

Table 3. Hydrogen-bond distances (Å) to Cl⁻ ions

C11...H11 ⁱ	2.21 (5)	C11...N11 ⁱ	3.069 (3)
C11...H13 ⁱ	2.14 (4)	C11...N13	3.017 (3)
C11...H31 ⁱⁱ	2.33 (6)	C11...N31 ⁱ	3.106 (3)
C12...H313	2.00 (5)	C12...N31	3.020 (3)
C12...H231 ⁱⁱ	2.27 (3)	C12...N23 ⁱⁱ	3.049 (3)
C13...H211	2.47 (4)	C13...N21	3.140 (3)
C13...H311	2.39 (3)	C13...N31	3.187 (3)

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

The title compound was prepared by the procedure reported by Joseph, Leigh & Swain (1977). 0.5 g of the crude compound was dissolved in 25 ml of a water/ethanol mixture (1:1 v/v). Crystals were grown by slow evaporation. After 20 d, crystals were filtered off, washed with a small amount of cold solvent, dried in a flow of air and crystallized in the form of slightly pink elongated prisms with well developed faces.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.2 ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal3.2*. Program(s) used to refine structure: *Xtal3.2 CRYLSQ*. Molecular graphics: *PLATON93* (Spek, 1993) and *PLUTON92* (Spek, 1992). Software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond angles involving H atoms, have been deposited with the IUCr (Reference: BK1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl *N*-(4-Chlorophenylaminothiocarbonyl)benzimidate

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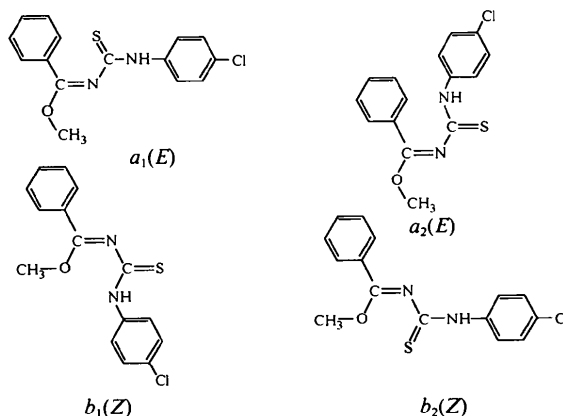
(Received 22 June 1994; accepted 13 October 1994)

Abstract

The conformation of the title compound, C₁₅H₁₃ClN₂OS, corresponds to that of methyl 4-chloro-*N*-(2-tolyl)benzimidate [Kallel, Hajjem, Baccar & Svoboda (1992). *Acta Cryst.* **C48**, 536–538]. The planes composed of atoms O, C8, N2 and N2, C7, S make an angle of 104.3 (2)° with one another. The two phenyl rings are not coplanar. The N—H bond participates in intermolecular hydrogen bonding.

Comment

The reaction of 4-chlorophenylthioisocyanate with methyl benzimidate leads to the formation of methyl *N*-(4-chlorophenylaminothiocarbonyl)benzimidate. This method of preparation has been described previously (Etienne, Le Berre, Lonchambon, Roques & Lemmens, 1976). Four stereoisomers may exist for the title compound. They are characterized as *a*₁(*E*), *a*₂(*E*), *b*₁(*Z*) and *b*₂(*Z*). ¹H and ¹³C NMR spectroscopic analysis confirms that the title compound exists in one isomeric form and X-ray diffraction studies show this configuration to be *a*₁(*E*).



Adjacent molecules in the crystal are linked by an N—H...S hydrogen bond [N1...S(−*x*, −*y*, 1−*z*) 3.382 (2), H1...S 2.58 (2) Å and N1—H1...S 167 (2)°]. The geometrical conformation *a*₁(*E*) adopted by the

molecule does not allow atoms O, C8, N2, C7 and S to be coplanar. X-ray data indicate an angle of $104.3(2)^\circ$ between the planes formed by atoms O, C8, N2 and N2, C7, S. The C8—N2(sp^2) and C7—S(sp^2) bond lengths of 1.265(2) and 1.678(2) Å, respectively, are in agreement with values of 1.279(8) and 1.671(24) Å given by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). These observations lead to the conclusion that the C=N and C=S groups are not conjugated.

