CARRUTHERS, T., BLOCH, A. N. & COWAN, D. O. (1976). *Bull. Amer. Phys. Soc.* **21**, 313.

CARRUTHERS, T., BLOCH, A. N., KISTENMACHER, T. J., PYLE, R. E., PHILLIPS, T. E. & COWAN, D. O. (1977). To be published.

DISALVO, F. J., READ, W., BLOCH, A. N. & COWAN, D. O. (1977). To be published.

ETEMAD, S. (1976). *Phys. Rev.* (*B*), **13**, 2254–2261.

FERRARIS, J. P., POEHLER, T. O., BLOCH, A. N. & COWAN, D. O. (1973). *Tetrahedron Lett.* **27**, 2552–2556.

GLEITER, R., KOBAYASKI, M., SPANGET-LARSEN, J., FERRARIS, J. P., BLOCH, A. N., BECHGAARD, K. & COWAN, D. O. (1975). *Ber. Bunsenges. Phys. Chem.* **79**, 1218–1226.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HERBSTEIN, F. H. (1971). *Perspectives in Structural Chemistry*, Vol. IV, pp. 166–395. New York: John Wiley.

HORN, P. M. & RIMAI, D. (1976). *Phys. Rev. Lett.* **36**, 809–813.

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

KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* B**30**, 763–768.

KISTENMACHER, T. J., PHILLIPS, T. E., COWAN, D. O., FERRARIS, J. P., BLOCH, A. N. & POEHLER, T. O. (1976). *Acta Cryst.* B**32**, 539–547.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

PHILLIPS, T. E., FERRARIS, J. P., KISTENMACHER, T. J., POEHLER, T. O., BLOCH, A. N. & COWAN, D. O. (1974). Unpublished.

PHILLIPS, T. E., KISTENMACHER, T. J., BLOCH, A. N. & COWAN, D. O. (1976). *Chem. Commun.* pp. 334–335.

PIPPY, M. E. & AHMED, F. R. (1968). NRC Crystallographic Programs, National Research Council, Ottawa, Canada.

POEHLER, T. O., BOHANDY, J., BLOCH, A. N. & COWAN, D. O. (1976). *Bull. Amer. Phys. Soc.* **21**, 287.

POEHLER, T. O., BOHANDY, J., BLOCH, A. N. & COWAN, D. O. (1977). To be published.

STEWART, J. M. (1967). The X-RAY 67 system. Tech. Rep. TR-67-58. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TOMKIEWICZ, Y., SCHULTZ, T. D., ENGLER, E. M., TARANKO, A. R. & BLOCH, A. N. (1976). *Bull. Amer. Phys. Soc.* **21**, 287–288.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1977). B**33**, 428–433

The Crystal Structure of Onitin, a Phenolic Illudoid Sesquiterpene from the Fern *Onychium auratum*

BY V. K. WADHAWAN, S. K. SIKKA AND R. CHIDAMBARAM

Neutron Physics Section, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, *India*

(*Received* 7 *June* 1976; *accepted* 16 *July* 1976)

Onitin monomethyl ether (6-hydroxyethyl-4-methoxy-2,2,5,7-tetramethyl-1-indanone), $C_{16}H_{22}O_3$, crystallizes in the space group *Pbca*, with $a = 16{\cdot}14$ (1), $b = 16{\cdot}95$ (1), $c = 10{\cdot}59$ (1) Å and $Z = 8$. Its structure has been determined by the symbolic addition method from visually estimated Weissenberg data, and refined by least squares to an R of 0·075 for 1266 observed reflexions. The 1-indanone skeleton deviates significantly from planarity. There is considerable distortion of valence angles in the region of the *gem*-dimethyl. Rotational disorder is observed in the hydroxyethyl part of the molecule: the OH group is statistically distributed over two of the three possible orientational sites. This is attributed to the fact that $O–H\cdots O$ bond formation occurs for both these configurations. The crystal structure is stabilized by these intermolecular hydrogen bonds spiralling around the 2_1 axes along **c**.

