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The Crystal and Molecular Structure of Palythine Trihydrate

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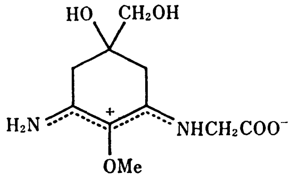
The molecular structure of palythine, $C_{10}H_{16}N_2O_5$, has been confirmed by means of an X-ray crystal analysis of its trihydrate. The crystals are monoclinic, with two formula units in a unit cell with dimensions of $a=10.499$, $b=12.812$, $c=5.322$ Å, and $\beta=98.53°$; the space group is $P2_1$. 1377 unique intensity data were collected on a four-circle diffractometer with LiF-monochromated Cu $K\alpha$ radiation. The structure was solved by the Monte Carlo direct method, using the 20 strongest reflections as a starting set, and was refined by the block-diagonal least-squares method. The final R value was 3.1%. The molecular structure thus obtained corresponds to that proposed by Tsujino *et al.* and Takano *et al.* on the basis of the chemical evidence. Palythine exists as a zwitter ion in the crystal. The palythine and water molecules are connected by twelve types of hydrogen bonds, forming a three-dimensional hydrogen-bonded structure.

Palythine is a new amino acid isolated from the red alga *Chondrus yendoi* and the zoanthid *Palythoa tuberculosa*.[1,2] On the basis of the chemical evidence, the **1** structure has been proposed for this compound. However, because of the remarkable lability of palythine, there was some doubt about the proposed structure. Therefore, in order to confirm **1**, we have now undertaken an X-ray crystallographic study of palythine trihydrate.



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Experimental

Colorless, single crystals of palythine trihydrate were obtained from an aqueous solution. A crystal with dimensions of about $0.1\times0.3\times0.4$ mm³ was used for the X-ray measurement. The crystal data are summarized in Table 1. The cell dimensions and diffraction intensities were measured on an automatic, four-circle diffractometer using Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) monochromatized with an LiF crystal. The intensity measurement was made by using an ω-2θ continuous scan at a rate of about $1°(\omega)$/min; the background was measured for 20—30 s at each end of the scan range. The intensities thus obtained were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 140°, 1377 unique structure factor magnitudes above $2\sigma(F)$ were selected for the structure determination.

TABLE 1. THE CRYSTAL DATA

Formula	$C_{10}H_{16}N_2O_5\cdot3H_2O$
Formula weight	298.29
Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions	$a=10.499(5)$ Å
	$b=12.812(6)$
	$c=\ 5.322(3)$
	$\beta=98.53(5)°$
	$V=708.0$ Å³
Z	2
D_x	1.399 g cm⁻³

Structure Determination

At the early stage of the structure determination, attempts were made to solve the structure by the symbolic-addition method.[3] Although a phase set which showed a low R_K value of 32.8% ($R_K=\sum||E_o|-k|E_c||/\sum|E_o|$) gave an E-map which contained a six-membered ring, it did not lead to the elucidation of the whole structure. It was found afterwards that the six-membered ring in the E-map deviated from its correct position, nearly perpendicular to the ($\bar{2}$ 0 1) plane by

TABLE 2. THE 54th RANDOM PHASE SET AND CORRECT PHASES (IN $10^{-3}\pi$)

	h	k	l	$\lvert E\rvert$	No. 54	Correct	ϕ[a]
1	$\overline{10}$	0	2	3.79	1000	0	0
2	$\bar{3}$	8	2	2.93	1000	1012	1021
3	3	0	5	2.79	0	0	1000
4	$\bar{2}$	4	3	2.73	0	4	10
5	7	8	0	2.52	750	953	1021
6	4	0	2	2.46	0	0	0
7	$\bar{3}$	4	1	2.46	750	587	1009
8	4	2	5	2.46	1250	1002	1006
9	$\bar{5}$	10	1	2.39	0	261	25
10	$\bar{2}$	3	2	2.38	1000	1288	1506
11	6	6	2	2.35	1000	949	1015
12	$\overline{11}$	6	1	2.27	1250	912	1016
13	1	12	1	2.27	1750	1286	1032
14	$\overline{11}$	6	2	2.27	250	489	1013
15	$\bar{4}$	1	5	2.25	1250	1388	1502
16	$\bar{6}$	0	3	2.24	0	0	0
17	8	3	0	2.24	1250	1461	1507
18	$\overline{10}$	1	2	2.21	500	880	1501
19	$\bar{5}$	4	5	2.16	1750	995	1010
20	$\bar{5}$	1	4	2.16	1250	650	502

a) Phase values obtained from the starting phase set, different from the 54th set only in the phase of $\overline{10}$ 0 2.

