

The theophylline molecule is linked to a *p*-nitrophenol molecule through a hydrogen bond between the carbonyl O(2) of theophylline and the hydroxyl O(13) of *p*-nitrophenol (2.71 Å).

The intermolecular contacts less than 3.35 Å are shown in Fig. 3. Nitro groups come into contact with a N—O...O—N distance of 3.04 Å. This short contact has also been observed in other nitro compounds (see Ichikawa, Aoki & Iitaka, 1978). There is another short contact: C(8)—H...O(10) of distance 2.40 Å [C(8)...O(10) 3.43 Å], which is less than the sum of the van der Waals radii of the H and O atoms (2.60 Å). This interaction seems to be an electrostatic one between the negative charge of the nitro group and the positive charge of H(C8). The acidic character of H(C8) may be due to the resonance contribution in the purine system (Shefter, 1968). In the crystal structures of theophylline monohydrate (Sutor, 1958*a*), theophylline-5-chlorosalicylic acid (Shefter, 1969), caf-

feine monohydrate (Sutor, 1958*b*), and caffeine-5-chlorosalicylic acid (Shefter, 1968), H(C8) interactions with a carbonyl O atom have also been observed.

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A 1:1 Complex of 2-Methylthio-6-benzamidopurine and *p*-Nitrophenol

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Abstract. (C₁₃H₁₁N₅OS)(C₆H₅NO₃), monoclinic, C2/c, $a = 25.63$ (4), $b = 9.64$ (2), $c = 16.90$ (3) Å, $\beta = 112.9$ (2)°, $Z = 8$. Block-diagonal least-squares refinement with anisotropic temperature factors yielded a final R value of 0.11. The complex is linked by three hydrogen bonds which form a three-dimensional network, and the benzoyl moiety is fixed by an intramolecular hydrogen bond (2.63 Å).

Introduction. Sekiya, Yoshino, Tanaka & Ishido (1973) and Nakazaki, Sekiya, Yoshino & Ishido (1973) have found that the formation of complexes of purine derivatives with *p*-nitrophenol activates the reaction of acetylated sugars with purines giving *N*-glycosides.

Pale-green single crystals were grown from a solution of chloroform. The lattice constants were measured from precession photographs taken with Cu $K\alpha$ radiation. Intensity data were collected from equi-inclination Weissenberg photographs taken with Cu $K\alpha$

radiation on multiple-film packs. Intensities were measured with the aid of a Narumi microdensitometer and were corrected for Lorentz, polarization and spot-shape (Phillips, 1954) factors, but no correction was applied for the absorption effect. 1251 independent structure factors were obtained (1657 being theoretically observable).