Introduction

A new class of illudoid sesquiterpenes, collectively called pterosins, has come to be known after the first report of their isolation by Yoshihira, Fukuoka, Kuroyanagi & Natori (1971) from *Pteridium aquilinum*, a fern known for its radiomimetic and carcinogenic properties (Evans, 1968; Price & Pamukcu, 1968; Hirono, Shibuya, Fushimi & Haga, 1970). More members of this class have since been discovered, all from closely related ferns (Fukuoka, Kuroyanagi, Toyama, Yoshihira & Natori, 1972; Hayashi, Nishizawa & Sakan, 1973; Hasegawa & Akabori, 1974). The pterosins have a 1-indanone type of skeleton. Banerji, Ramakrishnan & Chadha (1974) have isolated two phenolic pterosins, onitin* and onitisin, from the fern *Onychium auratum* (*Cryptogrammatacea*). Along with pterosin M (Hasegawa & Akabori, 1974), these are the only phenolic pterosins known so far. The structure of onitin monomethyl ether (Fig. 1) is presented in this paper. As far as the authors are aware, this is the first report of an X-ray study of a pterosin.

Experimental

As onitin did not form good crystals, its monomethyl ether was used for the X-ray analysis. Lattice parameters were determined from zero-layer Weissenberg data by least-squares refinement (*CELPAR*, Wadhawan, 1973); the refinement included an adjustable correction term for film shrinkage and radius error. The density was measured by flotation in a mixture of petroleum spirit and CCl_4.

Crystal data

$C_{16}H_{22}O_3$, $M_r = 262{\cdot}3$, $a = 16{\cdot}14\,(1)$, $b = 16{\cdot}95\,(1)$, $c = 10{\cdot}59\,(1)$ Å, $V = 2896\,(4)$ Å^3, $D_x = 1{\cdot}203\,(2)$, $D_m = 1{\cdot}21\,(1)$ g cm^{-3}, $Z = 8$, $F(000) = 1136$. Systematic absences: $0kl$, k odd; $h0l$, l odd; $hk0$, h odd. Space group: *Pbca*. μ(Cu $K\alpha$) = $6{\cdot}62$ cm^{-1}.

Multiple-film equi-inclination Weissenberg photographs were taken with Ni-filtered Cu $K\alpha$ radiation up to the ninth layer along **c** and the third layer along **b**. Nearly spherical specimens were used for both zones, with effective μR values of 0·19 and 0·10 respectively. Intensities of 2685 unique reflexions (81% of the total in the Cu sphere) were estimated visually by comparison with a calibrated film strip. Corrections were applied for absorption, Lp factor and spot length with *VALPS* (Wadhawan, 1976). A K plot was then made to obtain a set of E values.

Structure determination

The structure was solved by the symbolic addition method. *SIGFMULA* (Sikka, 1971) was used for choosing the starting reflexions and for the sign determination. Signs of 307 E values $>1{\cdot}3$ were determined, and an E map computed. All 19 non-hydrogen atoms could be located.

The atomic parameters were then subjected to full-matrix least-squares refinement with *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\Sigma\, w(F_o - K\,|F_c|)^2$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Zero weights were assigned to unobserved reflexions. For observed reflexions, unit weights were taken initially, but in the later stages of refinement weights based on error-analysis plots were used. A variable parameter for isotropic extinction was also included. With isotropic temperature factors, a value of 0·174 was obtained for R for 1266 observed reflexions.

