

ideal  $109^\circ$  in order to minimize the angular strain in the eight-membered ring and to accommodate the relatively bulky cyclopentadienyl ligands. The Ti-Cl distances vary from 2.263–2.270 ( $\sigma=0.004$ ) Å, the Ti-O distances from 1.776–1.799 ( $\sigma=0.007$ ) Å, and the Ti-( $\pi$ -C<sub>5</sub>H<sub>5</sub>) distances (taken to the centres of the rings) from 2.02–2.04 Å. These can best be compared with the distances found in the two structures [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>2</sub>]<sub>2</sub>O (Allegra & Ganis, 1962) and ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> (Ganis & Allegra, 1962) which were determined from two-dimensional projections. They found Ti-Cl distances varying from 2.27–2.30 Å, and Ti-O and Ti-( $\pi$ -C<sub>5</sub>H<sub>5</sub>) distances of 1.74 and 2.04 Å respectively. Thus all the bond lengths in the different structures are similar. There are no unusual intermolecular contacts and therefore the crystal structure is determined only by the efficient packing of the molecules.

The tetrameric ring structure of [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiClO]<sub>4</sub> is the first of its type containing a transition metal; the nearest equivalent is the cyclic P<sub>4</sub>O<sub>11</sub><sup>4-</sup> ion found in the metaphosphates Al<sub>4</sub>(P<sub>4</sub>O<sub>12</sub>)<sub>3</sub> (Pauling & Sherman, 1957) and (NH<sub>4</sub>)<sub>4</sub>P<sub>4</sub>O<sub>12</sub> (Romers, Ketelaar & MacGillavry, 1951). Tetrameric alkoxides of titanium are known (Ibers, 1963; Witters & Caughlan, 1965; Wright & Williams, 1966), but in these the titanium atoms are octahedrally coordinated and the tetramer consists of four such octahedra joined by edges.

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## The Crystal Structure of DL-4 $\beta$ ,10 $\beta$ -Dimethyl-6-ethylamino-4-hydroxycarbonyl-2, 3, 5 $\beta$ , 10-tetrahydrophenanthr-1-one lactam, C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N\*

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The title compound crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in a unit cell of dimensions  $a=10.901$ ,  $b=9.738$ ,  $c=16.389$  Å;  $\beta=117.17^\circ$ . The structure was determined by the symbolic-addition procedure using low-temperature diffractometer data and refined by the least-squares method to  $R=3.9\%$  for 3101 observed reflexions.

### Introduction

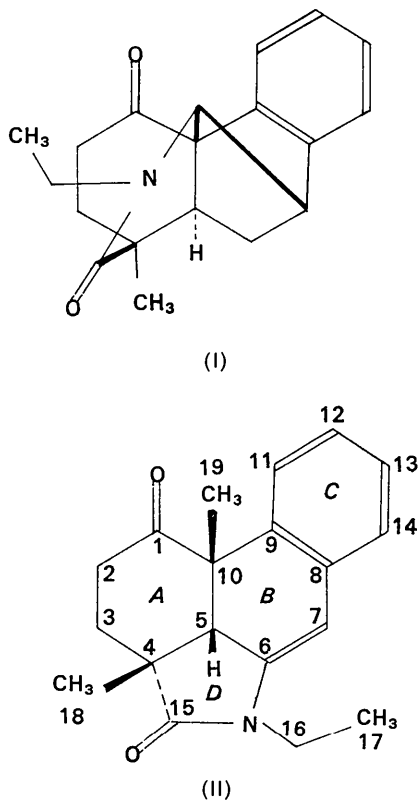
Wiesner and Ho recently attempted to prepare the lactam (I) and intended to use it as an intermediate for a

synthesis of hexacyclic diterpene alkaloids. Although the material which they obtained gave the correct elemental analysis, its ultraviolet and nuclear magnetic-resonance spectra did not agree with the proposed structure. This crystal structure determination, which was undertaken in order to establish unambiguously the structure of the synthetic intermediate, revealed the

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structure to be (II). The synthesis of this compound and the results of this X-ray analysis were published in a preliminary communication (Birnbaum, Wiesner & Ho, 1969).



### Crystal data

DL-4 $\beta$ ,10 $\beta$ -Dimethyl-6-ethylamino-4-hydroxycarbonyl-2,3,5 $\beta$ ,10-tetrahydrophenanthr-1-one lactam,  
C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N, F. W. 295.38, m.p. 138–139°C. Monoclinic.

At -160°C	At +21°C
$a = 10.901 \pm 0.002 \text{ \AA}$	$a = 10.979 \pm 0.002 \text{ \AA}$
$b = 9.738 \pm 0.001$	$b = 9.841 \pm 0.001$
$c = 16.389 \pm 0.003$	$c = 16.585 \pm 0.003$
$\beta = 117.17 \pm 0.02^\circ$	$\beta = 117.00 \pm 0.02^\circ$
$V = 1547.7 \text{ \AA}^3$	$V = 1596.6 \text{ \AA}^3$

Cu  $K\alpha_1$  ( $\lambda = 1.54051 \text{ \AA}$ ) and Cu  $K\alpha_2$  ( $\lambda = 1.54433 \text{ \AA}$ ) radiation was used.  $D_m = 1.229 \text{ g.cm}^{-3}$  (by flotation in aqueous potassium iodide)  $D_x = 1.229 \text{ g.cm}^{-3}$ ,  $Z = 4$ ,  $F(000) = 632$ . Space group  $P2_1/c$  (from precession photographs, systematic absences:  $h0l$  for  $l$  odd,  $0k0$  for  $k$  odd). Linear absorption coefficient  $\mu(\text{Cu } K\alpha) = 6.4 \text{ cm}^{-1}$ .

### Experimental

Crystallization from an ethyl acetate–n-pentane solution yielded well-formed colourless crystals. A crystal of dimensions  $0.36 \times 0.43 \times 0.50 \text{ mm}$  was mounted

along the  $b$  axis. The cell dimensions and the intensities were measured with a General Electric XRD-5 manual four circle diffractometer equipped with a scintillation counter and a pulse-height analyser. Ni-filtered Cu radiation was employed. Measurements of the cell constants were carried out using  $1^\circ$  take-off angle,  $0.02^\circ$  slit at  $-160^\circ\text{C}$  and  $0.05^\circ$  slit at room temperature. The intensity data were collected by the moving-crystal moving-counter ( $\theta/2\theta$ ) scan technique at a take-off angle of  $2^\circ$ , the crystal being bathed in a stream of cold nitrogen gas and thus kept at  $-160^\circ\text{C}$ . Brass attenuation filters were used when the count rate exceeded 20,000 c. p. s. A standard reflexion was measured after every 20–50 reflexions and used for scaling the data. The crystal showed no evidence of deterioration during the data collection. Of the 3439 independent reflexions within the range of the diffractometer ( $2\theta \leq 165^\circ$ ) 3101 were observed above threshold value. The threshold count was taken as a net count of 150 (15 decacounts as recorded) or 10% of the background, whichever was higher. The intensities were corrected for Lorentz and polarization factors but an absorption correction was considered unnecessary.

