The structure obtained shows that the benzyltrimethylammonium cation does not lie close to the phenolic oxygen atom (see Fig. 2) and is thus an appropriate cation for the study. The phenolic oxygen is, however, hydrogen-bonded to three water molecules [O···O distances 2·756 (7), 2·795 (6), 2·714 (7) Å] and, in turn, each water molecule is further hydrogen-bonded to two waters at distances of 2·818 (7), 2·834 (7) and 2·771 (7) Å.*

Although the C1—O bond length of 1·302 (9) Å indicates a significant double-bond character, the C4—N bond length of 1·452 (10) Å and the mean lengths C1—C2 1·416 (11), C2—C3 1·383 (12) and C3—C4 1·380 (11) Å which lie within 2σ of the values reported for these lengths in the *p*-nitrophenols and *p*-nitroanisole (see Table 3), do not indicate a significant contribution of the quinonoid form (VII).

It would thus appear that the three water molecules that are hydrogen-bonded to the nitrophenolate anion significantly reduce the negative charge on the oxygen atom and so lead to a decreased need to spread the charge into the ring. Work is proceeding in an attempt to produce the anhydrous salt of benzyltrimethylammonium *p*-nitrophenolate for further study.

---

* See deposition footnote.

References

Coppens, P. & Schmidt, G. M. (1965*a*). *Acta Cryst.* **18**, 62–67.
Coppens, P. & Schmidt, G. M. (1965*b*). *Acta Cryst.* **18**, 654–663.
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.
Higashi, T. & Osaki, K. (1977). *Acta Cryst.* B**33**, 2337–2339.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
O'Connell, A. M. & Maslen, E. N. (1967). *Acta Cryst.* **22**, 134–145.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Talberg, H. J. (1974). *Acta Chem. Scand. Ser. A*, **28**, 593.
Talberg, H. J. (1975). *Acta Chem. Scand. Ser A*, **29**, 919–926.
Talberg, H. J. (1977*a*). *Acta Chem. Scand. Ser. A*, **31**, 743–751.
Talberg, H. J. (1977*b*). *Acta Chem. Scand Ser. A*, **31**, 37–46.
Talberg, H. J. (1978). *Acta Chem. Scand. Ser. A*, **32**, 373–374.
Topsom, R. D. (1987). *Prog. Phys. Org. Chem.* **16**. In the press.
Von Nagy Felsobuki, E., Topsom, R. D., Pollack, S. & Taft, R. W. (1982). *J. Mol. Struct.* **88**, 255–260.

Acta Cryst. (1987). C**43**, 1094–1097

Structure of 1,2,3,3a-Tetrahydro-3a,7-diphenyl-5-(*p*-tolyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile

By Nelly O. Pante, Hector Beltrami and Xavier Ysern*

Departamento de Quimica, Universidad Simon Bolivar, Apartado 80659, *Caracas* 1081-*A*, *Venezuela*

and Mario V. Capparelli

Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, *Caracas* 1041-*A*, *Venezuela*

(*Received* 9 *October* 1986; *accepted* 17 *December* 1986)

Abstract. $C_{27}H_{23}N_3$, $M_r = 389{\cdot}5$, monoclinic, $P2_1$, $a = 8{\cdot}783$ (1), $b = 11{\cdot}988$ (2), $c = 10{\cdot}961$ (1) Å, $\beta = 111{\cdot}26$ (1)°, $V = 1075{\cdot}5$ (3) Å^3, $Z = 2$, D_m(flotation) $= 1{\cdot}19$ (2), $D_x = 1{\cdot}202$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}2$ cm^{-1}, $F(000) = 412$, $T = 292$ K. Final $R = 0{\cdot}033$ for 1498 observed reflections. The compound has two non-planar *cis*-fused heterocycles. The six-membered heterocycle adopts a sofa conformation due to the participation of the nitrogen atom's lone pair in the diene conjugated system. The five-membered ring shows an envelope conformation and a torsionally strained C—C bond [central C—C = 1·582 (4) Å in anticlinal φ—C—C—CN].

