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Crystal and Molecular Structures of Octaethylporphinium(monocation) Triiodide and Its Benzene Hemisolvate

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The structure of the triclinic form of octaethylporphinium (monocation) triiodide was determined by X-ray analysis. The structure of the previously determined orthorhombic form was refined using diffractometer data. The final R values for the triclinic and the orthorhombic forms were 0.060 and 0.069, respectively. The present analysis has established the inherent structure of porphyrin monocations; three pyrrole rings are coplanar and the plane of the fourth ring is tilted from the mean plane of the other three. The magnitude of the tilt angle is 12.5° for the triclinic form and 16.1° for the orthorhombic form.

Porphyrins exist in solution as the free base, monocationic and/or dicationic species, each of which shows the characteristic absorption spectrum.1) As the equilibrium between the free base and the monocation is sensitive to pH and other factors,2) the cationic species could be present in a biological environment.3) The resemblance of spectrum between the monocation and the reaction intermediate of metal incorporation4) suggests that in the final stage of oxidation from porphyrinogen to porphyrin, which occurs in the mitochondoria or in cytoplasm,5) the monocationic species plays a role in controlling the formation of metalloporphyrins.

For comprehensive studies in porphyrin stereochemistry, it is important to reveal the structure of porphyrin monocation, since structural studies have been done for the free base and dicationic species.6,7) As a first example, we have previously reported the structure of the orthorhombic form of octaethylporphinium (monocation) triiodide crystal,8) in which one pyrrole ring is inclined by 14° with respect to the plane of the remaining porphyrin nucleus. This is quite different from the typical structures of the other species; the free base is planar within ±0.05 Å,6) whilst the dication is deformed considerably, assuming $\bar{4}$ symmetry.7) Although the inner hydrogen atoms are expected to determine the stereochemistry of monocation, their positions were not directly obtained owing to the low accuracy of intensity data. We have tried to refine the structure using new diffractometer data. On the other hand, we obtained the triclinic crystals of octaethylporphinium(monocation) triiodide [$(H_3OEP)^+I_3^-$], in which benzene molecules are solvated. The structure of this crystal has been determined in order to examine the packing effect of the crystal upon the structural feature of the monocation. A comparison of the two structures in detail will give the inherent structure of porphyrin monocation.

Experimental and Structure Determination

Triclinic Crystal. Triclinic crystals of $(H_3OEP)^+I_3^-$, reddish brown plates, were obtained from a dichloromethane–benzene solution of octaethylporphinium(dication) tetraiodide, A crystal $0.16 \times 0.16 \times 0.32$ mm^3 was used for data collection on a Rigaku automated, four-circle diffractometer with graphite monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. Density measured by the flotation method suggested the benzene hemi-solvate. The unit-cell dimensions were determined by least-squares calculations with 47 high-angle reflexions. Intensities of the independent reflexions within the range $2\theta \leqq 55°$ were measured by use of the $\omega/2\theta$ scan mode with a scanning rate of 2° (2θ) min^{-1}. Stationary background counts were accumulated for 30 s before and after each scan. Periodic checks of the intensity values of five standard reflexions showed no significant X-ray damage or crystal decay. Corrections for absorption or extinction were not applied. A total of 9099 independent reflexions were obtained, of which 3096 were zero; the observed threshold value, F_{llm}, was 5.56. The space group $P\bar{1}$ was deduced by the intensity statistics.

The structure was solved by the heavy-atom method. The structural parameters were refined by block-diagonal least-squares techniques; the quantity minimized was $\sum w\varDelta^2$, where $\varDelta = |F_o| - |F_c|$. All the hydrogen atoms were found by the difference synthesis. The zero-reflexions, for which $|F_c| > F_{\mathrm{llm}}$, were included in the least-squares calculation by assuming $F_o = F_{\mathrm{llm}}$. The following weights were applied; $w = \exp(-(As^2+Bt^2+Cst+Ds+Et+F))$ where $s = |F_o| \times 10^2$ and $t = \sin\theta/\lambda$ for $|F_o| \geqq F_{\mathrm{llm}}$. and $w = 1/\langle\varDelta^2\rangle$ for $|F_o| < F_{\mathrm{llm}}$. The coefficients, A–F, were evaluated by least-squares calculation at each cycle of structure refinement so that $\langle w\varDelta^2\rangle = 1$ in (s, t) space; their values in the final stage of refinement were, −0.8951, 14.35, −0.2166, 7.782, −6.059, and 1.845, respectively. The final R value was 0.06 for 6829 reflexions ($|F_o| > 3/\sqrt{w(s,t)}$). Atomic scattering factors were taken from "International Tables for X-Ray Crystallography" Vol.