### Structure determination

The structure was solved by the symbolic-addition procedure for centrosymmetric space groups (Karle & Karle, 1966). The scale factor and overall isotropic temperature factor were derived from a Wilson plot and used to calculate the normalized structure factors,

$$|E_h| = k |F_h| \exp(B \sin^2 \theta / \lambda) / (\epsilon \sum_j n f_j)^{1/2},$$

where  $\epsilon$  is 2 for  $h0l$  and  $0k0$  reflexions and is 1 for all other reflexions. The statistics of the  $E$ 's, with theoretical values for centrosymmetric space groups (Karle, Dragonette & Brenner, 1965) given in parentheses, are:  $\langle |E| \rangle = 0.818$  (0.798),  $\langle |E|^2 \rangle = 1.041$  (1.000),  $\langle |E^2 - 1| \rangle = 0.982$  (0.968); reflexions with  $|E| > 3.05\%$  (0.3%), those with  $|E| > 2.51\%$  (5.0%), and those with  $|E| > 1.323\%$  (32.0%).

The 471 reflexions with  $|E| \geq 1.5$  were used in the sign-determining procedure using the  $\sum_2$  relationship,  $sE_h \approx s \sum_k E_k E_{h-k}$ , but only reflexions with  $|E| \geq 2.0$  were used in the right-hand side of this formula. Signs were accepted when the probability, given by  $P_+(\mathbf{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} |E_h| \sum_k E_k E_{h-k}$ , was 98.2% or higher. The

origin-defining reflexions were  $\bar{9}23$ ,  $348$  and  $\bar{1}31$ . Of the 471 reflexions 452 signs were determined (later inspection showed all these signs to be correct) while 19 were undetermined. An  $E$  map computed with these 452 terms revealed all the 22 non-hydrogen atoms in the asymmetric unit. There were no spurious peaks as high as the ones selected for the molecule.

A structure-factor calculation based on the coordinates derived from the  $E$  map and the scale factor and

isotropic temperature parameter ( $B=1.07 \text{ \AA}^2$ ) derived from the Wilson plot gave an  $R$  value of 28% ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ).

The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used throughout the analysis for carbon, nitrogen, and oxygen atoms and those for bonded hydrogen atoms were taken from Stewart, Davidson & Simpson (1965).

### Structure refinement

Coordinates, thermal parameters, and the scale factor were refined by the block-diagonal approximation of the least-squares method, minimizing the expression  $\sum w(|F_o| - |F_c|)^2$ . The matrices used were  $9 \times 9$  for coordinates and thermal parameters ( $4 \times 4$  for isotropic thermal motion) of each atom. The scale factor and the overall isotropic thermal parameter were refined by a  $2 \times 2$  matrix. A shift factor of 0.8 was used throughout the refinement.

Progress of the refinement is outlined in Table 1. A low-angle ( $\sin\theta/\lambda \leq 0.40$ ) difference Fourier synthesis

was calculated after the 5th cycle of refinement and all the hydrogen atoms were located on peaks varying in height from 0.45 to 0.68  $e. \text{\AA}^{-3}$  (Fig. 1). Residual electron density, lower than any of the peaks representing the hydrogen atoms, was present between some atoms and near the oxygen and nitrogen atoms but it is excluded from this Figure. After the 11th cycle of least squares the eight strongest reflexions were corrected empirically for extinction in the manner described by Pinnock, Taylor & Lipson (1956). Three other reflexions showed poor agreement between the observed and calculated structure factors, their  $F_c$ 's being very close to zero. An inspection of these reflexions on the diffractometer by gradually offsetting  $\varphi$  and adjusting  $\omega$  and  $\chi$  correspondingly, a method similar to that described by Coppens (1968), revealed that they were double reflexions and that their actual intensities were below the threshold value. The following weighting scheme, chosen so as to reflect the trends in  $|\Delta F|$ 's, was introduced at this stage:  $\sqrt{w} = \sqrt{w_1} \cdot \sqrt{w_2}$  where  $\sqrt{w_1} = 1$  when  $|F_o| \leq p_1$ ,  $\sqrt{w_1} = (p_1/|F_o|)^{1/2}$  when  $|F_o| > p_1$ ,  $\sqrt{w_2} = (\sin^2\theta/p_2)^{p_3}$  when  $\sin^2\theta \leq p_2$ , and  $\sqrt{w_2} = (p_2/\sin^2\theta)^{p_3}$  when

Table 1. Progress of the refinement

Cycle No.	Final $R$	Parameters refined
1—5	10.0%	$x, y, z, U_{iso}$ for C, N, O + overall scale factor
6—9	5.9%	as above + $x, y, z, U_{iso}$ for H
10	4.3%	$x, y, z, U_{ij}$ ( $i, j = 1, 2, 3$ ) for C, N, O; $x, y, z, U_{iso}$ for H + overall scale factor
11—15*	3.9%	as above
16*	3.9%	structure factors only

\* The scattering curve of oxygen was corrected for  $\Delta f''$ .

