Fig. 3. A projection of the unit-cell contents down b.

Fig. 3 is a projection of the crystal structure down b. The molecules are packed in layers along the xz plane.

We thank the Chlorocarbon Group of the Instituto de Química Orgánica Aplicada de Catalunya (CSIC) for valuable discussions and for providing us with the samples of perchlorodiphenylnitroxide, and Enraf–Nonius, who kindly supplied us with a CAD-4 diffractometer.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa.

ANDERSEN, B. & ANDERSEN, P. (1966). *Acta Chem. Scand.* 20, 2728–2730.

BALLESTER, M., RIERA, J. & ONRUBIA, C. (1976). *Tetrahedron Lett.* 12, 945–946.

BROWN, G. M. & STRYDOM, O. A. W. (1974). *Acta Cryst.* B30, 801–804.

FORRESTER, A. R., HAY, J. M. & THOMSON, R. H. (1968). *Organic Chemistry of Stable Free Radicals*, pp. 208–210. London, New York: Academic Press.

FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* 12, 412–415.

GALÍ, S. (1975). *Crystal and Molecular Structures of Perchlorinated Organic Compounds.* Thesis. Univ. of Barcelona, Spain.

HANSON, A. W. (1953). *Acta Cryst.* 6, 32–35.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* 3, 210–214.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KOCHI, J. K. (1972). *Free Radicals*, pp. 541–542, Vol. II. New York: Interscience.

LAJZÉROWICZ-BONNETEAU, J. (1968). *Acta Cryst.* B24, 196–199.

LINNETT, J. W. (1961). *J. Chem. Phys.* 29, 2643–2654.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. York, England, and Louvain, Belgium.

PEDERSEN, B. F. (1975). *Acta Cryst.* B31, 2931–2933.

SILVERMAN, J., SOLTZBERG, L. J., YANNONI, N. F. & KRUKONIS, A. P. (1971). *J. Phys. Chem.* 75, 1246–1250.

SOLANS, X. (1977). Thesis, Univ. of Barcelona, Spain.

SOLANS, X. & FONT-ALTABA, M. (1975). *Acta Geol. Hisp.* 3, 116–117.

A 1:1 Complex of Theophylline and p-Nitrophenol

BY KATSUYUKI AOKI AND TADAYOSHI ICHIKAWA

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

AND YOKO KOINUMA AND YOICHI IITAKA*

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan

Abstract. $(C_7H_8N_4O_2)(C_6H_5NO_3)$, triclinic, $P\bar{1}$, $a = 8\cdot29$ (2), $b = 11\cdot56$ (3), $c = 8\cdot95$ (2) Å, $\alpha = 114\cdot0$ (2), $\beta = 108\cdot9$ (2), $\gamma = 75\cdot4$ (2)°, $Z = 2$. Block-diagonal least-squares refinement gave a final R value of $0\cdot095$. The theophylline molecules are in a dimeric arrangement by virtue of two centrosymmetrically related

* To whom correspondence should be addressed.

hydrogen bonds [N(7)···O(6) 2·81 Å], and are linked to *p*-nitrophenol molecules by another hydrogen bond (2·71 Å).

Introduction. Because *p*-nitrophenol activates the glycosidic bond formation reaction of purine derivatives (Sekiya, Yoshino, Tanaka & Ishido, 1973; Nakazaki, Sekiya, Yoshino & Ishido, 1973), the present study has been carried out.

White crystals were grown from a solution of chloroform. The lattice constants were obtained from precession photographs. Intensity data were collected by the use of the multiple-film equi-inclination Weissenberg technique with Cu $K\alpha$ radiation, and were measured with the aid of a microdensitometer. 1205 independent structure factors, which correspond to 36% of those theoretically possible, were obtained; these were corrected for Lorentz and polarization factors but not for the absorption effect.