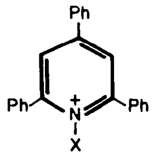
Introduction. From the reaction of the 1-amino-2,4,6-triphenylpyridinium ion (1) with a variety of reactives, Katritzky, Grzeskowiack. Alajarin-Ceron, bin Bahari, Beltrami & Keay (1982) reported the synthesis of some 60 novel derivatives (2,3,4). Unique among the products obtained was (5), which resulted from cycloaddition of acrylonitrile to (1), in spite of the steric impediment imposed by the flanking Ph groups.

---

* Present address: Johns Hopkins Medical Institutions, Biophysics Dept., 725 N. Wolfe St., Baltimore, MD 21205, USA. To whom to address correspondence.

0108-2701/87/061094-04$01.50

Following a similar procedure, Beltrami & Mallen (1984) synthetized the title compound and established its chemical formula (6) from elemental analysis and spectroscopic data. We undertook this study to confirm their assignment and to reveal finer conformational details.

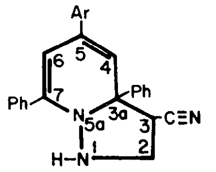


(1) X = NH_2

(2) X = $N\langle^{R}_{R'}$

(3) X = $\ddot{N}-R$

(4) X = $N{=}C\langle^{R}_{R'}$



(5) Ar = Ph

(6) Ar = $4\text{-}MeC_6H_4$

Experimental. Pale-green prisms (elongated along [010]) were obtained from a chloroform/petroleum ether solution. A crystal of *ca* 0·40 × 0·25 × 0·13 mm was used for both cell-parameter determination and data collection, utilizing a Nicolet *R*3*m*/Eclipse S140 diffractometer system equipped with a graphite monochromator; Cu $K\alpha$ radiation. Cell parameters were determined by least-squares fit of 24 high-angle reflections ($35{\cdot}6 \leq \theta \leq 47{\cdot}3°$). Intensities were measured using an ω scan with variable speed (2·0 to 29·3° $\min^{-1}$) for all reflections ($\theta \leq 57°$) within one quadrant (h −9→8, k 0→12, l 0→11); no significant change was observed, as monitored by the two standard reflections ($13\bar{2}$, 210) after every 50 measurements; a total of 1525 unique reflections were measured; 27 reflections were considered unobserved [$|F| \leq 3\sigma(F)$]; Lorentz and polarization but no absorption [$(\mu R)_{\max} \simeq 0{\cdot}1$] or extinction corrections were applied. Direct-methods solution; full-matrix least-squares refinement on $|\Delta F|^2$ of atomic coordinates and anisotropic thermal parameters for all non-H atoms. H atoms riding on parent C atoms in calculated positions [C—H = 0·960 Å, H—C—H = 109·5°, U(H) = 1·2 × $U_{\rm eq}$(C)]; same treatment for N—H, but without constraints on angles; Me group as rigid body, with same geometry and common $U_{\rm iso}$ refined. For the last cycle of refinement: $R = 0{\cdot}033$; $wR = 0{\cdot}038$, with $w = 1/[\sigma^2(F_o) + 0{\cdot}0041|F_o^2|]$ (refined); maximum shift = $0{\cdot}10\sigma$, mean shift = $0{\cdot}012\sigma$; residual electron density within −0·15 to +0·10 e Å^{-3}. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP* (Johnson, 1965).