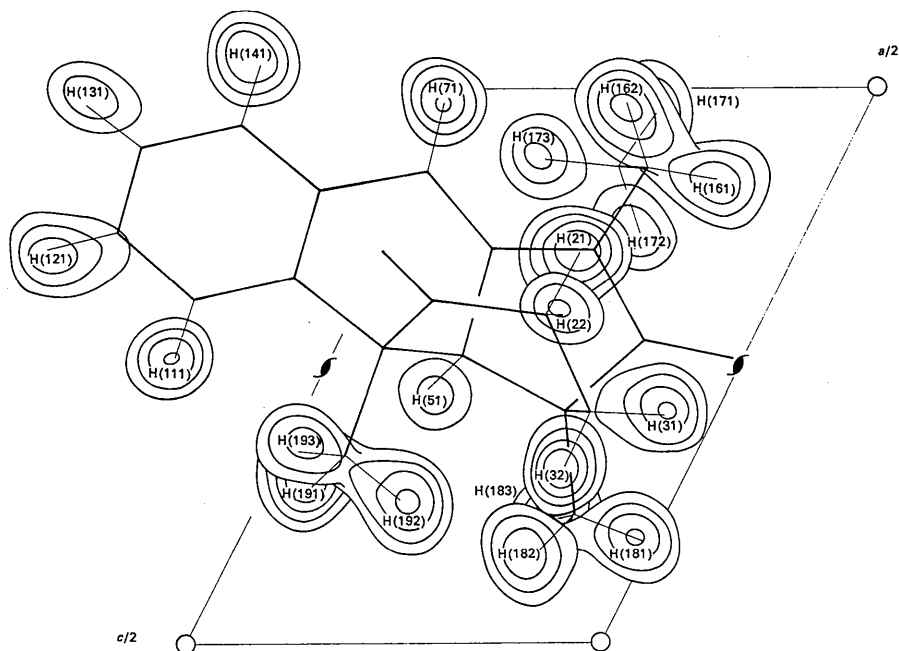


Fig. 1. Composite three-dimensional difference Fourier synthesis viewed along the  $b$  axis, showing the hydrogen atoms. The contours, starting at  $0.3 e. \text{\AA}^{-3}$ , are drawn at intervals of  $0.1 e. \text{\AA}^{-3}$ . The e.s.d. is  $0.13 e. \text{\AA}^{-3}$ .

$\sin^2\theta > p_2$ . The parameters were adjusted during the refinement in order to make  $w(\Delta F)^2$  as linear as possible with respect to  $|F_o|$  and to  $\sin\theta$ . The final values were  $p_1 = 13.5$ ,  $p_2 = 0.80$ , and  $p_3 = 0.153$ .

During the last cycles of the anisotropic refinement the oxygen atoms were corrected for the imaginary part of the anomalous dispersion [taken from *International Tables for X-ray Crystallography* (1962)]. The refinement converged to an  $R$  value of 3.9% ( $R' = 5.0\%$

where  $R' = (\sum w(\Delta F)^2 / \sum wF_o^2)^{1/2}$  for the 3101 observed reflexions. No shifts in any of the parameters were greater than  $0.1\sigma$  after the last cycle of refinement.

The final coordinates and thermal parameters are listed in Table 2. The listed estimated standard deviation values are those given by the inverse of the least-squares matrix. Table 3 shows the observed and calculated structure factors. The unobserved reflexions are marked with an asterisk. They were given the

Table 2. Final fractional coordinates and thermal parameters ( $\text{\AA}^2$ )

The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions.

(a) Non-hydrogen atoms

The temperature-factor expression used was

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

	$x$ ( $\times 10^5$ )	$y$ ( $\times 10^5$ )	$z$ ( $\times 10^5$ )	$U_{11}$ ( $\times 10^4$ )	$U_{22}$ ( $\times 10^4$ )	$U_{33}$ ( $\times 10^4$ )	$2U_{23}$ ( $\times 10^4$ )	$2U_{13}$ ( $\times 10^4$ )	$2U_{12}$ ( $\times 10^4$ )
C(1)	9025 (13)	64894 (12)	18988 (8)	147 (5)	88 (5)	113 (5)	-39 (9)	124 (9)	-16 (9)
C(2)	23649 (13)	66602 (13)	20374 (9)	142 (6)	112 (5)	203 (7)	62 (9)	181 (10)	-13 (9)
C(3)	34507 (12)	59329 (13)	28860 (9)	111 (5)	116 (5)	186 (5)	-36 (9)	115 (9)	-42 (9)
C(4)	31609 (12)	43795 (13)	28820 (8)	91 (5)	107 (5)	129 (5)	2 (9)	83 (9)	11 (8)
C(5)	15949 (11)	40534 (12)	24006 (8)	89 (5)	82 (5)	94 (5)	5 (8)	70 (9)	2 (8)
C(6)	13120 (12)	35974 (12)	14498 (8)	123 (5)	83 (5)	129 (5)	3 (9)	138 (9)	15 (8)
C(7)	451 (12)	35625 (13)	7419 (8)	133 (6)	120 (5)	117 (5)	5 (9)	123 (9)	5 (9)
C(8)	-11180 (12)	39602 (12)	9102 (8)	110 (5)	99 (5)	121 (5)	57 (9)	99 (9)	12 (9)
C(9)	-8792 (12)	47233 (12)	17014 (8)	106 (5)	82 (5)	123 (5)	51 (9)	96 (9)	33 (8)
C(10)	5911 (12)	52118 (12)	23281 (8)	95 (5)	84 (5)	115 (5)	3 (9)	97 (9)	20 (8)
C(11)	-19889 (12)	50235 (13)	18757 (9)	118 (5)	131 (5)	159 (5)	20 (9)	135 (9)	31 (9)
C(12)	-33209 (13)	45994 (14)	12820 (9)	112 (5)	175 (6)	199 (5)	76 (10)	156 (9)	41 (9)
C(13)	-35578 (13)	38658 (13)	4953 (9)	95 (5)	151 (6)	179 (5)	74 (9)	49 (9)	0 (9)
C(14)	-24674 (13)	35499 (13)	3126 (8)	133 (5)	121 (5)	128 (5)	33 (9)	75 (9)	-4 (9)
C(15)	36737 (13)	36686 (13)	22592 (9)	119 (5)	123 (6)	164 (5)	4 (9)	128 (9)	11 (9)
C(16)	26892 (13)	25381 (15)	7232 (9)	151 (6)	246 (7)	151 (5)	-65 (10)	183 (10)	36 (10)
C(17)	23645 (15)	10151 (16)	7287 (10)	213 (7)	248 (7)	241 (7)	-205 (12)	237 (12)	-13 (11)
C(18)	39335 (13)	37797 (14)	38460 (9)	133 (6)	181 (6)	128 (5)	31 (9)	49 (9)	38 (10)
C(19)	7744 (13)	56085 (13)	32866 (8)	135 (5)	127 (6)	131 (5)	-39 (9)	134 (9)	15 (9)
N(1)	25635 (10)	32619 (11)	14637 (7)	108 (5)	157 (5)	145 (4)	-33 (8)	138 (8)	28 (8)
O(1)	103 (9)	73177 (9)	14625 (6)	165 (4)	117 (4)	178 (4)	47 (7)	121 (7)	56(7)
O(2)	48755 (9)	35058 (11)	24326 (7)	101 (4)	274 (5)	241 (4)	-94 (8)	145 (7)	35 (7)

