

magnitudes of χ_N and χ_C indicate easier deformability at the nitrogen atom, in agreement with the observation of Winkler & Dunitz.

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The Crystal Structure and Absolute Configuration of the Antibiotic Actinobolin

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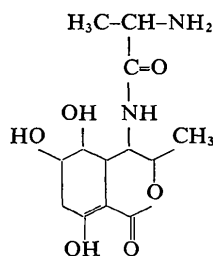
The structure of a solvated derivative of the title compound ($C_{13}H_{21}N_2O_6^+I^- \cdot H_2O \cdot \frac{1}{4}C_2H_5N$) has been determined from diffractometer data and refined to an R_1 of 0.089. The crystals are monoclinic, $P2_1$, $a = 19.340$ (2), $b = 24.202$ (3), $c = 7.968$ (3) Å and $\beta = 102.32$ (2)°, with four molecules of actinobolin. HI, four water molecules and one acetonitrile per asymmetric unit. The absolute configuration was determined from the anomalous scattering of the iodides. The four independent molecules of actinobolin have similar molecular conformations and are involved with the iodides and solvate molecules in a complex network of intermolecular, intramolecular and bifurcated hydrogen bonds.

Introduction

The antibiotic actinobolin was first isolated in 1959 as a sulfate salt from submerged aerated broth cultures of *Streptomyces griseoviridis* var. *atrofaciens* (Pitillo, Fischer, McAlpine, Thompson & Ehrlich, 1959; Haskell & Bartz, 1959). Initial investigations of its biological activity showed actinobolin to be a broad-spectrum antibiotic exhibiting low toxicity (Haskell & Bartz,

1959) and mild anticarcinogenic activity (Sugiura & Reilly, 1959; Burchenal, Holmberg, Reilly, Hemphill & Reppert, 1959; Teller, Wolff & Wagshul, 1964; Cappuccino, Oettgen, Murphy, Reilly & Burchenal, 1960; Merker, Bowie & Ando, 1962).

In 1968 the structure of actinobolin free base was shown by Munk, Nelson, Antosz, Herald & Haskell (1968) to be 4-(2-aminopropionamido)-3,4,4 α ,5,6,7-hexahydro-5,6,8-trihydroxy-3-methyl isocoumarin.



Additional evidence was later presented for the structure of actinobolin and the absolute configuration was proposed based on n.m.r. studies and the isolation of L-alanyl-L-threonine following mild permanganate oxidation of the free base (Antosz, Nelson, Herald & Munk, 1970).

In 1970 actinobolin was shown to be a potentially useful cariostatic agent (Hunt, Sandham & Caldwell, 1970; Hunt, Navia & Lopez, 1971). Additional studies demonstrated that actinobolin exhibits low oral toxicity (Hunt, Bradley & Bachmann, 1970), inhibits protein synthesis in bacteria (Hunt & Narkates, 1971) and serves to increase the hardness of human enamel (Hunt, Armstrong, Black & Narkates, 1972). Actinobolin has also been found to be inhibitory for mixed bacteria associated with periodontal disease (Armstrong & Hunt, 1972). *In vitro* studies have demonstrated that actinobolin has comparable activity with other antibiotics used in the treatment of periodontal disease and dental caries (Hunt, Armstrong, Black & Narkates, 1972). In addition, cross-resistance studies have shown that laboratory-derived strains of bacteria resistant to actinobolin were not resistant to several commonly used antibiotics; the converse was also found to be true (Hunt, Armstrong, Black & Narkates, 1972).

Owing to the current interest in the biological activity of actinobolin, especially as related to the problems of dental caries and periodontal disease, a crystal-structure determination was begun on an iodide salt of actinobolin with X-ray diffraction data collected by Professor Charles E. Bugg.

Experimental*

Crystals of actinobolin.HI were obtained by passing a solution of actinobolin sulfate, $(C_{13}H_{20}N_2O_6)_2H_2SO_4 \cdot H_2O$, through a strong anion exchange column charged with NaI. The resulting material was recrystallized from acetonitrile. Examination of the crystals revealed a monoclinic space group with systematic absences $0k0$, k odd. These absences with the known optical activity of the compound established the space group as $P2_1$. Immediately after diffraction-data collection accurate values of the cell parameters were determined by least-squares refinement of 2θ val-

ues for seven high-angle $Cu K\alpha_1$ and nine low-angle $Cu K\alpha_2$ reflections. These cell parameters with other physical and crystallographic data are given in Table 1. A preliminary density calculation indicated eight molecules per unit cell, four per asymmetric unit.

Table 1. Summary of physical and crystallographic data for actinobolin.HI

Stoichiometry	$C_{13}H_{21}N_2O_6I \cdot H_2O \cdot \frac{1}{4}C_2H_5N$
Space group	$P2_1$
a	19.340 (2) Å
b	24.202 (3)
c	7.968 (3)
β	102.32 (2)°
Density (obs)	1.64 (1) g cm ⁻³
Density (calc)	1.66
Z	8
μ	144.3 cm ⁻¹
Reflections:	
$F^2 > 2\sigma_I$	4792
Total	6233
$R_1 (F^2 > 2\sigma_I)$	0.086
R_1 (all data)	0.110

Intensities were collected on a Picker FACS-1 diffractometer with a scintillation counter and nickel-filtered $Cu K\alpha$ radiation. A θ - 2θ scanning technique was used for measurement of the 6233 independent reflections with $2\theta < 128^\circ$. Three standard reflections monitored periodically showed decreases in intensity of 23, 33, and 20%. A scaling procedure similar to that described by Ibers (1969) was used to correct for this decline. Variances, $\sigma(I)^2$, were assigned to the intensities where

$$\sigma(I)^2 = \sigma^2 (\text{counting statistics}) + (0.03S)^2,$$

S being the scan counts. The data were corrected for Lorentz and polarization effects and for absorption.

Structure determination and refinement

The coordinates of the four independent iodide ions were determined from a Patterson map by vector superposition techniques. From an electron-density map computed with the iodides as a phasing model, the coordinates of 46 atoms were determined. Repeated Fourier synthesis resulted in the location of all 88 expected lighter atoms; $R_1 = 0.30$.

Block-diagonal least-squares refinement of all positional and anisotropic thermal parameters lowered R_1 to 0.11. A difference map was computed which revealed the presence of four water molecules and one molecule of acetonitrile per asymmetric unit.

Absolute configuration determination

After convergence of the 95-atom model at $R = 0.089$, terms due to the anomalous scattering of iodine were included in further block-diagonal least-squares refinement, resulting in $R_1 = 0.096$ for the original and $R_1 = 0.086$ for the opposite enantiomer. The weighted R