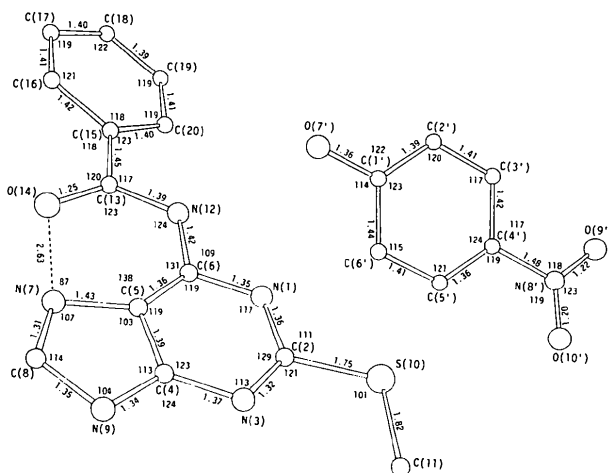
The structure was solved by the symbolic addition method (Karle & Karle, 1966). Refinement of the structure by the block-diagonal least-squares method with anisotropic thermal parameters for all the non-hydrogen atoms reduced the R value to 0.11. The following weighting system was adopted at the final stage of the refinement: $w = 0$ when $|F_o| \leq 2.0$; $w = 1$ when $2.0 < |F_o| \leq 8.0$; and $\sqrt{w} = 8/|F_o|$ when $|F_o| > 8.0$. The final atomic coordinates are listed in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33457 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. The final positional parameters ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	2839 (4)	4357 (10)	-322 (7)
C(2)	3183 (4)	5107 (13)	364 (8)
N(3)	3040 (3)	5984 (10)	842 (7)
C(4)	2467 (5)	6061 (13)	616 (10)
C(5)	2080 (4)	5363 (12)	-90 (9)
C(6)	2274 (5)	4480 (12)	-538 (9)
N(7)	1549 (4)	5803 (10)	-88 (7)
C(8)	1660 (6)	6717 (15)	533 (10)
N(9)	2217 (4)	6878 (11)	1006 (7)
S(10)	3893 (1)	4835 (4)	542 (2)
C(11)	4246 (5)	5922 (15)	1480 (9)
N(12)	1982 (4)	3636 (10)	-1267 (7)
C(13)	1404 (5)	3352 (14)	-1571 (10)
O(14)	1086 (4)	3872 (10)	-1245 (8)
C(15)	1173 (5)	2429 (13)	-2305 (8)
C(16)	594 (5)	2572 (15)	-2853 (9)
C(17)	341 (6)	1680 (15)	-3560 (11)
C(18)	680 (7)	698 (17)	-3739 (10)
C(19)	1249 (7)	543 (14)	-3216 (10)
C(20)	1499 (5)	1449 (13)	-2519 (10)
C(1')	3268 (4)	2035 (13)	-1966 (10)
C(2')	3550 (5)	1740 (14)	-2504 (10)
C(3')	4133 (6)	1428 (13)	-2144 (10)
C(4')	4397 (5)	1425 (13)	-1235 (8)
C(5')	4123 (5)	1701 (13)	-710 (10)
C(6')	3540 (5)	2029 (14)	-1042 (10)
O(7')	2713 (3)	2428 (10)	-2278 (6)
N(8')	5016 (4)	1221 (12)	-849 (8)
O(9')	5244 (4)	812 (11)	-1317 (8)
O(10')	5263 (4)	1375 (12)	-87 (7)


 Fig. 1. Bond lengths (Å) and angles ($^\circ$) (see text for standard deviations). The broken line represents the hydrogen bond.

Discussion. 2-Methylthio-6-benzamidopurine (MSBP) molecule: Fig. 1 shows the bond lengths and angles. The standard deviations of these values are estimated to be about 0.02 Å and 1.2° . As listed in Table 2, the atoms in the purine base show a slight puckering but the degree of puckering is not unusual as compared

Table 2. Least-squares planes and the deviations (Å) of individual atoms from these planes

In each of the equations of the planes, *X*, *Y*, and *Z* are coordinates (Å) referred to the orthogonal axes *a**, *b*, and *c*. Atoms designated by a dagger were given zero weight in calculating the plane; other atoms were weighted equally.

(a) The 2-methylthio-6-benzamide ring

$$-0.0138X + 0.7529Y - 0.6580Z = 5.2841 \text{ \AA}$$

N(1)	0.01	N(9)	-0.03
C(2)	0.00	N(12)†	0.00
N(3)	0.02	C(13)†	-0.23
C(4)	-0.03	O(14)†	0.41
C(5)	0.01	C(15)†	-0.23
C(6)	-0.02	S(10)†	0.05
N(7)	-0.01	C(11)†	0.02
C(8)	0.04		

(b) The benzene ring of the benzoyl group

$$0.2240X + 0.6578Y - 0.7191Z = 5.8261$$

C(15)	-0.02	C(19)	-0.02
C(16)	-0.01	C(20)	0.02
C(17)	-0.01	C(13)†	-0.04
C(18)	0.01		

 (c) The benzene ring of *p*-nitrophenol

$$0.2182X + 0.9702Y - 0.1051Z = 4.2775 \text{ \AA}$$

C(1')	0.002	C(6')	0.001
C(2')	-0.004	O(7')†	0.08
C(3')	0.002	N(8')†	0.13
C(4')	0.002	O(9')†	-0.03
C(5')	-0.003	O(10')†	0.29

Table 3. Hydrogen bonds

<i>D</i>	<i>A</i>	<i>D</i> ... <i>A</i>		
N(7)	O(14) ^a	2.63 (1) Å	C(5)—N(7)...	O(14) ^a 87 (1) ^o
			C(8)—N(7)...	O(14) ^a 165 (1)
N(7)	O(9') ^b	3.18 (1)	C(5)—N(7)...	O(9') ^b 107 (1)
			C(8)—N(7)...	O(9') ^b 111 (1)
N(12)	O(7') ^a	3.20 (2)	C(6)—N(12)...	O(7') ^a 117 (1)
			C(13)—N(12)...	O(7') ^a 119 (1)
O(7')	N(9) ^c	2.76 (2)	C(1')—O(7')...	N(9) ^c 117 (1)
			C(1')—O(7')...	N(12) ^a 129 (1)
			N(12)—O(7')...	N(9) ^c 110 (1)