(b) Hydrogen atoms\*

	$x$ ( $\times 10^4$ )	$y$ ( $\times 10^4$ )	$z$ ( $\times 10^4$ )	$U_{iso}$ ( $\times 10^4$ )
H(21)	2394 (17)	6287 (18)	1467 (12)	162 (41)
H(22)	2575 (19)	7606 (19)	2043 (13)	217 (44)
H(31)	4395 (18)	6049 (18)	2945 (12)	199 (43)
H(32)	3488 (18)	6387 (18)	3445 (12)	181 (42)
H(51)	1408 (16)	3269 (16)	2711 (11)	83 (35)
H(71)	-156 (16)	3246 (17)	129 (11)	79 (35)
H(111)	-1851 (16)	5544 (17)	2426 (11)	95 (37)
H(121)	-4085 (17)	4794 (18)	1418 (12)	156 (41)
H(131)	-4461 (18)	3540 (19)	102 (12)	190 (43)
H(141)	-2616 (16)	2970 (17)	-225 (11)	89 (35)
H(161)	3647 (19)	2703 (19)	845 (13)	230 (46)
H(162)	2047 (17)	3002 (18)	138 (12)	162 (41)
H(171)	2472 (21)	522 (22)	199 (14)	329 (52)
H(172)	3041 (19)	577 (20)	1335 (13)	248 (47)
H(173)	1415 (20)	822 (21)	652 (14)	302 (49)
H(181)	4938 (18)	3938 (18)	4076 (12)	180 (42)
H(182)	3638 (18)	4245 (19)	4263 (12)	200 (43)
H(183)	3744 (19)	2762 (20)	3853 (13)	258 (47)
H(191)	540 (17)	4827 (17)	3563 (11)	135 (38)
H(192)	1731 (17)	5868 (17)	3697 (11)	108 (37)
H(193)	206 (17)	6378 (17)	3254 (11)	118 (38)

\* The hydrogen atoms are numbered according to the carbon atoms to which they are attached.

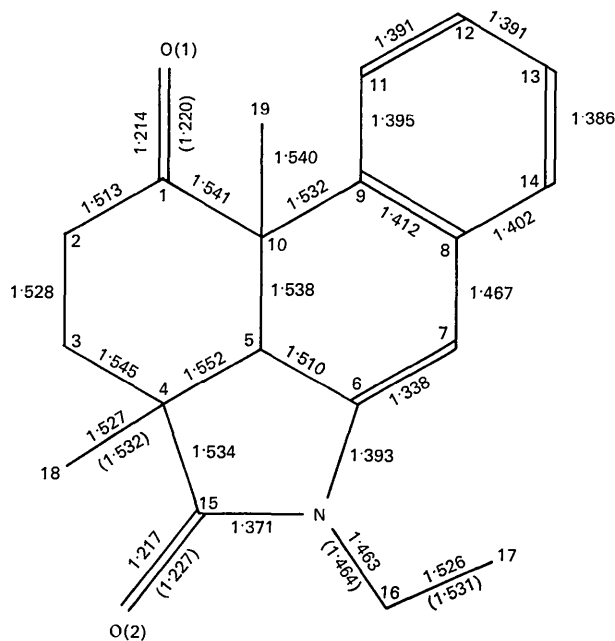


Table 3 (cont.)

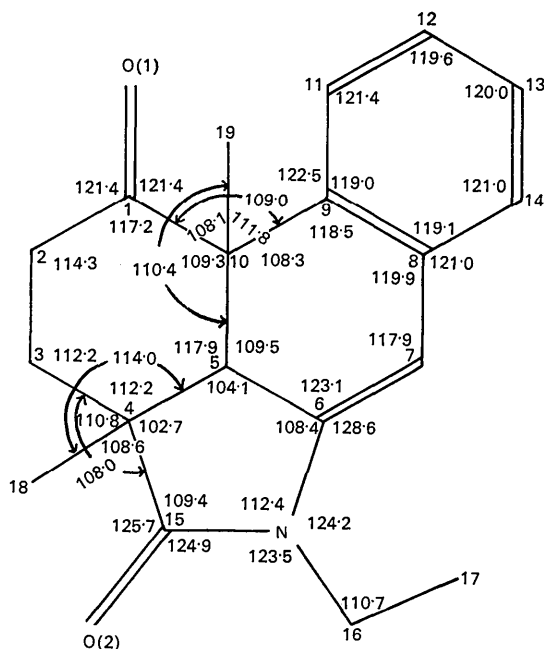
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threshold value but were excluded from the least-squares refinement. A summary of the agreement between  $|F_o|$  and  $|F_c|$  can be seen in Table 4.



(a)



(b)

Fig. 3. (a) Bond lengths (in parentheses bond lengths corrected for thermal vibration assuming riding motion). Their mean e.s.d. is 0.0019 Å. (b) Valency angles. Their mean e.s.d. is 0.11°.

### Thermal motion and correction of bond lengths

Due to the small vibration of the skeleton, corrections of bond lengths, assuming rigid-body vibration, would be insignificant and were therefore not attempted. However, the side groups, except C(19), vibrate appreciably even at  $-160^\circ\text{C}$ . The lengths of the bonds N(1)-C(16), C(16)-C(17), C(4)-C(18), C(1)-O(1), and C(15)-O(2) were corrected for thermal vibration under the assumption of riding motion (Busing & Levy, 1964). These corrected bond lengths are shown in parentheses in Fig. 3(a).

### Description and discussion of the structure

This structure has been determined to be (II) (and its enantiomer), and not the predicted (I). The conformation and molecular structure can be seen on the stereoscopic diagram (Fig. 2). The bond lengths and angles for non-hydrogen atoms are shown in Fig. 3. The range of e.s.d.'s for these bond lengths is 0.0016–0.0022 Å with a mean value of 0.0019 Å. For the valency angles the e.s.d.'s range from 0.10 to 0.13° with a mean value of 0.11°. Table 5 shows bond lengths and angles involving hydrogen atoms. All the least-squares planes described below are listed in Table 6.

Table 5. Bond lengths and angles involving hydrogen atoms with their e.s.d.'s.