TABLE 1. CRYSTAL DATA

Triclinic form	Orthorhombic form
$C_{36}H_{47}I_3N_4 \cdot 1/2C_6H_6$	$C_{36}H_{47}I_3N_4$
$F.W. = 955.6$	$F.W. = 916.5$
$P\bar{1}$	Cmca
$a = 16.047(6)$ Å	$a = 29.564(4)$ Å
$b = 15.762(4)$ Å	$b = 14.512(5)$ Å
$c = 14.251(6)$ Å	$c = 17.385(3)$ Å
$\alpha = 122.69(2)°$	$U = 7459(3)$ Å^3
$\beta = 139.15(2)°$	$D_m = 1.61$ g cm^{-3}
$\gamma = 63.84(2)°$	$D_x = 1.63$ g cm^{-3}
$U = 1981(1)$ Å^3	$Z = 8$
$D_m = 1.60$ g cm^{-3}	μ(Mo $K\alpha$) $= 26.7$ cm^{-1}
$D_x = 1.602$ g cm^{-3}	
$Z = 2$	
μ(Mo $K\alpha$) $= 25.7$ cm^{-1}	

4.[9] Anomalous dispersion effect was taken into account with f' and f'' for iodine atom.[10]

Table 2. Fractional coordinates and temperature factors (triclinic form)

The B values for non-hydrogen atoms are equivalent isotropic temperature factors calculated from anisotropic thermal parameters using the equation $B=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, and U_3 are the principal components of mean square displacement matrix $\boldsymbol{U}$. The e.s.d.'s in ( ) refer to last dicimal places.

Atom	x	y	z	B/Å^2
I(1)	0.13695(6)	0.22348(6)	0.09973(9)	6.86
I(2)	0.30733(5)	0.24553(4)	0.41499(8)	6.64
I(3)	0.47593(7)	0.25735(6)	0.73001(9)	7.46
N(1)	1.0850(5)	0.1331(4)	0.6791(7)	3.7
N(2)	0.9480(5)	0.0498(4)	0.6738(7)	3.4
N(2*)	1.2519(5)	−0.0443(4)	0.6961(7)	3.6
N(3)	1.1114(5)	−0.1390(4)	0.6815(6)	3.3
C(1)	1.0267(7)	0.3012(5)	0.6922(8)	3.4
C(2)	1.0047(6)	0.2142(5)	0.6800(8)	3.2
C(3)	0.9097(6)	0.2177(5)	0.6722(8)	3.0
C(4)	0.8839(6)	0.1427(5)	0.6688(7)	2.9
C(5)	0.7892(6)	0.1454(5)	0.6623(8)	3.0
C(6)	0.7995(6)	0.0565(5)	0.6653(8)	3.1
C(7)	0.9030(6)	−0.0053(5)	0.6749(8)	3.2
C(8)	0.9467(7)	−0.1008(5)	0.6834(9)	3.8
C(9)	1.0479(7)	−0.1594(5)	0.6980(9)	3.4
C(10)	1.1152(8)	−0.2432(6)	0.748(1)	4.7
C(11)	0.9568(7)	0.4029(5)	0.700(1)	4.3
C(12)	1.004(1)	0.463(1)	0.856(1)	7.0
C(13)	0.7010(6)	0.2371(6)	0.6629(9)	3.6
C(14)	0.7587(8)	0.3110(6)	0.820(1)	5.1
C(15)	0.7240(8)	0.0264(6)	0.667(1)	4.3
C(16)	0.790(1)	0.037(1)	0.820(1)	6.7
C(17)	1.0898(1)	−0.284(1)	0.799(1)	5.8
C(18)	1.018(1)	−0.378(1)	0.679(2)	8.9
C(1*)	1.1253(1)	0.2705(6)	0.6992(8)	3.5
C(2*)	1.1602(6)	0.1677(5)	0.6939(8)	3.0
C(3*)	1.2621(7)	0.1072(5)	0.7035(8)	3.4
C(4*)	1.3060(6)	0.0118(5)	0.7083(8)	2.9
C(5*)	1.4126(6)	−0.0483(5)	0.7259(8)	3.0
C(6*)	1.4198(6)	−0.1388(5)	0.7240(8)	3.2
C(7*)	1.3175(6)	−0.1370(5)	0.7064(8)	3.1
C(8*)	1.2965(6)	−0.2120(5)	0.7074(9)	3.5
C(9*)	1.2074(6)	−0.2122(5)	0.7051(8)	3.3
C(10*)	1.2142(8)	−0.2758(6)	0.754(1)	4.4
C(11*)	1.1879(8)	0.3325(6)	0.7162(1)	4.6
C(12*)	1.295(1)	0.391(1)	0.880(1)	7.0
C(13*)	1.5042(7)	−0.0123(6)	0.7524(9)	3.8
C(14*)	1.6054(9)	0.0483(8)	0.918(1)	6.0
C(15*)	1.5184(7)	−0.2244(6)	0.7463(9)	4.1
C(16*)	1.6214(8)	−0.2237(8)	0.911(1)	5.9
C(17*)	1.3182(9)	−0.3573(8)	0.813(1)	5.8
C(18*)	1.290(1)	−0.451(1)	0.683(2)	8.4
CB(1)	0.389(1)	0.498(1)	0.357(2)	8.5
CB(2)	0.392(1)	0.473(1)	0.436(2)	7.6
CB(3)	0.500(1)	0.475(1)	0.577(2)	7.9
HN(2)	1.017(6)	0.033(5)	0.697(8)	0.0
HN(2*)	1.204(7)	−0.016(5)	0.710(8)	1.7
HN(3)	1.070(5)	−0.114(4)	0.617(7)	0.0

Table 3. Fractional coordinates and temperature factors (orthorhombic form)

The B values for non-hydrogen atoms are equivalent isotropic temperature factors calculated from anisotropic thermal parameters using the equation $B=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, andU_3 are the principal components of mean square displacement matrix $\boldsymbol{U}$. The e.d.s.'s in ( ) refer to last dicimal places.

