Fig. 3. Least-squares plane through atoms C(5)–C(17) of 2,4-dioxa-5α-androstan-17β-ol acetate.

the natural androgen suggests considerable flexibility in the target site requiring the hydrophilic contact.

Reference

ZANATI, G. & WOLFF, M. E. (1971). *J. Med. Chem.* **14**, 958–961; 961–962.

2,7-Dimethyl-5-acetylaminopyrazolo[1,5-a]pyrimidine

BY R. E. BALLARD AND E. K. NORRIS

School of Chemical Sciences, University of East Anglia, Norwich NOR 88 C, England

AND G. M. SHELDRICK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Abstract. $C_{10}N_4H_{12}O$, monoclinic, space group $C2/c$, $a = 14\cdot24$ (5), $b = 16\cdot70$ (5), $c = 9\cdot43$ (2) Å, $\beta = 110\cdot5$ (5)°, $Z = 8$, $D_m = 1\cdot29$ (1), $D_x = 1\cdot29$ g cm^{-3}. The structure of the acetyl derivative of the isomer which melts at 185–186 °C is found to be that of the acetyl derivative of 2,7-dimethyl-5-aminopyrazolo[1,5-a]pyrimidine (I) rather than (II). The molecules are arranged in planes separated by $a/4$; within the layers the amide groups are linked into O···H–N hydrogen-bonded chains.

(I)   (II)
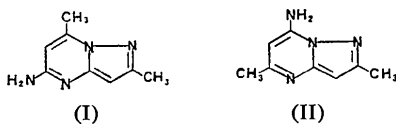
Introduction. Compounds containing the pyrazolo-[1,5-a]pyrimidine ring with structures (I) and (II) have important pharmacological properties (Takamizawa & Sawashima, 1966; Takamizawa & Hamajima, 1966; Takamizawa, Hayashi & Hamajima, 1969). The structure of the product, m.p. 201–202°, formed by the reaction of β-aminocrotonitrile and hydrazine at 100° or less has been variously assigned as (I) (von Meyer, 1915) and (II) (Takamizawa & Sawashimo, 1966). It has been suggested by Kobylecki (1973) that both (I) and (II) can in fact be made from the same reactants, the isomer m.p. 201–202° probably having structure (II) and the isomer m.p. 185–186° structure (I). Both analyse as $C_8N_4H_{10}$; the low m.p. isomer is formed by mixing cold aqueous solutions of the reactants and heating the precipitate to about 250 °C, whereas the high m.p. isomer is formed by refluxing the aqueous solutions. Since the usual spectroscopic techniques are unable to distinguish between the isomers, it was decided to acetylate the –NH₂ group and to determine the crystal structure of the low m.p. isomer. The result confirms the assignment suggested by Kobylecki.

The low m.p. isomer was prepared by Kobylecki's (1973) method. It was refluxed with acetic anhydride and the product precipitated by the addition of water. Crystallization from ethanol followed by slow crystallization (two weeks) from a dilute solution in chloroform gave transparent needles, m.p. 238–239°. Intensities were estimated visually from equi-inclination Weissenberg photographs (layers hk0 to hk5 and h0l to h3l) of a crystal of dimensions 0·43 × 0·11 × 0·16 mm taken with Cu Kα radiation ($\lambda = 1\cdot5418$ Å). No correction was made for absorption.

Conventional symbolic-addition and multisolution $\sum_2$ refinement (in space group $C2/c$) and multisolution tangent refinement (in Cc) failed to solve the structure, possibly because the arrangement of molecules into planes perpendicular to x^* invalidated the statistical assumptions. Eventually the structure was solved (in $C2/c$) by a multisolution technique (Sheldrick, 1975). A large number (here 2^{16}) of sign permutations were expanded by the $\sum_2$ formula. If the internal consistency of a permutation fell below a preset value at any stage during the expansion, the permutation was rejected. Finally a 'similarity test' was applied to avoid having to calculate too many virtually identical E maps. 21 E maps were computed, of which the eighth (in terms of $\sum_2$ consistency) revealed the complete structure except for C(15). We subsequently found that if a quartet test (Giacovazzo, 1974; Schenk, 1974) was included in the index of merit, the second E map in the ranking order was essentially correct. The structure was refined by full-matrix least-squares calculations with anisotropic temperature factors for all atoms; no attempt was made to locate the hydrogen atoms. Neutral-atom scattering factors were employed (Cromer & Mann, 1968; Cromer & Liberman, 1970). The final weighted residual $R' = \sum w^{1/2}\Delta / \sum w^{1/2}|F_o|$ was 0·126, with a corresponding unweighted R of 0·113. The weighting scheme em-