#### (a) Bond lengths

C(2)—H(21)	10.16 (18) Å
C(2)—H(22)	0.948 (19)
C(3)—H(31)	0.995 (22)
C(3)—H(32)	1.001 (18)
C(5)—H(51)	0.989 (17)
C(16)—H(161)	0.983 (22)
C(16)—H(162)	1.000 (17)
C(17)—H(171)	1.044 (22)
C(17)—H(172)	1.022 (19)
C(17)—H(173)	1.002 (25)
C(18)—H(181)	0.994 (21)
C(18)—H(182)	0.988 (20)
C(18)—H(183)	1.014 (20)
C(19)—H(191)	0.978 (18)
C(19)—H(192)	0.981 (18)
C(19)—H(193)	0.958 (18)
C(7)—H(71)	0.975 (16)
C(11)—H(111)	0.984 (16)
C(12)—H(121)	0.974 (20)
C(13)—H(131)	0.952 (20)
C(14)—H(141)	0.995 (16)

#### (b) Valency angles

C(1)—C(2)—H(21)	107.2 (1.0)°
C(1)—C(2)—H(22)	110.0 (1.2)
C(3)—C(2)—H(21)	109.5 (1.0)
C(3)—C(2)—H(22)	111.0 (1.2)
H(21)—C(2)—H(22)	104.3 (1.6)
C(2)—C(3)—H(31)	111.9 (1.1)
C(2)—C(3)—H(32)	108.6 (1.1)
C(4)—C(3)—H(31)	108.2 (1.1)
C(4)—C(3)—H(32)	111.0 (1.1)
H(31)—C(3)—H(32)	104.6 (1.6)
C(4)—C(5)—H(51)	109.5 (1.0)
C(6)—C(5)—H(51)	108.1 (1.0)

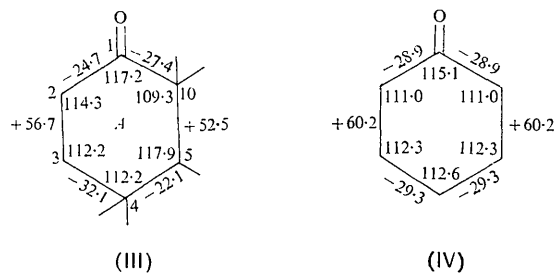


Table 5 (cont.)

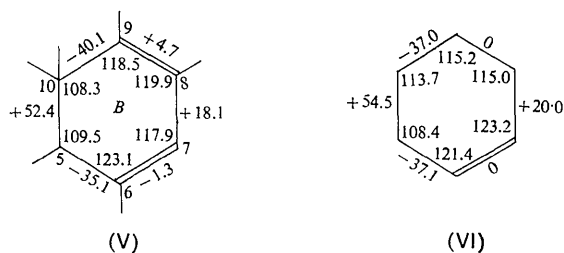
C(10)—C(5)—H(51)	107.5 (1.0)
C(17)—C(16)—H(161)	112.7 (1.2)
C(17)—C(16)—H(162)	112.5 (1.1)
N(1)—C(16)—H(161)	104.3 (1.2)
N(1)—C(16)—H(162)	106.7 (1.1)
H(161)—C(16)—H(162)	109.5 (1.6)
C(16)—C(17)—H(171)	109.1 (1.2)
C(16)—C(17)—H(172)	110.2 (1.2)
C(16)—C(17)—H(173)	114.3 (1.3)
H(171)—C(17)—H(172)	108.1 (1.7)
H(171)—C(17)—H(173)	108.1 (1.7)
H(172)—C(17)—H(173)	106.8 (1.7)
C(4)—C(18)—H(181)	109.0 (1.1)°
C(4)—C(18)—H(182)	109.9 (1.1)
C(4)—C(18)—H(183)	111.5 (1.2)
H(181)—C(18)—H(182)	108.5 (1.6)
H(181)—C(18)—H(183)	110.0 (1.6)
H(182)—C(18)—H(183)	107.9 (1.6)
C(10)—C(19)—H(191)	109.8 (1.1)
C(10)—C(19)—H(192)	111.5 (1.0)
C(10)—C(19)—H(193)	111.1 (1.1)
H(191)—C(19)—H(192)	107.6 (1.5)
H(191)—C(19)—H(193)	109.6 (1.5)
H(192)—C(19)—H(193)	107.1 (1.5)
C(6)—C(7)—H(71)	124.0 (1.0)
C(8)—C(7)—H(71)	118.1 (1.0)
C(9)—C(11)—H(111)	120.8 (1.0)
C(12)—C(11)—H(111)	117.9 (1.0)
C(11)—C(12)—H(121)	120.7 (1.1)
C(13)—C(12)—H(121)	119.7 (1.1)
C(12)—C(13)—H(131)	119.7 (1.2)
C(14)—C(13)—H(131)	120.3 (1.2)
C(8)—C(14)—H(141)	118.4 (1.0)
C(13)—C(14)—H(141)	120.5 (1.0)

### Conformation

The ring junctions *A/B* and *A/D* are both *cis*. Ring *A* occurs in the twist-boat conformation [1,4-RT according to Djerassi & Klyne (1962)]. This form is preferred since the 1,3 diaxial interaction [C(18)...C(19)] which would be present in a chair is relieved. The C(18)...C(19) non-bonded distance is 3.604(2) Å while in a chair the 1,3 diaxial methyl-methyl distances are usually observed in the range 3.0–3.3 Å (Birnbaum & Ferguson, 1969). The shortest hydrogen-hydrogen contact, H(182)...H(192), of 2.433(27) Å is equal to the van der Waals distance of 2.4 Å (Pauling, 1960) and indicates the absence of strain. The twist-boat conformation is slightly distorted since only the atoms C(1), C(2), C(10) and O(1) are in a plane but not C(4), which is displaced by 0.158 Å. Also, C(5) is further away from the plane (+0.677 Å) than C(3) (−0.574 Å). The distortion can also be seen by comparison of the torsional angles, shown in (III), (for notation see Klyne & Prelog, 1960) with those obtained from theoretical calculations (Bucourt & Hainaut, 1967) for cyclohexanone in the twist-boat conformation (IV). All torsional angles in ring *A* except one are smaller than calculated, with the largest differences occurring at the ring junctions. There is thus a general flattening of ring *A*.



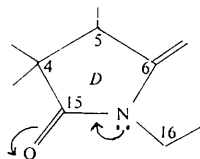
The conformation of ring *B*, determined by the fusion with the aromatic ring *C*, is a distorted half-boat. The atoms C(5), C(6), C(7) and C(8) are roughly in a plane and C(9) and C(10) are both displaced to the same side of that plane, but by the unequal amounts 0.358 and 0.856 Å respectively. Within experimental error H(71) lies in this 'best' plane. This conformation is the same as Bucourt & Hainaut (1967) found to be the third most stable form of cyclohexene (VI), as can be seen from the comparison of torsional angles. The largest discrepancy occurs at the junction of ring *B* with the aromatic ring *C*, indicating some distortion at this point.



