Refinement

Refinement on F
$R = 0.048$
$wR = 0.029$
$S = 2.80$
2760 reflections
293 parameters
H atoms refined isotropically
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 0.29 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—P2	1.913 (1)	N3—N8	1.420 (3)
P2—O1	1.594 (2)	O2—C9	1.218 (3)
P2—N1	1.647 (2)	N8—C9	1.370 (3)
P2—N3	1.663 (2)	N10—C9	1.390 (3)
N1—N10	1.429 (3)		
S—P2—O1	114.94 (7)	P2—N3—C4	123.3 (2)
S—P2—N1	114.67 (8)	N8—N3—C4	112.0 (2)
S—P2—N3	118.67 (8)	N3—N8—C7	113.9 (2)
O1—P2—N1	106.32 (1)	N3—N8—C9	122.0 (2)
O1—P2—N3	98.6 (1)	C7—N8—C9	121.6 (2)
N1—P2—N3	101.6 (1)	N1—N10—C9	117.6 (2)
P2—O1—C1	125.2 (2)	N1—N10—C11	111.0 (2)
P2—N1—N10	111.2 (2)	C9—N10—C11	118.0 (2)
P2—N1—C14	124.7 (2)	O2—C9—N8	124.0 (2)
N10—N1—C14	113.3 (2)	O2—C9—N10	123.3 (2)
P2—N3—N8	116.6 (2)	N8—C9—N10	112.7 (2)
N3—P2—N1—N10	42.4 (2)	N10—C9—N8—N3	29.1 (3)
P2—N1—N10—C9	−66.0 (2)	C9—N8—N3—P2	−44.9 (3)
N1—N10—C9—N8	28.4 (3)	N8—N3—P2—N1	5.6 (2)

Reflections with $F_o^2 < 2\sigma(F_o^2)$ and $F_o > F_c$ were included in the refinement. Atomic form factors for non-H atoms are from Cromer & Mann (1968), and for H atoms from Stewart, Davidson & Simpson (1965).

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *Express*. Data reduction: *CAD*-4 *Express*. Program(s) used to solve structure: *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Program(s) used to refine structure: *Xtal*3.0 (Hall & Stewart, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 775–777

3,4-Dimethoxybenzaldehyde Isonicotinoylhydrazone†

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Abstract

Hydrogen bonds between the N2 and O1 atoms [2.879 (3) Å] link molecules of the title Schiff base, $C_{15}H_{15}N_3O_3$, into a zigzag chain along the *c* axis.

Comment

Conjugated organic molecules have attracted a great deal of interest in recent years because of their large optical non-linearities (Cheng, Tam, Stevenson & Meredith, 1991). Non-linear optical molecules must possess

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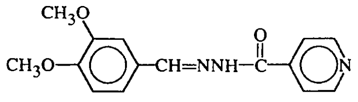
† Alternative name: *N*-(3,4-dimethoxybenzylideneamino)isonicotinamide.

two parts, *i.e.* donor and acceptor (Chemla & Zyss, 1987).

The title compound, (I), is a new Schiff base derived from isonicotinic hydrazide and 3,4-dimethoxybenzaldehyde, which contains delocalized electrons. The methoxy and pyridine groups may be regarded as electron donor and acceptor groups, respectively. As the crystal is centrosymmetric, it may possess third-order non-linear optical properties. Further research is being carried out.



(I)

The molecule of (I) is not completely planar. The planar 3,4-dimethoxybenzylidene moiety makes an interplanar angle of 49.1 (1)° with the pyridine ring. The C7—N3—N2—C6, N3—N2—C6—O1 and N3—N2—C6—C3 torsion angles have values of −168.6 (2), −0.9 (4) and 117.6 (2)°, respectively. Intramolecular bond parameters are close to the usual reported values (Allen *et al.*, 1987). The O1 and H2 atoms are *anti* with respect to one another and both form intermolecular hydrogen bonds with neighbouring molecules [N2—H2···O1(x, $\frac{3}{2}-y$, $\frac{1}{2}+z$) 2.879 (3) Å]. These hydrogen bonds link the molecules into a zigzag chain running parallel to the c axis (Fig. 2).

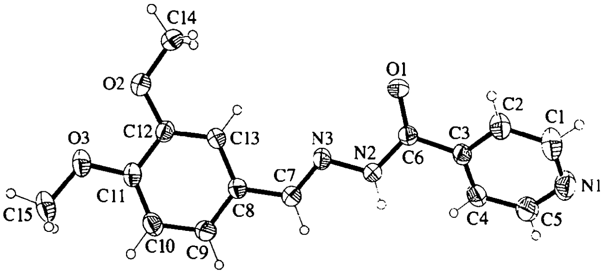


Fig. 1. *ORTEP* (Johnson, 1965) plot of the title compound at the 30% probability level, with H atoms drawn as spheres of arbitrary radii.

