

Acta Cryst. (1995). **C51**, 924–926

m-Anisidinium Dihydrogenmonophosphate

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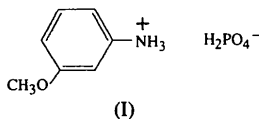
(Received 21 July 1994; accepted 12 October 1994)

Abstract

The structure of *m*-anisidinium dihydrogenmonophosphate, C₇H₁₀NO⁺·H₂PO₄⁻, is built from monophosphoric acid and *m*-anisidine units connected through hydrogen bonds. Layers of H₂PO₄⁻ anions alternate with layers of (1,3-CH₃O—C₆H₄—NH₃)⁺ organic cations parallel to the *ab* plane. Two types of hydrogen bond, O—H···O and N—H···O, ensure the cohesion and stability of the structure.

Comment

Our recent study of the anisidine–H₃PO₄ system resulted in the new organic cation monophosphate, *o*-anisidinium dihydrogenmonophosphate (Abdellahi & Jouini, 1995). In this work, we present the structure determination of a related novel compound, *m*-anisidinium dihydrogenmonophosphate (I).



The molecular packing projected along the *b* axis is shown in Fig. 1. It consists of alternating layers of organic cations and inorganic anions. Each cation is anchored by three N—H···O hydrogen bonds to three different H₂PO₄⁻ tetrahedral units and each H₂PO₄⁻ anion is in turn connected through strong O—H···O hydrogen bonds to three other anions. The geometrical features of the H₂PO₄⁻ groups are quite regular and can be compared to those observed in similar structures (Abdellahi & Jouini, 1995; Averbuch-Pouchot & Durif, 1987; Averbuch-Pouchot, Durif & Guitel, 1987; Riou, Loiseau & Ferey, 1993). The two benzene rings are planar within experimental error. The interatomic distances are in the ranges 1.363 (7)–1.393 (6) and 1.365 (7)–1.387 (6) Å, for the two molecules of the asymmetric unit, with a mean value of 1.378 Å, which is shorter than the normal aromatic bond length. The O5—C3 and O5'—C3' bond distances of 1.363 (5) and 1.366 (5) Å, respectively, are comparable to the C—O single bond length under the influence of an aromatic ring (partial double bond), e.g. 1.36 Å (*International Tables for X-ray Crystallography*, 1968, Vol. III), while the O5—C7

and O5'—C7' bond lengths of 1.415 (6) and 1.424 (6) Å, respectively, are near to the expected value of 1.43 (1) Å for a paraffinic C—O bond (*International Tables for X-ray Crystallography*, 1968, Vol. III). Twist angles between the methoxy groups and benzene rings are about 2 and 3° for the two molecules of the asymmetric unit.

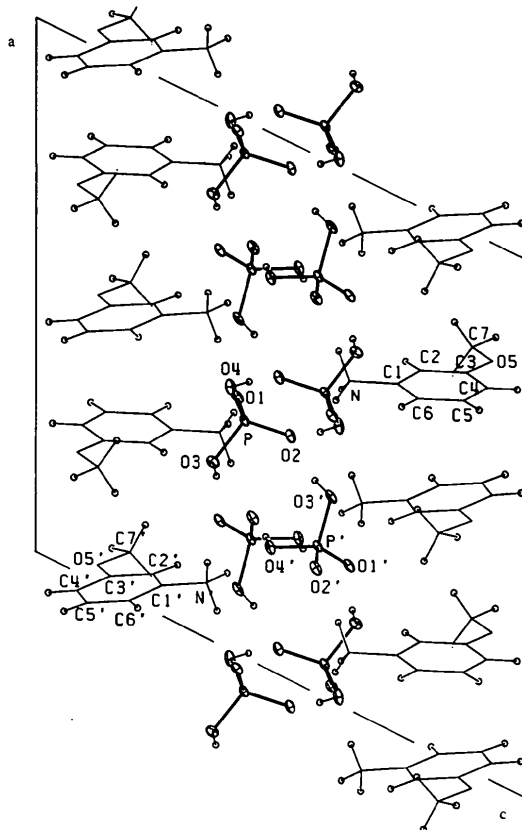


Fig. 1. Projection along the (010) direction of the atomic arrangement of the title compound. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radius.

Experimental

A solution of monophosphoric acid (84%, *d* = 1.70) was mixed with a stoichiometric amount of *m*-anisidine (98%, *d* = 1.102). Slow evaporation at room temperature of an aqueous solution of the resultant product yielded colourless crystals of the title compound.