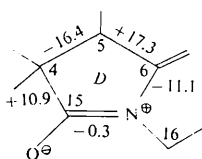
With a  $\chi^2$  of 30.7 the six atoms of the aromatic ring *C* are not coplanar. Non-planar aromatic rings have also been found in protopine (Hall & Ahmed, 1968a) and in cryptopine (Hall & Ahmed, 1968b) where they were slightly boat-shaped. In the present structure aromatic ring *C* adopts a quasi half-boat conformation with C(9), C(11), C(12) and C(13) coplanar and C(14) and C(8) both displaced to the same side of this plane (−0.009 and −0.020 Å respectively). The hydrogen atoms H(111), H(121) and H(131) lie in this plane while H(141) is displaced significantly from it (−0.072 Å). The non-planarity of ring *C* seems to be caused by non-bonded interaction between H(141) and H(21) and by the strain due to the fusion of rings *B* and *C*. The intermolecular distance H(141)<sub>I</sub>...H(21)<sub>II</sub> of 2.276(25) Å is shorter than twice the van der Waals radius of 1.2 Å (Pauling, 1960). This distance would have been even shorter if H(141) had not been displaced from the aromatic plane. The strain present at the junction between rings *B* and *C* causes not only C(8) to be displaced from the aromatic plane but also C(7) and C(10) (−0.103 and +0.042 Å respectively). A similar effect was observed in sultone B (Bjåmer & Ferguson, 1967)

where two substituent atoms were displaced from the aromatic plane by  $-0.085$  and  $+0.070$  Å.

Ring *D* is envelope-shaped with C(5) displaced by  $0.281$  Å from the plane through the other ring atoms. The torsional angles are marked in (VIIb). As will be seen below, this ring exists in two resonance forms, (VIIa) and (VIIb), and its conformation is in agreement with this.



(VIIa)



(VIIb)

Due to this resonance one would expect O(2) and C(16) to lie in the same plane. Although they are both displaced significantly from this plane, the displacements are small ( $+0.013$  and  $-0.014$  Å respectively). The stereochemical arrangement around the nitrogen atom is thus close to being planar.

#### Bond lengths

There are no unusual bond lengths in this structure, but some comments should be made about several of them. Five bond lengths, C(4)–C(5) ( $1.552$  Å), C(9)–C(10) ( $1.532$  Å), C(1)–C(10) ( $1.541$  Å), C(4)–C(15) ( $1.534$  Å) and C(8)–C(9) ( $1.412$  Å), apparently are significantly longer than the values given by Sutton (1965): C–C single,  $1.537 \pm 0.005$ ; C–C<sub>6</sub>H<sub>5</sub>,  $1.505 \pm 0.005$ ;

C–C(=O),  $1.506 \pm 0.005$ ; C–C aromatic,  $1.394 \pm 0.005$  Å. (Note that the uncertainty as indicated by Sutton is  $2\sigma$ .) Their ratios of  $\Delta l/\sigma(\Delta l)$ , where  $\Delta l$  is the difference between observed and accepted bond lengths, range from  $4.8\sigma$  to  $11.7\sigma$ . However, these bond lengths are all between highly substituted carbon atoms and lengthening of such bonds is common. For instance, in a derivative of  $\epsilon$ -caesalpin two C–C single bonds were observed as  $1.603(17)$  and  $1.591(17)$  Å (Birnbaum & Ferguson, 1969), and in naphthalene C–C bond lengths up to  $1.422(4)$  Å were observed (Almenningen, Bastiansen & Dyvik, 1961).

Before correction for thermal vibration the bonds C(4)–C(18) and C(16)–C(17) were significantly shorter than the usual C–C single bond [ $1.537 \pm 0.005$  Å (Sutton, 1965)]. However, the corrected values ( $1.532$  and  $1.531$  Å respectively) are both normal. The C<sub>sp</sub><sup>2</sup>–C<sub>sp</sub><sup>2</sup> bond C(7)–C(8) of  $1.467$  Å agrees well with the values determined by electron diffraction,  $1.462(2)$  Å in 1,3,5-*cis*-hexatriene (Trätteberg, 1968*a*) and  $1.465(2)$  Å in 1,3-cyclohexadiene (Trätteberg, 1968*b*). The C(6)–C(7) bond length ( $1.338$  Å) corresponds to a normal double bond [ $1.335 \pm 0.005$  Å (Sutton, 1965)].

The bond lengths associated with the five-membered ring *D* show that there is resonance between the two forms (VIIa) and (VIIb). By the use of Pauling's (1960) formula the N(1)–C(15) bond has 8% double-bond character and, in good agreement with this, the C(15)=O(2) bond has 9% single-bond character. Thus the resonance form (VIIb) contributes 8–9% to this structure. The following bond lengths were used in these calculations: C<sub>sp</sub><sup>2</sup>–N,  $1.393$  [C(6)–N(1) in this

Table 6. Least-squares planes

Plane A (ring A)		Plane B (ring B)		Plane C (ring C)		Plane D (ring D)	
	$\Delta$		$\Delta$		$\Delta$		$\Delta$
C(1)	$-0.003$ Å	C(5)	$0.003$ Å	C(9)	$-0.001$ Å	C(4)	$0.001$ Å
C(2)	$0.001$	C(6)	$-0.006$	C(11)	$0.001$	C(6)	$-0.001$
C(10)	$0.001$	C(7)	$0.006$	C(12)	$-0.001$	C(15)	$-0.002$
O(1)	$0.001$	C(8)	$-0.003$	C(13)	$0.001$	N(1)	$0.001$
C(4)*	$0.158$	H(71)*	$-0.025$	C(14)*	$-0.009$	C(5)*	$-0.281$
C(3)*	$-0.574$	C(9)*	$0.358$	C(8)*	$-0.020$	O(2)*	$0.013$
C(5)*	$0.677$	C(10)*	$0.856$	H(111)*	$0.003$	C(16)*	$-0.014$
		N(1)*	$-0.010$	H(121)*	$-0.023$		
				H(131)*	$-0.040$		
				H(141)*	$-0.072$		
				C(7)*	$-0.103$		
				C(10)*	$0.042$		
r.m.s.d. = $0.002$		r.m.s.d. = $0.005$		r.m.s.d. = $0.001$		r.m.s.d. = $0.001$	
$\chi^2 = 8.3$		$\chi^2 = 54.7$		$\chi^2 = 2.0$		$\chi^2 = 3.9$	

\* Atoms excluded from the calculation of the plane.