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
N(1)	2954 (3)	3748 (3)	3204 (2)	5·0
N(2)	3544 (2)	2762 (3)	3953 (2)	3·8
N(3)	3240 (4)	4706 (4)	7406 (3)	7·5
C(1)	2740 (4)	4520 (3)	4144 (3)	5·1
C(2)	4140 (3)	4306 (3)	5434 (2)	3·7
C(3)	4600 (2)	3045 (3)	5312 (2)	3·3
C(4)	4317 (3)	2277 (3)	6288 (2)	3·4
C(5)	3439 (2)	1334 (3)	5953 (2)	3·1
C(6)	2570 (3)	1098 (3)	4580 (2)	3·3
C(7)	2563 (2)	1819 (3)	3635 (2)	3·3
C(8)	3652 (3)	4523 (4)	6558 (3)	4·8
C(9)	6409 (3)	2939 (3)	5493 (2)	3·6
C(10)	7595 (3)	3323 (3)	6640 (3)	4·4
C(11)	9247 (3)	3167 (4)	6866 (3)	5·6
C(12)	9708 (4)	2625 (4)	5949 (4)	6·3
C(13)	8555 (4)	2252 (4)	4819 (4)	6·2
C(14)	6905 (3)	2398 (3)	4586 (3)	4·8
C(15)	3362 (3)	534 (3)	6962 (2)	3·2
C(16)	4681 (3)	383 (1)	8118 (2)	4·1
C(17)	4617 (4)	−364 (4)	9055 (2)	5·4
C(18)	3235 (4)	−999 (4)	8866 (2)	5·6
C(19)	1910 (4)	−846 (3)	7720 (2)	5·0
C(20)	1970 (3)	−105 (3)	6780 (2)	4·0
C(21)	3165 (6)	−1811 (6)	9890 (4)	10·5
C(22)	1719 (3)	1564 (3)	2231 (2)	3·9
C(23)	2388 (4)	1815 (4)	1299 (2)	5·6
C(24)	1624 (5)	1490 (5)	4 (3)	7·4
C(25)	184 (5)	924 (5)	−371 (3)	7·2
C(26)	−510 (4)	669 (4)	530 (4)	6·3
C(27)	236 (3)	993 (4)	1816 (2)	4·7

Discussion. Refined atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* A view of the molecule is shown in Fig. 1, while bond lengths and angles are in Table 2. The results of the structural analysis are consistent with formula (6), thus confirming the interpretation of IR and NMR data made by Beltrami & Mallen (1984).

The lengths of C(5)—C(6) and C(7)—C(22) are in the range found in conjugated systems [*e.g.* 1·442 (7)–1·482 (8) Å in the 9-Et analogue of vitamin A acid (Schenk, Kops, van der Putten & Bode, 1978)]; also C(7)—N(2), which is shorter than either C(1)—N(1) or C(3)—N(2), shows some degree of π bonding.

As expected, the aromatic rings are planar (r.m.s.d. ≤0·005 Å). Owing to intramolecular non-bonded H···H interactions, the *D* and *E* rings are similarly twisted (34·4 and 37·7°) with respect to the C(15)—C(5)—C(6)—C(7)—C(22) plane, thus decreasing π-orbital overlapping in C(5)—C(15) and C(7)—C(22) [which are significantly longer than C(5)—C(6)]. Ring *C* is nearly eclipsed (14·1°) with the C(3)—C(4) bond, possibly to minimize interactions between H(C10) and H(C4).

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, selected torsion angles and relevant least-squares mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43660 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ring *A* has an envelope conformation, with N(1) 0·51 Å out of the mean plane through the other four atoms (r.m.s.d. = 0·029 Å); the pucker angle is 34·8°, and H(N1) is in an axial position. The eclipsed conformation about C(2)—C(3) (Fig. 2) places considerable torsional strain on this bond [C(2)—C(3) = 1·582 (4) Å]. Model manipulation shows that ring *A* has some flexibility, in spite of being connected to ring *B*. Model rotation about C(2)—C(3) would produce a different envelope conformation [with C(2) in the flap and C(8) axially bonded], increasing C(8)—C(2)—C(3)—C(9) to *ca* 148°. This seems to be a more favorable conformation than −115·8° and it is not clear why the molecule does not adopt it in the crystal. On the other hand, Beltrami & Mallen (1984) interpreted the NMR data of (5) as being produced by a 1/10 mixture of *cis/trans* isomers about C(2)—C(3). It is an open question whether that mixture contains conformers like those described above, or one of them and one of the diastereoisomers obtained by interchanging the positions of H(C2) and C(8) in those conformers.