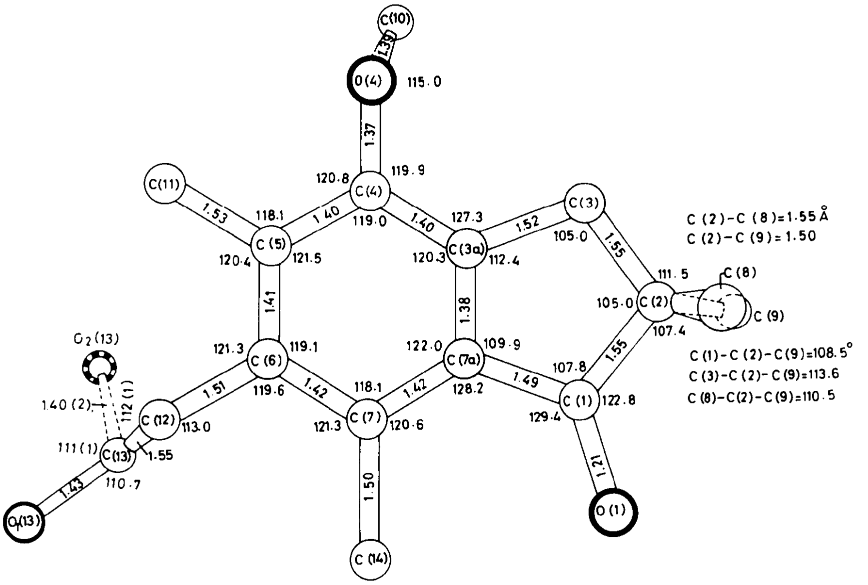

Fig. 1. Projection of the molecule of onitin monomethyl ether along the normal to the mean plane through the 1-indanone skeleton. Except when indicated otherwise, the e.s.d.'s of bond lengths and angles are 0·01 Å and 0·5° respectively.

---

* Hayashi, Nishizawa & Sakan (1974) have suggested the name 4-hydroxypterosin Z for onitin.

Introduction of anisotropic temperature factors and a weighting scheme based on an analysis of residuals made R fall to 0·126, and a value 0·173 was obtained for R_w $[=\{\Sigma\, w(F_o-|F_c|)^2/\Sigma\, wF_o^2\}^{1/2}]$. Because of the large number of parameters involved, the anisotropic refinement was done in two batches.

A difference synthesis located 20 of the 22 H atoms at this stage. These were included in the refinement with a common, variable, isotropic temperature factor. Scattering factors for H were taken from Stewart, Davidson & Simpson (1965). The refinement resulted in R and R_w falling to 0·093 and 0·122 respectively.

In a difference synthesis made at the end of this refinement, a prominent peak of almost half the usual C peak height was observed at (0·44, 0·42, 0·90), *i.e.* almost at the position expected for one of the H atoms bonded to C(13) (Fig. 1). Rotational disorder about C(12)–C(13) was suspected. A model was proposed in which the O atom attached to C(13) is randomly distributed over the sites marked O_1(13) and O_2(13) in Fig. 1. To gain some confidence in the model, an unconstrained refinement was first carried out in which the occupancy factors of O_1(13) and O_2(13) were allowed to vary independently and contributions of the two H atoms near each of these sites were ignored. R fell to 0·076 and the occupancy factors for O_1(13) and O_2(13) refined to 0·856 (16) and 0·290 (19) respectively. In addition, O_2(13) refined to a position giving a C(13)–O_2(13) length of 1·4 Å and very reasonable angles around C(13).

A constrained refinement was next carried out. O_1(13) was assigned a variable occupancy x, and an occupancy factor $(1-x)$ was taken for O_2(13). Also, H_1(13) and H_2(13), with occupancy factors $(1-x)$ and x respectively, were kept fixed at points corresponding to C–H = 1 Å and lying on the lines joining C(13) to

Table 2. *Fractional coordinates and thermal parameters* (*all* $\times 10^4$)