Atom	x	y	z	B/Å^2
I(1)	0.18254(8)	0.0	0.0	10.9
I(2)	0.18189(7)	0.1457(2)	0.1150(1)	12.8
N(1)	0.5	0.429(1)	0.3946(9)	2.2
N(2)	0.4285(6)	0.565(1)	0.412(1)	3.1
N(3)	0.5	0.709(2)	0.438(1)	3.1
C(1)	0.4771(5)	0.279(1)	0.3670(9)	2.6
C(2)	0.4626(7)	0.375(1)	0.385(1)	3.1
C(3)	0.4187(8)	0.401(2)	0.387(1)	3.0
C(4)	0.4012(6)	0.491(2)	0.402(1)	3.0
C(5)	0.3565(6)	0.521(2)	0.403(1)	3.6
C(6)	0.3567(7)	0.614(2)	0.417(1)	3.8
C(7)	0.4031(6)	0.641(2)	0.423(1)	2.9
C(8)	0.4194(9)	0.728(2)	0.435(1)	4.0
C(9)	0.4617(7)	0.765(2)	0.435(1)	2.8
C(10)	0.4769(5)	0.856(1)	0.426(1)	2.8
C(11)	0.4459(7)	0.199(1)	0.353(1)	4.5
C(12)	0.4321(7)	0.193(1)	0.268(1)	7.2
C(13)	0.3159(6)	0.458(1)	0.389(1)	4.6
C(14)	0.3050(7)	0.445(2)	0.306(1)	9.2
C(15)	0.3155(7)	0.676(1)	0.422(1)	5.0
C(16)	0.3093(6)	0.733(2)	0.348(1)	7.8
C(17)	0.4450(6)	0.938(1)	0.412(1)	4.5
C(18)	0.4290(6)	0.939(1)	0.330(1)	7.6
HN(2)	0.458(5)	0.55(1)	0.413(8)	0.0
HN(3)	0.5	0.66(2)	0.46(1)	0.0

Orthorhombic Crystal. Orthorhombic crystals, reddish brown hexagonal plates, were obtained from methylenechloride-benzene solution. A crystal with dimensions of 0.15×0.10×0.02 mm^3 was used for data collection on the automated, four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The unit-cell dimensions were determined by least-squares calculations with 34 high-angle reflexions. Diffraction intensities of all the independent reflexions within the range $2\theta\leq 40°$ were measured by use of the ω scan mode at a scanning rate of 1° min^{-1}. Stationary background counts were accumulated for 50 s before and after each scan. Periodic checks of the intensity of three standard reflexions showed no significant X-ray damage or crystal decay. Corrections for absorption and extinction were not applied. A total of 1784 independent reflexions were obtained, of which 731 were zero. The structural parameters, determined by photographic data,[8] were used as the initial values. They were refined by the full-matrix least-squares methods. All the hydrogen atoms were located by the difference synthesis. The final R value was 0.069 for 1345 reflexions $(|F_o|>3/\sqrt{w(s,t)})$. The atomic parameters of most of the hydrogen atoms were fixed during the refinement. Details of refinement including anomalous dispersion effect of iodine were the same as those for the triclinic crystal. F_{lim} was 9.00 and the weighting coefficients A—F were 0.4916, 22.01, −0.03600, −1.585, −6.020, and 6.661, respectively. Crystal data are summarized in Table 1, and the final coordinates of both crystals are

Table 4. Bond lengths (l/Å) and angles (ϕ/°) in triclinic form

Some nonbonded distances of interest are also given. CB's denote the carbon atoms of the benzene molecule.