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Table 2. Final atomic positions ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) with their estimated standard errors for actinobolin. HI
$$T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(A1)	3940 (6)	4809 (4)	7501 (15)	41 (4)	9 (2)	235 (24)	8 (5)	31 (16)	-6 (12)
C(A2)	3826 (8)	4307 (7)	6859 (21)	36 (5)	14 (3)	192 (32)	4 (7)	53 (21)	-42 (18)
C(A3)	3228 (7)	4027 (6)	6646 (17)	33 (4)	10 (3)	101 (23)	12 (6)	65 (15)	-12 (14)
C(A4)	2665 (8)	4287 (7)	7259 (17)	34 (5)	17 (3)	70 (23)	-20 (7)	31 (17)	-21 (15)
O(A5)	2691 (6)	4765 (4)	7832 (14)	41 (4)	12 (2)	221 (23)	-15 (5)	60 (15)	-40 (12)
O(A6)	2069 (5)	4033 (5)	7220 (14)	25 (3)	23 (3)	214 (22)	-4 (5)	64 (12)	-6 (14)
C(A7)	1954 (7)	3440 (7)	6434 (21)	14 (4)	19 (3)	195 (32)	20 (6)	19 (18)	17 (19)
C(A8)	1370 (9)	3187 (9)	7284 (24)	29 (5)	30 (5)	271 (42)	8 (9)	54 (23)	-19 (26)
C(A9)	2637 (7)	3116 (7)	6767 (18)	22 (4)	15 (3)	102 (25)	1 (7)	12 (17)	16 (16)
N(A10)	2906 (6)	3041 (5)	8574 (14)	30 (4)	14 (2)	88 (20)	5 (5)	32 (14)	-3 (13)
C(A11)	3003 (6)	3544 (6)	9309 (17)	20 (3)	10 (2)	136 (24)	-6 (6)	44 (15)	11 (16)
O(A12)	2842 (6)	2130 (5)	8546 (15)	49 (5)	12 (2)	203 (24)	5 (6)	15 (17)	7 (13)
C(A13)	3370 (7)	2531 (7)	11212 (19)	28 (4)	16 (3)	147 (27)	-15 (8)	31 (18)	-18 (19)
N(A14)	3113 (8)	2056 (5)	12032 (18)	64 (6)	11 (2)	176 (27)	24 (7)	45 (21)	-21 (14)
C(A15)	4174 (7)	2504 (10)	11403 (22)	16 (4)	44 (6)	192 (33)	16 (10)	19 (19)	30 (28)
C(A16)	3164 (7)	3443 (7)	5952 (18)	26 (4)	15 (3)	114 (25)	-7 (6)	53 (16)	15 (16)
C(A17)	3885 (8)	3169 (7)	6194 (21)	35 (5)	12 (3)	195 (31)	-19 (7)	72 (19)	-15 (18)
O(A18)	3782 (5)	2639 (5)	5368 (14)	37 (3)	22 (3)	199 (22)	-16 (6)	27 (14)	43 (14)
C(A19)	4414 (8)	3502 (7)	5540 (18)	31 (5)	20 (4)	115 (25)	-11 (7)	64 (17)	-20 (17)
O(A20)	5068 (5)	3243 (6)	5712 (15)	24 (3)	36 (3)	328 (25)	-36 (5)	133 (12)	-73 (16)
C(A21)	4542 (8)	4087 (8)	6418 (26)	21 (5)	25 (4)	339 (44)	-3 (8)	47 (23)	-32 (26)
O(B1)	6622 (5)	4773 (5)	1210 (16)	30 (3)	23 (3)	329 (29)	-38 (5)	67 (15)	-34 (16)
C(B2)	6773 (7)	4254 (7)	1812 (20)	20 (4)	19 (4)	182 (30)	-3 (7)	48 (17)	-13 (19)
C(B3)	7435 (7)	4052 (7)	2025 (15)	23 (4)	25 (4)	66 (20)	2 (7)	74 (12)	35 (15)
C(B4)	7973 (7)	4379 (6)	1499 (17)	29 (4)	12 (3)	82 (22)	-2 (6)	48 (15)	8 (14)
O(B5)	7878 (5)	4849 (5)	900 (13)	32 (3)	15 (2)	185 (21)	-1 (5)	43 (13)	-5 (12)
O(B6)	8608 (5)	4162 (4)	1468 (13)	33 (3)	14 (2)	156 (19)	10 (5)	42 (13)	-18 (12)
C(B7)	8789 (7)	3620 (6)	2228 (21)	20 (4)	11 (3)	261 (33)	-18 (6)	78 (17)	-40 (17)
C(B8)	9449 (7)	3437 (9)	1507 (24)	10 (4)	37 (5)	300 (38)	-8 (8)	70 (18)	26 (26)
C(B9)	8175 (6)	3233 (6)	1809 (18)	13 (3)	11 (3)	152 (26)	0 (6)	17 (16)	-34 (15)
N(B10)	7917 (6)	3142 (5)	-34 (14)	32 (4)	7 (2)	107 (20)	-13 (5)	32 (14)	1 (12)
C(B11)	7878 (6)	2649 (7)	-744 (15)	10 (3)	26 (4)	59 (20)	-8 (6)	22 (12)	39 (15)
O(B12)	8090 (7)	2232 (5)	10 (16)	65 (5)	13 (2)	218 (25)	-20 (6)	61 (18)	-54 (13)
C(B13)	7466 (8)	2651 (7)	-2595 (19)	39 (5)	16 (3)	170 (26)	23 (7)	97 (17)	58 (16)
N(B14)	7667 (8)	2180 (7)	-3509 (21)	58 (6)	21 (3)	385 (36)	30 (8)	160 (22)	116 (18)
C(B15)	6660 (7)	2627 (8)	-2719 (20)	30 (4)	28 (4)	167 (30)	40 (7)	40 (19)	17 (21)
C(B16)	7571 (8)	3452 (7)	2674 (18)	36 (5)	16 (3)	124 (25)	5 (7)	81 (16)	-28 (16)
C(B17)	6929 (7)	3118 (7)	2377 (19)	16 (4)	17 (3)	144 (28)	-5 (6)	12 (17)	9 (18)
O(B18)	7092 (5)	2603 (5)	3216 (13)	34 (3)	22 (3)	195 (21)	8 (6)	64 (13)	-12 (14)
C(B19)	6363 (8)	3425 (8)	3212 (19)	29 (5)	26 (4)	151 (27)	21 (8)	69 (17)	65 (18)
O(B20)	5752 (5)	3092 (6)	3036 (16)	25 (3)	39 (4)	315 (27)	39 (5)	104 (13)	39 (18)
C(B21)	6131 (8)	3950 (8)	2187 (24)	25 (5)	26 (4)	275 (39)	-23 (8)	58 (21)	-13 (24)
O(C1)	3154 (5)	-280 (6)	3922 (16)	27 (3)	27 (3)	274 (29)	8 (6)	22 (16)	-19 (17)
C(C2)	3252 (8)	25 (8)	4297 (18)	37 (5)	21 (4)	252 (28)	3 (9)	16 (19)	55 (21)
C(C3)	2569 (7)	-118 (6)	3963 (16)	29 (4)	14 (3)	105 (22)	10 (7)	16 (16)	23 (15)
C(C4)	2352 (7)	-648 (6)	3065 (17)	26 (5)	15 (3)	55 (23)	15 (6)	66 (17)	54 (14)
O(C5)	2800 (6)	-964 (5)	2662 (14)	35 (3)	14 (2)	105 (21)	13 (5)	15 (14)	-16 (12)
O(C6)	1701 (5)	-814 (4)	2732 (14)	29 (3)	11 (2)	219 (27)	-1 (4)	22 (14)	5 (14)
C(C7)	1144 (8)	-492 (7)	3234 (19)	30 (5)	22 (3)	213 (40)	-19 (8)	31 (22)	33 (21)
C(C8)	441 (9)	-683 (9)	2077 (24)	25 (5)	28 (3)	126 (46)	-12 (7)	-11 (24)	-57 (22)
C(C9)	1292 (8)	128 (6)	3099 (20)	29 (3)	12 (4)	248 (22)	-14 (7)	15 (13)	25 (20)
N(C10)	1265 (6)	307 (5)	1379 (14)	28 (4)	16 (3)	175 (22)	-8 (6)	46 (15)	-25 (14)
C(C11)	776 (7)	671 (6)	627 (17)	22 (4)	14 (3)	86 (21)	-1 (6)	32 (13)	22 (15)
O(C12)	314 (5)	867 (5)	1254 (13)	23 (3)	32 (2)	101 (18)	-38 (4)	112 (11)	-78 (11)
C(C13)	843 (8)	829 (7)	-1186 (19)	32 (5)	18 (3)	238 (24)	4 (7)	71 (18)	5 (15)
N(C14)	164 (7)	1112 (6)	-2057 (16)	28 (3)	26 (3)	140 (24)	-21 (6)	-28 (15)	-33 (15)
C(C15)	1472 (9)	1220 (8)	-1077 (19)	39 (6)	28 (5)	141 (36)	-13 (9)	13 (21)	7 (24)
C(C16)	1999 (8)	256 (7)	4395 (18)	28 (5)	15 (3)	84 (28)	-15 (7)	-27 (19)	29 (15)
C(C17)	2212 (7)	849 (6)	4233 (21)	22 (7)	10 (4)	85 (34)	-9 (10)	81 (24)	8 (20)
O(C18)	1709 (6)	1178 (6)	4700 (17)	38 (7)	23 (4)	280 (32)	-3 (10)	65 (21)	-14 (21)
C(C19)	2930 (9)	931 (7)	5608 (23)	40 (12)	13 (3)	353 (38)	7 (10)	67 (35)	41 (19)
O(C20)	3162 (6)	1470 (5)	5652 (16)	48 (8)	23 (3)	273 (28)	25 (8)	82 (23)	91 (15)
C(C21)	3508 (7)	577 (8)	5122 (20)	17 (7)	29 (4)	327 (38)	28 (9)	-35 (27)	41 (23)
O(D1)	5489 (5)	-309 (6)	7976 (16)	21 (3)	29 (3)	283 (27)	-8 (6)	6 (16)	-20 (16)
C(D2)	5981 (8)	-34 (9)	7452 (19)	28 (5)	27 (4)	127 (25)	-7 (9)	-3 (19)	38 (18)
C(D3)	6655 (7)	-195 (7)	7610 (17)	24 (4)	19 (3)	51 (20)	-3 (7)	1 (15)	-13 (14)
C(D4)	6831 (8)	-737 (6)	8450 (17)	30 (4)	12 (3)	71 (22)	-11 (6)	-1 (15)	-35 (14)

