Program, the Petroleum Research Foundation administered by the American Chemical Society, and the Robert A. Welch Foundation for support of this work.

References

BEDDOES, R. L., DALTON, L., JOULE, J. A., MILLS, O. S., STREET, D. & WATT, C. I. F. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 787–797.

CELLATLY, R. P., OLLIS, W. D. & SUTHERLAND, I. O. (1976). *J. Chem. Soc. Perkin Trans.* 1, pp. 913–925.

CESARIO, M. & GUILHEM, J. (1977). *Cryst. Struct. Commun.* **6**, 707–710.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

GUGGENBERGER, L. J. (1975). *Acta Cryst.* B**31**, 13–19.

SHELDRICK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1991). C**47**, 414–416

The Structure of 2-(3′-Hydroxy-2′,3′-dimethylbutan-2′-yl)pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one Hydrate, a Photoadduct of Allopurinol with 2-Propanol

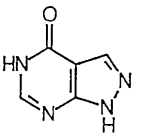
BY R. BRIAN LAMONT,* R. JEREMY H. DAVIES† AND JOHN F. MALONE*

Departments of Chemistry and Biochemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

(*Received* 22 *January* 1990; *accepted* 3 *July* 1990)

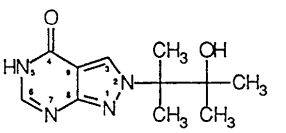
Abstract. $C_{11}H_{16}N_4O_2.H_2O$, $M_r = 254{\cdot}3$, monoclinic, $P2_1/c$, $a = 13{\cdot}343\ (13)$, $b = 6{\cdot}885\ (7)$, $c = 13{\cdot}334\ (13)$ Å, $\beta = 91{\cdot}76\ (10)°$, $V = 1224{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}38$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}064$ mm^{-1}, $F(000) = 544$, $T = 293$ K, final $R = 0{\cdot}038$ for 1191 unique reflections with $I > 3\sigma(I)$. The structure of the title compound, which is obtained by UV-irradiation of allopurinol in aqueous 2-propanol, is described. The crystals contain one molecule of water per asymmetric unit which is involved in a network of hydrogen bonding.

Introduction. Owing to its inhibition of the enzyme xanthine oxidase, the purine analogue allopurinol (1)



(1)

is an important therapeutic agent in the treatment of hyperuricaemic conditions, including gout. It also exhibits anti-trypanosomal activity (Marr, Berens & Nelson, 1978). When purines are irradiated with ultraviolet light in the presence of 2-propanol they undergo photoalkylation in which H atoms attached to ring C atoms are substituted by a 2-hydroxypropyl group (Elad, 1976). However, similar irradiation of allopurinol with 2-propanol (Bose & Davies, 1980) gave as the major photoproduct a compound identified, on the basis of spectroscopic inference, as 2-(3′-hydroxy-2′,3′-dimethylbutan-2′-yl)pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (2). This assignment is confirmed by the crystal structure analysis reported here. A feature of the molecule distinguishing it from allopurinol (Prusiner & Sundaralingam, 1972) and related pyrazolo[3,4-*d*]pyrimidine derivatives whose structures have been reported (Gadret, Goursolle & Leger, 1974; Sprang, Scheller, Rohrer & Sundaralingam, 1978; Srikrishnan, Parthasarathy, De & Chheda, 1983) is the requirement imposed by the substitution at N(2) for the distribution of π electrons in the allopurinol nucleus to reflect a 'quinonoid' arrangement of the conjugated double bonds.



(2)

Experimental. Crystals were obtained from water. Colourless rectangular plates, crystal dimensions 1·0 × 0·25 × 0·10 mm, Stöe-Stadi-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; unit-cell dimensions from 25 centred axial reflections in the range $3 < \theta < 20°$; the transformation (010/−10−1/−101) gives a metrically orthorhombic *A*-centred cell but Weissenberg photographs taken

* Department of Chemistry.
† Department of Biochemistry.