Thermal parameters for non-hydrogen atoms are defined by $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
For H atoms, a common isotropic temperature factor refined to a value 3·8 Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	2421 (3)	3899 (3)	3640 (4)	31 (2)	44 (2)	103 (5)	11 (2)	−9 (3)	−11 (3)
O(4)	5921 (3)	3132 (3)	4769 (6)	35 (2)	44 (2)	132 (6)	9 (2)	12 (3)	4 (3)
O_1(13)	4049 (4)	5337 (4)	9647 (5)	50 (3)	54 (3)	80 (7)	13 (3)	−15 (4)	−24 (4)
O_2(13)	4606 (15)	4102 (13)	9154 (20)	51 (13)	42 (11)	87 (26)	10 (9)	3 (14)	9 (13)
C(1)	3123 (4)	3653 (3)	3704 (6)	34 (3)	24 (2)	72 (7)	0 (2)	−1 (3)	4 (3)
C(2)	3483 (4)	3044 (3)	2754 (5)	38 (3)	25 (2)	63 (6)	3 (2)	3 (3)	−4 (3)
C(3)	4379 (4)	2888 (4)	3215 (6)	45 (3)	36 (3)	96 (8)	17 (3)	4 (4)	−18 (4)
C(3a)	4485 (4)	3413 (3)	4372 (5)	36 (3)	26 (2)	61 (7)	−1 (2)	13 (3)	−1 (3)
C(4)	5199 (4)	3506 (4)	5109 (6)	23 (3)	33 (2)	90 (7)	4 (2)	5 (3)	9 (4)
C(5)	5183 (4)	4035 (4)	6123 (6)	36 (3)	34 (3)	69 (7)	1 (2)	−5 (3)	10 (3)
C(6)	4475 (4)	4491 (3)	6394 (5)	38 (3)	23 (2)	62 (6)	1 (2)	−1 (3)	0 (3)
C(7)	3749 (4)	4382 (3)	5656 (5)	37 (3)	19 (2)	64 (7)	8 (2)	6 (3)	2 (3)
C(7a)	3783 (4)	3843 (3)	4637 (5)	32 (3)	21 (2)	64 (6)	3 (2)	5 (3)	7 (3)
C(8)	3475 (5)	3432 (5)	1433 (6)	67 (4)	54 (4)	75 (8)	14 (3)	7 (4)	1 (4)
C(9)	2944 (4)	2326 (8)	2767 (4)	63 (4)	31 (3)	146 (10)	7 (3)	0 (5)	−13 (4)
C(10)	5966 (4)	2342 (5)	5104 (9)	37 (4)	52 (4)	185 (12)	16 (3)	8 (5)	−10 (5)
C(11)	5969 (5)	4128 (5)	6912 (7)	42 (4)	61 (4)	95 (8)	10 (3)	5 (4)	3 (5)
C(12)	4470 (4)	5081 (4)	7461 (6)	43 (3)	27 (2)	75 (7)	−4 (2)	0 (4)	−6 (3)
C(13)	4125 (4)	4735 (4)	8711 (6)	50 (4)	38 (3)	69 (7)	5 (3)	7 (4)	−2 (4)
C(14)	2976 (5)	4844 (4)	5913 (6)	49 (3)	51 (3)	68 (7)	17 (3)	−8 (4)	−24 (4)

	x	y	z		x	y	z
H(3)*	4398 (35)	2292 (31)	3309 (52)	H(11)	5819 (36)	3921 (33)	7698 (52)
H(3′)	4868 (35)	3104 (31)	2603 (51)	H(11′)	5916 (34)	4852 (33)	7011 (51)
H(8)	3839 (35)	3953 (32)	1422 (51)	H(11″)	6321 (34)	3998 (33)	6536 (52)
H(8′)	3619 (35)	3038 (32)	846 (51)	H(12)	4061 (35)	5585 (32)	7277 (52)
H(8″)	2884 (35)	3467 (32)	1164 (50)	H(12′)	5049 (36)	5307 (31)	7613 (52)
H(9)	2944 (33)	1965 (32)	3549 (52)	H_1(13)	4072 (—)	5159 (—)	9370 (—)
H(9′)	2397 (35)	2280 (31)	2401 (50)	H_2(13)	4469 (—)	4283 (—)	9027 (—)
H(9″)	3165 (36)	1908 (32)	2363 (51)	H(13′)	3471 (35)	4550 (32)	8595 (50)
H(10)	6453 (34)	2165 (31)	4971 (51)	H(O13)	3587 (54)	5635 (45)	9454 (70)
H(10′)	5444 (34)	2024 (31)	5118 (50)	H(14)	2661 (34)	5001 (34)	5288 (52)
H(10″)	5977 (34)	2293 (32)	6016 (54)	H(14′)	2866 (33)	4978 (33)	6660 (53)
				H(14″)	2301 (35)	4406 (31)	6088 (51)

* H atom labels correspond to those of the heavy atoms to which they are bonded.