Table 2 (cont.)

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(D5)	6423 (5)	-1021 (4)	8963 (13)	35 (4)	13 (2)	178 (24)	-16 (5)	38 (16)	5 (13)
O(D6)	7509 (5)	-895 (5)	8685 (15)	25 (3)	15 (2)	318 (23)	-27 (5)	56 (14)	-35 (12)
C(D7)	8045 (9)	-618 (7)	8051 (24)	38 (5)	15 (4)	326 (28)	8 (7)	122 (19)	-19 (18)
C(D8)	8735 (8)	-814 (7)	9190 (25)	30 (5)	12 (5)	375 (41)	-10 (9)	73 (25)	-47 (25)
C(D9)	7949 (6)	-10 (8)	8019 (16)	17 (5)	30 (3)	108 (30)	-26 (7)	60 (20)	-17 (16)
N(D10)	8077 (7)	266 (6)	9754 (15)	47 (4)	14 (3)	124 (19)	24 (5)	73 (13)	15 (13)
C(D11)	8465 (7)	734 (7)	10011 (16)	22 (4)	18 (3)	93 (24)	-9 (6)	72 (16)	1 (15)
O(D12)	8671 (5)	1001 (4)	8886 (12)	36 (3)	12 (3)	157 (20)	20 (5)	86 (10)	1 (14)
C(D13)	8672 (8)	925 (7)	11875 (18)	38 (5)	16 (4)	92 (27)	-15 (7)	36 (17)	-44 (18)
N(D14)	9102 (6)	1458 (6)	11899 (15)	18 (4)	18 (3)	149 (25)	3 (7)	-8 (17)	10 (16)
C(D15)	8077 (9)	1036 (9)	12659 (23)	55 (6)	31 (4)	251 (26)	52 (9)	140 (21)	51 (21)
C(D16)	7219 (8)	137 (6)	6932 (19)	44 (5)	7 (3)	165 (25)	5 (7)	74 (18)	25 (15)
C(D17)	7024 (10)	758 (8)	6927 (22)	63 (4)	17 (3)	190 (35)	-13 (6)	102 (18)	-41 (18)
O(D18)	7501 (9)	1051 (7)	6176 (19)	105 (4)	35 (3)	379 (31)	22 (6)	232 (18)	-36 (18)
C(D19)	6252 (13)	814 (7)	5843 (24)	110 (6)	9 (3)	192 (39)	-33 (8)	47 (34)	39 (20)
O(D20)	6058 (9)	1383 (6)	5568 (17)	121 (4)	17 (3)	240 (29)	-32 (6)	160 (18)	-39 (15)
C(D21)	5710 (10)	524 (9)	6685 (24)	45 (4)	24 (4)	191 (30)	-24 (7)	-16 (19)	12 (19)
I(1)	1504 (1)	2500	2596 (2)	41 (0)	24 (0)	219 (2)	11 (1)	23 (2)	36 (2)
I(2)	441 (1)	4939 (1)	4405 (2)	44 (0)	27 (0)	183 (2)	-2 (1)	62 (1)	-4 (2)
I(3)	6000 (1)	1582 (1)	1140 (2)	55 (0)	32 (0)	240 (3)	34 (1)	35 (2)	13 (2)
I(4)	9280 (1)	2627 (1)	5953 (2)	41 (0)	55 (1)	300 (3)	-7 (1)	38 (2)	-133 (2)
W(1)	9931 (7)	2060 (6)	9928 (18)	38 (4)	26 (3)	286 (28)	9 (6)	28 (18)	38 (17)
W(2)	289 (7)	1564 (8)	4684 (16)	57 (5)	58 (5)	176 (26)	31 (10)	9 (19)	-24 (22)
W(3)	4800 (12)	1879 (8)	6867 (31)	120 (10)	38 (5)	757 (73)	-77 (11)	-193 (44)	86 (34)
W(4)	5397 (9)	2896 (14)	9316 (25)	82 (8)	128 (14)	576 (53)	0 (17)	214 (29)	156 (45)
N(1)	3416 (11)	972 (11)	782 (29)	68 (8)	54 (7)	433 (56)	-48 (13)	-1 (35)	62 (35)
C(2)	3955 (13)	753 (11)	814 (31)	75 (10)	35 (6)	339 (55)	40 (13)	94 (36)	25 (33)
C(3)	4632 (12)	393 (14)	1038 (37)	54 (9)	47 (9)	654 (85)	3 (16)	156 (41)	48 (49)

values for the two refinements are 0.082 and 0.078, respectively, yielding a weighted R value ratio of 1.0513. Only those data with intensities greater than twice their standard errors were included in these refinements and the weighting scheme $w = 1/\sigma_F^2$ was employed. The scattering factors for iodine are those of Cromer & Waber (1965) while those for carbon, nitrogen and oxygen were obtained from *International Tables for X-ray Crystallography* (1968). The values of f' and f'' for iodine were taken from Cromer (1965).

By application of Hamilton's (1965) R value ratio test the determination of the absolute configuration is significant at greater than the 0.5% level. The absolute configuration of actinobolin is R, R, S, R, R and R at C(7), C(9), C(13), C(16), C(17) and C(19), respectively, in agreement with previous findings (Antosz, Nelson, Herald & Munk, 1970). Hydrogen-atom positions were not determined. A final difference map revealed no residual electron density above $0.60 \text{ e } \text{Å}^{-3}$. The atomic coordinates and anisotropic thermal parameters and their estimated standard errors are given in Table 2.*

Discussion of the structure

The observed conformations of the four crystallographically independent molecules of actinobolin are

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30699 (44 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

similar except for small but significant differences in bond distances and angles. In addition, molecule D engages in an intramolecular hydrogen bond not present in the other three molecules (see section below on hydrogen bonding).

The observed bond distances and angles and their estimated standard errors are presented in Tables 3 and 4. The correct absolute configuration and the values of the bond distances and angles averaged over the four independent molecules are shown in Fig. 1. The average estimated standard errors of the bond distances and angles are rather large (0.02 Å and 1.3°), reflecting the size of the structure. Within these error limits the averaged values of the bond distances and angles in actinobolin are comparable with those observed in other structures (Pauling & Corey, 1953; Marsh & Donohue, 1967; Sutton, 1958).

The estimated standard errors of the positional and thermal parameters of the water molecules and the acetonitrile are larger than those of the other atoms, suggesting partial occupancy. Less than full occupancy of the solvent molecules is also supported by the observed density, which is significantly less than that calculated for four waters and one acetonitrile per asymmetric unit (Table 1).