about 1.1 Å. The structure was finally elucidated by the Monte Carlo direct method.[4] The 20 strongest reflections given in Table 2 were chosen as members of a starting set. The tentative phase values for the starting reflections were derived from successively-generated random numbers. In order to extend this tentative phase set, 10 cycles of the tangent procedure were performed using 331 $|E|$ values above 1.20; during the first 5 cycles, the phases of the starting reflections were kept constant. Since the 54th phase set showed a low R_K value of 28.2%,** 6 additional cycles of the tangent procedure were carried out. Consequently, the R_K value was reduced to 18.8%. An E-map based on 329 phases clearly revealed the locations of all 20 non-hydrogen atoms.

The 54th random phase set and the correct phases calculated with the final atomic parameters are given in Table 2. The two corresponding phase values are in substantial agreement with each other except for the $\overline{10}$ 0 2, $\bar{5}$ 4 5, and $\bar{5}$ 1 4 reflections. However, it should be noted that the phase value assigned to the strongest $\overline{10}$ 0 2 reflection is different from the correct phase by π. It was ascertained that, when this phase value was replaced by the correct one in the initial stage of the tangent procedure, the 54th random phase set no longer led to the correct solution. Of the phase values calculated in such a way, those for the starting reflections are given in the last column of Table 2. Especially great deviations from the correct phases can be seen for the 3 0 5, $\bar{3}$ 4 1, $\overline{11}$ 6 2, and $\overline{10}$ 1 2 reflections, those derivations being π, $0.422\,\pi$, $0.524\,\pi$, and $0.621\,\pi$ respectively. Since none of the 24 most probable phase relationships ($\kappa=2\sigma_3\sigma_2^{-3/2}|E_hE_kE_{h-k}>3.5$) associated with the $\overline{10}$ 0 2 reflection contain errors greater than

TABLE 3. THE FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS

(1) The non-hydrogen atoms

The positional and thermal parameters are multiplied by 10^4 and 10^5 respectively.
The latter ones are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−1030(2)	1458(1)	938(3)	50(1)	31(1)	185(5)	−1(2)	26(4)	19(4)
C(2)	−663(2)	2325(1)	2450(3)	50(1)	29(1)	219(6)	8(2)	45(5)	4(4)
C(3)	617(2)	2498(1)	3506(3)	53(1)	25(1)	194(5)	−6(2)	39(4)	11(4)
C(4)	1664(2)	1792(1)	2860(4)	47(1)	30(1)	250(6)	−6(2)	38(5)	−12(4)
C(5)	1186(2)	700(1)	2062(3)	46(1)	28(1)	202(5)	2(2)	39(4)	2(4)
C(6)	−34(2)	752(2)	114(4)	49(1)	36(1)	205(5)	4(2)	26(4)	−27(4)
C(7)	2232(2)	75(2)	1008(4)	56(2)	33(1)	214(6)	10(2)	38(5)	−4(4)
C(8)	−2183(2)	2716(2)	5141(5)	71(2)	50(1)	335(8)	−17(3)	125(6)	−53(5)
C(9)	2174(2)	3583(2)	6346(4)	60(2)	33(1)	210(6)	−23(2)	23(5)	−16(4)
C(10)	2954(2)	4225(2)	4682(4)	64(2)	34(1)	301(7)	−3(2)	78(5)	23(4)
N(1)	−2248(2)	1247(1)	116(3)	49(1)	37(1)	258(6)	3(2)	14(4)	−31(4)
N(2)	898(2)	3294(1)	5087(3)	53(1)	32(1)	280(6)	−7(2)	54(4)	−22(4)
O(1)	−1603(1)	3011(1)	2972(3)	55(1)	32(1)	271(5)	15(1)	59(4)	9(3)
O(2)	841(1)	131(1)	4182(3)	62(1)	37(1)	207(4)	−8(2)	49(3)	16(3)
O(3)	2549(1)	551(1)	−1239(3)	54(1)	53(1)	248(4)	12(2)	79(3)	16(4)
O(4)	2552(2)	4317(2)	2406(3)	109(2)	54(1)	289(5)	−8(2)	90(5)	64(4)
O(5)	3990(2)	4595(2)	5790(5)	88(2)	92(2)	500(9)	−97(3)	8(6)	88(6)
O(W1)	4754(2)	1462(2)	5129(4)	93(2)	62(1)	472(8)	36(3)	4(6)	20(5)
O(W2)	4873(2)	−533(2)	−684(4)	76(1)	64(1)	417(7)	25(2)	153(5)	26(5)
O(W3)	4702(2)	−2731(2)	−323(4)	96(2)	51(1)	477(8)	−22(2)	101(6)	21(5)