N(1)-C(2)	1.36(1)	C(6)-C(7)-N(2)	106.2(8)
N(1)-C(2*)	1.37(1)	C(6)-C(7)-C(8)	126.5(9)
N(2)-C(4)	1.37(1)	N(2)-C(7)-C(8)	127.3(9)
N(2)-C(7)	1.36(1)	C(7)-C(8)-C(9)	127.5(10)
N(2*)-C(4*)	1.36(1)	C(8)-C(9)-N(3)	125.0(9)
N(2*)-C(7*)	1.38(1)	C(8)-C(9)-C(10)	127.8(10)
N(3)-C(9)	1.39(1)	N(3)-C(9)-C(10)	106.9(9)
N(3)-C(9*)	1.37(1)	C(9)-C(10)-C(10*)	108.7(11)
C(1*)-C(1)	1.37(1)	C(10)-C(10*)-C(9*)	107.0(10)
C(1)-C(2)	1.46(1)	N(3)-C(9*)-C(10*)	107.8(9)
C(2)-C(3)	1.42(1)	C(8*)-C(9*)-C(10*)	126.5(10)
C(3)-C(4)	1.38(1)	N(3)-C(9*)-C(8*)	124.8(9)
C(4)-C(5)	1.43(1)	C(7*)-C(8*)-C(9*)	129.0(10)
C(5)-C(6)	1.36(1)	N(2*)-C(7*)-C(8*)	128.2(9)
C(6)-C(7)	1.50(1)	C(6*)-C(7*)-C(8*)	125.6(9)
C(7)-C(8)	1.38(2)	N(2*)-C(7*)-C(6*)	106.1(8)
C(8)-C(9)	1.38(2)	C(7*)-C(6*)-C(5*)	107.8(8)
C(9)-C(10)	1.42(2)	C(6*)-C(5*)-C(4*)	108.1(8)
C(10)-C(10*)	1.38(2)	C(5*)-C(4*)-N(2*)	107.2(8)
C(9*)-C(10*)	1.43(2)	C(5*)-C(4*)-C(3*)	128.9(9)
C(8*)-C(9*)	1.41(1)	C(3*)-C(4*)-N(2*)	123.9(9)
C(7*)-C(8*)	1.38(1)	C(2*)-C(3*)-C(4*)	128.2(9)
C(6*)-C(7*)	1.45(1)	N(1)-C(2*)-C(3*)	122.6(9)
C(5*)-C(6*)	1.37(1)	C(1*)-C(2*)-C(3*)	124.6(9)
C(4*)-C(5*)	1.44(1)	N(1)-C(2*)-C(1*)	112.9(8)
C(3*)-C(4*)	1.37(1)	C(2*)-N(1)-C(2)	103.7(8)
C(2*)-C(3*)	1.43(1)	C(4)-N(2)-C(7)	111.2(8)
C(1*)-C(2*)	1.44(1)	C(4*)-N(2*)-C(7*)	110.9(8)
C(1)-C(11)	1.50(2)	C(9*)-N(3)-C(9)	109.3(8)
C(11)-C(12)	1.50(2)	C(1*)-C(1)-C(2)	105.4(9)
C(5)-C(13)	1.51(1)	C(1)-C(2)-N(1)	112.5(9)
C(13)-C(14)	1.50(2)	C(1)-C(2)-C(3)	121.8(9)
C(6)-C(15)	1.50(2)	N(1)-C(2)-C(3)	125.7(9)
C(15)-C(16)	1.47(2)	C(2)-C(3)-C(4)	127.5(9)
C(10)-C(17)	1.53(2)	C(3)-C(4)-N(2)	125.6(9)
C(17)-C(18)	1.49(3)	C(2*)-C(1*)-C(1)	105.6(9)
C(1*)-C(11*)	1.51(2)	C(1*)-C(1)-C(11)	128.8(10)
C(11*)-C(12*)	1.50(2)	C(2)-C(1)-C(11)	125.8(9)
C(5*)-C(13*)	1.51(1)	C(1)-C(11)-C(12)	111.9(1)
C(13*)-C(14*)	1.50(2)	C(4)-C(5)-C(13)	123.5(8)
C(6*)-C(15*)	1.50(2)	C(6)-C(5)-C(13)	127.9(9)
C(15*)-C(16*)	1.54(2)	C(5)-C(13)-C(14)	113.3(9)
C(10*)-C(17*)	1.52(2)	C(5)-C(6)-C(15)	127.6(9)
C(17*)-C(18*)	1.48(3)	C(7)-C(6)-C(15)	124.5(9)
N(2)-HN(2)	0.83(10)	C(6)-C(15)-C(16)	114.1(11)
N(2*)-HN(2*)	0.82(10)	C(9)-C(10)-C(17)	125.3(11)
N(3)-HN(3)	0.83(8)	C(10*)-C(10)-C(17)	125.8(12)
HN(2)···HN(2*)	2.63(14)	C(10)-C(17)-C(18)	111.9(14)
HN(2)···HN(3)	2.06(13)	C(10)-C(10*)-C(17*)	127.9(12)
HN(2*)···HN(3)	2.28(14)	C(9*)-C(10*)-C(17*)	124.9(11)
N(1)···N(2)	2.96(1)	C(10*)-C(17*)-C(18*)	110.1(13)
N(1)···N(2*)	2.86(1)	C(7*)-C(6*)-C(15*)	123.9(9)
N(3)···N(2)	2.96(1)	C(5*)-C(6*)-C(15*)	128.2(9)
N(3)···N(2*)	3.05(1)	C(6*)-C(15*)-C(16*)	112.2(9)
N(2)···N(2*)	4.23(1)	C(6*)-C(5*)-C(13*)	127.2(9)
I(1)-I(2)	2.889(1)	C(4*)-C(5*)-C(13*)	124.6(9)
I(2)-I(3)	2.945(1)	C(5*)-C(13*)-C(14*)	111.6(10)
CB(1)-CB(2)	1.34(3)	C(2*)-C(1*)-C(11*)	127.1(10)
CB(2)-CB(3)	1.32(3)	C(1)-C(1*)-C(11*)	127.3(10)
CB(1)-CB(3')	1.40(3)	C(1*)-C(11*)-C(12*)	112.9(11)
C(3)-C(4)-C(5)	128.2(9)	I(1)-I(2)-I(3)	176.77(5)
N(2)-C(4)-C(5)	106.3(8)	CB(1)-CB(2)-CB(3)	120.2(18)
C(4)-C(5)-C(6)	108.5(8)	CB(2)-CB(3)-CB(1')	119.7(18)
C(5)-C(6)-C(7)	107.8(9)	CB(2)-CB(1)-CB(3')	120.2(18)

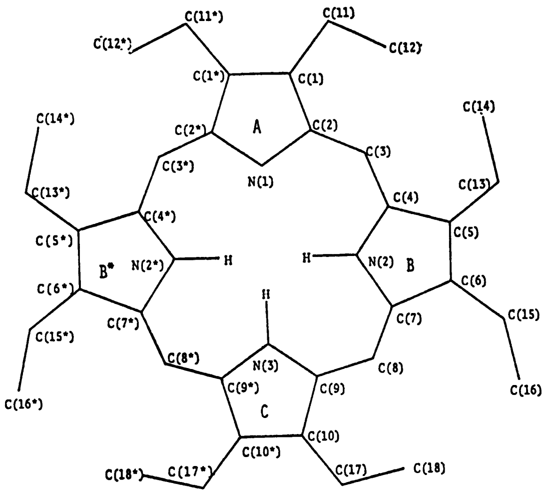


Fig. 1. The atom numbering system.

