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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>, are packed in layers. These layers are held together to form a sheet by a system of intermolecular hydrogen bonding which includes C—H···O hydrogen bonds.

## Comment

The structure determination of the title crystal was undertaken during the course of a study of a number of complexes involving methylxanthine. The structure of the 2:1 complex of theophylline and 5-fluorouracil has been reported (Zaitu, Miwa & Taga, 1995), and the structures of 1:1 theophylline-*p*-nitrophenol (Aoki, Ichikawa, Koinuma & Iitaka, 1987) and 1:1 theophylline-urea (Wiedenfeld & Knoch, 1986) have also been determined. Fig. 1 shows the molecular structure of the title complex, the 1:1 molecular complex of theophylline and *p*-nitroaniline, (I).

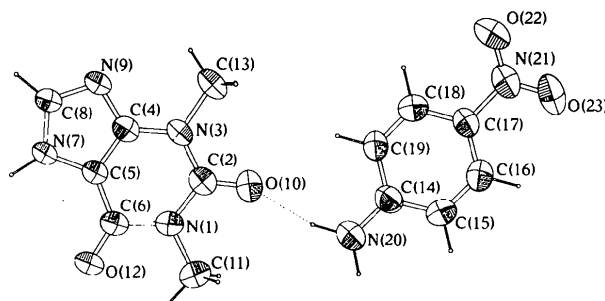
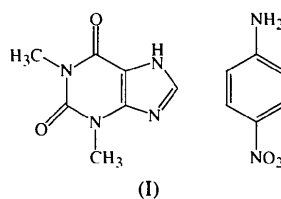


Fig. 1. Perspective view of the title complex with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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## 1:1 Molecular Complex of Theophylline and *p*-Nitroaniline

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### Abstract

Theophylline (3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione) and *p*-nitroaniline molecules in the title complex,

The fused theophylline rings are essentially planar and the bond lengths and angles within the molecule are in fairly good agreement with those observed in theophylline monohydrate (Sutor, 1958) and other theophylline complexes, *e.g.* 1:1 theophylline-sulfathiazole (Shefter & Sackman, 1971). The *p*-nitroaniline molecule has practically a twofold axis collinear with the C—N bonds and, as has been observed in *p*-nitroaniline itself (Colapietro, Domenicano, Marciante & Portalone, 1982), the C—C bonds of the six-membered ring along the long molecular axis are shorter than the other C—C bonds. The planar molecules are packed by stacking forces and hydrogen bonds (Table 3) to form theophylline-*p*-nitroaniline layers (Fig. 2). C(8)—H···O(12) interactions are considered to be C—H···O hydrogen bonds; similar C(8)—H hydrogen bonds to

carbonyl O atoms have been observed in a number of theophylline complexes, *e.g.* 5-fluorouracil (Zaitu, Miwa & Taga, 1995), urea (Wiedenfeld & Knoch, 1986), *p*-nitrophenol (Aoki, Ichikawa, Koinuma & Iitaka, 1978), phenobarbital (Nakao, Fujii, Sakaki & Tomita, 1977) and 5-chlorosalicylic acid (Shefter, 1969). C(15)—H···O(23) interactions are also important intermolecular hydrogen bonds; these connect the theophylline-*p*-nitroaniline layers to form a sheet (Fig. 2).

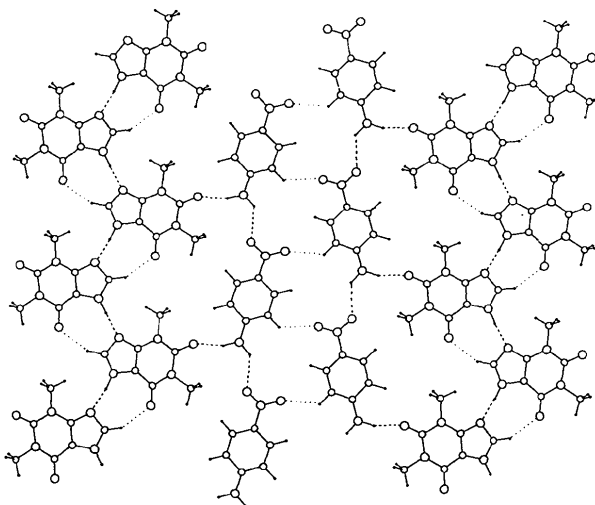


Fig. 2. A sheet of the molecular network in the crystal structure. Dotted lines indicate N—H···N, N—H···O and C—H···O hydrogen bonds.

## Experimental

Crystals of the title complex were obtained at room temperature by the slow evaporation of a solution containing equimolar amounts of theophylline and *p*-nitroaniline in chloroform-methanol (10:1) solvent. The density  $D_m$  was measured by flotation.