The most planar fragment in ring *B* is C(6)—C(7)—N(2)—C(3) (r.m.s.d. = 0·005 Å), C(4) and C(5) being on the same side of that plane, at 0·20 and 0·12 Å. The ring torsion angles about the double bonds C(4)—C(5) and C(6)—C(7) are larger (−7·0 and 6·9°) than those about C(5)—C(6) and C(7)—N(2) (−2·7 and −1·4°), which are nominally single bonds. Lack of data about similar ring systems, for comparison, makes it difficult to envisage the factors governing the shape of ring *B*, which is quite different to the half-chair conformation observed and calculated in the formally analogous ring of 1,3-cyclohexadiene [for references *cf.* Bohn (1977) and White (1978)]. Alternatively, ring *B* could be described as having a sofa conformation, with quaternary C(3) 0·13 Å out of the sofa mean plane (r.m.s.d. = 0·024 Å).

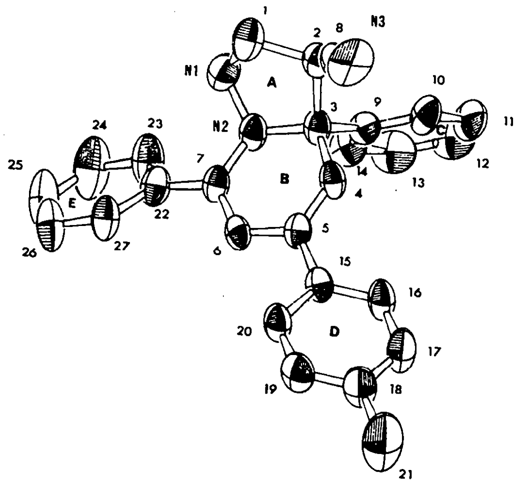


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the structure illustrating 44% probability ellipsoids. H atoms are omitted. C atoms are only numbered.

The *A*/*B* ring system is *cis*-fused at N(2)—C(3) with C(9) and (the position corresponding to) N(2)'s lone pair mutually eclipsed (Fig. 2).