Symmetry code: (a) *x*, *y*, *z*; (b) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (c) *x*, $1 - y, -\frac{1}{2} + z$.

with that in other purine derivatives. An intramolecular hydrogen bond between N(7) of the purine base and carbonyl O(14) of the amide group (2.63 Å) stabilizes the molecular structure, and causes the MSBP molecule to take an extended conformation. The MSBP molecule assumes a roughly planar conformation [torsion angles C(5)—C(6)—N(12)—C(13) and C(6)—N(12)—C(13)—C(15) are -14 and -178° respectively] and the dihedral angle between the phenyl and purine rings is 15° .

p-Nitrophenol molecule: The benzene ring is planar within experimental errors while the nitro group is displaced from the ring plane (Table 2). No contri-

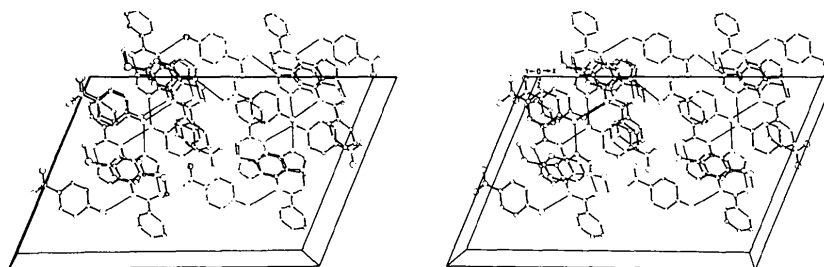


Fig. 2. Stereodrawing of the crystal packing. Long lines represent hydrogen bonds.

bution of the quinonoid resonance structure, which has been found in β -*p*-nitrophenol (Coppens & Schmidt, 1965*b*), has been observed. The two C—C—O angles are not equal, as in α -*p*-nitrophenol (Coppens & Schmidt, 1965*a*) and β -*p*-nitrophenol. This effect has been interpreted by Hirshfeld (1964) as evidence for bent orbitals resulting from the repulsion between the H atom and the C atom carrying the hydroxyl group.

Crystal structure: Hydrogen bonds appear to be predominant stabilizing forces in the crystal; these interactions are illustrated in Fig. 2 and are also listed in Table 3. The *p*-nitrophenol molecule is simultaneously linked by three hydrogen bonds to three MSBP molecules (3.20, 2.76 and 3.18 Å) so that a three-dimensional network of hydrogen bonds is formed.

The purine rings are stacked in relation to a centre of symmetry with perpendicular separations of 3.8 and 3.4 Å, but they are not stacked with the *p*-nitrophenol molecules.

Intermolecular contacts less than 3.35 Å, other than hydrogen bonds, are listed in Table 4. The shortest contact is that between carbonyl O(14) and nitro group O(9') (2.82 Å). Nitro groups come into contact with each other at a distance of 3.04 Å; such a short contact has also been observed in other nitro compounds, such as *o*-nitrobenzoic acid (3.05 Å) (Sakore, Tavale & Pant, 1967), *o*-nitrobenzaldehyde (2.95 and 3.05 Å) (Coppens & Schmidt, 1964), *s*-trinitrobenzene (2.97 and 2.84 Å) (Hanson, 1964), 9,10-dinitroanthracene (3.06 Å) (Trotter, 1959) and 1,4-dinitrobenzene (3.24 Å) (Abrahams, 1950).

Table 4. Intermolecular contacts less than 3.35 Å not involving hydrogen bonds

O(14)···O(9') ^a	2.82 (1) Å
N(7)···O(10') ^a	3.34 (2)
O(10')···O(10') ^b	3.04 (1)
O(10')···C(8) ^c	3.33 (2)
C(17)···O(10') ^d	3.13 (2)

Symmetry code: (a) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (b) $1 - x, 1 - y, 1 - z$; (c) $\frac{1}{2} + x, -\frac{1}{2} + y, z$; (d) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

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