The N(1)-C(2) distance of 1.164 Å in the acetonitrile is close to that observed in a microwave study (Thomas, Sherrard & Sheridan, 1955) of the free molecule (1.157 Å) and in the crystal structure (Massaux, Bernard & Le Bihan, 1971) of $\text{CuBr} \cdot \text{C}_2\text{H}_3\text{N}$ (1.158 Å). However, the C(2)-C(3) distance and the N(1)-C(2)-C(3) angle differ substantially from values previously observed

Table 3. Observed bond distances and their estimated standard errors (Å) for the four crystallographically independent molecules of actinobolin. HI

	Molecule A	Molecule B	Molecule C	Molecule D
O(1)—C(2)	1.314 (21)	1.352 (23)	1.302 (23)	1.302 (23)
C(2)—C(3)	1.378 (25)	1.347 (22)	1.336 (24)	1.340 (24)
C(2)—C(21)	1.530 (26)	1.526 (25)	1.525 (28)	1.528 (31)
C(3)—C(4)	1.433 (23)	1.441 (23)	1.486 (22)	1.478 (23)
C(3)—C(16)	1.514 (24)	1.543 (26)	1.521 (24)	1.543 (24)
C(4)—O(5)	1.239 (21)	1.232 (20)	1.248 (20)	1.182 (20)
C(4)—O(6)	1.301 (21)	1.342 (20)	1.294 (19)	1.340 (20)
O(6)—C(7)	1.560 (22)	1.458 (20)	1.453 (21)	1.414 (22)
C(7)—C(8)	1.562 (25)	1.556 (22)	1.542 (22)	1.524 (22)
C(7)—C(9)	1.509 (23)	1.506 (22)	1.537 (27)	1.480 (30)
C(9)—N(10)	1.435 (8)	1.464 (8)	1.426 (8)	1.507 (14)
C(9)—C(16)	1.541 (22)	1.570 (21)	1.558 (19)	1.534 (20)
N(10)—C(11)	1.333 (21)	1.315 (22)	1.336 (20)	1.350 (23)
C(11)—O(12)	1.180 (19)	1.203 (21)	1.209 (18)	1.238 (15)
C(11)—C(13)	1.531 (10)	1.517 (10)	1.527 (13)	1.525 (11)
C(13)—N(14)	1.462 (23)	1.450 (23)	1.512 (21)	1.532 (24)
C(13)—C(15)	1.530 (23)	1.542 (24)	1.529 (28)	1.446 (26)
C(16)—C(17)	1.519 (24)	1.460 (24)	1.508 (25)	1.550 (27)
C(17)—O(18)	1.436 (21)	1.417 (21)	1.370 (21)	1.395 (27)
C(17)—C(19)	1.481 (24)	1.585 (23)	1.588 (19)	1.563 (31)
C(19)—O(20)	1.391 (21)	1.413 (23)	1.380 (25)	1.431 (26)
C(19)—C(21)	1.575 (29)	1.527 (27)	1.520 (26)	1.529 (32)
Acetonitrile				
N(1)—C(2)	1.164 (38)			
C(2)—C(3)	1.555 (41)			

for acetonitrile complexes (Massaux, Bernard & Le Bihan, 1971; Marstokk & Strømme, 1968). These observed differences may possibly be attributed to the errors associated with the acetonitrile position, partial occupancy of the molecule and effects due to the N(A14)···N(1) hydrogen bond.

Fig. 2 is a stereoscopic drawing of the unit cell illustrating the molecular packing and conformation of actinobolin. HI. The hexahydroisocoumarin portion of the molecule has a double-chair conformation as pre-

dicted by Antosz, Nelson, Herald & Munk (1970) on the basis of n.m.r. studies. The conformation of the 2-aminopropionamido side chain is similar to that observed in the threonyl portion of L-threonyl-L-phenylalanine *p*-nitrobenzene ester hydrobromide (Mallikarjunan, Rao, Venkatesan & Sarma, 1965) and in L(*s*)-threonine (Shoemaker, Donohue, Schomaker & Corey, 1951).

Hydrogen bonding

The hydrogen-bonding scheme of actinobolin. HI is extremely complex. All 36 hydrogen atoms theoretically available to hydrogen bond appear to do so. Despite the absence of experimentally determined hydrogen positions, sufficient information is available from the 'heavy'-atom positions to make specific statements concerning donor-acceptor roles in the hydrogen-bonding scheme. Arguments similar to those below have previously been applied (Donohue, 1952) in the determination of self-consistent models for hydrogen bonding. Fig. 3 is a schematic representation of the proposed hydrogen-bonding network with distances given between 'heavy' atoms involved in hydrogen bonds. A complete set of interatomic angles appears in Table 5. In Fig. 3 the positioning of a filled circle (hydrogen atom) closer to one atom than another implies that the nearer atom is the hydrogen donor. In some situations the distinction between a close contact and a weak hydrogen bond is not clear and an alternative interpretation may be possible.

In each of the four crystallographically independent molecules of actinobolin. HI, intramolecular hydrogen bonds of the type O(1)—H···O(5) are observed with an average O(1)···O(5) distance of 2.50 Å. This distance is similar to the values 2.47 and 2.53 Å observed in the unsymmetrical O···O hydrogen bonds of harunganin (Alden, Stout, Kraut & High, 1964) and obtusi-

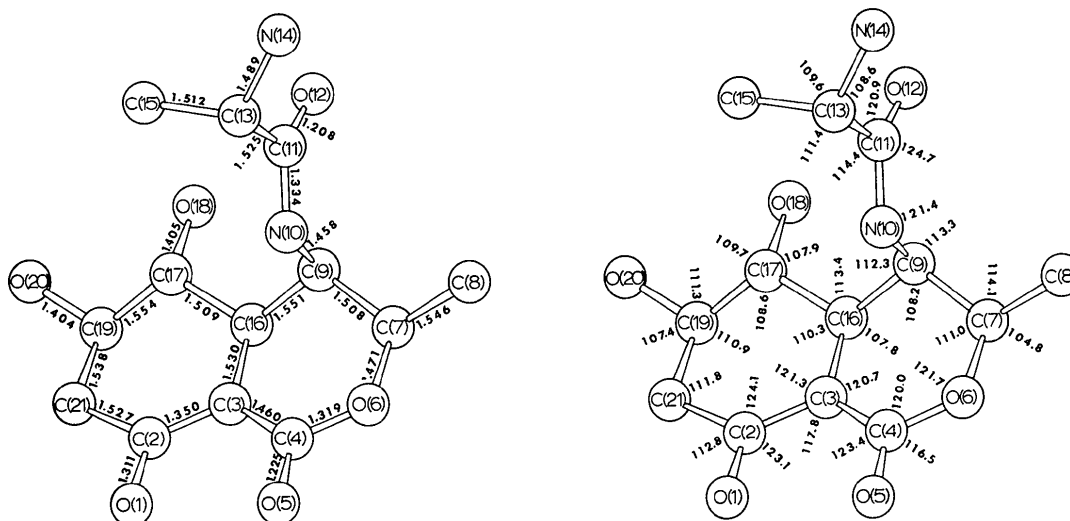


Fig. 1. Drawing of actinobolin showing the correct absolute configuration and values of the bond distances and angles averaged over the four crystallographically independent molecules.

folin (Narayanan, Zechmeister, Röhrli & Hoppe, 1971).