$O_1(13)$ and $O_2(13)$ respectively. The remaining H atom bonded to C(13), H(13′), was assigned full occupancy* and variable positional parameters. This refinement resulted in R falling from 0·093 to 0·075. From a difference synthesis made at this stage, the two missing H atoms could also be located. The refinement was repeated after inclusion of these and with the weighting scheme: $w^{-1/2} = 1{\cdot}320$ for $F_o \leq 18{\cdot}0$, $w^{-1/2} = 1{\cdot}320 + 0{\cdot}0269(F_o - 18{\cdot}0)$ for $F_o > 18{\cdot}0$. The final values for R and R_w are 0·075 and 0·099 respectively. The occupancy factors for $O_1(13)$ and $O_2(13)$ are 0·800 (12) and 0·200 (12). The extinction constant g' (Coppens & Hamilton, 1970) refined to 1·1 (2). This corresponds to an average value of 5·29″ for the equivalent mosaic spread parameter, η. Table 1 shows a comparison of the observed and calculated structure factors. Unobserved reflexions are not included in this table.† R for all 2685 reflexions (with unobserved reflexions taken at half the threshold intensity) is 0·165. Table 2 lists the atomic parameters.

Discussion

Fig. 1 shows a projection of the molecule along the normal to the mean plane through the 1-indanone skeleton. Atom labels, bond lengths, and bond angles are also indicated.‡ Onitin monomethyl ether has been found to be 6-hydroxyethyl-4-methoxy-2,2,5,7-tetramethyl-1-indanone, confirming the structure suggested by Banerji *et al.* (1974) from spectroscopic and biogenetic considerations.

Equations of weighted least-squares planes (*PLANE*, Ramanadham & Sikka, 1971, unpublished) through the five-membered ring (plane 1), the six-membered ring (plane 2), and the 14 atoms constituting the 1-indanone skeleton and those bonded directly to it (except the two *gem* methyls) (plane 3) are given in Table 3. The five- and six-membered rings are planar, though inclined to each other at an angle of 2·15°. But atoms defining plane 3 deviate from it by as much as 0·065 (5) Å. For this plane, $\chi^2 = 497{\cdot}4$, whereas $\chi^2_{11,0{\cdot}05} = 19{\cdot}7$. A similar departure from planarity is also observed in 2-dimethylsulphuranylidene-1,3-indandione (Christensen & Thom, 1971), and is probably attributable to steric effects in the strained indanone skeleton.

The strain caused by fusion of the two rings leads to considerable distortion of valence angles also. Whereas C(3)–C(2)–C(8) and C(3)–C(2)–C(9) are 111·5 (5) and 113·6 (5)° respectively, the corresponding angles with C(1) replacing C(3) are 107·4 (5) and 108·5 (5)°; that is, about 4° less. A similar difference of 4° is also found in 2-dimethylsulphuranylidene-1,3-indandione (Christensen & Thom, 1971) and in phthalimidocyclohexane (Groth, 1969). On the other hand, in tetragonal triketoindan (Bolton, 1965) an implied twofold axis of symmetry passes through the β keto bond and therefore the molecule is observed to be symmetrical; it is also reported to be planar within the error of measurement.

C(6)–C(7)–C(7a) [118·1 (5)°] in the present molecule is very similar to the 117·4° value in 2-dimethylsulphuranylidene-1,3-indandione, 116° in phthalimidocyclohexane, and 118·3° in triketoindan. The C(1)–C(2) and C(3)–C(2) distances [1·55 (1) Å each] compare well with the 1·526 Å in triketoindan. However, significantly shorter values of 1·437 and

Table 3. *Equations of weighted least-squares planes, and distances from these planes*

Plane 1 is defined by atoms 1 to 5, plane 2 by atoms 4 to 9, and plane 3 by atoms 1 to 14.

$$\text{Plane 1}: 0{\cdot}3275X + 0{\cdot}7427Y - 0{\cdot}5841Z - 3{\cdot}9649 = 0$$
$$\text{Plane 2}: 0{\cdot}3147X + 0{\cdot}7262Y - 0{\cdot}6112Z - 3{\cdot}6479 = 0$$
$$\text{Plane 3}: 0{\cdot}3075X + 0{\cdot}7363Y - 0{\cdot}6027Z - 3{\cdot}7391 = 0$$