### Crystal data

$C_7H_8N_4O_2 \cdot C_6H_6N_2O_2$

$M_r = 318.29$

Monoclinic

$P2_1/c$

$a = 7.693(2) \text{ \AA}$

$b = 9.178(1) \text{ \AA}$

$c = 22.982(4) \text{ \AA}$

$\beta = 116.59(2)^\circ$

$V = 1451.0 \text{ \AA}^3$

$Z = 4$

$D_x = 1.4568 \text{ Mg m}^{-3}$

$D_m = 1.43 \text{ Mg m}^{-3}$

### Data collection

Rigaku AFC-5 diffractometer

Cu  $K\alpha$  radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 17.9\text{--}27.3^\circ$

$\mu = 0.90 \text{ mm}^{-1}$

$T = 295.0 \text{ K}$

Prism

$0.40 \times 0.30 \times 0.30 \text{ mm}$

Yellow

$R_{\text{int}} = 0.021$

$\theta_{\text{max}} = 60^\circ$

$\theta/2\theta$  scans

Absorption correction:

none

2834 measured reflections

2621 independent reflections

1780 observed reflections

$[F > 3\sigma(F)]$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 10$

$l = -24 \rightarrow 24$

3 standard reflections

monitored every 150

reflections

intensity decay: 2%

### Refinement

Refinement on  $F$

$R = 0.070$

$wR = 0.075$

$S = 0.80$

1780 reflections

250 parameters

Only coordinates of H atoms

refined, all from  $\Delta F$  map

$w = 1/[\sigma^2(F) + 0.023F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.05$

$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

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

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	$B_{\text{eq}}$
N(1)	0.0012 (4)	0.2614 (3)	-0.0718 (1)	4.3 (1)
C(2)	0.0330 (6)	0.1112 (4)	-0.0677 (2)	4.7 (1)
N(3)	-0.0907 (5)	0.0289 (3)	-0.1193 (2)	4.4 (1)
C(4)	-0.2398 (6)	0.0960 (3)	-0.1710 (2)	4.2 (1)
C(5)	-0.2649 (5)	0.2419 (3)	-0.1740 (2)	4.1 (1)
C(6)	-0.1446 (5)	0.3381 (4)	-0.1235 (2)	4.2 (1)
N(7)	-0.4270 (5)	0.2673 (3)	-0.2316 (1)	4.6 (1)
C(8)	-0.4889 (6)	0.1377 (4)	-0.2591 (2)	4.9 (1)
N(9)	-0.3779 (5)	0.0279 (3)	-0.2235 (1)	4.6 (1)
O(10)	0.1657 (4)	0.0566 (3)	-0.0202 (1)	6.0 (1)
C(11)	0.1377 (8)	0.3481 (5)	-0.0162 (2)	6.0 (2)
O(12)	-0.1595 (4)	0.4700 (2)	-0.1219 (1)	5.5 (1)
C(13)	-0.0649 (9)	-0.1300 (5)	-0.1186 (3)	6.4 (2)
C(14)	0.5837 (6)	-0.1073 (4)	0.1103 (2)	4.8 (1)
C(15)	0.7458 (6)	-0.1492 (4)	0.1664 (2)	5.2 (1)
C(16)	0.7967 (6)	-0.2919 (4)	0.1791 (2)	5.1 (1)
C(17)	0.6849 (6)	-0.3977 (4)	0.1358 (2)	4.7 (1)
C(18)	0.5218 (6)	-0.3592 (4)	0.0798 (2)	5.2 (1)
C(19)	0.4709 (6)	-0.2162 (4)	0.0667 (2)	5.1 (1)
N(20)	0.5302 (6)	0.0353 (4)	0.0970 (2)	6.3 (1)
N(21)	0.7388 (6)	-0.5499 (4)	0.1480 (2)	6.0 (1)
O(22)	0.6367 (6)	-0.6399 (3)	0.1081 (2)	9.1 (2)
O(23)	0.8807 (5)	-0.5835 (3)	0.1975 (2)	8.2 (1)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

N(1)—C(2)	1.396 (5)	N(7)—C(8)	1.331 (4)
N(1)—C(6)	1.404 (4)	C(8)—N(9)	1.337 (4)
N(1)—C(11)	1.472 (5)	C(14)—C(15)	1.388 (5)
C(2)—N(3)	1.368 (5)	C(14)—C(19)	1.406 (5)
C(2)—O(10)	1.220 (4)	C(14)—N(20)	1.365 (5)
N(3)—C(4)	1.374 (5)	C(15)—C(16)	1.361 (5)
N(3)—C(13)	1.471 (5)	C(16)—C(17)	1.381 (5)
C(4)—C(5)	1.350 (4)	C(17)—C(18)	1.382 (5)
C(4)—N(9)	1.352 (4)	C(17)—N(21)	1.448 (5)
C(5)—C(6)	1.422 (5)	C(18)—C(19)	1.364 (5)
C(5)—N(7)	1.373 (4)	N(21)—O(22)	1.223 (5)
C(6)—O(12)	1.218 (4)	N(21)—O(23)	1.212 (5)
C(2)—N(1)—C(6)	127.0 (3)	C(5)—C(6)—O(12)	127.3 (3)
C(2)—N(1)—C(11)	116.1 (3)	C(5)—N(7)—C(8)	106.5 (3)
C(6)—N(1)—C(11)	116.9 (3)	N(7)—C(8)—N(9)	112.8 (3)
N(1)—C(2)—N(3)	117.0 (3)	C(4)—N(9)—C(8)	103.2 (3)
N(1)—C(2)—O(10)	121.2 (3)	C(15)—C(14)—C(19)	118.4 (3)
N(3)—C(2)—O(10)	121.9 (3)	C(15)—C(14)—N(20)	122.0 (3)
C(2)—N(3)—C(4)	119.3 (3)	C(19)—C(14)—N(20)	119.6 (3)