In each of the four crystallographically independent molecules of actinobolin.HI there exist intermolecular hydrogen bonds $N(10)-H \cdots O(5')$ with an average $N(10) \cdots O(5')$ distance of 3.02 Å. This average dis-

tance is similar to those observed in *N*-acetylglycine, 3.030 Å (Donohue & Marsh, 1962); glycylphenylalanyl-glycine, 2.89, 3.00 Å (Marsh & Glusker, 1961) and α -glycylglycine, 2.966 Å (Biswas, Hughes, Sharma & Wilson, 1968). In three of the four independent molecules the angle $C(9)-N(10) \cdots O(5')$ is significantly

Table 4. Observed bond angles ($^\circ$) and their estimated standard errors for the four crystallographically independent molecules of actinobolin.HI

	Molecule A	Molecule B	Molecule C	Molecule D
O(1)—C(2)—C(3)	121.9 (16)	120.7 (16)	124.2 (17)	125.6 (19)
O(1)—C(2)—C(21)	112.3 (16)	113.2 (14)	114.0 (15)	111.7 (16)
C(3)—C(2)—C(21)	125.8 (16)	126.2 (17)	121.8 (17)	122.7 (18)
C(2)—C(3)—C(4)	117.6 (15)	119.2 (17)	118.9 (15)	115.3 (16)
C(2)—C(3)—C(16)	120.4 (15)	118.4 (15)	122.5 (16)	124.0 (16)
C(4)—C(3)—C(16)	121.7 (15)	122.2 (14)	118.6 (13)	120.6 (14)
C(3)—C(4)—O(5)	124.1 (14)	124.2 (15)	120.9 (14)	124.5 (15)
C(3)—C(4)—O(6)	121.2 (16)	120.7 (15)	121.9 (14)	116.0 (14)
O(5)—C(4)—O(6)	114.7 (15)	114.6 (14)	117.1 (14)	119.4 (14)
C(4)—O(6)—C(7)	119.7 (12)	119.6 (12)	121.6 (13)	125.8 (13)
O(6)—C(7)—C(8)	104.0 (12)	104.6 (12)	106.6 (12)	104.7 (11)
O(6)—C(7)—C(9)	111.3 (11)	110.4 (11)	110.2 (13)	112.2 (14)
C(8)—C(7)—C(9)	113.9 (14)	114.4 (14)	113.9 (14)	114.2 (14)
C(7)—C(9)—N(10)	111.0 (10)	113.7 (10)	113.2 (10)	115.4 (10)
C(7)—C(9)—C(16)	106.9 (13)	109.0 (12)	107.2 (12)	109.6 (14)
N(10)—C(9)—C(16)	110.9 (11)	111.5 (10)	115.1 (13)	111.5 (13)
C(9)—N(10)—C(11)	122.9 (12)	123.1 (11)	120.5 (12)	119.2 (11)
N(10)—C(11)—O(12)	122.9 (7)	124.3 (7)	125.9 (9)	125.6 (8)
N(10)—C(11)—C(13)	116.5 (13)	112.7 (14)	113.3 (13)	115.1 (11)
O(12)—C(11)—C(13)	120.6 (14)	122.8 (15)	120.8 (13)	119.3 (14)
C(11)—C(13)—N(14)	109.2 (13)	110.2 (13)	107.9 (12)	107.2 (10)
C(11)—C(13)—C(15)	110.3 (10)	112.1 (9)	109.1 (9)	114.2 (13)
N(14)—C(13)—C(15)	111.0 (16)	108.3 (14)	110.4 (15)	108.6 (15)
C(3)—C(16)—C(9)	109.6 (11)	105.1 (11)	107.9 (11)	108.4 (10)
C(3)—C(16)—C(17)	111.1 (13)	112.9 (13)	108.7 (14)	108.5 (15)
C(9)—C(16)—C(17)	113.3 (13)	115.3 (13)	110.3 (11)	114.8 (14)
C(16)—C(17)—O(18)	107.3 (13)	108.5 (12)	107.9 (13)	108.0 (17)
C(16)—C(17)—C(19)	113.7 (14)	108.1 (14)	105.8 (12)	106.6 (15)
O(18)—C(17)—C(19)	111.3 (12)	108.6 (11)	107.9 (10)	111.1 (12)
C(17)—C(19)—O(20)	113.8 (15)	109.1 (15)	111.5 (13)	110.8 (17)
C(17)—C(19)—C(21)	112.8 (12)	108.5 (11)	109.7 (11)	112.5 (11)
O(20)—C(19)—C(21)	107.8 (13)	106.2 (13)	106.7 (16)	108.9 (20)
C(2)—C(21)—C(19)	110.7 (15)	110.3 (14)	114.5 (14)	111.7 (18)
Acetonitrile				
N(1)—C(2)—C(3)	170.7 (27)			

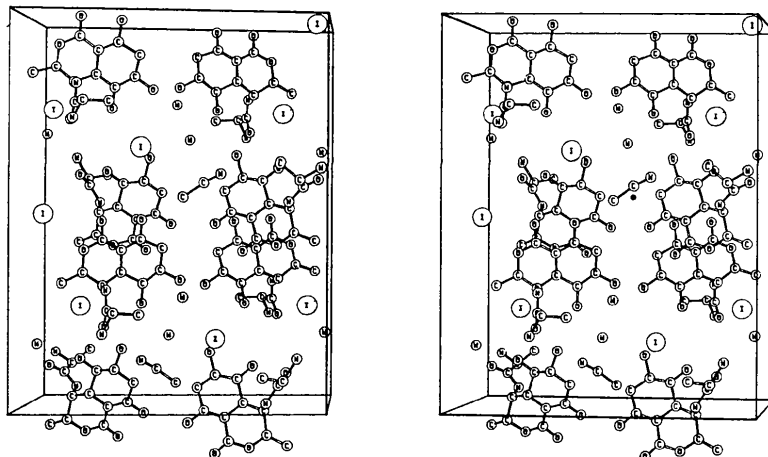


Fig. 2. Stereoscopic drawing of the unit-cell contents of actinobolin.HI. The horizontal axis is *a* and the vertical axis is *b*.

larger than the angle $C(11)-N(10)\cdots O(5')$ (average value of 127.9° as compared with 113.4°) as has previously been observed (see Fuller, 1959, for a review). In molecule *D* the $C(9)-N(10)\cdots O(A5)$ angle is observed to be smaller than the $C(11)-N(10)\cdots O(A5)$ angle, presumably because of a slight change in molecular conformation resulting from an $O(D18)-H\cdots O(D12)$ intramolecular hydrogen bond not observed in the other three independent molecules. In each of

the independent molecules the atoms $C(9)$, $N(10)$, $C(11)$ and $O(5')$ are nearly coplanar (sum of the angles about $N(10)$ averages 360.0°) as required for this type of hydrogen bonding (Donohue, 1952).

The charged amino nitrogen $N(A14)$ is approached closely by four possible hydrogen acceptors as shown in Fig. 3(a). The acetonitrile nitrogen $N(1)$ and the iodide ion $I(1)$ are both in positions suitable for the formation of rather strong hydrogen bonds. The