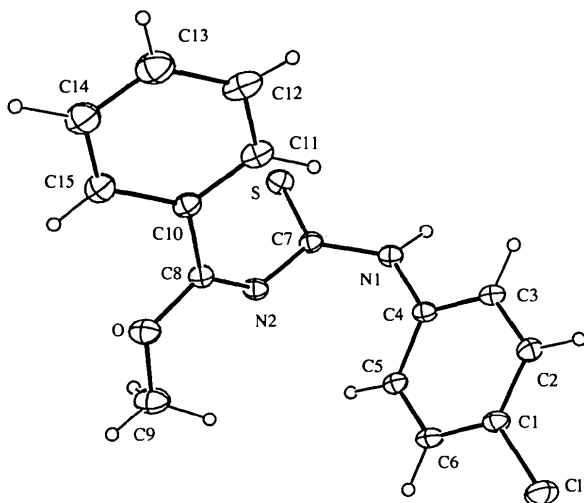


Fig. 1. ORTEP view (Johnson, 1965) of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

Crystal data

$C_{15}H_{13}ClN_2OS$

$M_r = 304.78$

Triclinic

$P\bar{1}$

$a = 7.3812(11) \text{ \AA}$

$b = 8.4422(9) \text{ \AA}$

$c = 12.4200(14) \text{ \AA}$

$\alpha = 73.243(9)^\circ$

$\beta = 81.924(11)^\circ$

$\gamma = 83.473(11)^\circ$

$V = 731.5(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.384 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction:
none

3136 measured reflections

2953 independent reflections

2693 observed reflections

$[I > 2\sigma(I)]$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25
reflections

$\theta = 14-16^\circ$

$\mu = 0.400 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.42 \times 0.36 \times 0.27 \text{ mm}$

Yellow

Crystal source: from
methanol

$R_{int} = 0.0061$

$\theta_{max} = 29.88^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = 0 \rightarrow 14$

3 standard reflections

frequency: 120 min

intensity decay: 0.0255%

Refinement

Refinement on F^2

$R(F) = 0.0382$

$wR(F^2) = 0.0869$

$S = 1.302$

2953 reflections

234 parameters

All H-atom parameters
refined

$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2$
 $+ 0.2194P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.309$

$\Delta\rho_{max} = 0.277 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.529 \text{ e \AA}^{-3}$

Extinction correction:

$F_c^* = 1/kF_c[1 +$
 $0.001\chi F_c^2\lambda^3/\sin(2\theta)]^{1/4}$

Extinction coefficient:

0.0139 (39)

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$$

	x	y	z	U_{eq}
Cl	0.76026 (7)	0.42281 (7)	0.65722 (5)	0.0723 (2)
S	-0.00180 (7)	-0.23886 (6)	0.63479 (4)	0.0547 (2)
O	0.3600 (2)	-0.3215 (2)	0.91881 (10)	0.0613 (4)
N1	0.1893 (2)	0.0207 (2)	0.60279 (12)	0.0438 (3)
N2	0.2672 (2)	-0.2034 (2)	0.74711 (12)	0.0460 (3)
C1	0.5927 (2)	0.3057 (2)	0.63961 (14)	0.0480 (4)
C2	0.4161 (2)	0.3758 (2)	0.6270 (2)	0.0512 (4)
C3	0.2836 (2)	0.2795 (2)	0.61536 (15)	0.0467 (4)
C4	0.3280 (2)	0.1167 (2)	0.61614 (12)	0.0396 (4)
C5	0.5085 (2)	0.0495 (2)	0.62500 (14)	0.0450 (4)
C6	0.6400 (2)	0.1445 (2)	0.63756 (15)	0.0481 (4)
C7	0.1547 (2)	-0.1330 (2)	0.66448 (13)	0.0417 (4)
C8	0.2295 (2)	-0.2424 (2)	0.85353 (14)	0.0451 (4)
C9	0.5356 (3)	-0.3603 (5)	0.8612 (2)	0.0828 (9)
C10	0.0559 (2)	-0.2120 (2)	0.92237 (15)	0.0495 (4)
C11	-0.0639 (3)	-0.0750 (3)	0.8838 (2)	0.0626 (5)
C12	-0.2235 (3)	-0.0490 (4)	0.9520 (3)	0.0858 (8)
C13	-0.2630 (4)	-0.1597 (5)	1.0570 (3)	0.0931 (9)
C14	-0.1462 (4)	-0.2952 (4)	1.0946 (2)	0.0820 (7)
C15	0.0146 (3)	-0.3210 (3)	1.0289 (2)	0.0631 (5)