0108-2701/91/020414-03$03.00

Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3$.

	x	y	z	U_{eq}
N(1)	0·6932 (1)	0·1511 (4)	0·4757 (1)	0·048 (1)
N(2)	0·7002 (1)	0·1918 (3)	0·5772 (1)	0·045 (1)
C(3)	0·6121 (2)	0·2458 (4)	0·6144 (2)	0·045 (1)
C(4)	0·4388 (2)	0·2935 (4)	0·5240 (2)	0·046 (1)
N(5)	0·4055 (2)	0·2768 (4)	0·4250 (2)	0·052 (1)
C(6)	0·4641 (2)	0·2190 (5)	0·3480 (2)	0·056 (1)
N(7)	0·5571 (2)	0·1689 (4)	0·3550 (1)	0·052 (1)
C(8)	0·5968 (2)	0·1857 (4)	0·4518 (2)	0·045 (1)
C(9)	0·5430 (2)	0·2433 (4)	0·5353 (2)	0·044 (1)
C(10)	0·7998 (2)	0·1955 (4)	0·6310 (2)	0·047 (1)
C(11)	0·7822 (2)	0·1410 (6)	0·7409 (2)	0·058 (1)
C(12)	0·8672 (2)	0·0449 (6)	0·5851 (3)	0·063 (1)
C(13)	0·8426 (2)	0·4051 (5)	0·6212 (2)	0·050 (1)
C(14)	0·8589 (2)	0·4615 (6)	0·5128 (2)	0·059 (1)
C(15)	0·9415 (2)	0·4290 (7)	0·6823 (2)	0·062 (1)
O(1)	0·3829 (1)	0·3492 (3)	0·5900 (1)	0·060 (1)
O(2)	0·7708 (1)	0·5379 (3)	0·6572 (1)	0·054 (1)
O(3)	0·2126 (2)	0·1327 (5)	0·6462 (1)	0·065 (1)

about the unique monoclinic axis show the true Laue group to be $2/m$; ω scans, scan width 2°, scan speed 1·5° min^{-1}. 2215 reflections were reviewed ($6 \le 2\theta \le 60°$; h: $-18 \rightarrow 18$, k: $0 \rightarrow 7$, l: $0 \rightarrow 18$) and the 1305 registering >5 counts s^{-1} were measured. No significant variations in intensity for control reflections; Lp corrections, no absorption corrections. 1192 unique reflections with $I > 3\sigma(I)$ were deemed to be observed. The structure was determined by the direct methods of *SHELX*76 (Sheldrick, 1976) and refined by least-squares calculations on F with non-H atoms anisotropic, H atoms located from a difference Fourier map and refined with individual isotropic temperature factors, atomic scattering factors for all atoms as in *SHELX*76. Final $R = 0·038$, $wR = 0·043$, $w = 1·0/[\sigma^2(F_o) + 0·00352(F_o)^2]$; 235 parameters, maximum $(\Delta/\sigma) = 0·002$, residual electron-density fluctations on final difference Fourier synthesis +0·08 and −0·11 e Å^{-3}.

Discussion. Final atomic coordinates for non-H atoms are given in Table 1.* A *PLUTO* (Motherwell & Clegg, 1978) picture of the molecule is shown in Fig. 1. Bond lengths and angles are given in Table 2, together with those of their counterparts in allopurinol (Prusiner & Sundaralingam, 1972).

Like allopurinol, the photoadduct is found in the C(4) keto form with the carbonyl bond having a distinctly skewed disposition [N(5)—C(4)—O(1) =

* Lists of structure factors, anisotropic thermal parameters, full bond lengths, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53377 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