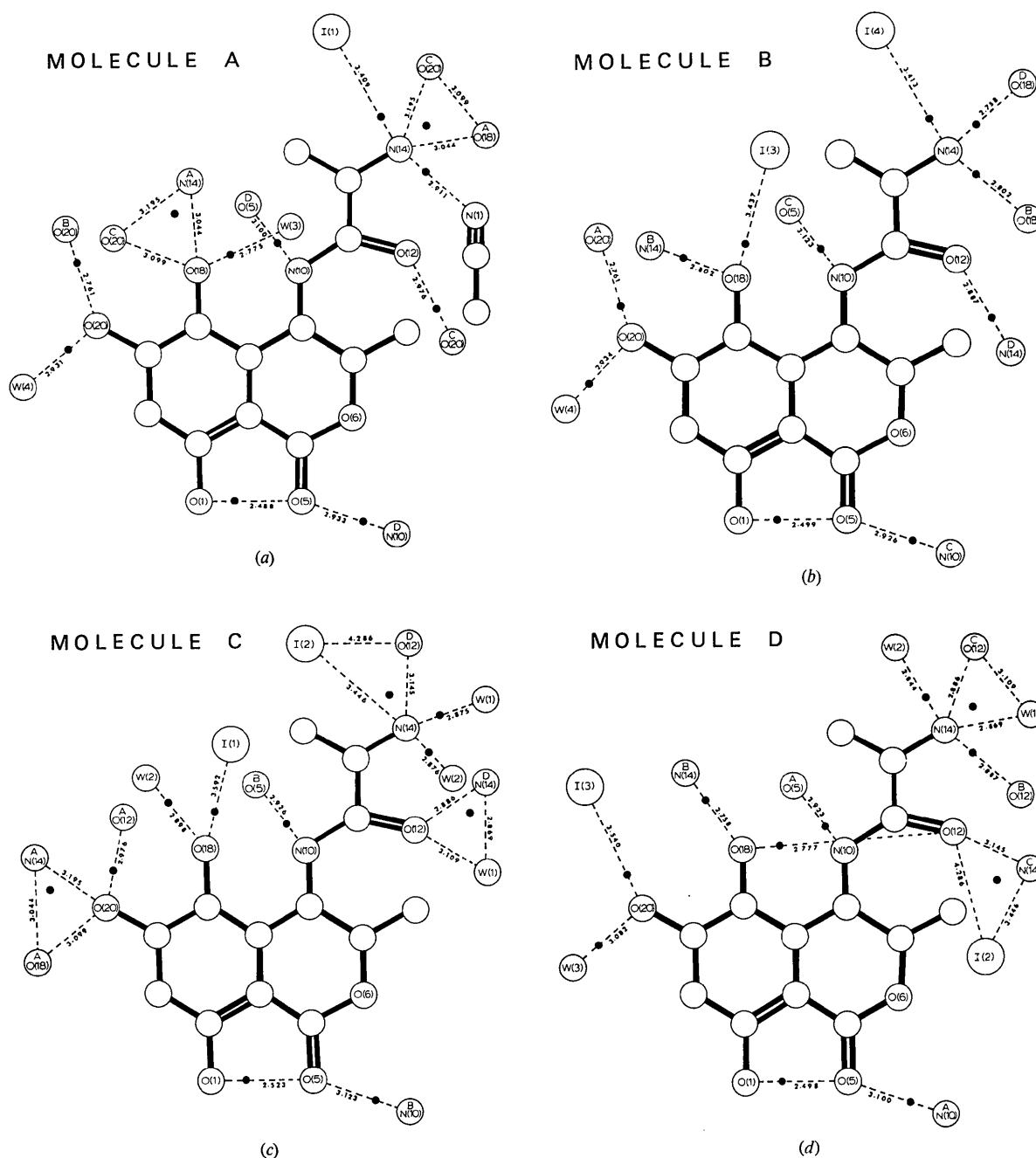


Fig. 3. Schematic representations of the hydrogen bonding of actinobolin.HI. See text for further explanation.

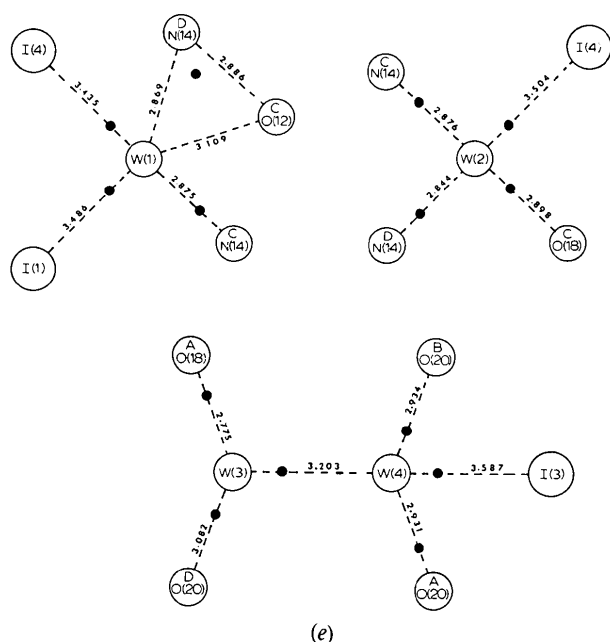


Fig. 3 (cont.)

$N(A14)\cdots I(1)$ distance of 3.409 \AA is the shortest iodine contact observed in this structure and is significantly shorter than the values of 3.54 and 3.52 \AA reported for the charged amino $N\cdots I$ hydrogen bonds in *L*-leucine hydroiodide (Chaney, Seely & Steinrauf, 1971). The $N(A14)\cdots N(1)$ hydrogen bond is to the authors' knowledge the first report of an NH_3^+ -acetonitrile hydrogen bond. The $N(A14)\cdots N(1)$ distance of 2.911 \AA is somewhat shorter than the values of 3.12 , 3.12 and 3.21 \AA reported for amino-nitrile hydrogen bonds in diaminomaleonitrile (Penfold & Lipscomb, 1961). The two hydroxide oxygens $O(C20)$ and $O(A18')$ both approach $N(A14)$ at distances slightly longer than the average $N\cdots O$ hydrogen-bond distance (Fuller, 1959), and with $C-N\cdots O$ angles widely different from the desired near-tetrahedral value. The situation is similar to that found in the crystal structures of the α and β forms of glycine (Marsh, 1958; Iitaka, 1960) where bifurcated hydrogen bonds were observed. If a hydrogen atom were to be placed along the line bisecting the $O(C20)\cdots N(A14)\cdots O(A18')$ angle and in the plane of the three atoms, the $C(A13)-N(A14)\cdots H$ angle would be 115° , close to the expected value. On the basis of this evidence and the further hydrogen-bonding activity of $O(C20)$ and $O(A18)$ such a bifurcated hydrogen bond is likely.

$N(B14)$ is observed to form three hydrogen bonds with $I(4)$, $O(D18)$, and $O(B18')$. The $C(B13)-N(B14)\cdots O(D18)$ angle of 141.8° deviates strongly from the tetrahedral value but the short $N(B14)\cdots O(D18)$ distance of 2.785 \AA is highly suggestive of the presence of a hydrogen bond (Fuller, 1959).

$N(C14)$ forms two hydrogen bonds to water mol-

ecules $W(1)$ and $W(2)$ with $N(C14)\cdots W$ distances similar to those tabulated by Fuller (1959). The $C(C13)-N(C14)\cdots W$ and the $W\cdots N(C14)\cdots W$ angles are also close to the expected tetrahedral values. The iodide ion $I(2)$ and the amido oxygen $O(D12)$ also form close contacts with $N(C14)$. Although the $N(C14)\cdots O(D12)$ distance of 3.145 \AA is rather long for hydrogen bonding, the $N(C14)\cdots I(2)$ angle of 92.0° casts some doubt upon $I(2)$ being the sole acceptor of the third hydrogen of $N(C14)$. If, as with $N(A14)$, a bifurcated hydrogen bond is considered and a hydrogen is placed along a line bisecting the $I(2)\cdots N(C14)\cdots H$ angle and in the plane of the three atoms, the $C(C13)-N(C14)\cdots H$ angle would be 114° . In Fig. 3(c) such a bifurcated hydrogen bond is indicated. Alternatively, the structure may be viewed as a 'bent' $N(C14)\cdots I(2)$ hydrogen bond with the displacement in the direction of $O(D12)$.

A situation similar to that encountered in $N(A14)$ also exists for $N(D14)$. Two water molecules and two amido oxygens approach $N(D14)$ with an average $N(D14)\cdots O$ distance of 2.87 \AA . Water molecule $W(2)$ and the amido oxygen $O(B12)$ are both in suitable hydrogen acceptor positions. As in molecule *A*, two additional oxygen atoms $O(C12)$ and $W(1)$ form an approximate equilateral triangle with $N(D14)$. While the $C(D13)-N(D14)\cdots O(B12)$ angle of 103.5° is reasonable for a hydrogen bond, the close contact with $W(1)$ is left unexplained. Placement of a hydrogen atom along the line bisecting the $O(C12)\cdots N(D14)\cdots W(1)$ angle and in the plane of the three atoms would result in a $C(D13)-N(D14)\cdots H$ angle of 119° . Such a bifurcated hydrogen bond explains in part the rather close $O(C12)\cdots W(1)$ contact of 3.109 \AA .

The hydroxide oxygen $O(A18)$ acts as the donor atom in a hydrogen bond to $W(3)$. The $O(A18)\cdots W(3)$ distance of 2.775 \AA is typical of those reported by Donohue (1952) and Fuller (1959).

The hydroxide oxygen $O(A20)$ donates a hydrogen to water molecule $W(4)$ and accepts a hydrogen from the hydroxide oxygen $O(B20)$. A water molecule $W(4')$ translated one unit cell in the z direction donates a hydrogen to $O(B20)$ thus linking the *A* and *B* molecules in an infinite chain parallel to *c*. It is possible, although the angles are less favorable, that $O(A20)$ is the acceptor of a hydrogen from $W(4)$ and $O(B20)$ in turn accepts from $O(A20)$ and donates to $W(4')$.