There are no intermolecular distances shorter than the sums of the van der Waals radii.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·522 (4)	C(11)—C(12)	1·376 (5)
C(1)—N(1)	1·447 (4)	C(12)—C(13)	1·360 (5)
C(2)—C(3)	1·582 (4)	C(13)—C(14)	1·388 (4)
C(2)—C(8)	1·467 (4)	C(15)—C(16)	1·384 (3)
C(3)—C(4)	1·499 (3)	C(15)—C(20)	1·394 (3)
C(3)—C(9)	1·534 (3)	C(16)—C(17)	1·379 (4)
C(3)—N(2)	1·480 (3)	C(17)—C(18)	1·384 (4)
C(4)—C(5)	1·342 (3)	C(18)—C(19)	1·381 (4)
C(5)—C(6)	1·447 (3)	C(18)—C(21)	1·503 (5)
C(5)—C(15)	1·484 (3)	C(19)—C(20)	1·376 (4)
C(6)—C(7)	1·347 (3)	C(22)—C(23)	1·383 (4)
C(7)—C(22)	1·478 (3)	C(22)—C(27)	1·394 (4)
C(7)—N(2)	1·387 (3)	C(23)—C(24)	1·387 (4)
C(8)—N(3)	1·135 (4)	C(24)—C(25)	1·361 (6)
C(9)—C(10)	1·389 (3)	C(25)—C(26)	1·371 (5)
C(9)—C(14)	1·383 (3)	C(26)—C(27)	1·377 (4)
C(10)—C(11)	1·393 (4)	N(1)—N(2)	1·426 (3)
C(2)—C(1)—N(1)	106·5 (2)	C(12)—C(13)—C(14)	120·6 (3)
C(1)—C(2)—C(3)	103·2 (2)	C(9)—C(14)—C(13)	120·5 (3)
C(1)—C(2)—C(8)	111·5 (2)	C(5)—C(15)—C(16)	121·2 (2)
C(3)—C(2)—C(8)	113·7 (2)	C(5)—C(15)—C(20)	121·5 (2)
C(2)—C(3)—C(4)	114·4 (2)	C(16)—C(15)—C(20)	117·3 (2)
C(2)—C(3)—C(9)	110·6 (2)	C(15)—C(16)—C(17)	121·3 (2)
C(4)—C(3)—C(9)	106·9 (2)	C(16)—C(17)—C(18)	121·1 (2)
C(2)—C(3)—N(2)	102·6 (2)	C(17)—C(18)—C(19)	117·8 (2)
C(4)—C(3)—N(2)	111·8 (2)	C(17)—C(18)—C(21)	121·1 (3)
C(9)—C(3)—N(2)	110·7 (2)	C(19)—C(18)—C(21)	121·1 (3)
C(3)—C(4)—C(5)	123·4 (2)	C(18)—C(19)—C(20)	121·3 (2)
C(4)—C(5)—C(6)	118·9 (2)	C(15)—C(20)—C(19)	121·1 (2)
C(4)—C(5)—C(15)	121·2 (2)	C(7)—C(22)—C(23)	122·5 (2)
C(6)—C(5)—C(15)	120·0 (2)	C(7)—C(22)—C(27)	119·9 (2)
C(5)—C(6)—C(7)	121·9 (2)	C(23)—C(22)—C(27)	117·5 (2)
C(6)—C(7)—C(22)	122·0 (2)	C(22)—C(23)—C(24)	121·1 (3)
C(6)—C(7)—N(2)	120·0 (2)	C(23)—C(24)—C(25)	120·1 (3)
C(22)—C(7)—N(2)	117·5 (2)	C(24)—C(25)—C(26)	120·0 (3)
C(2)—C(8)—N(3)	178·1 (3)	C(25)—C(26)—C(27)	120·3 (3)
C(3)—C(9)—C(10)	119·4 (2)	C(22)—C(27)—C(26)	120·9 (3)
C(3)—C(9)—C(14)	121·8 (2)	C(1)—N(1)—N(2)	103·5 (2)
C(10)—C(9)—C(14)	118·6 (2)	C(7)—N(2)—C(3)	123·1 (2)
C(9)—C(10)—C(11)	120·5 (3)	C(3)—N(2)—N(1)	110·7 (2)
C(10)—C(11)—C(12)	119·8 (3)	C(7)—N(2)—N(1)	117·9 (2)
C(11)—C(12)—C(13)	120·1 (3)		

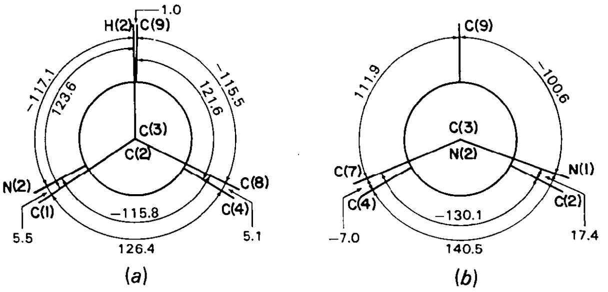


Fig. 2. Newman projections (*a*) along the C(2)—C(3) bond, and (*b*) along the N(2)—C(3) bond. Torsional angles are in °; average e.s.d. 0·2°.

We wish to thank Dr A. C. Skapski (Imperial College, London) for allowing the use of the diffractometer. We acknowledge the use of the Interactive Graphics Facility of the Department of Biophysics, Johns Hopkins University School of Medicine. This facility was established and maintained by NIH and NSF grants and by a gift from the Richard King Mellon Foundation.