Crystal data

C₇H₁₀NO⁺·H₂PO₄⁻
M_r = 221.15
 Monoclinic
*P*2₁/*a*
a = 16.095 (1) Å
b = 8.490 (1) Å
c = 16.9070 (1) Å
 β = 116.104 (1)°

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 22 reflections
 θ = 14–16°
 μ = 0.262 mm⁻¹
T = 293 (2) K
 Plate

$V = 2074.6 (3) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.416 \text{ Mg m}^{-3}$

$0.24 \times 0.18 \times 0.05 \text{ mm}$
 Colourless

N—C1	1.461 (4)	N'—C1'	1.468 (4)
C1—C6	1.370 (5)	C1'—C6'	1.371 (5)
C1—C2	1.387 (5)	C1'—C2'	1.379 (5)
C2—C3	1.383 (5)	C2'—C3'	1.385 (5)
C3—C4	1.384 (6)	C3'—C4'	1.385 (6)
C4—C5	1.363 (7)	C4'—C5'	1.365 (7)
C5—C6	1.393 (6)	C5'—C6'	1.387 (6)

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none

$R_{\text{int}} = 0.0212$
 $\theta_{\text{max}} = 25.02^\circ$
 $h = -19 \rightarrow 17$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 20$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.78%

O1—P—O2	114.89 (14)	O1'—P'—O2'	116.45 (13)
O1—P—O3	107.29 (15)	O1'—P'—O3'	104.56 (14)
O2—P—O3	110.22 (15)	O2'—P'—O3'	111.74 (15)
O1—P—O4	107.83 (14)	O1'—P'—O4'	111.46 (14)
O2—P—O4	109.30 (13)	O2'—P'—O4'	105.44 (14)
O3—P—O4	107.0 (2)	O3'—P'—O4'	106.9 (2)
C3—O5—C7	117.7 (3)	C3'—O5'—C7'	118.4 (3)
C6—C1—C2	122.7 (3)	C6'—C1'—C2'	122.9 (3)
C6—C1—N	120.2 (3)	C6'—C1'—N'	118.1 (3)
C2—C1—N	117.1 (3)	C2'—C1'—N'	119.0 (3)
C3—C2—C1	118.6 (4)	C1'—C2'—C3'	118.2 (4)
O5—C3—C2	124.4 (4)	O5'—C3'—C4'	115.5 (3)
O5—C3—C4	116.1 (4)	O5'—C3'—C2'	124.4 (4)
C2—C3—C4	119.5 (4)	C4'—C3'—C2'	120.1 (4)
C5—C4—C3	120.7 (4)	C5'—C4'—C3'	120.0 (4)
C4—C5—C6	121.2 (4)	C4'—C5'—C6'	121.4 (4)
C1—C6—C5	117.4 (4)	C1'—C6'—C5'	117.5 (4)
C7—O5—C3—C4	-178.0 (5)	C7'—O5'—C3'—C4'	177.1 (4)

3770 measured reflections
 3640 independent reflections
 2772 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2
 $R(F) = 0.0484$
 $wR(F^2) = 0.1064$
 $S = 1.282$
 3640 reflections
 349 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 2.2384P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.068$
 $\Delta\rho_{\text{max}} = 0.205 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.284 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N—H2...O2	0.95 (4)	2.00 (4)	2.921 (4)	163 (3)
N'—H1'...O4'	0.98 (4)	1.89 (4)	2.861 (4)	169 (3)
O3'—H11'...O2	0.81 (4)	1.80 (4)	2.601 (3)	167 (4)
N—H1...O2' ⁱ	0.97 (4)	1.78 (5)	2.746 (4)	176 (4)
N—H3...O1 ⁱⁱ	0.91 (4)	1.78 (4)	2.681 (4)	168 (3)
N'—H2'...O1' ⁱⁱⁱ	0.94 (4)	1.87 (4)	2.801 (4)	170 (3)
O3—H11...O1' ⁱⁱⁱ	0.75 (4)	1.83 (4)	2.566 (3)	166 (4)
N'—H3'...O1' ^{iv}	0.91 (4)	1.86 (4)	2.757 (4)	172 (3)
O4—H12...O2' ^v	0.85 (4)	1.71 (5)	2.543 (3)	167 (4)
O4'—H12'...O2' ^{vi}	0.80 (5)	1.78 (5)	2.572 (3)	175 (5)

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

The θ -scan width was $(0.75 + 0.35\tan\theta)^\circ$. Data were corrected for Lorentz and polarization effects.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: DU1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. Selected geometric parameters (\AA , $^\circ$)