Table 5. Bond lengths (l/Å) and angles (ϕ/°) in orthorhombic form
Some nonbonded distances of interest are also given.

N(1)–C(2)	1.37(2)	C(4)–N(2)–C(7)	110(2)
N(2)–C(4)	1.36(3)	C(9)–N(3)–C(9*)	109(2)
N(2)–C(7)	1.34(3)	C(1*)–C(1)–C(2)	107(1)
N(3)–C(9)	1.39(3)	C(1)–C(2)–N(1)	110(2)
C(1)–C(2)	1.49(3)	C(1)–C(2)–C(3)	123(2)
C(2)–C(3)	1.35(3)	N(1)–C(2)–C(3)	128(2)
C(3)–C(4)	1.43(3)	C(2)–C(3)–C(4)	127(2)
C(4)–C(5)	1.39(3)	C(3)–C(4)–N(2)	122(2)
C(5)–C(6)	1.38(3)	C(3)–C(4)–C(5)	129(2)
C(6)–C(7)	1.43(3)	N(2)–C(4)–C(5)	109(2)
C(7)–C(8)	1.37(3)	C(4)–C(5)–C(6)	108(2)
C(8)–C(9)	1.36(3)	C(5)–C(6)–C(7)	107(2)
C(9)–C(10)	1.41(3)	C(6)–C(7)–N(2)	108(2)
C(10)–C(10*)	1.37(3)	C(6)–C(7)–C(8)	127(2)
C(1)–C(1*)	1.36(3)	N(2)–C(7)–C(8)	125(2)
C(1)–C(11)	1.50(3)	C(7)–C(8)–C(9)	133(2)
C(11)–C(12)	1.54(3)	C(8)–C(9)–N(3)	121(2)
C(5)–C(13)	1.52(3)	C(8)–C(9)–C(10)	131(2)
C(13)–C(14)	1.49(3)	N(3)–C(9)–C(10)	107(2)
C(6)–C(15)	1.52(3)	C(9)–C(10)–C(10*)	109(2)
C(15)–C(16)	1.54(3)	C(11)–C(1)–C(1*)	128(2)
C(10)–C(17)	1.53(3)	C(1)–C(11)–C(12)	112(2)
C(17)–C(18)	1.51(3)	C(2)–C(1)–C(11)	125(2)
N(2)–HN(2)	0.88(14)	C(4)–C(5)–C(13)	124(2)
N(3)–HN(3)	0.82(18)	C(5)–C(13)–C(14)	113(2)
HN(2)···HN(2*)	2.50(28)	C(6)–C(5)–C(13)	128(2)
HN(2)···HN(3)	2.62(18)	C(5)–C(6)–C(15)	126(2)
N(1)···N(2)	2.90(2)	C(7)–C(6)–C(15)	127(2)
N(2)···N(3)	3.00(3)	C(6)–C(15)–C(16)	122(2)
N(2)···N(2*)	3.49(2)	C(9)–C(10)–C(17)	123(2)
I(1)–I(2)	2.910(3)	C(10*)–C(10)–C(17)	128(2)
C(2)–N(1)–C(2*)	107(1)	C(10)–C(17)–C(18)	110(2)
		I(1)–I(2)–I(3)	180