ployed was $w = (5\cdot49 + |F_o| + 0\cdot0101|F_o|^2)^{-1}$. Final atomic coordinates are given in Table 1 and anisotropic temperature factors in Table 2. The full covariance matrix was used in estimating the standard deviations in the bond lengths (Table 3) and angles (Table 4).*

Table 1. *Fractional coordinates* ($\times 10^4$)

	x/a	y/b	z/c
N(1)	1264 (6)	1188 (4)	−289 (12)
C(2)	1146 (7)	1096 (6)	1024 (14)
C(3)	1104 (6)	1845 (5)	1756 (10)
N(4)	1122 (5)	3222 (4)	747 (8)
C(5)	1204 (5)	3582 (4)	−429 (9)
C(6)	1298 (6)	3203 (5)	−1730 (10)
C(7)	1308 (5)	2379 (5)	−1717 (10)
N(8)	1249 (5)	2002 (4)	−515 (10)
C(9)	1130 (6)	2406 (5)	669 (12)
N(10)	1225 (5)	4419 (4)	−239 (8)
C(11)	1213 (6)	5000 (4)	−1324 (11)
C(12)	1296 (8)	5833 (5)	−722 (11)
O(13)	1197 (5)	4822 (3)	−2599 (9)
C(14)	1381 (7)	1910 (5)	−3080 (10)
C(15)	1181 (8)	285 (6)	1646 (14)

Table 2. *Anisotropic temperature factors* ($\text{Å}^2 \times 10^3$)

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\right].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	85 (5)	38 (4)	75 (7)	2 (4)	8 (5)	−9 (3)
C(2)	78 (6)	62 (6)	65 (8)	10 (6)	21 (6)	−13 (4)
C(3)	56 (5)	62 (5)	45 (6)	7 (5)	17 (4)	3 (4)
N(4)	68 (4)	54 (4)	34 (4)	17 (4)	23 (3)	6 (3)
C(5)	52 (4)	39 (4)	25 (4)	−6 (4)	11 (3)	5 (3)
C(6)	55 (5)	51 (5)	35 (6)	2 (4)	16 (4)	5 (3)
C(7)	49 (4)	46 (5)	37 (5)	−9 (5)	15 (4)	−1 (3)
N(8)	56 (4)	41 (3)	59 (5)	5 (4)	16 (4)	−2 (3)
C(9)	58 (5)	42 (5)	68 (8)	−5 (5)	23 (4)	−9 (3)
N(10)	65 (4)	41 (3)	37 (4)	−4 (4)	14 (3)	−2 (3)
C(11)	67 (5)	44 (4)	25 (5)	−3 (4)	23 (4)	3 (3)
C(12)	113 (8)	43 (4)	45 (6)	−8 (4)	34 (5)	−2 (4)
O(13)	107 (5)	45 (3)	61 (5)	−5 (4)	38 (4)	−2 (3)
C(14)	99 (7)	45 (4)	42 (6)	−20 (5)	26 (5)	−1 (4)
C(15)	100 (8)	67 (6)	93 (9)	28 (7)	29 (7)	1 (5)

Table 3. *Selected interatomic distances* (Å)

