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CRYSTAL AND MOLECULAR STRUCTURE OF PALYTHENE POSSESSING A NOVEL 360 NM CHROMOPHORE

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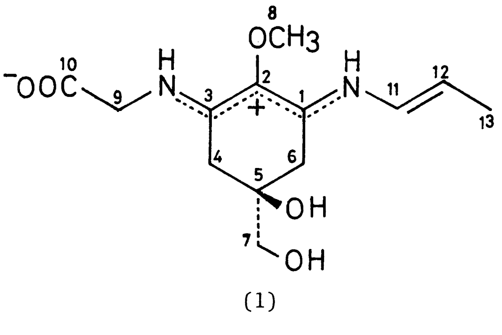
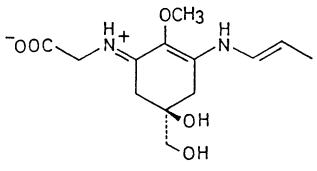
Crystal and molecular structure of palythene isolated from Palythoa tuberculosa (Coelenterata) was unambiguously determined by X-ray analysis including its absolute configuration. The structure of palythene was defined as an inner salt and then features of delocalization of the positive charge were elucidated.

We described the isolation and structures of a series of compounds possessing characteristic UV-absorption at 310-360 nm from Palythoa tuberculosa1) and Porphyra tenera Kjellmann2). Some of them are well known to exist in species of red algae, corals, jellyfishes and planktons, and have attracted much attention with respect to their roles in these living systems. Each UV-absorbing compound contains a glycine moiety and a vinylog of amidine or an enaminone system. As shown in structure 1, palythene which belongs to the group of these compounds is represented as a resonance hybrid between two canonical forms 2 and 3. It is interesting to determine the extent of contribution of each canonical form from a structural point of view. Therefore, we attempted the structural elucidation by X-ray crystallography of palythene with a strong maximum at 360 nm.

The recrystallization of palythene from ethanol gave well formed and orthormbic crystals $(C_{13}H_{20}N_2O_5 \cdot H_2O)$. The space group is $P2_12_12_1$ and lattice constants are a= 8.660 Å, b= 11.176 Å, c= 15.056 Å and α= β= γ= 90°. The structure was solved by using of MULTAN and refined to R= 8.2 % by full matrix least-squares. Absolute configuration was determined by comparison of calculated and observed intensities of 15 reflections using Cu $K\alpha$ radiation.



(1)



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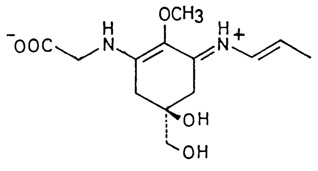

(3)

A view of the molecule of palythene 1 is shown in the Figure 1 and then Table lists each bond lengths and angles. The bond length between C(2) and C(3) is obviously great in comparison with C(1)-C(2) bond and the N(2)-C(1) bond is longer than the N(1)-C(3) bond. These results indicate that the canonical form 2 contributes more effectively than the form 3. Therefore, it is apparently suggested that the positive and negative charges in the inner salt such as palythene are favorable to exist in the near position each other. On the other hand, the conversion of carboxylate to carboxylic acid or its ester causes remarkable delocalization of the positive charge judging from the observation of their CMR spectra1).

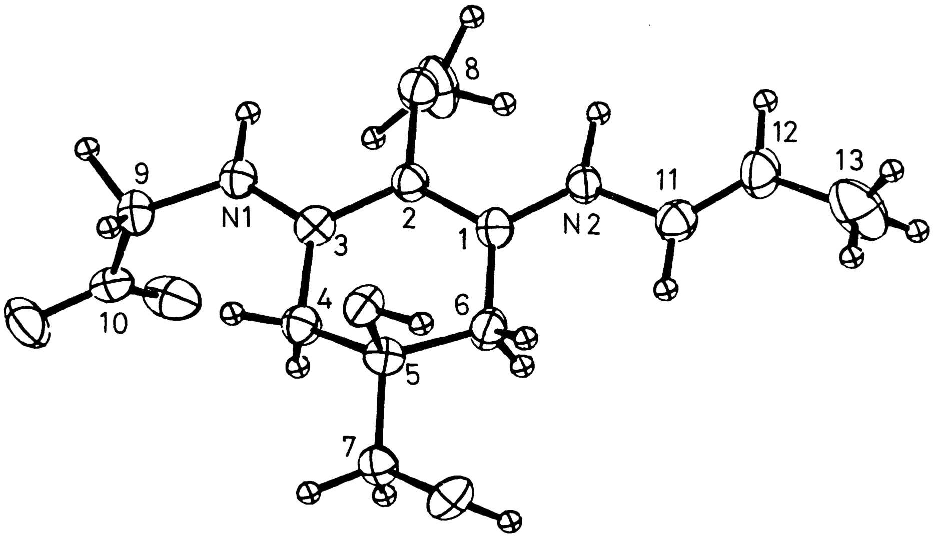

Figure 1. Palythene, shown in the best plane of the vinylog of amidine.

Table. Bond lengths and bond angles in palythene.

Bond Lengths				Bond Angles			
N1-H	1.057 Å	C1-C6	1.496 Å	H-N1-C9	116.65°	O-C2-C3	118.30°
N2-H	1.084	C2-O	1.376	H-N1-C3	121.80	O-C2-C1	119.36
N2-C1	1.341	C2-C3	1.409	C3-N1-C9	126.06	C1-C2-C3	122.32
N2-C9	1.423	C3-C4	1.494	N1-C3-C2	118.86	H-N2-C1	126.38
N1-C3	1.323	C9-C10	1.311	N1-C3-C4	120.76	H-N2-C11	107.71
N1-C9	1.463	C11-C12	1.494	C2-C3-C4	120.36	C1-N2-C11	125.90
C1-C2	1.381						

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References

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2) S. Takano, A. Nakanishi, D. Uemura, and Y. Hirata, Chem. Lett., 1979, 419, and references cited therein.

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