(2) The hydrogen atoms

The positional and thermal parameters are multiplied by 10^3 and 10 respectively.

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
H(4a)	231(3)	173(2)	432(5)	27(5)	H(N1a)	−242(3)	71(2)	−82(5)	27(5)
H(4b)	201(3)	211(2)	143(5)	24(4)	H(N1b)	−283(3)	166(3)	52(6)	33(6)
H(6a)	−36(3)	2(3)	−19(6)	35(6)	H(N2)	29(3)	371(3)	534(6)	31(5)
H(6b)	19(3)	106(3)	−135(6)	37(6)	H(O2)	140(3)	24(2)	552(5)	26(5)
H(7a)	189(3)	−59(2)	57(5)	23(4)	H(O3)	320(4)	28(3)	−156(7)	42(7)
H(7b)	295(2)	5(2)	228(5)	20(4)	H(W1a)	517(5)	101(4)	509(9)	53(8)
H(8a)	−290(4)	323(3)	523(7)	47(7)	H(W1b)	490(5)	172(4)	665(9)	59(10)
H(8b)	−153(3)	282(3)	667(6)	38(6)	H(W2a)	539(4)	−52(4)	−167(8)	51(8)
H(8c)	−249(4)	198(3)	496(7)	43(7)	H(W2b)	529(4)	−49(4)	83(8)	53(8)
H(9a)	211(3)	397(2)	786(6)	29(5)	H(W3a)	506(5)	−294(4)	−150(9)	57(9)
H(9b)	265(3)	299(3)	685(7)	40(6)	H(W3b)	476(5)	−214(5)	−40(10)	65(11)

** The second lowest of the R_K values for the 54 sets was 30.7%.

$\pi/3$, such serious deviations may be due to the accidental accumulation of rather large errors produced by these phase relationships.

The structure thus obtained was refined by the block-diagonal-matrix least-squares method, first with isotropic and then with anisotropic temperature factors. After all the 22 hydrogen atoms had been located in a difference Fourier map, further least-squares refinement including these hydrogen atoms with isotropic temperature factors was carried out. For this refinement, the following weighting scheme was used:

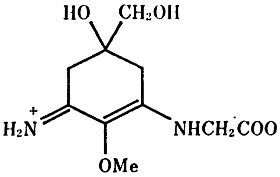
$$W = 1/\{\sigma(F)^2 \exp(AX^2+BY^2+CXY+DX+EY)\}$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The A, B, C, D, and E coefficients are constants which were determined from the $(\Delta F)^2$ values in each cycle of the refinement. In this manner, the R value reached 3.1%. The atomic parameters thus obtained are listed in Table 3. The tables of the observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8003).

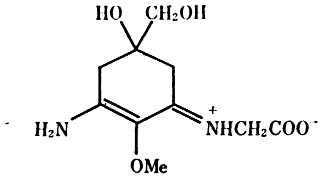
All the calculations were performed on a FACOM 230-75 computer at the Hokkaido University Computing Center, using our own programs. Random numbers were generated by calling a function RANDOM which existed in a program library of the Computing Center. The atomic scattering factors were taken from the International Tables.[5]

Results and Discussion

Molecular Structure. The molecular structure of palythine is illustrated in Fig. 1, where each atom is represented as a thermal ellipsoid enclosing a 50% probability. As can be seen in Fig. 1, the molecular framework obtained corresponds to the structure **1.** Since the proton of the carboxyl group is transferred to the nitrogen atom, in the crystalline state palythine exists as a zwitter ion which is stabilized by resonance between the two nearly-equivalent structures, **2a** and **2b**. The bond distances and angles and the dihedral angles are listed in Tables 4 and 5 respectively. If the H(N1a) atom and the CH_2COO^- group are excluded,



2a



2b

TABLE 4. THE BOND DISTANCES (l/Å) AND ANGLES (ϕ/°), WITH THEIR STANDARD DEVIATIONS
The standard deviations given in parentheses refer to the last decimal position.