N(1)–C(2)	1·316 (16)	C(5)—N(10)	1·407 (13)
N(1)–N(8)	1·374 (13)	C(7)—N(8)	1·324 (14)
C(2)–C(3)	1·440 (17)	C(7)—C(14)	1·539 (16)
C(2)–C(15)	1·470 (18)	N(8)—C(9)	1·366 (15)
C(3)–C(9)	1·399 (16)	N(10)–C(11)	1·406 (15)
N(4)–C(5)	1·302 (14)	C(11)–C(12)	1·491 (15)
N(4)–C(9)	1·365 (14)	C(11)–O(13)	1·231 (14)
C(5)–C(6)	1·428 (15)	N(10)–O(13)	2·806 (16)
C(6)–C(7)	1·376 (15)		

Discussion. The identification of the ring nitrogen and carbon atoms (Fig. 1) was based on chemical considerations, but the assignment is consistent with the shorter bonds involving nitrogen and the reasonable

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30673 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
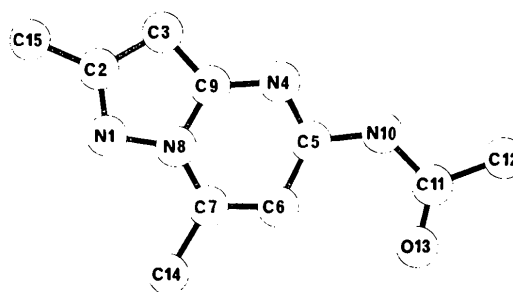

Fig. 1. The molecule of 2,7-dimethyl-5-acetylaminopyrazolo-[1,5-*a*]pyrimidine.

Table 4. *Selected bond angles* (°)

N(8)—N(1)—C(2)	105·2 (11)	C(14)–C(7)—N(8)	121·0 (9)
C(3)—C(2)–N(1)	112·9 (10)	C(7)—N(8)—N(1)	126·9 (11)
C(15)–C(2)–N(1)	119·1 (12)	C(9)—N(8)—N(1)	111·2 (11)
C(15)–C(2)–C(3)	127·6 (13)	C(9)—N(8)—C(7)	121·8 (9)
C(9)—C(3)–C(2)	102·4 (10)	N(4)–C(9)—C(3)	128·8 (12)
C(9)—N(4)–C(5)	114·2 (10)	N(8)—C(9)—C(3)	108·1 (10)
C(6)—C(5)–N(4)	126·1 (9)	N(8)—C(9)—N(4)	122·9 (11)
N(10)-C(5)–N(4)	110·8 (10)	C(11)-N(10)–C(5)	126·8 (10)
N(10)-C(5)–C(6)	123·1 (10)	C(12)-C(11)–N(10)	112·8 (10)
C(7)—C(6)–C(5)	116·1 (11)	O(13)-C(11)–N(10)	122·4 (9)
N(8)—C(7)–C(6)	118·6 (11)	O(13)-C(11)–C(12)	124·7 (10)
C(14)–C(7)–C(6)	120·3 (11)		

temperature factors obtained. The bond lengths indicate appreciable electron delocalization in the aromatic system, with (I) representing the most important valence bond extreme; C(7)–N(8) is also short. The molecules are arranged in planes at $x/a = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$; within the layers the amide groups are linked into O$\cdots$H–N hydrogen-bonded chains, with N(10)$\cdots$ O(13) = 2·806 (16) Å. Apart from this, there are no particularly short intermolecular interactions.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
GIACOVAZZO, C. (1974). *Acta Cryst.* A**30**, 481–484.
KOBYLECKI, R. J. (1973). Ph. D. thesis, Univ. of East Anglia.
MEYER, E. VON (1915). *J. Prakt. Chem.* **92**, 174–193.
SCHENK, H. (1974). *Acta Cryst.* A**30**, 477–481.
SHELDRICK, G. M. (1975). To be published.
TAKAMIZAWA, A. & HAMAJIMA, Y. (1966). Japanese Patent 12735; *Chem. Abs.* **65**, 16984.
TAKAMIZAWA, A. HAYASHI, S. & HAMAJIMA, Y. (1969). Japanese Patent 25504; *Chem. Abs.* **70**, 57886.
TAKAMIZAWA, A. & SAWASHIMA, Y. (1966). Japanese Patent 18755; *Chem. Abs.* **64**, 12696.