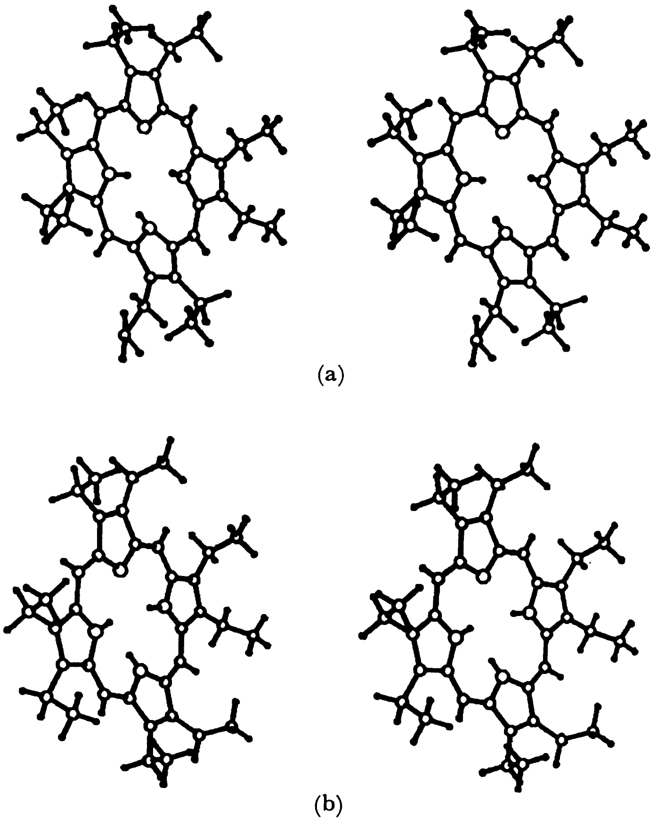
given in Tables 2 and 3.††

Results and Discussion

Cation. Figure 1 shows the atom numbering system used for both crystals. The monocation in the orthorhombic crystal has a crystallographic mirror plane perpendicular to the mean molecular plane through N(1) and N(3). Similar approximate local mirror symmetry is also observed in the triclinic monocation. The symmetry-related atoms are indicated with asterisk. The bond lengths and angles are listed in Tables 4 and 5 for triclinic and orthorhombic forms, respectively.

In the both crystals the imino hydrogen atoms are localized on rings B, B*, and C just as we postulated from the geometrical considerations in the previous paper on the orthorhombic form.[8)] In the triclinic form, the C_α–N–C_α bond angle in the ring A, pyrrolenine ring, is 103.7°, while those of the ring B, B*, and C are 111.2, 110.9, and 109.3°, respectively. The corresponding values in the orthorhombic form are 107, 110, 110, and 109°, respectively. These values are consistent with those of pyrrole rings with and without attached hydrogen atoms.[11)]

The stereoscopic drawings of the cations are shown in Fig. 2. Both cations take essentially the same architecture except the orientation of the peripheral ethyl groups. In the triclinic form the two ethyl groups attached to the ring C are oriented opposite to the other six ethyl groups with respect to the plane of the porphyrin nucleus, while all ethyl groups stick out on the same side in the orthorhombic form.


(a)

(b)

Fig. 2. The stereoscopic drawings of the molecules.
(a) Triclinic form. (b) Orthorhombic form.

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†† The tables of thermal parameters, hydrogen coordinates, and observed and calculated structure factors are kept as Document No. 8125 at the Chemical Society of Japan.

TABLE 6A. LEAST-SQUARES PLANES IN THE ORTHORHOMBIC MONOCATION WITH DISPLACEMENTS OF ATOMS FROM THESE PLANES

(a) Displacements from the mean plane (l/Å)

Plane (1); N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), N(2*), C(1*), C(2*), C(3*), C(4*), C(5*), C(6*), C(7*), C(8*)

N(1) 0.06, N(2) 0.02,C(1) −0.04, C(2) 0.03, C(3) −0.01, C(4) 0.03, C(5) −0.04, C(6) −0.02, C(7) 0.01, C(8) −0.01

Plane (2); ring A

N(1) −0.00, C(1) −0.00, C(2) 0.00

Plane (3); ring B

N(2) −0.01, C(4) 0.02, C(5) −0.01, C(6) 0.01

Plane (4); ring C

N(3) −0.02, C(9) 0.02, C(10) −0.01, HN(3) 0.24

(b) Plane equations in the form $Px+Qy+Rz=S$

	P	Q	R	S
(1)	0.000	−0.174	0.985	5.62
(2)	0.000	−0.216	0.976	5.36
(3)	−0.025	−0.171	0.985	5.35
(4)	0.000	0.106	0.994	8.68

(c) Angles (τ/°) between the planes. Estimated standard deviations are in parentheses.

(1)/(2) 2.4(5) (1)/(3) 1.5(6) (1)/(4) 16.1(6)
(2)/(3) 3.0(8) (2)/(4) 18.5(7) (3)/(4) 16.0(8)

TABLE 6B. LEAST-SQUARES PALNES IN THE TRICLINIC MONOCATION WITH DISPLACEMENTS OF ATOMS FROM THESE PLANES

(a) Displacements from the mean plane (l/Å)

Plane (1); N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), N(2*), C(1*), C(2*), C(3*), C(4*), C(5*), C(6*), C(7*), C(8*)

N(1) −0.09, N(2) −0.03, N(2*) −0.07, C(1) −0.07, C(2) −0.02, C(3) −0.01, C(4) −0.02, C(5) −0.00, C(6) 0.02, C(7) 0.02, C(8) 0.06, C(1*) 0.06, C(2*) −0.02, C(3*) −0.02, C(4*) −0.01, C(5*) 0.07, C(6*) 0.04, C(7*) −0.03, C(8*) −0.01

Plane (2); ring A

N(1) −0.01, C(1) 0.00, C(2) 0.00, C(1*) −0.01, C(2*) 0.01

Plane (3); ring B

N(2) −0.01, C(4) 0.01, C(5)−0.00, C(6) −0.01, C(7) 0.01, HN(2) 0.15

Plane (4); ring B*

N(2*) −0.01, C(4*) 0.00, C (5*) 0.00, C(6*) −0.00, C(7*) 0.01, HN(2*) 0.21

Plane (5); ring C

N(3) 0.03, C(9) −0.02, C(10) 0.01, C(9*) −0.03, C(10*) 0.02, HN(3) −0.33

(b) Plane equations in the form $Px+Qy+Rz=S$

	P	Q	R	S
(1)	0.643	0.413	0.645	5.431
(2)	0.651	0.351	0.673	5.155
(3)	0.652	0.425	0.628	5.551
(4)	0.598	0.417	0.684	4.580
(5)	0.612	0.639	0.466	5.146

(c) Angles (τ/°) between the planes. Estimated standard deviations are in parentheses.