P—O1	1.495 (2)	P'—O1'	1.492 (2)
P—O2	1.512 (2)	P'—O2'	1.499 (2)
P—O3	1.555 (3)	P'—O3'	1.559 (2)
P—O4	1.555 (3)	P'—O4'	1.571 (3)
O5—C3	1.363 (5)	O5'—C3'	1.366 (5)
O5—C7	1.415 (6)	O5'—C7'	1.424 (6)

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Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). **C51**, 926–927

N,N-Diethyl-4-(methylsulfonyl)-2-nitroaniline

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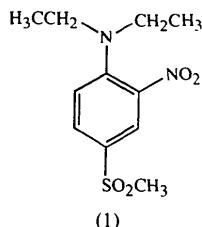
(Received 22 September 1994; accepted 9 November 1994)

Abstract

The title compound, C₁₁H₁₆N₂O₄S, shows significant rotation of the NEt₂ and NO₂ groups from the benzene plane, which reduces the steric compression of these *ortho* substituents. The methyl groups of the NEt₂ substituent adopt a *syn* arrangement, unlike the *anti* arrangement in *N,N*-diethyl-2,4-dinitroaniline.

Comment

The methyl groups in the NEt₂ unit of the title compound (1) adopt a *syn* arrangement. The NEt₂ and NO₂ N atoms are displaced by $-0.139(3)$ and $0.283(3)$ Å from the mean plane of the benzene ring whilst the S atom lies $0.008(1)$ Å from it. The orientations of the NEt₂ and NO₂ groups are described, respectively, by the torsion angles C5—C4—N2—C10 $22.6(4)$, C3—C4—N2—C8 $31.0(4)$, C4—C3—N1—O3 $38.1(4)$, C2—C3—N1—O4 $40.6(4)^\circ$. The NEt₂ N atom is slightly pyramidal, N2 being displaced from the plane of the directly attached C atoms by $0.070(3)$ Å. The nitro group is almost planar with the N atom $0.030(3)$ Å from the O3—O4—C3 plane. The differences between the two N—C(ethyl) and between the two C—C(ethyl) bond lengths are probably due to librational effects. One large anisotropic displacement parameter for C11 suggests either a large component of vibration amplitude or slight disorder.



The *syn* arrangement of the methyl groups contrasts with an *anti* arrangement in *N,N*-diethyl-2,4-dinitroaniline (MacNicol & Mallinson, unpublished results). The N2—C4 and N1—C3 distances in the title compound are $1.366(5)$ and $1.462(5)$ Å compared with $1.353(5)$ and $1.458(5)$ Å in the dinitro compound. The significantly closed angle C3—C4—C5 here, $114.0(4)^\circ$, may be compared with $115.2(4)^\circ$ in the dinitro compound.

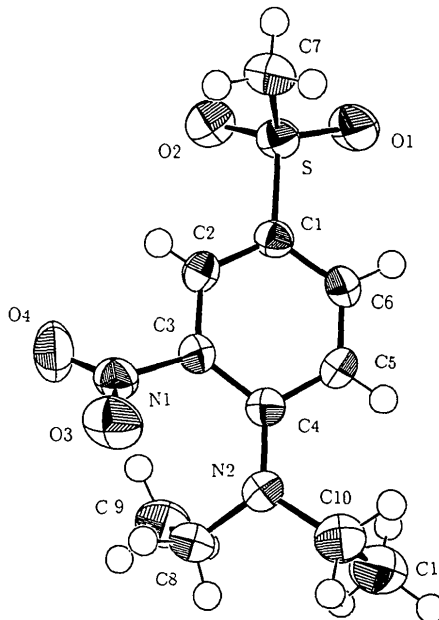


Fig. 1. A view of the molecular structure showing the atom labels. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as circles of arbitrary radii and are labelled according to the atoms to which they are attached.

Experimental

Crystals, m.p. 359 K, were prepared at Glasgow University by Dr C. W. N. Horning.

Crystal data

C₁₁H₁₆N₂O₄S
M_r = 272.32
 Monoclinic
*P*2₁/*n*
a = 5.035 (1) Å
b = 11.684 (1) Å
c = 21.792 (3) Å
 β = 90.54 (2) $^\circ$
V = 1282 (1) Å³
Z = 4
D_x = 1.41 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 11–15 $^\circ$
 μ = 0.249 mm⁻¹
T = 293 K
 Needle
 0.8 × 0.1 × 0.1 mm
 Yellow

Data collection

Enraf–Nonius CAD-4
 diffractometer

*R*_{int} = 0.023
 θ _{max} = 27 $^\circ$