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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1536). Services for accessing these data are described at the back of the journal.

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## Methylphenylammonium Hydrogen 2,6-Pyridinedicarboxylate at 158 K

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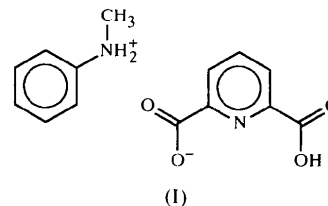
### Abstract

The hydrogen 2,6-pyridinedicarboxylate anions in methylphenylammonium hydrogen 2,6-pyridinedicarboxylate,  $C_7H_{10}N^+ \cdot C_7H_4NO_4^-$ , are linked by a hydrogen bond [ $O \cdots O = 2.472(2) \text{ \AA}$ ] into a zigzag chain; the methylphenylammonium cations are linked to the chain by four  $N \cdots O/N \cdots N$  hydrogen bonds.

### Comment

In the crystal structure of 2,6-pyridinedicarboxylic acid monohydrate, the 2,6-pyridinedicarboxylic acid molecules are linked into a linear chain through an

intermolecular hydrogen bond involving the carboxy COOH group of one molecule and the carboxy COO<sup>-</sup> group of an adjacent molecule [ $O \cdots O = 2.584(7) \text{ \AA}$ ]. The doubly-bonded carbonyl O atom of the first group and the hydroxyl O atom of the second group are linked to the water molecule, these hydrogen bonds giving rise to a sheet structure (Takusagawa *et al.*, 1973). In methylphenylammonium hydrogen 2,6-pyridinedicarboxylate, (I), the hydrogen 2,6-pyridinedicarboxylate anion is similarly linked into a chain running parallel to the *c* axis by a hydrogen bond involving the carboxy COOH group of one anion and the negatively charged carboxyl COO<sup>-</sup> group of a symmetry-related anion, but the hydrogen bond is much stronger [ $O \cdots O = 2.472(2) \text{ \AA}$ ]. The carbon–oxygen bonds in the carboxy [ $C—O = 1.310(3)$  and  $C=O = 1.216(3) \text{ \AA}$ ] and carboxyl [ $C—O = 1.283(3)$  and  $C=O = 1.242(3) \text{ \AA}$ ] groups can be differentiated into single and double bonds, with the difference in the pair of distances for the carboxy group being more marked. The ammonium cations surround the chain; one of the H atoms is linked to the pyridyl N atom and the singly-bonded O atom of the carboxyl group [ $N2 \cdots N1 = 3.074(3)$  and  $N2 \cdots O3 = 2.904(3) \text{ \AA}$ ]; the other H atom is linked to the carboxy O atom as well as to the doubly-bonded carboxyl O atom of the adjacent anion [ $N2 \cdots O1 = 2.809(3)$  and  $N2 \cdots O4 = 2.784(3) \text{ \AA}$ ].



The hydrogen-bonding distance that links the anions into a polyanionic zigzag chain is similar to that [2.484(3) Å] found in the (dimethyldithiocarbamyl)-acetate–(dimethyldithiocarbamyl)acetic acid monoanion (Ng, 1997b), as well as to that [2.448(3) Å] found in the

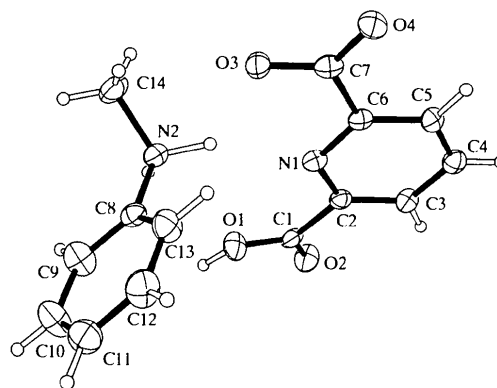


Fig. 1. ORTEP (Johnson, 1976) plot of (I) at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

trithiocarbodiglycolate–tricarbodiglycolic acid dianion (Ng, 1995). These distances are, however, much shorter than the hydrogen bond [2.710 (3) Å] that links the non-planar hydrogen oxalate anion into a helical chain in the dicyclohexylammonium salt (Ng, 1994). The hydrogen 2,6-pyridinedicarboxylate anion is flat, a conformation also adopted by the 2,6-pyridinedicarboxylate dianion in its dihydrated bis(dicyclohexylammonium) salt (Ng, 1997a).