No.	Atom	Plane 1	Plane 2	Plane 3
1	C(1)	−0·006 (6) Å	0·038 (6) Å	0·006 (6) Å
2	C(2)	0·005 (6)	0·086 (6)	0·032 (6)
3	C(3)	−0·003 (7)	0·050 (7)	−0·013 (7)
4	C(3a)	−0·002 (6)	0·002 (6)	−0·043 (6)
5	C(7a)	0·005 (5)	0·003 (5)	−0·025 (5)
6	C(7)	0·035 (5)	−0·010 (5)	−0·019 (5)
7	C(6)	0·099 (6)	0·015 (6)	0·006 (6)
8	C(5)	0·067 (6)	−0·011 (6)	−0·038 (6)
9	C(4)	0·037 (6)	0·002 (6)	−0·044 (6)
10	O(1)	−0·029 (4)	0·025 (4)	0·005 (4)
11	O(4)	0·158 (5)	0·128 (5)	0·065 (5)
12	C(11)	0·111 (8)	−0·009 (8)	−0·036 (8)
13	C(12)	0·180 (6)	0·048 (6)	0·059 (6)
14	C(14)	0·049 (7)	−0·001 (7)	0·010 (7)
15	C(8)	1·307 (8)	1·415 (8)	1·355 (8)
16	C(9)	−1·192 (10)	−1·080 (10)	−1·141 (10)
17	C(10)	−1·021 (8)	−1·039 (8)	−1·113 (8)
18	C(13)	−1·211 (7)	−1·362 (7)	−1·342 (7)
19	$O_1(13)$	−1·073 (6)	−1·266 (6)	−1·226 (6)
20	$O_2(13)$	−2·029 (22)	−2·185 (22)	−2·177 (22)

---

* The possibility that this site may also be partially occupied by O was also checked. Fractional occupancies x_1, $1 - x_1 - x_3$, and x_3 were assigned to $O_1(13)$, $O_2(13)$ and $O_3(13)$, the last being for the possible O site near H(13′). In addition, $H_1(13)$, $H_2(13)$, and H(13′), fixed in position 1 Å from C(13) and having appropriate valence angles, were assigned occupancies $1 - x_1$, $x_1 + x_3$, and $1 - x_3$. The refinement was carried out with the temperature factor of $O_3(13)$ held fixed at 3·8 Å^2. The parameter x_1 refined to 0·794 (12) and x_3 fell from an arbitrarily chosen initial value 0·050 to 0·014 (8) in two cycles. There was no improvement in R. It appears that x_3 is not significantly different from zero. This conclusion is also supported by the absence of any significant peak in the difference map.

† Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32052 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

‡ Bond distances and angles involving H atoms are not indicated in Fig. 1. These distances range from 0·73 (6) to 1·33 (6) Å, and the angles from 78 (4) to 126 (5)°.

1·420 Å are observed in 2-dimethylsulphuranylidene-1,3-indandione.

The conformation around C(12)–C(13) is predominantly antiperiplanar [C(6)–C(12)–C(13)–O_1(13) = −173·6°]. Only in 20% of the molecules is the synclinal conformation adopted [C(6)–C(12)–C(13)–O_2(13) = 61·6°], and that too is because the molecule can form hydrogen bonds in this conformation also. This can be seen from Table 4, which lists interatomic distances less than 3·75 Å between molecules. Two types of intermolecular O–H···O bonds occur in the structure: O_1(13)–H···O(1) bonds, for which O_1(13)···O(1) = 2·905 (8) Å and C(13)–O_1(13)–O(1) = 97·7 (4)°, and O_2(13)–H···O_1(13) bonds, for which O_2(13)···O_1(13) = 2·69 (2) Å and C(13)–O_2(13)–O_1(13) = 120·7 (7)°. These hydrogen bonds are indicated by broken lines in Fig. 2, which shows a projection of the crystal structure along **c**.

The possibility of formation of the second type of hydrogen bond is the reason for the OH group bonded to C(13) being statistically distributed over the two sites O_1(13) and O_2(13). An energy calculation was performed to confirm this observation. Contributions of the non-bonded interaction and the bent O–H···O bond interaction to the total potential energy were calculated. For the latter type of interaction, the modified Lippincott–Schroeder potential was employed

Table 4. *Intermolecular distances less than* 3·75 Å *between non-hydrogen atoms*

(i)	x	y	z	(ix)	$\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$
(ii)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	(x)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
(iii)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	(xi)	$1-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
(iv)	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$	(xii)	$1-x$	$1-y$	$2-z$
(v)	$-x$	$-y$	$-z$	(xiii)	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
(vi)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z	(xiv)	$1-x$	$1-y$	$1-z$
(vii)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(xv)	x	y	$1+z$
(viii)	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$				