The hydroxide oxygen $O(B18)$ donates a hydrogen to the iodide ion $I(3)$ and accepts a hydrogen from $N(B14)$. The $O(B18)\cdots I(3)$ distance of 3.437 \AA is slightly shorter than the 3.57 and 3.54 \AA distances observed in other structures (Fridrichsons & Matheison, 1963; Pilotti, 1971).

The hydroxide oxygen $O(C18)$ donates a hydrogen to the iodide ion $I(1)$ and accepts a hydrogen from water molecule $W(2)$.

The hydroxide oxygen $O(D18)$ donates a hydrogen to the amido oxygen $O(D12)$ of the same molecule. Such an intramolecular hydrogen bond is not observed

Table 5. *Interatomic angles (°) involved in the hydrogen-bonding network of actinobolin. HI*

C(A2) — O(A1) ··· O(A5)	88.2	C(C11) — O(C12) ··· N(D14)	165.4
C(B2) — O(B1) ··· O(B5)	87.9	C(C11) — O(C12) ··· W(1)	111.6
C(C2) — O(C2) ··· O(C5)	86.9	N(D14) ··· O(C12) ··· W(1)	57.0
C(D2) — O(D2) ··· O(D5)	85.8	C(D11) — O(D12) ··· N(C14)	132.1
C(A4) — O(A5) ··· O(A1)	88.0	C(D11) — O(D12) ··· I(2)	111.3
C(B4) — O(B5) ··· O(B2)	87.8	C(D11) — O(D12) ··· O(D18)	104.5
C(C4) — O(C5) ··· O(C2)	89.1	N(C14) ··· O(D12) ··· I(2)	52.9
C(D4) — O(D5) ··· O(D2)	88.9	N(C14) ··· O(D12) ··· O(D18)	116.6
C(A4) — O(A5) ··· N(D10)	129.9	I(2) ··· O(D12) ··· O(D18)	85.2
C(B4) — O(B5) ··· N(C10)	122.2	C(A13) — N(A14) ··· I(1)	102.6
C(C4) — O(C5) ··· N(B10)	111.4	C(A13) — N(A14) ··· N(1)	116.4
C(D4) — O(D5) ··· N(A10)	115.2	C(A13) — N(A14) ··· O(C20)	143.6
O(A1) ··· O(A5) ··· N(D10)	133.7	C(A13) — N(A14) ··· O(A18)	84.4
O(B1) ··· O(B5) ··· N(C10)	141.3	I(1) ··· N(A14) ··· O(C20)	82.7
O(C1) ··· O(C5) ··· N(B10)	154.8	I(1) ··· N(A14) ··· O(A18)	88.2
O(D1) ··· O(D5) ··· N(A10)	151.8	I(1) ··· N(A14) ··· N(1)	125.8
C(A9) — N(A10) ··· O(D5)	123.8	O(C20) ··· N(A14) ··· O(A18)	59.5
C(B9) — N(B10) ··· O(C5)	125.1	O(C20) ··· N(A14) ··· N(1)	86.5
C(C9) — N(C10) ··· O(B5)	124.9	O(A18) ··· N(A14) ··· N(1)	129.6
C(D9) — N(D10) ··· O(A5)	114.3	C(B13) — N(B14) ··· I(4)	99.5
C(A11) — N(A10) ··· O(D5)	112.5	C(B13) — N(B14) ··· O(D18)	141.8
C(B11) — N(B10) ··· O(C5)	111.3	C(B13) — N(B14) ··· O(B18)	94.9
C(C11) — N(C10) ··· O(B5)	114.3	I(4) ··· N(B14) ··· O(D18)	113.2
C(D11) — N(D10) ··· O(A5)	126.2	I(4) ··· N(B14) ··· O(B18)	87.7
C(A11) — O(A12) ··· O(C20)	141.3	O(D18) ··· N(B14) ··· O(B18)	105.2
C(B11) — O(B12) ··· N(D14)	158.0	C(C13) — N(C14) ··· I(2)	92.0
C(C13) — N(C14) ··· O(D12)	127.1	N(B14) ··· O(B18) ··· I(3)	105.4
C(C13) — N(C14) ··· W(1)	109.7	C(C17) — O(C18) ··· W(2)	156.0
C(C13) — N(C14) ··· W(2)	110.8	C(C17) — O(C18) ··· I(1)	113.8
I(2) ··· N(C14) ··· O(D12)	80.6	W(2) ··· O(C18) ··· I(1)	72.6
I(2) ··· N(C14) ··· W(1)	151.2	C(D17) — O(D18) ··· N(B14)	122.6
I(2) ··· N(C14) ··· W(2)	84.7	C(D17) — O(D18) ··· O(D12)	98.5
O(D12) ··· N(C14) ··· W(1)	71.2	N(D14) ··· O(D18) ··· O(D12)	85.0
O(D12) ··· N(C14) ··· W(2)	120.4	C(A19) — O(A20) ··· O(B20)	124.0
W(1) ··· N(C14) ··· W(2)	104.3	C(A19) — O(A20) ··· W(4)	103.2
C(D13) — N(D14) ··· W(2)	115.5	O(B20) ··· O(A20) ··· W(4)	132.7
C(D13) — N(D14) ··· O(C12)	92.3	C(B19) — O(B20) ··· O(A20)	112.1
C(D13) — N(D14) ··· W(1)	141.8	C(B19) — O(B20) ··· W(4)	101.7
C(D13) — N(D14) ··· O(B12)	103.5	O(A20) ··· O(B20) ··· W(4)	138.9
W(2) ··· N(D14) ··· O(C12)	68.4	C(C19) — O(C20) ··· O(A12)	114.0
W(2) ··· N(D14) ··· W(1)	89.5	C(C19) — O(C20) ··· N(A14)	116.8
W(2) ··· N(D14) ··· O(B12)	133.8	C(C19) — O(C20) ··· O(A18)	172.5
O(C12) ··· N(D14) ··· W(1)	65.4	O(A12) ··· O(C20) ··· N(A14)	119.4
O(C12) ··· N(D14) ··· O(B12)	135.6	O(A12) ··· O(C20) ··· O(A18)	73.4
W(1) ··· N(D14) ··· O(B12)	77.4	N(A14) ··· O(C20) ··· O(A18)	57.8
C(A17) — O(A18) ··· O(C20)	143.1	C(D19) — O(D20) ··· I(3)	103.6
C(A17) — O(A18) ··· N(A14)	143.7	C(D19) — O(D20) ··· W(3)	121.5
C(A17) — O(A18) ··· W(3)	112.3	I(3) ··· O(D20) ··· W(3)	115.0
O(C20) ··· O(A18) ··· N(A14)	57.8	C(2) — N(1) ··· O(A12)	141.3
O(C20) ··· O(A18) ··· W(3)	67.2	I(1) ··· W(1) ··· I(4)	122.7
N(A14) ··· O(A18) ··· W(3)	101.5	I(1) ··· W(1) ··· N(D14)	109.8
C(B17) — O(B18) ··· N(B14)	139.9	O(B20) ··· W(4) ··· W(3)	135.7
C(B17) — O(B18) ··· I(3)	110.7	O(B20) ··· W(4) ··· I(3)	75.5
I(4) ··· W(1) ··· N(D14)	124.7	O(B20) ··· W(4) ··· O(A20)	154.0
I(4) ··· W(1) ··· O(C12)	134.3	W(3) ··· W(4) ··· I(3)	66.9
I(4) ··· W(1) ··· N(C14)	83.2	W(3) ··· W(4) ··· O(A20)	69.4
N(D14) ··· W(1) ··· O(C12)	57.6	I(3) ··· W(4) ··· O(A20)	129.4
N(D14) ··· W(1) ··· N(C14)	93.9	W(1) ··· I(1) ··· N(A14)	121.7
O(C12) ··· W(1) ··· N(C14)	52.6	N(C14) ··· I(2) ··· O(D12)	46.4
N(C14) ··· W(2) ··· I(4)	81.9	I(1) ··· W(1) ··· O(C12)	87.8
N(C14) ··· W(2) ··· O(C18)	97.8	I(1) ··· W(1) ··· N(C14)	111.1
N(C14) ··· W(2) ··· N(D14)	117.5	O(B18) ··· I(3) ··· W(3)	119.7
I(4) ··· W(2) ··· O(C18)	145.1	O(B18) ··· I(3) ··· W(4)	70.2
I(4) ··· W(2) ··· N(D14)	83.4	O(B18) ··· I(3) ··· O(D20)	74.5
O(C18) ··· W(2) ··· N(D14)	125.5	W(3) ··· I(3) ··· W(4)	51.7
I(3) ··· W(3) ··· O(A18)	139.6	W(3) ··· I(3) ··· O(D20)	144.2
I(3) ··· W(3) ··· O(D20)	81.4	W(4) ··· I(3) ··· O(D20)	117.6
I(3) ··· W(3) ··· W(4)	61.4	W(1) ··· I(4) ··· W(2)	81.7
O(A18) ··· W(3) ··· O(D20)	130.7	W(1) ··· I(4) ··· N(B14)	85.6
O(A18) ··· W(3) ··· W(4)	83.2	W(2) ··· I(4) ··· N(B14)	112.6
O(D20) ··· W(3) ··· W(4)	107.3		

