ \AA}$	$T = 297 (2) \text{ K}$
$\beta = 104.96 (4)^\circ$	Plate, colorless
$V = 975.5 (8) \text{ \AA}^3$	$0.52 \times 0.28 \times 0.02 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART CCD area-detector diffractometer	1731 independent reflections
$\varphi$ and $\omega$ scans	1155 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS, Blessing, 1995)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.678$ , $T_{\text{max}} = 1.00$	$\theta_{\text{max}} = 25.1^\circ$
6692 measured reflections	$h = -18 \rightarrow 18$
	$k = -7 \rightarrow 7$
	$l = -11 \rightarrow 12$

### Refinement

Refinement on $F^2$	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0903P)^2]$
$wR(F^2) = 0.154$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1731 reflections	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
178 parameters	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

O1—C7	1.189 (3)	N—H51N	0.84 (3)
O2—C7	1.315 (3)	N—H52N	0.95 (4)
O3—C8	1.243 (3)	N—H53N	0.88 (3)
O4—C8	1.260 (3)	N—H54N	0.85 (4)
H51N—N—H52N	117 (3)	H51N—N—H54N	110 (3)
H51N—N—H53N	104 (3)	H52N—N—H54N	102 (3)
H52N—N—H53N	116 (3)	H53N—N—H54N	108 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H2O···O4 <sup>i</sup>	0.95 (3)	1.66 (3)	2.601 (3)	169 (3)
N—H51N···O3 <sup>ii</sup>	0.84 (3)	2.58 (3)	3.321 (3)	148 (2)
N—H51N···O4 <sup>ii</sup>	0.84 (3)	2.10 (3)	2.895 (3)	158 (3)
N—H52N···O4 <sup>iii</sup>	0.95 (3)	1.87 (3)	2.824 (4)	176 (3)
N—H53N···O3	0.88 (3)	1.95 (3)	2.819 (3)	168 (3)
N—H54N···O3 <sup>iv</sup>	0.86 (3)	1.96 (4)	2.806 (3)	169 (3)
C1—H1···O4	0.96 (2)	2.57 (2)	2.919 (3)	101.3 (16)

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

H atoms were located in a difference electron-density map and refined isotropically [C—H = 0.93 (4)–1.02 (3) Å, O—H = 0.95 (4) Å and N—H = 0.84 (3)–0.95 (4) Å].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE-Plus*; data reduction: *SAINTE-Plus* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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