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 non-hydrogen atoms and isotropic for H led to the final R value of 0·095. In this calculation, two reflexions ($\bar{1}12$ and $\bar{1}10$) having the largest calculated structure factors were excluded, since they are obviously affected by the secondary-extinction effect. The following weighting system was adopted at the final stage of the refinement: $w = 0$ when $|F_o| < 1·5$; $w = 1$ when $1·5 \le |F_o| \le 20·0$; and $\sqrt{w} = 20/F_o$ when $|F_o| > 20·0$. The final atomic coordinates are listed in Table 1.*

Discussion. Fig. 1 shows the bond lengths and angles. The standard deviations are estimated to be about 0·01 Å and 0·8°.

Table 1. *The final positional parameters* ($\times 10^4$ *for the non-hydrogen atoms;* $\times 10^3$ *for the hydrogen atoms*)

|	x	y	z
N(1)	−1144 (8)	−1637 (7)	2685 (9)
C(2)	594 (10)	−1416 (8)	3365 (12)
N(3)	1038 (8)	−444 (7)	3119 (9)
C(4)	−241 (10)	260 (8)	2214 (11)
C(5)	−1889 (9)	−18 (8)	1561 (11)
C(6)	−2474 (9)	−981 (8)	1764 (10)
N(7)	−2743 (8)	829 (7)	745 (9)
C(8)	−1563 (10)	1578 (8)	988 (11)
N(9)	12 (9)	1231 (7)	1888 (10)
C(1)	−1560 (11)	−2683 (9)	3018 (14)
O(2)	1653 (7)	−2037 (6)	4150 (8)
C(3)	2870 (10)	−228 (9)	3672 (13)
O(6)	−3943 (6)	−1268 (6)	1262 (8)
C(10)	3695 (10)	4867 (8)	1903 (11)
C(11)	2443 (10)	4177 (9)	1783 (12)
C(12)	2912 (10)	3291 (9)	2523 (12)
C(13)	4640 (10)	3055 (8)	3380 (11)
C(14)	5893 (10)	3711 (8)	3489 (12)
C(15)	5438 (10)	4638 (8)	2787 (11)
N(10)	3214 (9)	5807 (7)	1132 (10)
O(10)	1710 (8)	5985 (7)	318 (10)
O(10')	4305 (9)	6460 (7)	1320 (10)
O(13)	4999 (8)	2155 (6)	4094 (9)
H(C1)	−268 (9)	−285 (6)	222 (9)
H'(C1)	−123 (21)	−238 (16)	450 (21)
H''(C1)	−82 (16)	−338 (12)	258 (16)
H(C3)	377 (19)	−103 (14)	320 (18)
H'(C3)	322 (12)	0 (9)	485 (12)
H''(C3)	283 (16)	47 (12)	317 (16)
H(N7)	383 (12)	85 (9)	−3 (12)
H(C8)	−179 (11)	216 (8)	22 (11)
H(C11)	122 (12)	442 (10)	107 (13)
H(C12)	210 (11)	296 (8)	268 (11)
H(C14)	698 (12)	368 (9)	428 (12)
H(C15)	620 (12)	523 (9)	281 (12)
H(O13)	579 (12)	212 (9)	478 (12)
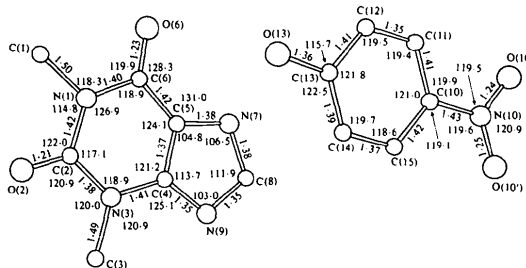
Fig. 1. Bond lengths (Å) and angles (°) (see text for standard deviations).

Table 2. *Least-squares planes and 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, where Z is along **c**, X is in the *ac* plane and Y is along **b***. Atoms designated by a dagger were given zero weight in calculating the plane; other atoms were weighted equally.