C(1)-C(2)	1.392(2)	O(W1)-H(W1a)	0.73(5)	C(5)-C(7)-O(3)	110.7(2)
C(1)-C(6)	1.496(3)	O(W1)-H(W1b)	0.87(5)	C(5)-C(7)-H(7a)	107(2)
C(1)-N(1)	1.317(2)	O(W2)-H(W2a)	0.81(5)	C(5)-C(7)-H(7b)	107(2)
C(2)-C(3)	1.394(2)	O(W2)-H(W2b)	0.86(4)	O(3)-C(7)-H(7a)	108(2)
C(2)-O(1)	1.381(2)	O(W3)-H(W3a)	0.82(5)	O(3)-C(7)-H(7b)	111(2)
C(3)-C(4)	1.503(3)	O(W3)-H(W3b)	0.76(6)	H(7a)-C(7)-H(7b)	113(2)
C(3)-N(2)	1.327(2)	C(2)-C(1)-C(6)	120.4(2)	O(1)-C(8)-H(8a)	106(2)
C(4)-C(5)	1.525(3)	C(2)-C(1)-N(1)	121.9(2)	O(1)-C(8)-H(8b)	107(2)
C(4)-H(4a)	0.96(3)	C(6)-C(1)-N(1)	117.7(2)	O(1)-C(8)-H(8c)	110(2)
C(4)-H(4b)	0.98(3)	C(1)-C(2)-C(3)	121.8(2)	H(8a)-C(8)-H(8b)	108(3)
C(5)-C(6)	1.525(2)	C(1)-C(2)-O(1)	118.6(2)	H(8a)-C(8)-H(8c)	113(3)
C(5)-C(7)	1.531(3)	C(3)-C(2)-O(1)	119.5(2)	H(8b)-C(8)-H(8c)	113(3)
C(5)-O(2)	1.434(2)	C(2)-C(3)-C(4)	120.4(2)	C(10)-C(9)-N(2)	113.9(2)
C(6)-H(6a)	1.01(4)	C(2)-C(3)-N(2)	119.2(2)	C(10)-C(9)-H(9a)	108(2)
C(6)-H(6b)	0.93(4)	C(4)-C(3)-N(2)	120.4(2)	C(10)-C(9)-H(9b)	107(2)
C(7)-O(3)	1.425(2)	C(3)-C(4)-C(5)	113.2(2)	N(2)-C(9)-H(9a)	110(2)
C(7)-H(7a)	0.94(3)	C(3)-C(4)-H(4a)	109(2)	N(2)-C(9)-H(9b)	110(2)
C(7)-H(7b)	0.93(2)	C(3)-C(4)-H(4b)	107(2)	H(9a)-C(9)-H(9b)	107(3)
C(8)-O(1)	1.433(3)	C(5)-C(4)-H(4a)	108(2)	C(9)-C(10)-O(4)	119.1(2)
C(8)-H(8a)	1.01(4)	C(5)-C(4)-H(4b)	108(2)	C(9)-C(10)-O(5)	115.6(2)
C(8)-H(8b)	0.99(3)	H(4a)-C(4)-H(4b)	112(2)	O(4)-C(10)-O(5)	125.2(2)
C(8)-H(8c)	1.00(4)	C(4)-C(5)-C(6)	111.0(1)	C(1)-N(1)-H(N1a)	118(2)
C(9)-C(10)	1.531(3)	C(4)-C(5)-C(7)	110.9(2)	C(1)-N(1)-H(N1b)	119(2)
C(9)-N(2)	1.455(2)	C(4)-C(5)-O(2)	111.0(1)	H(N1a)-N(1)-H(N1b)	123(3)
C(9)-H(9a)	0.96(3)	C(6)-C(5)-C(7)	110.5(1)	C(3)-N(2)-C(9)	126.2(2)
C(9)-H(9b)	0.93(4)	C(6)-C(5)-O(2)	105.8(1)	C(3)-N(2)-H(N2)	119(2)
C(10)-O(4)	1.228(3)	C(7)-C(5)-O(2)	107.5(1)	C(9)-N(2)-H(N2)	115(2)
C(10)-O(5)	1.251(3)	C(1)-C(6)-C(5)	112.3(2)	C(2)-O(1)-C(8)	113.3(2)
N(1)-H(N1a)	0.86(3)	C(1)-C(6)-H(6a)	112(2)	C(5)-O(2)-H(O2)	110(2)
N(1)-H(N1b)	0.86(3)	C(1)-C(6)-H(6b)	105(2)	C(7)-O(3)-H(O3)	108(3)
N(2)-H(N2)	0.86(3)	C(5)-C(6)-H(6a)	108(2)	H(W1a)-O(W1)-H(W1b)	108(5)
O(2)-H(O2)	0.86(3)	C(5)-C(6)-H(6b)	107(2)	H(W2a)-O(W2)-H(W2b)	108(4)
O(3)-H(O3)	0.80(4)	H(6a)-C(6)-H(6b)	113(3)	H(W3a)-O(W3)-H(W3b)	103(6)