(1)/(2) 3.9(5) (1)/(3) 1.3(11) (1)/(4) 3.4(4)
(1)/(5) 16.7(3) (2)/(3) 4.9(4) (2)/(4) 4.9(4)
(2)/(5) 20.6(4) (3)/(4) 4.5(4) (3)/(5) 15.6(4)
(4)/(5) 17.9(4)

The common feature of the cations in the two different crystalline field is of particular interest. As shown in Table 6, three of the four pyrrole rings, each of which are planar within the experimental errors, are approximately coplanar. The fourth ring C is tilted from the plane consisting of the three rings by 16.1(6) and 12.5(8)° for orthorhombic and triclinic forms, respectively. The difference between the two values may be due to the packing effects. Similar deformation mode is seen in octaethylporphinium tri-μ-chloro-hexacarbonyldirhenate[12] and in 21-ethoxycarbonylmethyl-2,3,7,-8,12,13,17,18-octaethylporphyrin.[13] In the former case the corresponding tilt angle is smaller (8.6°) probably due to the hydrogen bonding between the pyrrole nitrogen atoms and the water molecule of solvation. In the latter case the angle is much larger apparently due to the bulky alkyl substituents.

The tilt of the fourth pyrrole ring is believed to be due

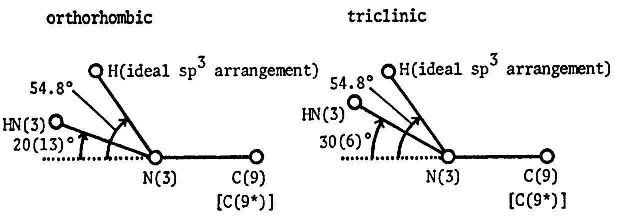

Fig. 3. Deviations of HN(3) atoms from the plane defined by N(3), C(9), and C(9*) atoms. The degree of deviations is expressed by the angle between N(3)→H vector and the plane. Estimated standard deviations are in parentheses.

mainly to the steric hindrance of the imino hydrogen atoms. As shown in Tables 4 and 5, H···H distances are 2.06 to 2.63 Å which indicate the relieved nonbonded H···H repulsion, if we take 1.9—2.0 Å as the minimum H···H nonbonded contact.[14] While HN(2)···HN(2*) distance are longer than 2.5 Å, HN(2)···HN(3) and HN(2*)···HN(3) distances are shorter than 2.3 Å. These distances suggest that the steric hindrance is effectively relieved by the tilt of the ring C. In addition, it is noted that the imino hydrogen atom of the ring C deviates from the plane of C_α–N–C_α. Figure 3 illustrates the angles between the N–H vector and the C_α–N–C_α planes for orthorhombic and triclinic cations, together with the N–H vector for the ideal sp³ hybridization. Although these differences are not statistically significant enough, it may be concluded that the nitrogen atoms of the ring C have some sp³ character. Such sp³ character of N(3) is favourable for relieving the steric hindrance.

The values of corresponding bond lengths and angles in both cations are quite similar. In addition to this, the crystallographic and local mirror symmetries justify averaging equivalent bond lengths and angles to give the typical molecular dimensions as shown in Fig. 4.

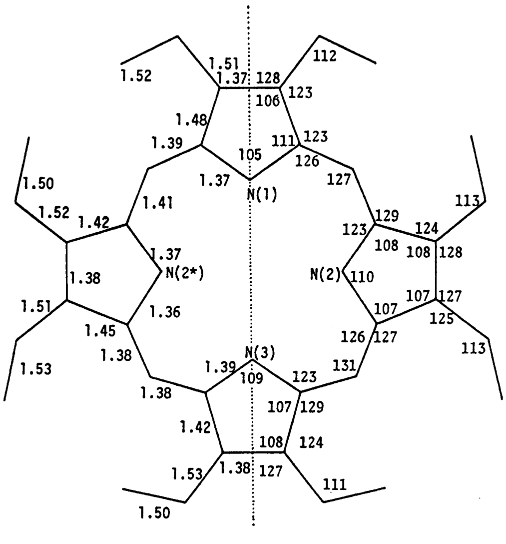

Fig. 4. Bond lengths and angles obtained by averaging equivalent halves of the two independent molecules. The dotted line reveals the crystallographic or local mirror plane.

The C_α–N distances are slightly longer in the ring C than in the other rings. The C_α–C_m–C_α angles, especially C(7)–C(8)–C(9), are larger than those normally found.[11] These features are similar to those of octaethylporphinium tri-μ-chloro-hexacarbonyldirhenate.[14] Other bond lengths and angles fall within the range tabulated by Hoard.[11]

The observed structures are the essential feature of monocationic species of porphyrins. Absorption spectra of many porphyrin monocations exhibit a similar pattern,[3,15] which reflects the common conjugate system determined by the present steric structure.