(*a*) The theophylline ring

$$-0\cdot1410X + 0\cdot6521Y + 0\cdot7449Z = 1\cdot6313 \text{ Å}$$

N(1)	0·01	C(8)	0·01
C(2)	−0·01	N(9)	0·01
N(3)	−0·01	C(1)†	0·04
C(4)	0·01	O(2)†	−0·01
C(5)	−0·01	C(3)†	−0·14
C(6)	0·01	O(6)†	0·05
N(7)	−0·02		

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

$$-0\cdot0953X + 0\cdot6950Y + 0\cdot7126Z = 2\cdot0714 \text{ Å}$$

C(10)	0·00	C(15)	0·01
C(11)	−0·01	N(10)†	−0·01
C(12)	0·01	O(10)†	−0·06
C(13)	0·00	O(10')†	0·07
C(14)	−0·01	O(13)†	0·02

Table 3. *Hydrogen bonds*

D	A	D—H	D···A	H···A	∠H—D···A
N(7)	O(6)^a	0·94 (8) Å	2·806 (8) Å	1·88 (9) Å	9 (6)°
O(13)	O(2)^b	0·74 (9)	2·711 (8)	2·02 (9)	19 (6)

Angle subtended at each atom (°)

C(5)—N(7)···O(6)^a	136·3 (6)		C(13)—O(13)···O(2)^b	109·2 (6)
C(8)—N(7)···O(6)^a	117·2 (6)			

Symmetry code: (a) $-1 - x, -y, -z$; (b) $1 - x, -y, 1 - z$.
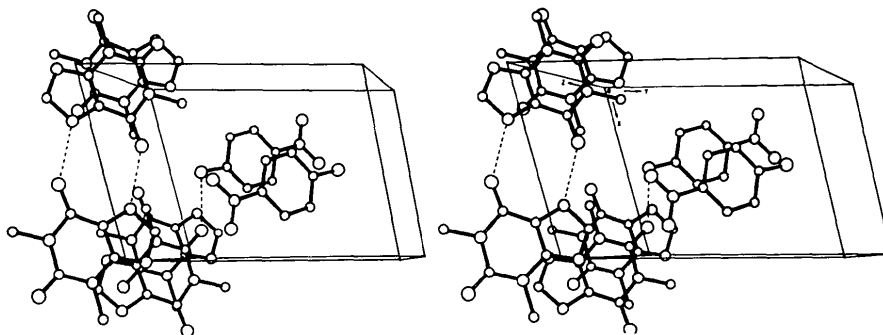
Fig. 2. Crystal packing viewed down the *c* axis. Broken lines represent hydrogen bonds.

Theophylline molecule: The bond lengths and angles are mostly as expected, except N(7)—C(8) = 1·38 Å, which is somewhat larger than values found in other purine derivatives (Voet & Rich, 1970). The purine ring is essentially planar within experimental errors (Table 2).

p-Nitrophenol molecule: The lengths of the two C—C bonds parallel to the long molecular axis, C(11)—C(12) and C(14)—C(15), are shorter than those of the other four C—C bonds. Moreover, C(10)—N(10) = 1·43 Å is significantly shorter than the usual C—N single-bond length of 1·475 Å (*International Tables for X-ray Crystallography*, 1962), and C(13)—O(13) = 1·36 Å exhibits partial double-bond character [the C—O single-bond length is 1·43 Å (*International Tables for X-ray Crystallography*, 1962)]. These shortenings show that *p*-nitrophenol takes a partial quinonoid resonance structure. As in other nitrophenols, the benzene ring is planar but the nitro group is displaced from the ring plane (Table 2); the dihedral angle between the benzene and nitro-group planes is 3·6°. The angle C—C—OH is appreciably larger on the H side, as observed in many phenols.

Crystal structure: Crystal packing is dominated by hydrogen bonds and stacking interactions. Hydrogen bonds are listed in Table 3 and are also shown in Figs. 2 and 3.