References

Beltrami, H. & Mallen, J. (1984). *Tetrahedron*, **40**, 1683–1690.

Bohn, R. K. (1977). *Mol. Struct. Diffr. Methods*, **5**, 23–94.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Katritzky, A. R., Grzeskowiack, N. E., Alajarin-Ceron, M., bin Bahari, Z., Beltrami, H. B. & Keay, J. G. (1982). *J. Chem. Res.* (*M*), pp. 2164–2195.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. A program for crystallographic calculations. Univ. of Cambridge, England.

Schenk, H., Kops, R. T., van der Putten, N. & Bode J. (1978). *Acta Cryst.* B**34**, 505–507.

Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

White, D. N. J. (1978). *Mol. Struct. Diffr. Methods*, **6**, 38–92.

Acta Cryst. (1987). C**43**, 1097–1100

Triamterene*

By Carl H. Schwalbe†

*Drug Development Research Group, Pharmaceutical Sciences Institute, Department of Pharmaceutical Sciences, Aston University, Aston Triangle, Birmingham B*4 *7ET, England*

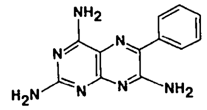
and Graheme J. B. Williams‡

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, *USA*

(*Received* 20 *October* 1986; *accepted* 4 *February* 1987)

Abstract. 2,4,7-Triamino-6-phenylpteridine, $C_{12}H_{11}N_7$, $M_r = 253{\cdot}28$, triclinic, $P\bar{1}$, $a = 7{\cdot}440\,(1)$, $b = 10{\cdot}164\,(1)$, $c = 16{\cdot}666\,(2)$ Å, $\alpha = 77{\cdot}43\,(1)$, $\beta = 88{\cdot}75\,(1)$, $\gamma = 88{\cdot}56\,(1)°$, $V = 1229{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}37$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 6{\cdot}59$ cm^{-1}, $F(000) = 528$, $T = 291\,(2)$ K, final $R = 0{\cdot}090$ for 3186 observed reflections. The two independent molecules are similar in geometry, with the bonds between phenyl and pteridine rings twisted by 31·1 and 33·4° respectively. Molecules are linked into ribbons by hydrogen bonds between both H atoms of the 2-amino groups and N(1) and N(3) of adjacent rings. The ribbons are connected by paired N(7)—H···N(8) hydrogen bonds around centers of symmetry; pteridine rings are also stacked.

Introduction. Triamterene (I) is a valuable potassium-sparing diuretic and also a modest inhibitor of dihydrofolate reductase (DHFR). It contains the same 2,4-diaminopteridine moiety as active DHFR inhibitors such as methotrexate, but the 6-phenyl and 7-amino substituents are evidently not conducive to maximum antifolate activity. The present study was undertaken with the intention of comparing the molecular geometry of triamterene with that of the parent compound 2,4-diaminopteridine (Schwalbe & Williams, 1986*a*) and other antifolates and diuretics.



(I)

Experimental. Platelets grown by slow evaporation from dimethyl sulfoxide with a small quantity of acetone added near the end. Specimen 0·27 × 0·24 × 0·03 mm. Unit-cell dimensions by least-squares analysis of setting angles of 25 reflections, $10{\cdot}7 \le \theta \le 59{\cdot}0°$, graphite-monochromated Cu $K\alpha$ radiation, Enraf–Nonius CAD-4 diffractometer. Data collection by ω–2θ scans, ω-scan rate 1·2 to 3·4° min^{-1}, ω-scan

---

* This research was carried out in part at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the US Department of Energy, Office of Basic Energy Sciences.

† Research collaborator at Brookhaven National Laboratory.

‡ Present address: Enraf–Nonius, 390 Central Avenue, Bohemia, New York 11716, USA.

0108-2701/87/061097-04$01.50