Equations of the planes ( $X', Y, Z'$  are orthogonal coordinates in Å, *i.e.*  $X' = X - Z \cos \beta^*$ ,  $Z' = Z \sin \beta^*$ ):

$$\begin{aligned} A: & 0.174X' - 0.517Y - 0.838Z' = -5.661 \text{ Å} \\ B: & 0.228X' + 0.946Y - 0.231Z' = 2.910 \\ C: & 0.039X' + 0.856Y - 0.509Z' = 2.477 \\ D: & 0.220X' + 0.880Y - 0.420Z' = 2.274 \end{aligned}$$

Dihedral angles between the planes

$\angle AB$	$\angle AC$	$\angle AD$	$\angle BC$	$\angle BD$	$\angle CD$
$104.8^\circ$	$90.0^\circ$	$93.7^\circ$	$18.7^\circ$	$11.5^\circ$	$9.2^\circ$

analysis]; C=N<sup>+</sup>, 1.24; C-O<sup>-</sup>, 1.45 (Gerdil, 1961); and C=O, 1.215 Å (Sutton, 1965). These results corroborate the bond length of 1.393 Å as being appropriate for a C<sub>sp</sub><sup>2</sup>-N single bond.

All the C-H bond lengths agree within experimental error with their mean values, 0.994(5) Å for C<sub>sp</sub><sup>3</sup>-H bonds and 0.976(8) Å for C<sub>sp</sub><sup>2</sup>-H bonds. These mean values are significantly shorter (by 0.102 and 0.108 Å respectively) than the corresponding spectroscopic values of 1.096 ± 0.005 and 1.084 ± 0.005 Å (Sutton, 1965). Such results are usually obtained from X-ray analyses. In L-ascorbic acid (Hvoslef, 1968) the C-H bonds were observed to be 0.08 Å shorter from X-ray diffraction than from neutron diffraction.

#### Valency angles

The angles in ring *A* may be compared with those in cyclohexanone (IV). As already mentioned, ring *A* is flattened and this is also evidenced by a general increase in valency angles. The largest deviation occurs in the angle C(4)-C(5)-C(10). This can most likely be attributed to strain present at the junction between the three rings. One angle, C(1)-C(10)-C(5), is smaller

than the calculated value. From a survey of several steroid structures Geise, Altona & Romers (1967) observed that the valency angles in six-membered rings are smaller than the tetrahedral value at quaternary carbon atoms. The angle C(1)-C(10)-C(5) can therefore be considered normal.

It is interesting to compare the bond angles in the five-membered ring *D* with those of the five-membered ring in a photolysis product (VIII) (Karle, Karle & Estlin, 1967).

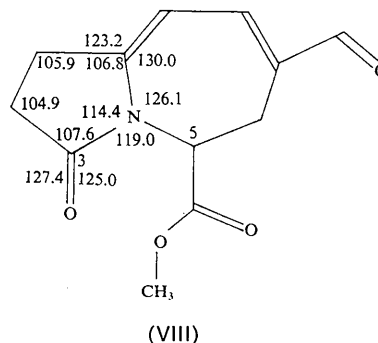


Table 7. Mean values of valency angles involving hydrogen atoms at sp<sup>3</sup>-carbon atoms

The numbers given in the square brackets indicate the number of angles used to calculate the mean value.

Angle	Primary carbon atom	Secondary carbon atom	Tertiary carbon atom
C-C-H	110.7 (0.4)° [9]	110.3 (0.4)° [10]	108.4 (0.6)° [3]
N-C-H		107.5 (0.8)° [2]	
H-C-H	108.2 (0.5)° [9]	106.1 (0.9)° [3]	

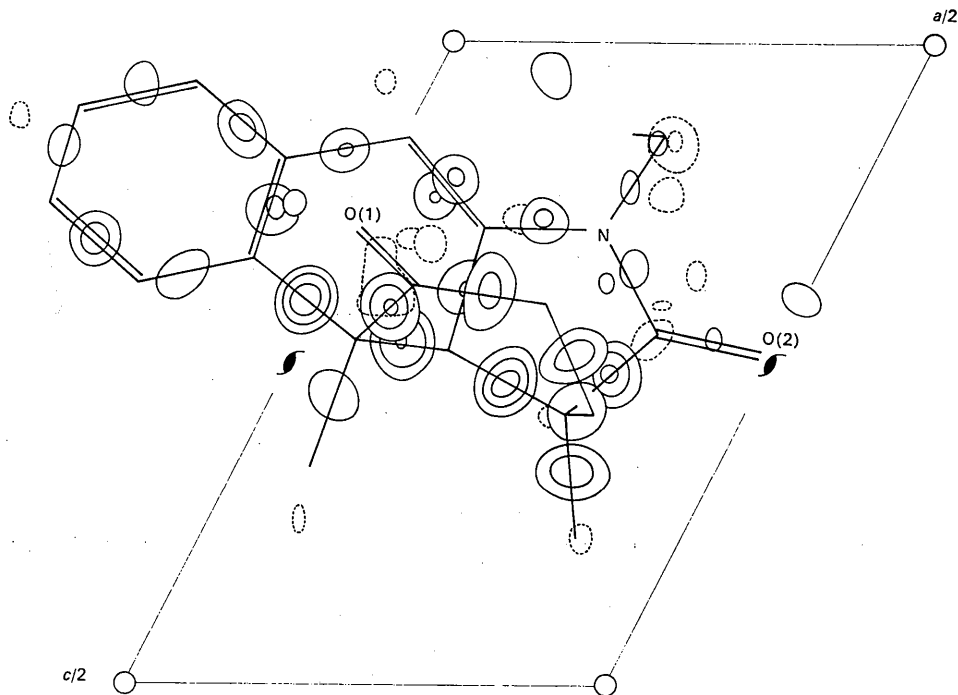


Fig. 4. Composite final three-dimensional difference Fourier synthesis viewed along the *b* axis. The contours, starting at ±0.15 e.Å<sup>-3</sup>, are drawn at intervals of 0.1 e.Å<sup>-3</sup>. The e.s.d. is 0.05 e.Å<sup>-3</sup>.

Except for C(5)–N–C(3) ( $119.0^\circ$ ), which is significantly smaller than C(16)–N(1)–C(15) ( $123.5^\circ$ ), all the angles in (VIII) agree within experimental error with the corresponding ones in this structure. Their root-mean-square deviation of  $1.6^\circ$  is close to the e.s.d. of the angles in (VIII) ( $1.3^\circ$ ).

All angles involving hydrogen atoms at  $sp^2$ -carbon atoms agree within experimental error with the expected value of  $120^\circ$  except C(6)–C(7)–H(71) ( $124.0^\circ$ ) which deviates significantly. The mean values of the angles involving hydrogen atoms at  $sp^3$ -carbon atoms are listed in Table 7. No angle deviates from the corresponding mean value. The C–C–H and H–C–H angles tend to decrease with increased substitution at the carbon atom. Also, the mean values decrease when the size of a substituent atom decreases (*i.e.* C > N > H).