O(1)–$O_1(13)^{ix}$	2·91 (1)	O_2(13)–$C(8)^{xv}$	3·23 (2)
–$C(13)^{ix}$	3·40 (1)	–$C(10)^{vii}$	3·44 (2)
–$C(10)^{x}$	3·42 (1)	–$C(3)^{vii}$	3·54 (2)
–$C(14)^{ix}$	3·65 (1)	–$C(13)^{xii}$	3·63 (2)
–$C(12)^{ix}$	3·72 (1)	C(3a)–$C(12)^{xiv}$	3·62 (1)
O_1(13)–$O_2(13)^{vii}$	2·69 (2)	C(4)–$C(12)^{xiv}$	3·67 (1)
–$O_1(13)^{vii}$	3·36 (1)	C(5)–$C(6)^{xiv}$	3·69 (1)
–$C(10)^{xi}$	3·41 (1)	–$C(7)^{xiv}$	3·70 (1)
–$C(13)^{xii}$	3·42 (1)	C(7)–$C(11)^{xiv}$	3·74 (1)
–$C(14)^{xiii}$	3·55 (1)		

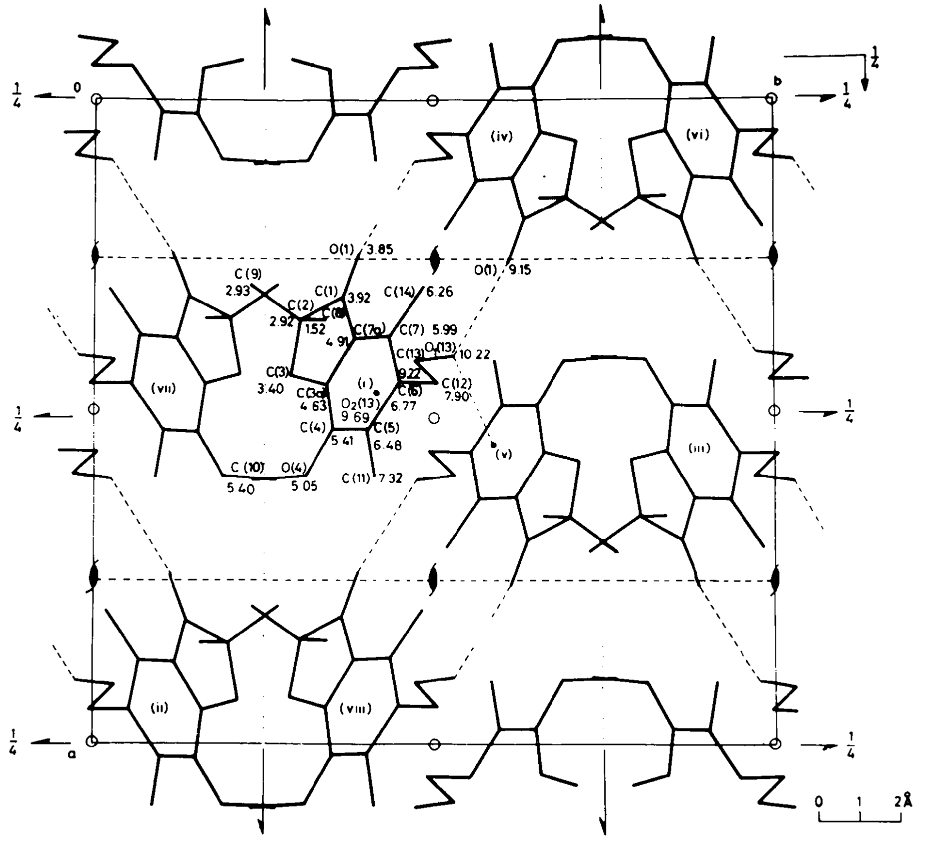

Fig. 2. The crystal structure viewed down **c**. Numbers near each atom label are z coordinates in Å. Broken lines between atoms represent hydrogen bonds.

(Chidambaram & Sikka, 1968; Chidambaram, 1968). Preliminary calculations show the occurrence of an energy minimum at $O_2(13)$. If the O atom occurs at $O_2(13)$ with a probability x, the probability of forming the hydrogen bond $O_2(13)$—H $\cdots$ $O_1(13)$ will be between x and $x(1-x)$ depending on the correlations between the occupances of $O_2(13)$ and $O_1(13)$ in neighbouring molecules.