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

Cl—C1	1.742 (2)	C3—C4	1.374 (2)
S—C7	1.678 (2)	C4—C5	1.394 (2)
O—C8	1.339 (2)	C5—C6	1.379 (2)
O—C9	1.441 (3)	C8—C10	1.477 (2)
N1—C7	1.335 (2)	C10—C11	1.384 (3)
N1—C4	1.431 (2)	C10—C15	1.392 (3)
N2—C8	1.265 (2)	C11—C12	1.386 (3)
N2—C7	1.368 (2)	C12—C13	1.382 (4)
C1—C6	1.373 (3)	C13—C14	1.360 (4)
C1—C2	1.379 (3)	C14—C15	1.376 (3)
C2—C3	1.389 (2)		
C8—O—C9	116.6 (2)	N1—C7—S	122.31 (12)
C7—N1—C4	126.59 (14)	N2—C7—S	122.24 (13)
C8—N2—C7	129.46 (15)	N2—C8—O	119.1 (2)
C6—C1—C2	121.1 (2)	N2—C8—C10	129.45 (15)
C6—C1—Cl	118.97 (13)	O—C8—C10	111.41 (14)
C2—C1—Cl	119.94 (15)	C11—C10—C15	119.6 (2)
C1—C2—C3	119.1 (2)	C11—C10—C8	121.1 (2)
C4—C3—C2	120.4 (2)	C15—C10—C8	119.3 (2)
C3—C4—C5	119.8 (2)	C12—C11—C10	119.3 (2)
C3—C4—N1	119.25 (14)	C11—C12—C13	120.2 (3)
C5—C4—N1	120.9 (2)	C14—C13—C12	120.5 (2)
C6—C5—C4	119.9 (2)	C13—C14—C15	119.9 (3)
C5—C6—C1	119.7 (2)	C14—C15—C10	120.4 (2)
N1—C7—N2	115.21 (14)		

The ω -scan angle was $(0.90 + 0.34\tan\theta)^\circ$ and the background was measured by the usual scan on each side of the reflection.

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, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

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: TA1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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o-Anisidinium Dihydrogenmonophosphate

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Abstract

The structure of *o*-anisidinium dihydrogenmonophosphate, C₇H₁₀NO⁺·H₂PO₄[−], consists of layers containing H₂PO₄[−] anions alternating with layers built up of C₇H₁₀NO⁺ cations, both layers being parallel to the *ab* plane. In the first type of layer, the H₂PO₄[−] tetrahedra are connected through strong hydrogen bonds forming infinite (H₂PO₄)_n chains with rather short internal P··P distances of 4.16 and 4.27 Å.

Comment

The present study is part of a program aimed at examining the packing characteristics of compounds resulting from the interaction of various phosphoric acids and aromatic amines. To our knowledge, the anisidine–H₃PO₄

system has not yet been investigated. In the present work, we describe the chemical preparation and structure of *o*-anisidinium dihydrogenmonophosphate, (I), an example of such a compound.

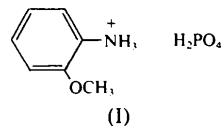


Fig. 1 shows the general atomic arrangement of (I) projected along the *c* axis. It can be described as an alternate stacking of planes containing H₂PO₄[−] tetrahedra and planes built up of organic cations, the two types of layer being parallel to the *ab* plane. In the inorganic layers, the phosphoric entities form infinite zigzag (H₂PO₄)_n chains parallel to the *a* direction. The H₂PO₄[−] tetrahedra are connected through strong hydrogen bonds with O··O distances of 2.573 and 2.627 Å. Consequently, the P··P distance appears relatively short (4.16 and 4.27 Å). All bond distances and angles are normal and correspond well with those observed in similar structures (Averbuch-Pouchot & Durif, 1987; Averbuch-Pouchot, Durif & Guitel, 1988; Kamoun, Jouini, Kamoun & Daoud, 1989; Averbuch-Pouchot, 1993). The benzene ring is practically planar with the greatest deviation from the six-atom least-squares plane being 0.005 Å. The methoxy group makes an angle of 10° with the plane of the phenyl ring. The stability of the structure results from two types of hydrogen bond: the O—H··O type connecting the phosphoric entities in the (H₂PO₄)_n chains and the N—H··O type connecting the NH₃⁺ radicals, originating from the organic cation, to the external O atoms of the phosphoric entities of the inorganic chain. The first type of hydrogen bond is strong but the second is relatively weak according to the criterion of the donor–acceptor distance being less than or greater than 2.7 Å (Brown, 1976).

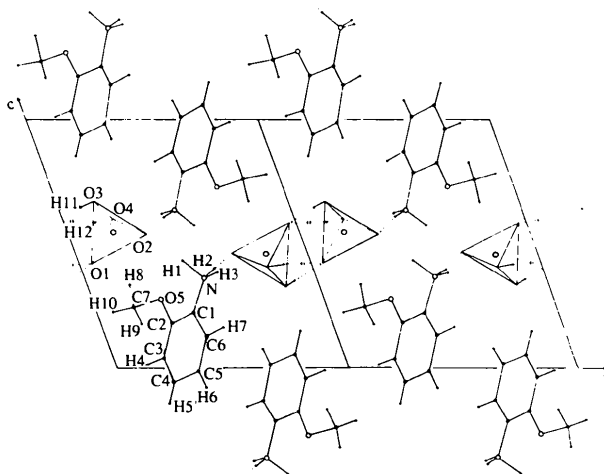


Fig. 1. Projection of the title structure onto the (100) plane.