in the other three independent molecules of actinobolin. HI. O(D18) also acts as the acceptor in a hydrogen bond with N(B14).

The hydroxide oxygen O(D20) acts as the donor in a hydrogen bond with iodide ion I(3) and as the acceptor in a hydrogen bond with water molecule W(3).

Fig. 3(e) summarizes the hydrogen-bonding activity of the four independent water molecules. The distances and angles (Table 5) between the atoms involved in these hydrogen bonds often differ from the values found in less complicated hydrogen-bond networks [see Donohue (1952), Fuller (1959) and Baur (1965) for reviews]. The likelihood of partial occupancy of the waters together with the steric factors involved in such a complex network of hydrogen bonds are likely explanations for these anomalies.

Table 6 is a summary of the observed hydrogen-bond parameters averaged according to the appropriate classifications. It is remarkable how well these distances and angles conform to the values observed in much less complicated systems. These stringent steric requirements possibly explain the presence of four molecules of actinobolin. HI per asymmetric unit and the inclusion of solvent molecules.

Table 6. Summary of observed hydrogen-bond parameters averaged according to classification

The number in parentheses indicates the number of independent hydrogen bonds used in the average.

Donor	Acceptor	Average X...Y distance (Å)	Average C-X...Y angle (°)
NH	C=O (lactone)	3.02 (4)	See text
NH ₃ ⁺	C=O (amido)	2.97 (3)†	103.5 (1)
NH ₃ ⁺	C-OH	2.95 (4)†	118.4 (2)
NH ₃ ⁺	H ₂ O	2.87 (4)†	112.0 (3)
NH ₃ ⁺	I	3.42 (3)†	101.1 (2)
NH ₃ ⁺	C ₂ H ₅ N	2.91 (1)	116.4 (1)
C-OH	C=O (lactone)	2.50 (4)*	87.2 (4)*
C-OH	C=O (amido)	2.88 (2)*	106.3 (2)*
C-OH	C-OH	2.76 (1)	112.1 (1)
C-OH	H ₂ O	2.85 (2)	107.8 (1)
C-OH	I	3.52 (3)	109.4 (3)
H ₂ O	C=O (amido)	3.10 (1)†	
H ₂ O	C-OH	2.79 (4)	
H ₂ O	H ₂ O	3.20 (1)	
H ₂ O	I	3.51 (3)	

* Includes intramolecular hydrogen bonds.

† Includes bifurcated hydrogen bonds.

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Structure Cristalline de l'Orthostannate de Potassium K_4SnO_4

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Potassium orthostannate, K_4SnO_4 , crystallizes in the triclinic system with $a=6.48$ (2), $b=6.51$ (2), $c=9.70$ (2) Å, $\alpha=71.82$ (20), $\beta=99.89$ (20), $\gamma=113.13$ (20)°, space group $P\bar{1}$. The structure was determined from 4006 independent reflexions collected on an automatic diffractometer with Mo $K\alpha$ radiation. The crystal structure was refined by the full-matrix least-squares method to an unweighted R value of 0.029 and a weighted R_w value of 0.029. This compound consists of discrete tetrahedral SnO_4 groups which are bounded by potassium cations. The Sn–O distances are between 1.947 (3) and 1.960 (3) Å. The O–Sn–O angles are between 105.72 (9) and 114.37 (9)°.

Introduction

L'orthostannate de potassium K_4SnO_4 peut être préparé par action à 900°C du nitrate de potassium KNO_3 sur l'oxyde stannique SnO_2 (Tournoux & Hagenmuller, 1963). L'examen des diagrammes de poudre a indiqué une relation d'isotypie entre les phases $K_4M^{IV}O_4$ ($M=Si, Ti, Cr, Mn, Co, Ge, Sn, Pb$) et Na_4MO_4 ($M=Ti, Cr, Mn, Ge, Zr, Sn, Hf, Pb$) (Olazcuaga, Reau, Devalette, Le Flem & Hagenmuller, 1974). Le spectre de réflectance diffuse et les propriétés magnétiques de K_4CrO_4 et K_4MnO_4 ont montré que dans ces phases le cation M^{IV} a une coordinence tétraédrique. Il était donc intéressant de déterminer la structure d'un de ces composés d'autant que l'existence de phases du type K_4MO_4 avait récemment été mise en doute (Schartau & Hoppe, 1973). La relation d'isotypie entre une série de composés $M_4^{II}M^{IV}O_4$ allant du silicate au stannate et au plombate peut paraître *a priori* surprenante, les cations Sn^{IV} et Pb^{IV} exerçant habituellement une coordinence octaédrique dans leurs composés oxygénés. Cette remarque nous a conduit à déterminer la structure cristalline de K_4SnO_4 .

Partie expérimentale

Les monocristaux de K_4SnO_4 sont obtenus par action d'un excès de nitrate de potassium sur l'oxyde stan-

nique. Les cristaux se présentent sous forme de plaquettes incolores. Leur extrême sensibilité à l'humidité atmosphérique nécessite leur manipulation en boîte sèche ou sous un liquide inerte. Un monocristal de dimensions $0,4 \times 0,2 \times 0,2$ mm a été placé dans un tube de verre de Lindemann.

L'enregistrement des réflexions a été effectué à l'aide d'un diffractomètre automatique Nonius CAD 3 (rayonnement Mo $K\alpha$, monochromateur en graphite) avec un balayage $\theta-2\theta$. L'affinement de la structure a été conduit à partir des 4006 réflexions indépendantes satisfaisant au test $\sigma(I)/I < 0,20$ avec $\sigma(I)/I = [I_M + \tau^2(F_1 + F_2)]^{1/2} / [I_M - \tau(F_1 + F_2)]$ où τ est le rapport du temps de comptage de la réflexion I_M sur le temps de comptage du fond continu ($F_1 + F_2$); dans le cas présent $\tau = \frac{1}{2}$. Les intensités ont été corrigées du facteur de Lorentz-polarisation, les corrections d'absorption ont été négligées ($\mu = 58 \text{ cm}^{-1}$).

La transformation de Delaunay (1932) appliquée aux paramètres donnés dans le Tableau 1 permet d'obtenir la maille: $a=6,50$; $b=9,85$; $c=7,18$ Å; $\alpha=104,25$; $\beta=123,42$; $\gamma=94,81$ °; qui a été utilisée pour indexer les diagrammes de poudre des phases K_4MO_4 (Olazcuaga *et al.*, 1974). Elle peut être obtenue à partir de celle donnée au Tableau 1 à l'aide de la matrice

$$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 1 \\ 1 & 1 & 0 \end{pmatrix}.$$

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