We thank Dr M. S. Chadha for suggesting the problem and for his interest in the work. Crystals of the compound were kindly supplied by Dr G. Ramakrishnan. Useful discussions with Dr G. Ramakrishnan and Dr A. Banerji are also acknowledged.

References

Banerji, A., Ramakrishnan, G. & Chadha, M. S. (1974). *Tetrahedron Lett.* pp. 1369–1370.

Bolton, W. (1965). *Acta Cryst.* **18**, 5–10.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305 (with modifications by W. C. Hamilton, J. A. Ibers, C. K. Johnson, S. Srikanta & S. K. Sikka). The BESM-6 version is by H. Rajagopal.

Chidambaram, R. (1968). *Nucl. Phys. Solid State Phys. (India)*, **11A**, 215–234.

Chidambaram, R. & Sikka, S. K. (1968). *Chem. Phys. Lett.* **2**, 162–165.

Christensen, A. T. & Thom, E. (1971). *Acta Cryst.* **B27**, 581–586.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

Evans, I. A. (1968). *Cancer Res.* **28**, 2252–2261.

Fukuoka, M., Kuroyanagi, M., Toyama, M., Yoshihira, K. & Natori, S. (1972). *Chem. Pharm. Bull.* **20**, 2282–2285.

Groth, P. (1969). *Acta Chem. Scand.* **23**, 1076–1078.

Hasegawa, M. & Akabori, Y. (1974). *Phytochemistry*, **13**, 509–511.

Hayashi, Y., Nishizawa, M. & Sakan, T. (1973). *Chem. Lett.* pp. 63–64.

Hayashi, Y., Nishizawa, M. & Sakan, T. (1974). *Chem. Lett.* pp. 945–946.

Hirono, I., Shibuya, C., Fushimi, K. & Haga, M. (1970). *J. Natl. Cancer Inst.* **45**, 179–188.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.

Price, J. M. & Pamukcu, A. M. (1968). *Cancer Res.* **28**, 2247–2250.

Sikka, S. K. (1971). *SIGFMULA*. Report BARC 576, Bhabha Atomic Research Centre, Bombay.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wadhawan, V. K. (1973). *CELPAR*. Program No. 193, *World List of Crystallographic Computer Programs*, 3rd ed., edited by G. C. Bassi. *J. Appl. Cryst.* (1973), **6**, 309.

Wadhawan, V. K. (1976). Ph.D. thesis, Univ. of Bombay, Bombay.

Yoshihira, K., Fukuoka, M., Kuroyanagi, M. & Natori, S. (1971). *Chem. Pharm. Bull.* **19**, 1491–1495.

Acta Cryst. (1977). B33, 433–437

The Crystal and Molecular Structure of Bis(L-asparaginato)zinc(II), $[Zn(OOC.CHNH_2.CH_2.CONH_2)_2]_n$

By F. S. Stephens, R. S. Vagg and P. A. Williams

School of Chemistry, Macquarie University, North Ryde, NSW 2113, Australia

(*Received* 9 *June* 1976; *accepted* 16 *July* 1976)

The structure of bis(L-asparaginato)zinc(II) has been determined by counter methods and refined to R 0·045 for 1531 unique reflexions by least squares. The monoclinic unit cell, space group $P2_1$, has a = 12·323 (1), b = 5·027 (2), c = 9·702 (2) Å, β = 99·12 (4)°, Z = 2. The Zn atom is in a distorted octahedral environment. A carboxylic O atom and the α-amino N atom from each ligand coordinate to the Zn atom in a *trans* square-planar configuration (Zn—O 2·09, Zn—N 2·08 Å). The octahedral environment is completed by carbonyl O atoms from neighbouring molecules (Zn—O 2·28, 2·48 Å) creating infinite chains linked in the [011] direction.

Introduction

Both L-asparagine and L-glutamine are known to be essential growth factors (Williams, 1972) for a variety of tumours, particularly animal lymphomas. Recently it has been shown that the activity of L-asparaginase can be inhibited (Charlson, Coman, Karossi, Stephens, Vagg & Watton, 1976, unpublished) by a number of