		Photoadduct (2)	Allopurinol (1)
Pyrimidine ring			
C(4)—N(5)		1·385 (3)	1·399 (5)
N(5)—C(6)		1·369 (4)	1·364 (5)
C(6)—N(7)		1·289 (3)	1·292 (5)
N(7)—C(8)		1·385 (3)	1·379 (4)
C(8)—C(9)		1·400 (3)	1·395 (5)
C(9)—C(4)		1·436 (4)	1·432 (5)
C(4)—O(1)		1·233 (3)	1·227 (4)
Pyrazole ring			
N(1)—C(8)		1·338 (3)	1·338 (4)
N(1)—N(2)		1·383 (3)	1·374 (4)
N(2)—C(3)		1·342 (3)	1·325 (5)
C(3)—C(9)		1·380 (3)	1·414 (5)
Hydroxyalkyl side chain			
N(2)—C(10)	1·492 (3)	C(13)—C(14)	1·518 (4)
C(10)—C(11)	1·538 (4)	C(13)—C(15)	1·538 (4)
C(10)—C(12)	1·514 (4)	C(13)—O(2)	1·419 (3)
C(10)—C(13)	1·559 (4)		
Hydrogen bonds			
O(1)···O(3)	2·838 (3)	O(3)···O(2^{ii})	2·705 (3)
O(3)···N(1^{i})	2·857 (4)	O(2)···N(5^{iii})	2·863 (3)

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

	Photoadduct (2)	Allopurinol (1)
Pyrimidine ring		
C(9)—C(4)—N(5)	111·3 (2)	111·1 (3)
C(4)—N(5)—C(6)	124·4 (2)	125·6 (3)
N(5)—C(6)—N(7)	126·5 (3)	125·0 (3)
C(6)—N(7)—C(8)	112·6 (2)	112·4 (3)
N(7)—C(8)—C(9)	125·1 (2)	127·3 (3)
C(8)—C(9)—C(4)	120·1 (2)	118·6 (3)
N(5)—C(4)—O(1)	121·5 (2)	
C(9)—C(4)—O(1)	127·2 (2)	
C(4)—C(9)—C(3)	134·4 (2)	
N(7)—C(8)—N(1)	122·9 (2)	
Pyrazole ring		
C(8)—N(1)—N(2)	103·4 (2)	110·7 (2)
N(1)—N(2)—C(3)	112·7 (2)	106·4 (3)
N(2)—C(3)—C(9)	106·6 (2)	110·4 (3)
C(3)—C(9)—C(8)	105·4 (2)	104·6 (3)
C(9)—C(8)—N(1)	112·0 (2)	107·8 (3)

Hydroxyalkyl side chain			
N(1)—N(2)—C(10)	120·4 (2)	C(12)—C(10)—C(13)	112·1 (3)
C(3)—N(2)—C(10)	126·5 (2)	C(10)—C(13)—C(14)	112·4 (2)
N(2)—C(10)—C(11)	107·1 (2)	C(10)—C(13)—C(15)	111·4 (3)
N(2)—C(10)—C(12)	109·0 (2)	C(10)—C(13)—O(2)	108·4 (2)
N(2)—C(10)—C(13)	107·4 (2)	C(14)—C(13)—C(15)	109·4 (2)
C(11)—C(10)—C(12)	109·1 (3)	C(14)—C(13)—O(2)	106·0 (2)
C(11)—C(10)—C(13)	111·9 (2)	C(15)—C(13)—O(2)	109·2 (2)

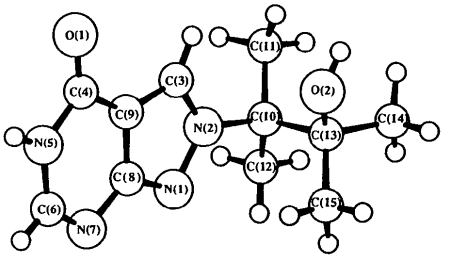


Fig. 1. The molecular structure of photoadduct (2).

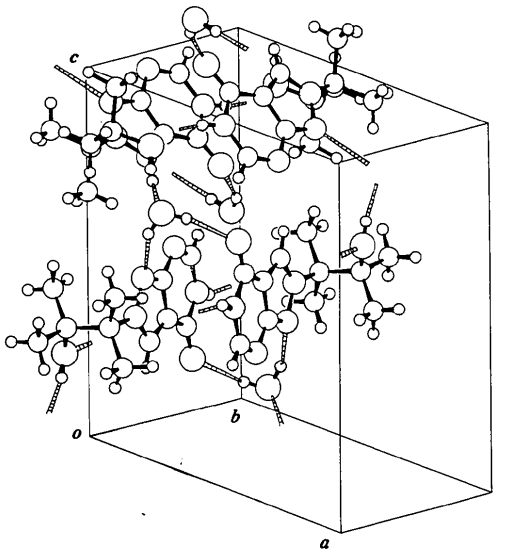


Fig. 2. The unit cell of photoadduct (2).