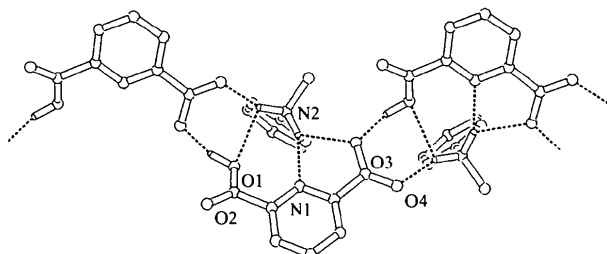


Fig. 2. *PLUTON* (Spek, 1994) plot of the hydrogen-bonded zigzag chain.

## Experimental

The compound was synthesized by neutralizing 2,6-pyridinedicarboxylic acid with an equimolar quantity of *N*-methyl-aniline in ethanol. Crystals of the compound did not diffract well at room temperature, hence necessitating low-temperature measurements.

### Crystal data

C<sub>7</sub>H<sub>10</sub>N<sup>+</sup>·C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub><sup>-</sup>  
*M<sub>r</sub>* = 274.27  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 11.834 (2) Å  
*b* = 8.841 (2) Å  
*c* = 12.889 (2) Å  
 $\beta$  = 93.41 (2)°  
*V* = 1346.1 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.353 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 21 reflections  
 $\theta$  = 4.0–12.5°  
 $\mu$  = 0.101 mm<sup>-1</sup>  
*T* = 158 (2) K  
 Triangular block  
 0.45 × 0.35 × 0.21 mm  
 Colorless

### Data collection

Siemens *P4* diffractometer  
 $\omega$  scan  
 Absorption correction: none  
 2843 measured reflections  
 2372 independent reflections  
 1167 reflections with  
 $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.052

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042  
*wR*(*F*<sup>2</sup>) = 0.071

$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

*S* = 0.737

2372 reflections

193 parameters

O- and N-bonded H atoms were located and refined; riding model for the C-bonded H atoms, with *U* = 1.5*U*<sub>eq</sub>(C)

$\Delta\rho_{\max} = 0.171 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.252 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.310 (3)	C3—C4	1.384 (3)
O2—C1	1.216 (3)	C4—C5	1.383 (3)
O3—C7	1.283 (3)	C5—C6	1.385 (3)
O4—C7	1.242 (3)	C6—C7	1.513 (3)
N1—C2	1.347 (3)	C8—C9	1.372 (3)
N1—C6	1.353 (3)	C8—C13	1.379 (3)
N2—C8	1.470 (3)	C9—C10	1.388 (4)
N2—C14	1.494 (3)	C10—C11	1.382 (4)
C1—C2	1.508 (3)	C11—C12	1.377 (4)
C2—C3	1.384 (3)	C12—C13	1.388 (4)
C2—N1—C6	117.1 (2)	C5—C6—C7	121.1 (2)
C3—N2—C14	112.4 (2)	O3—C7—O4	126.1 (2)
O1—C1—O2	125.5 (2)	O3—C7—C6	115.3 (2)
O1—C1—C2	112.9 (2)	O4—C7—C6	118.6 (3)
O2—C1—C2	121.5 (3)	C9—C8—C13	121.1 (3)
N1—C2—C1	116.2 (2)	C9—C8—N2	119.5 (2)
N1—C2—C3	123.3 (2)	C13—C8—N2	119.4 (3)
C1—C2—C3	120.5 (2)	C8—C9—C10	119.7 (3)
C2—C3—C4	119.1 (3)	C9—C10—C11	119.9 (3)
C3—C4—C5	118.2 (3)	C12—C11—C10	119.7 (3)
C4—C5—C6	119.7 (2)	C11—C12—C13	120.7 (3)
N1—C6—C5	122.5 (2)	C8—C13—C12	118.9 (3)
N1—C6—C7	116.4 (2)		

Data collection: *XSCANS* (Siemens, 1990). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1269). Services for accessing these data are described at the back of the journal.