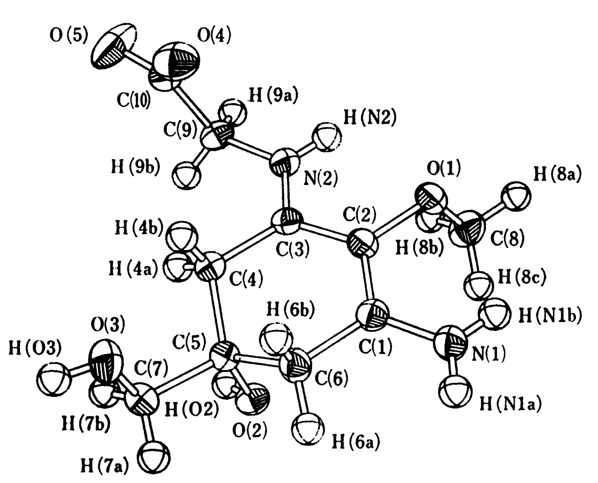


Fig. 1. A perspective view of the palythine molecule. For hydrogen atoms, a *B* value of $2\ \text{Å}^2$ was used.

the zwitter ion is almost symmetrical with respect to the plane determined by the C(2), C(5), and O(2) atoms.

The six-membered ring takes an envelope-like form in which the C(5) atom is 0.579 Å apart from the least-squares plane for the other five atoms. The deviations of the other atoms from this plane are as follows: C(1), 0.039 Å; C(2), −0.031 Å; C(3), 0.006 Å; C(4), 0.009 Å; C(6), −0.023 Å; N(1), 0.117 Å; N(2), 0.038 Å; O(1), −0.097 Å. All the bond distances in the ring are normal. The average of the C(1)–N(1) and C(3)–N(2) bond distances is 1.322 Å, which is somewhat small compared with the C–N distances (1.334 Å) in pyrazine[6] and 1,2,4,5-tetrazine,[7] and almost equal to the lengths of amide linkages, CO–NH.[8] This bond shortening may be related to the cationic nature of the conjugated system, since the C–NH part in amides also carries a considerable positive charge.

In a crystalline state, a carbon atom of a methoxyl group attached to an aromatic ring usually lies nearly on the ring plane. However, since the present molecule has amino or imino groups at both of the two positions *ortho* to the methoxyl group, the C(8) atom deviates remarkably from the C(1)–C(2)–C(3) plane in the same direction as the O(2) atom. The H(N1b) and H(N2) atoms are situated at distances of 2.42 and 2.37 Å from the O(1) atom respectively. An NMR study of 2-substituted 1,3-phenylenediamines and their *N,N′*-diacyl derivatives has revealed that, for the 2-methoxy compound in a deuterochloroform solution, a weak, but still effective, dual intramolecular hydrogen bonding is formed.[9] Accordingly, the N(1)···O(1) and N(2)···O(1) contacts in the palythine molecule can be taken as intramolecular hydrogen bonds.