### Residual electron density

A difference Fourier synthesis based on the final parameters was calculated with all the observed terms (Fig. 4), its standard deviation being  $0.05 \text{ e. \AA}^{-3}$  (Cruickshank, 1949). Only contours exceeding  $3\sigma$  are drawn. Regions of residual electron density can be seen near the centres of all bonds except the C(1)=O(1) bond where there is only a peak of  $0.07 \text{ e. \AA}^{-3}$ . At the double (or partially double) bonds C(6)=C(7), C(15)–N(1), and C(15)=O(2) there are two separate peaks halfway between the two atoms, one below and one above the bond. The one below the C(15)=O(2) bond has the height  $0.13 \text{ e. \AA}^{-3}$  and is therefore not shown in the diagram.

There are two peaks near each of the oxygen atoms at distances ranging from  $0.8$  to  $1.1 \text{ \AA}$ ; they presumably correspond to the lone-pair electrons. However, two of

these peaks (one at each oxygen atom) are lower than  $0.15 \text{ e. \AA}^{-3}$  ( $0.10$  and  $0.13 \text{ e. \AA}^{-3}$ ) and are therefore not shown in the Figure.

The peak near the hydrogen atom H(173) is part of a pattern of peaks and valleys typical for anisotropically vibrating atoms for which isotropic vibration was assumed.

### Packing

The molecular arrangement parallel to (010) can be seen in Fig. 5. Of the intermolecular non-bonded distances only H(141)<sub>I</sub>...H(21)<sub>II</sub> ( $2.276(25) \text{ \AA}$ ) and H(191)<sub>I</sub>...O(1)<sub>III</sub> ( $2.512(17) \text{ \AA}$ ) are shorter than the corresponding van der Waals distances of  $2.4$  and  $2.6 \text{ \AA}$  (I at  $x, y, z$ ; II at  $\bar{x}, 1-y, \bar{z}$ ; III at  $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$ ). The packing can thus be described as consisting of infinite chains of molecules running parallel to [001] with short van der Waals contacts in this direction.

I wish to thank Professor K. Wiesner for suggesting this problem and for supplying me with the material. I am also indebted to Dr Maria Przybylska for her constant encouragement during this work. Computer programs used were those of Ahmed, Hall, Pippy & Huber (1966).

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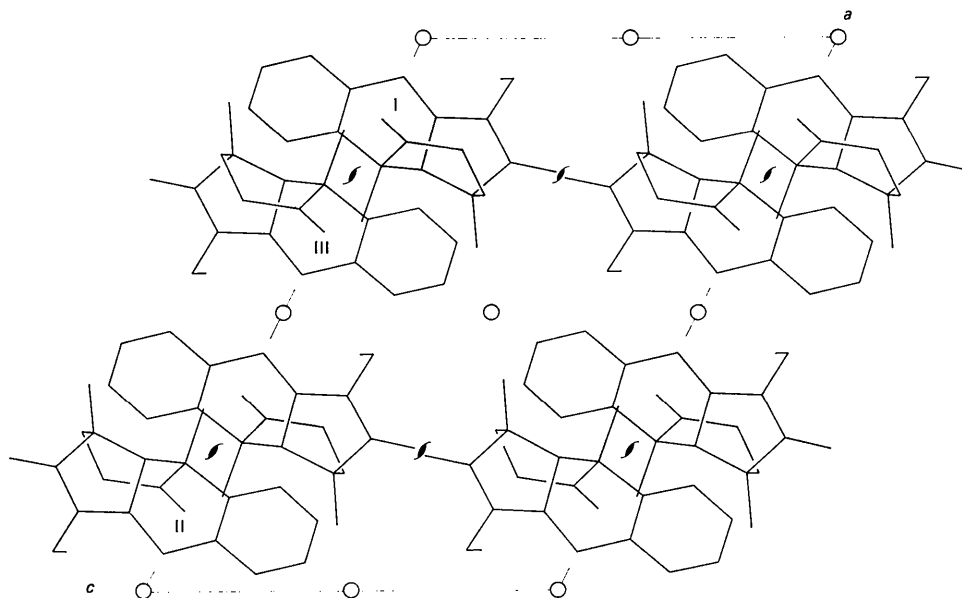


Fig. 5. Packing diagram viewed along the  $b$  axis.

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## The Crystal Structures of Two Derivatives of 8-Hydroxyquinoline-5-sulfonic Acid, 2-Methyl-8-hydroxyquinoline-5-sulfonic Acid Monohydrate, and 7-Iodo-8-hydroxyquinoline-5-sulfonic Acid\*

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The crystal structures of 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate and 7-iodo-8-hydroxyquinoline-5-sulfonic acid have been determined by Fourier syntheses and refined by the method of least squares using three-dimensional photographic data. The 2-methyl derivative crystallizes from water as the monohydrate and the monoclinic unit cell has the dimensions  $a = 13.35$ ,  $b = 9.11$ ,  $c = 17.84$  Å;  $\beta = 90.3^\circ$ . The space group is  $C2/c$  with eight molecules in the unit cell. The molecule exists as a zwitterion and hydrogen bonds of lengths ranging from 2.65 to 2.94 Å link molecules together to form a three-dimensional hydrogen-bonded network in the structure. The final  $R$  was 0.087 for 1926 observed reflections. The 7-iodo derivative has a monoclinic unit cell of dimensions:  $a = 9.55$ ,  $b = 13.35$ ,  $c = 8.83$  Å,  $\beta = 109.2^\circ$ , and the space group is  $P2_1/c$  with  $Z = 4$ . The structure consists of sheets of molecules parallel to (010), the molecules being related by unit-cell translations in the  $a$  and  $c$  directions and linked by interactions of length 3.07 Å between iodine and oxygen atoms and hydrogen bonds of length 2.80 Å between oxygen atoms and quinoline nitrogen atoms. Sheets are bonded in pairs by hydrogen bonds between sulfonic acid oxygen atoms and hydroxyl groups, and distances between adjacent double sheets correspond to normal van der Waals interactions. The final  $R$  was 0.14 for 954 observed reflections.

### Introduction

Structures of chelating organic molecules and the chelate complexes they form with inorganic ions, especially those complexes used by the analytical chemist, have long been of special interest to this laboratory.

The compound 8-hydroxyquinoline forms complexes with a large number of inorganic ions and so do most of its derivatives. However, substitution in the 2-position of the parent molecule prevents reaction with aluminum ions (Merritt & Walker, 1944) and it was felt desirable to determine the structures of derivatives with a 2-substituent and a 7-substituent, as these positions are adjacent to the chelate forming groups in the 1,8 positions of the 8-hydroxyquinoline molecule, in order to learn, if possible, what influences structure has on the formation and properties of the chelate

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