Theophylline molecules are in a dimeric arrangement by virtue of centrosymmetrically related hydrogen bonds between N(7) and O(6) (2·81 Å), and they are
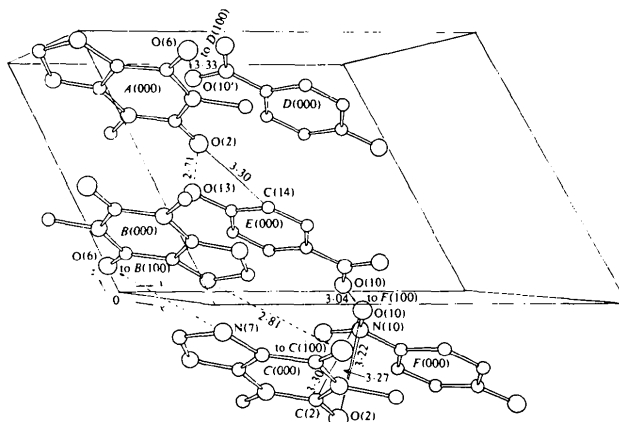

Fig. 3. Crystal packing viewed down the *a* axis. Broken lines represent hydrogen bonds. Single lines represent intermolecular contacts less than 3·35 Å. The symmetry transformations of the labelled molecules relative to Table 1 are as follows: A(000) $1 - x, -y, 1 - z$; B(000) $1 + x, y, z$; C(000) $1 - x, -y, -z$; D(000) $1 - x, 1 - y, 1 - z$; E(000) x,y,z; F(000) $1 - x, 1 - y, -z$.

stacked in relation to a centre of symmetry at separations of about 3·41 Å (molecules A and B in Fig. 3) and 3·25 Å (molecules B and C). *p*-Nitrophenol molecules are also stacked at a separation of about 3·35 Å (molecules D and E), but their degree of overlap is small.

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, 1958a), theophylline–5-chlorosalicylic acid (Shefter, 1969), caf-feine monohydrate (Sutor, 1958b), and caffeine–5-chlorosalicylic acid (Shefter, 1968), H(C8) interactions with a carbonyl O atom have also been observed.

References

Ichikawa, T., Aoki, K. & Iitaka, Y. (1978). Acta Cryst. B34, 2336–2338.
International Tables for X-ray Crystallography (1962). Vol. III, p. 276. Birmingham: Kynoch Press.
Karle, J. & Karle, I. L. (1966). Acta Cryst. 21, 849–859.
Nakazaki, N., Sekiya, M., Yoshino, T. & Ishido, Y. (1973). Bull. Chem. Soc. Jpn, 46, 3858–3863.
Sekiya, M., Yoshino, T., Tanaka, H. & Ishido, Y. (1973). Bull. Chem. Soc. Jpn, 46, 556–561.
Shefter, E. (1968). J. Pharm. Sci. 57, 1163–1169.
Shefter, E. (1969). J. Pharm. Sci. 58, 710–714.
Sutor, D. J. (1958a). Acta Cryst. 11, 83–87.
Sutor, D. J. (1958b). Acta Cryst. 11, 453–458.
Voet, D. & Rich, A. (1970). Prog. Nucleic Acid Res. Mol. Biol. 10, 183–265.

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

By Tadayoshi Ichikawa and Katsuyuki Aoki

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

and Yoichi Iitaka*

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan

Abstract. $(C_{13}H_{11}N_5OS)(C_6H_5NO_3)$, monoclinic, $C2/c$, $a = 25\cdot63$ (4), $b = 9\cdot64$ (2), $c = 16\cdot90$ (3) Å, $\beta = 112\cdot9$ (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 Kα radiation. Intensity data were collected from equi-inclination Weissenberg photographs taken with Cu Kα 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 $|F_o| \leq 2\cdot0$; $w = 1$ when $2\cdot0 < |F_o| \leq 8\cdot0$; and $\sqrt{w} = 8/|F_o|$ when $|F_c| > 8\cdot0$. The final atomic coordinates are listed in Table 1.†

---

* To whom correspondence should be addressed.