Of the two groups bonded to the C(5) atom, the larger, CH_2OH group occupies the equatorial position, and the smaller, OH group, the axial. Although, from the standpoint of steric repulsion, a structure in which the O(3)H group takes a *trans* conformation with one of the two bulky methylene groups around the C(5)–C(7) bond can be expected to be the most stable, in fact,

Table 5. The dihedral angles (ϕ/°)

The A–B–C–D angle is positive if, when looking along B to C, A has to be rotated clockwise to eclipse D.

C(6)–C(1)–C(2)–C(3)	−8.0	C(4)–C(5)–C(6)–C(1)	−49.9
C(6)–C(1)–C(2)–O(1)	174.0	C(4)–C(5)–C(6)–H(6a)	−173
N(1)–C(1)–C(2)–C(3)	174.2	C(4)–C(5)–C(6)–H(6b)	65
C(2)–C(1)–C(6)–C(5)	31.1	C(7)–C(5)–C(6)–C(1)	−173.3
C(2)–C(1)–C(6)–H(6a)	152	O(2)–C(5)–C(6)–C(1)	70.6
C(2)–C(1)–C(6)–H(6b)	−85	C(4)–C(5)–O(2)–H(O2)	−42
N(1)–C(1)–C(6)–C(5)	−151.1	C(6)–C(5)–O(2)–H(O2)	−162
C(2)–C(1)–N(1)–H(N1a)	179	C(7)–C(5)–O(2)–H(O2)	80
C(2)–C(1)–N(1)–H(N1b)	0	C(4)–C(5)–C(7)–O(3)	−63.3
C(6)–C(1)–N(1)–H(N1a)	2	C(4)–C(5)–C(7)–H(7a)	179
C(1)–C(2)–C(3)–C(4)	5.1	C(4)–C(5)–C(7)–H(7b)	58
C(1)–C(2)–C(3)–N(2)	−174.9	C(6)–C(5)–C(7)–O(3)	60.2
O(1)–C(2)–C(3)–C(4)	−177.0	O(2)–C(5)–C(7)–O(3)	175.2
C(1)–C(2)–O(1)–C(8)	86.5	C(2)–O(1)–C(8)–H(8a)	−175
C(3)–C(2)–O(1)–C(8)	−91.5	C(2)–O(1)–C(8)–H(8b)	70
C(2)–C(3)–C(4)–C(5)	−25.6	C(2)–O(1)–C(8)–H(8c)	−53
C(2)–C(3)–C(4)–H(4a)	−146	C(3)–N(2)–C(9)–C(10)	81.7
C(2)–C(3)–C(4)–H(4b)	93	C(3)–N(2)–C(9)–H(9a)	−156
N(2)–C(3)–C(4)–C(5)	154.4	C(3)–N(2)–C(9)–H(9b)	−39
C(2)–C(3)–N(2)–C(9)	180.0	H(N2)–N(2)–C(9)–C(10)	−94
C(2)–C(3)–N(2)–H(N2)	−5	N(2)–C(9)–C(10)–O(4)	−10.2
C(4)–C(3)–N(2)–C(9)	0.1	N(2)–C(9)–C(10)–O(5)	171.7
C(3)–C(4)–C(5)–C(6)	47.4	H(9a)–C(9)–C(10)–O(4)	−133
C(3)–C(4)–C(5)–C(7)	170.6	H(9b)–C(9)–C(10)–O(4)	112
C(3)–C(4)–C(5)–O(2)	−70.0	C(5)–C(7)–O(3)–H(O3)	168
H(4a)–C(4)–C(5)–C(6)	168	H(7a)–C(7)–O(3)–H(O3)	−75
H(4b)–C(4)–C(5)–C(6)	−71	H(7b)–C(7)–O(3)–H(O3)	49

the O(3)H group has *gauche* relations with both of the methylene groups. The preference of the present conformation may be due not only to the electrostatic repulsion between the negatively-charged atoms, O(2) and O(3), but also to the hydrogen-bond formation of the O(3)H group with adjacent molecules.