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### 4-Benzoyl-6-(4-methoxybenzylidene)-3-phenyl-2-oxa-3-azabicyclo[3.3.0]oct-7-ene

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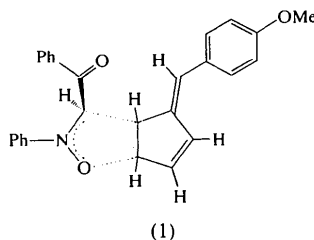
(Received 20 November 1997; accepted 30 January 1998)

#### Abstract

The title compound, C<sub>27</sub>H<sub>23</sub>NO<sub>3</sub>, consists of a fulvene–1,3-dipolar-nitrone adduct with a five-membered C<sub>3</sub>NO saturated heterocycle.

#### Comment

The 1,3-dipolarophilic reactivity of fulvenes towards some 1,3-dipoles has been studied for many years (Alder *et al.*, 1961; Houk & Luskus, 1970; Caramella *et al.*, 1971) but, to the best of our knowledge, nitrones have never been used as 1,3-dipole targets. The structure of the title compound, (1), shows that the fulvene–1,3-dipolar-nitrone reaction proceeds through the usual pathway. Cycloaddition involves one of the two fulvenic



double bonds (C2=C3 and C4=C5). The second one, equal to 1.324 (3) Å in (1), is not affected by cycloaddition. The central saturated cycle is puckered and exhibits a 'boat-like' geometry over the planar C1–C2–C3–O1 unit. The dihedral angles involving this unit with the O1–N–C1 and C2–C6 planes are equal to 37.1 (2) and 58.7 (2)°, respectively. The fulvene-

derived fragment in (1) remains almost planar, with the dihedral angle between the C2–C6 and C8–C13 planes equal to 6.6 (1)°. A perspective view of the title molecule is shown in Fig. 1.

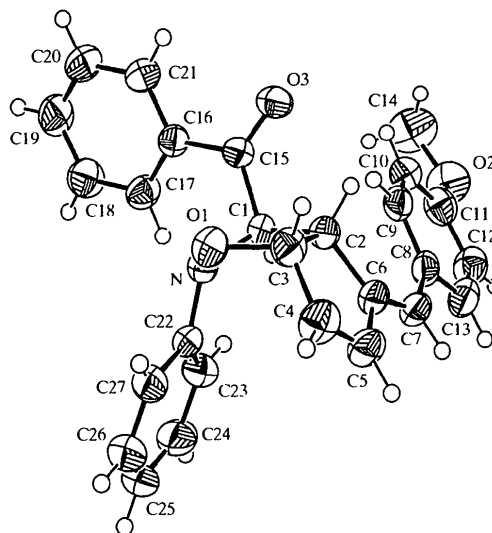


Fig. 1. View of the molecular structure of (1) showing 50% probability displacement ellipsoids.

#### Experimental

In the course of our studies on 1,3-dipolar cycloadditions, the reaction involving a fulvene and a nitrone has been carried out. A mixture of 3 mmol of 6-*p*-anisylpentafulvene and 5 mmol of nitrone were refluxed for 15 h in THF. After evaporation of the solvent, the crude oil, containing formally at least eight regio- and stereoisomers, was dissolved in ethanol and the major product, (1), was separated by thin-layer chromatography on silica gel (57% yield). Crystals of (1) suitable for X-ray measurements were grown from ethanol.

#### Crystal data

C<sub>27</sub>H<sub>23</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 409.46  
 Triclinic  
*P* $\bar{1}$   
*a* = 9.542 (5) Å  
*b* = 10.327 (6) Å  
*c* = 11.857 (9) Å  
 $\alpha$  = 114.41 (5)°  
 $\beta$  = 90.70 (5)°  
 $\gamma$  = 96.61 (5)°  
*V* = 1054.5 (11) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.290 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 8.74–18.07°  
 $\mu$  = 0.084 mm<sup>-1</sup>  
*T* = 296 (1) K  
 Irregular  
 0.25 × 0.15 × 0.15 mm  
 Pale yellow

Data collection  
 Enraf–Nonius CAD-4 diffractometer

*R*<sub>int</sub> = 0.030  
 $\theta$ <sub>max</sub> = 26.31°