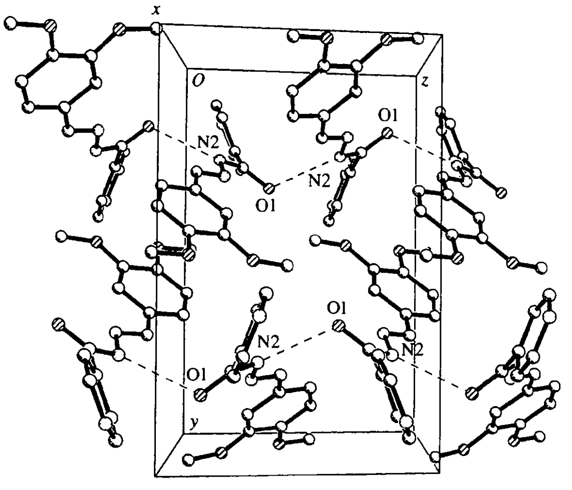


Fig. 2. Packing diagram viewed down the a axis.

Experimental

Equimolar amounts of isonicotinic hydrazide and 3,4-dimethoxybenzaldehyde were reacted in methanol. The product was recrystallized from acetonitrile at room temperature.

Crystal data

$C_{15}H_{15}N_3O_3$
$M_r = 285.30$
Monoclinic
$P2_1/c$
$a = 11.810\,(1)$ Å
$b = 13.8044\,(7)$ Å
$c = 8.925\,(1)$ Å
$\beta = 101.320\,(8)°$
$V = 1426.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.328$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$13°$
$\mu = 0.095$ mm^{-1}
$T = 300\,(2)$ K
Cut from a thick needle
$0.50 \times 0.43 \times 0.22$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2675 measured reflections
2511 independent reflections
1510 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0158$
$\theta_{\rm max} = 24.97°$
$h = -13 \rightarrow 14$
$k = -16 \rightarrow 0$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0595$
$wR(F^2) = 0.1405$
$S = 0.973$
2511 reflections
191 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.507$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.457$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.063 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

H atoms were placed in calculated positions.

Data collection: *CAD*-4 *VAX*/*PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX*/*PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methylxanthines. I. Anhydrous Theophylline

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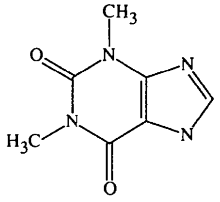
Abstract

Clear crystals of anhydrous theophylline (3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione), $C_7H_8N_4O_2$, were grown by sublimation and the X-ray structure determined. The planar molecules are stacked in columns along [010] and are inclined at an angle of 26.05 (10)° relative to (010). The melting point has been determined to be 548.8 (5) K.

Comment

There is considerable interest in the structures of methylxanthines such as theophylline owing to their pharmacological use. Theophylline is often used as a muscle relaxant or vasodilator. However, the X-ray structure of pure theophylline has not been reported since it is difficult to obtain crystals not containing solvent or other complexing agents. As part of our research on the methylxanthines, we report the structure of anhydrous theophylline, (I).



(I)

The unit-cell dimensions and space-group assignment determined in the present work agree well with crystal data from previously reported powder diffraction data (Naqvi & Bhattacharyya, 1981).

The numbering scheme is shown in Fig. 1. Bond lengths and angles (Table 1) agree well with previously reported theophylline-complex structures (Aoki & Ichikawa, 1978; Karczmarzyk, Karolak-Wojciechowska & Pawłowski, 1995; Sutor, 1958; Zaitu, Miwa & Taga, 1995*a*,*b*; Nakao, Fujii, Sakaki & Tomita, 1977). The molecular packing and the hydrogen-bonding scheme can be seen in Fig. 2. The planar molecules are stacked in columns along [010]. The molecular plane is inclined at an angle of 26.05 (10)° relative to (010). The mean separation between molecular planes is 3.425 (7) Å.

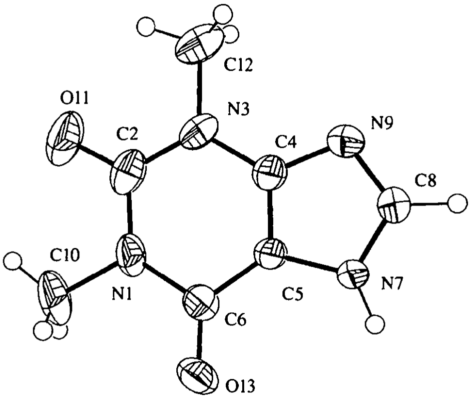


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of theophylline showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres with arbitrary radii.

The theophylline molecules form hydrogen-bonded networks as shown in Fig. 2. The networks are composed of one N—H···N hydrogen bond and two (bifurcated) C—H···O hydrogen bonds. The values for these interactions are given in Table 2. As would be expected from hydrogen-bonding rules (Etter, 1990), the best pro-

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