121·5 (2), C(9)—C(4)—O(1) = 127·2 (2)°]. The irregular geometry of the six-membered pyrimidine ring is very similar in both molecules; corresponding bond lengths and endocyclic bond angles are within 0·014 Å and 2·2° respectively (Table 2). However, there are marked differences in bond angles in the five-membered pyrazole ring moieties, reflecting the alternative tautomeric distribution of the π electrons. In particular, the sum of the endocyclic angles at C(3) and N(1) is 11° smaller in the photoadduct than in allopurinol, while the N(2) angle is 6° larger.

The hydroxyalkyl side chain on N(2) is fully extended with a terminal methyl group, and all substituents are in staggered conformations.

The water molecule of crystallization [O(3)] is involved in hydrogen bonding to three different molecules of the photoadduct, using its own H atoms to bond to the carbonyl O atom [O(1) at x, y, z] and to N(1) at $1-x, -y, 1-z$ as well as bonding, *via* the hydroxyl H atom, to O(2) at $1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$. The hydroxyl O atom, O(2), in turn hydrogen bonds *via* H(5) to N(5) at $1-x, 1-y, 1-z$. Thus, each formula unit is involved in seven hydrogen bonds leading to the network illustrated in Fig. 2.

References

BOSE, S. N. & DAVIES, R. J. H. (1980). *Photochem. Photobiol.* **31**, 195–199.

ELAD, D. (1976). In *Photochemistry and Photobiology of Nucleic Acids*, VOL. I, edited by S.Y. WANG, pp. 357–380. New York: Academic Press.

GADRET, M., GOURSOLLE, M. & LEGER, J. M. (1974). *Acta Cryst.* B**30**, 1598–1602.

MARR, J. J., BERENS, R. L. & NELSON, D. J. (1978). *Science*, **201**, 1018–1020.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

PRUSINER, P. & SUNDARALINGAM, M. (1972). *Acta Cryst.* B**28**, 2148–2152.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SPRANG, S., SCHELLER, R., ROHRER, D. & SUNDARALINGAM, M. (1978). *J. Am. Chem. Soc.* **100**, 2867–2872.

SRIKRISHNAN, T., PARTHASARATHY, R., DE, N. C. & CHHEDA, G. B. (1983). *Acta Cryst.* C**39**, 1441–1445.

Acta Cryst. (1991). C**47**, 416–418

Structure of Dicyanodurene*

BY DOYLE BRITTON AND COBY VAN RIJ

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, *USA*

(*Received* 14 *March* 1990; *accepted* 2 *July* 1990)

Abstract. $C_{12}H_{12}N_2$, $M_r = 184·24$, monoclinic, $C2/c$, $a = 17·176$ (9), $b = 5·055$ (2), $c = 12·460$ (8) Å, $\beta = 113·27$ (5)°, $Z = 4$, $V/Z = 248·5$ (4) Å^3, $D_x = 1·231$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·69$ cm^{-1}, $F(000) = 392$, $T = 183$ (3) K, $R = 0·055$ for 977 reflections. The bond lengths and angles are normal. The molecule is slightly puckered into a chair form owing to the crowding of the substituents. A further consequence of the crowding is that the CH_3 groups are rotated away from the eclipsed orientation found in durene by 8 (2) and 15 (3)°. Adjacent methyl groups rotate in the same direction in order to minimize the H···H contacts. There are no special intermolecular interactions apparent from the packing.

* 2,3,5,6-Tetramethyl-1,4-benzenedicarbonitrile.

Introduction. The crystal structure of dicyanodurene was originally determined (van Rij, 1976) as

0108-2701/91/020416-03$03.00