Anion and Molecular Packing. In the orthorhombic crystal, the central iodine atom of the triiodide anion is on the two-fold axis; therefore it has a symmetrical structure with the I–I distance of 2.910(3) Å and the I–I–I angle of 180°. In the triclinic crystal, on the other hand, the anion is free from any crystallographic restriction; the I(1)–I(2) distance of 2.889 Å is significantly shorter than the I(2)–I(3) of 2.945 Å, and I(1)–I(2)–I(3) angle is 176.77(5)°. The asymmetry may be due to the asymmetric environment around the anion in the crystal.[16] The gravity centre of benzene molecule in the triclinic crystal is placed on the centre of symmetry at (1/2, 1/2, 1/2).

The stereoscopic drawings of the crystal structures of both polymorphs are shown in Fig. 5. The common packing feature is "face-to-face" stacking of the porphyrin nuclei. There is no NH···N hydrogen bond between the faces. The similar packing mode is found in the crystal of other octaethylporphyrin derivatives.[12,13] This "face-to-face" stacking well explains the orientation of the terminal ethyl groups. The exceptional direction of the two ethyl groups attached to the C ring is seen in the triclinic crystal.

No unusual van der Waals contact is seen between the anion and the peripheral part of the cations. There is no charge transfer interaction between the benzene molecule and the anion in the triclinic crystal.

Figures 2 and 5 were drawn by TSD : XTAL, which is a computer-graphics interactive modeling programme for the NOVA3 computer.[17]

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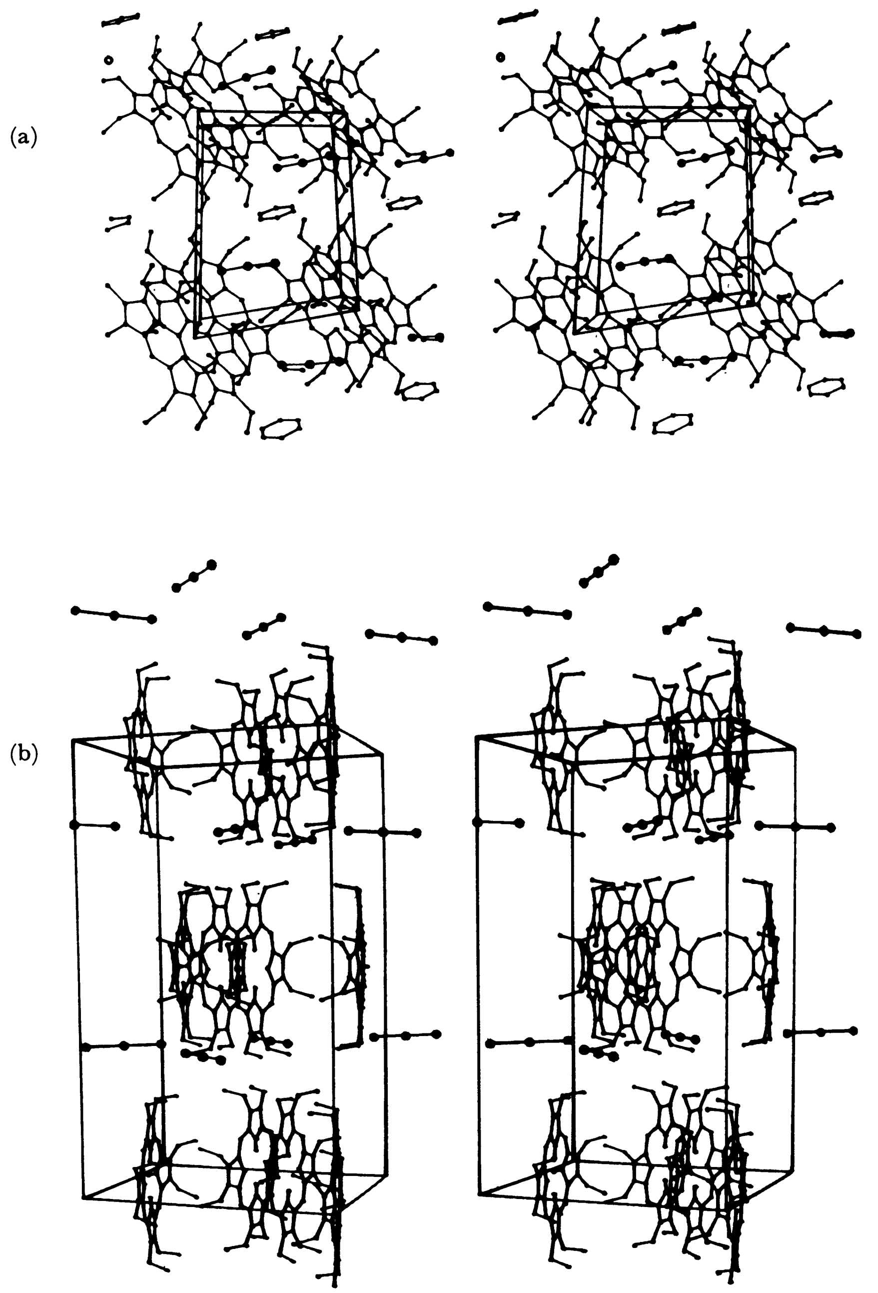

Fig. 5. The stereoscopic drawings of the crystal structures. (a) Triclinic form. The origin is at the lower left rear corner, c points to the viewer, b upward, and a rightward. (b) Orthorhomibc form. The origin is at the lower left rear corner, b points to the viewer, a upward, and c rightward.

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