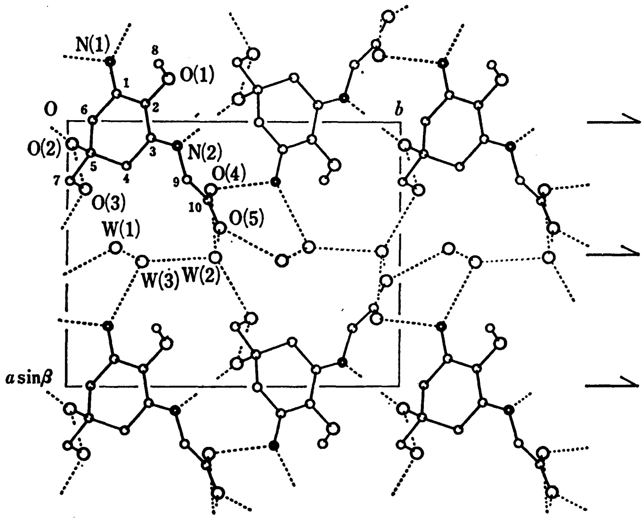


Fig. 2. The crystal structure viewed along the c axis.

Table 6. The hydrogen bonds, X–H···Y

X	Y	X···Y (*l*/Å)	H···Y (*l*/Å)	X–H···Y (*ϕ*/°)
(1) intramolecular				
N(1)	O(1)	2.751(2)	2.42(3)	104(2)
N(2)	O(1)	2.723(2)	2.37(3)	105(2)
(2) intermolecular				
N(1)	O(4)$^{b)}$	2.809(3)	1.97(3)	167(3)
N(1)	O(W3)$^{c)}$	2.906(3)	2.11(3)	156(3)
N(2)	O(2)$^{d)}$	3.039(2)	2.20(3)	163(3)
O(2)	O(3)$^{e)}$	2.855(2)	1.99(3)	174(3)
O(3)	O(W2)$^{a)}$	2.785(2)	2.04(4)	154(4)
O(W1)	O(5)$^{f)}$	2.810(3)	2.10(5)	166(5)
O(W1)	O(W3)$^{g)}$	2.927(3)	2.06(5)	177(5)
O(W2)	O(4)$^{h)}$	2.987(3)	2.26(4)	149(4)
O(W2)	O(5)$^{h)}$	3.130(3)	2.38(4)	154(4)
O(W2)	O(5)$^{f)}$	2.704(3)	1.85(4)	174(5)
O(W3)	O(W1)$^{h)}$	2.893(3)	2.12(5)	159(4)
O(W3)	O(W2)$^{a)}$	2.831(3)	2.07(6)	178(5)

The symmetry codes are: a) x, y, z (given in Table 3); b) $-x, -1/2+y, -z$; c) $-x, 1/2+y, -z$; d) $-x, 1/2+y, 1-z$; e) $x, y, 1+z$; f) $1-x, -1/2+y, 1-z$; g) $1-x, 1/2+y, 1-z$; h) $1-x, -1/2+y, -z$.

The carboxylate ion group is placed on the opposite side of the mean plane for the N(1)–C(1)–C(2)–C(3)–N(2) conjugated system to the C(8)H_3 group. The carboxylate plane is approximately perpendicular to the C(3)–N(2)–C(9) plane, and the O(4) atom nearly eclipses the N(2) atom around the C(9)–C(10) bond. As a result, the H(4a) and H(9b) atoms are very close to each other, the distance between them being only 2.10 Å.

Crystal Structure. The projection of the crystal structure viewed along the c axis is shown in Fig. 2, while the details of the hydrogen bonds are given in Table 6. The palythine and water molecules are joined together into a three-dimensional hydrogen-bonded structure by twelve types of hydrogen bonds. Three groups, N(1)–H(N1b), N(2)–H(N2), and O(W2)–H(W2a), take part in bifurcated hydrogen bonds.[10] The first two make intermolecular hydrogen bonds with the O(W3)$^{c)}$ and O(2)$^{d)}$ atoms respectively, besides intramolecular ones with the O(1) atom. The last group donates its proton, H(W2a), to both of the two oxygen atoms in the same carboxylate group, O(4)$^{h)}$ and O(5)$^{h)}$. Although the O(W2)···O(4)$^{h)}$ and O(W2)···O(5)$^{h)}$ distances are somewhat different, the O(W2)–H(W2a)···O(4)$^{h)}$ and O(W2)–H(W2a)···O(5)$^{h)}$ angles are nearly equal to each other, 149 and 154° respectively.

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