C(2)—N(3)—C(13)	120.0 (3)	C(14)—C(15)—C(16)	121.2 (3)
C(4)—N(3)—C(13)	120.7 (3)	C(15)—C(16)—C(17)	119.7 (3)
N(3)—C(4)—C(5)	122.3 (3)	C(16)—C(17)—C(18)	120.3 (3)
N(3)—C(4)—N(9)	125.7 (3)	C(16)—C(17)—N(21)	120.4 (3)
C(5)—C(4)—N(9)	112.1 (3)	C(17)—C(17)—N(21)	119.3 (3)
C(4)—C(5)—C(6)	123.2 (3)	C(17)—C(18)—C(19)	120.2 (3)
C(4)—C(5)—N(7)	105.4 (3)	C(14)—C(19)—C(18)	120.1 (3)
C(6)—C(5)—N(7)	131.3 (3)	C(17)—N(21)—O(22)	118.3 (3)
N(1)—C(6)—C(5)	111.2 (3)	C(17)—N(21)—O(23)	119.1 (3)
N(1)—C(6)—O(12)	121.5 (3)	O(22)—N(21)—O(23)	122.6 (4)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N(7)—H(7)...N(9 <sup>i</sup> )	1.76 (3)	2.766 (4)	171 (3)
N(20)—H(20B)...O(10)	1.91 (4)	2.897 (4)	163 (3)
N(20)—H(20A)...O(22 <sup>ii</sup> )	2.31 (4)	3.072 (4)	132 (3)
C(8)—H(8)...O(12 <sup>iii</sup> )	2.30 (4)	3.247 (4)	149 (2)
C(15)—H(15)...O(23 <sup>iv</sup> )	2.45 (3)	3.218 (4)	131 (2)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *MULTAN88* (Main *et al.*, 1988). Program(s) used to refine structure: *KPPXRAY* (Taga, Masuda, Higashi & Iizuka, 1991) including a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *KPPXRAY*. Software used to prepare material for publication: *EDCIF-J* (Osaki & Taga, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## $\alpha$ - and $\gamma$ -Polymorphs of Dimethyl 9-Chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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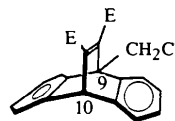
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### Abstract

Two further polymorphic forms ( $\alpha = P2_1$  and  $\gamma = P2_1/c$ ) of the title compound (C<sub>21</sub>H<sub>17</sub>ClO<sub>4</sub>) have been obtained and their crystal structures determined. The molecular geometries and photochemical behaviour are very similar to those of the previously described  $\beta$ -form reported in the  $P2_1/c$  space group [Chen, Pokkuluri, Scheffer & Trotter (1993). *Acta Cryst.* **B49**, 905–909].

### Comment

The crystal structure and photochemistry of the title compound have been described previously (Chen, Pokkuluri, Scheffer & Trotter, 1991, 1993). Further study of the material (Chen, 1991) led to isolation of two other polymorphic modifications. Crystallization from chloroform/methanol gives the previously described prismatic crystals (now named the  $\beta$ -form). Crystallization from diethyl ether/petroleum ether gives needles ( $\alpha$ -form) and prisms ( $\beta$ -form), while crystallization from acetone/hexane gives block-shaped crystals ( $\gamma$ -form). The  $\alpha$ -form has a melting point 6 K higher than the other two forms, and the three forms have slightly different FTIR (Fourier transform infrared) spectra and photochromic behaviour (Chen, 1991).



E = CO<sub>2</sub>Me  
(I)

The molecules in all three polymorphic forms have very similar conformations and dimensions (Table 2). The ester group remote from the chloromethyl substituent is conjugated with the C11=C12 double bond in each molecule; the C11—C12—C15—O4 torsion angles are not far from 0 or 180°, with  $\cos^2(\text{angle}) = 0.88$ – $1.00$  (0.67 for the disordered group of the  $\gamma$ -form). The ester group adjacent to the chloromethyl group is not conjugated, presumably as a result of steric interactions; the