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Porphyrins with Four Azole Substituents in *meso* Positions. Part 2. X-Ray Crystal Structure of *meso*-tetrakis{1-[2-(trimethylsilyl)ethoxymethyl]pyrazol-5-yl}-porphyrin at 200 K

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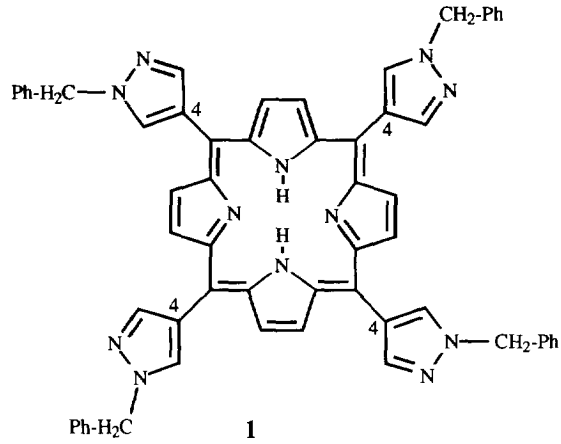
Abstract.—The crystal and molecular structure of *meso*-tetrakis{1-[2-(trimethylsilyl) ethoxymethyl]pyrazol-5-yl}porphyrin **2** has been solved by X-ray analysis. The porphyrin core appears to be distorted from planarity and the conformation of the pyrazole rings is such that pyrazole N_2 atoms are situated *up*, *up*, *down*, *down* with regard to the macrocyclic ring ($\alpha\alpha\beta\beta$ atropisomer). A new porphyrin *meso*-tetrakis[1-benzyloxy-3-methylpyrazol-5-yl]-porphyrin **3** has been obtained from 1-benzyloxy-5-formylpyrazole. Zn(II) and Co(III) complexes of *meso*-tetrakis-(1-benzylpyrazol-4-yl)-porphyrin **1** have been prepared and characterized by MS, NMR and UV.

INTRODUCTION

In part 1 of this series some *meso*-pyrazolyl substituted porphyrins were described.[1] Most of these compounds were *meso*-tetrakis(pyrazol-4-yl)porphyrins derived from 4-formylpyrazoles and the first X-ray structure of this family of compounds was reported, that of *meso*-tetrakis-(1-benzylpyrazol-4-yl)-porphyrin (**1**) [compound **4a** in reference 1].



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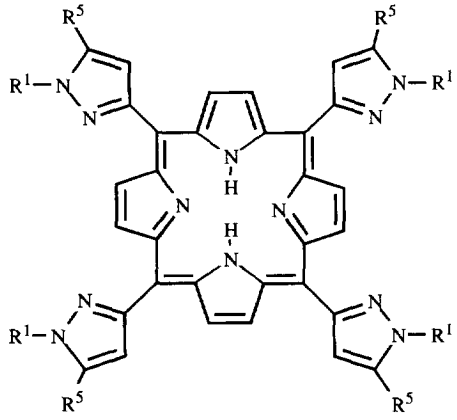
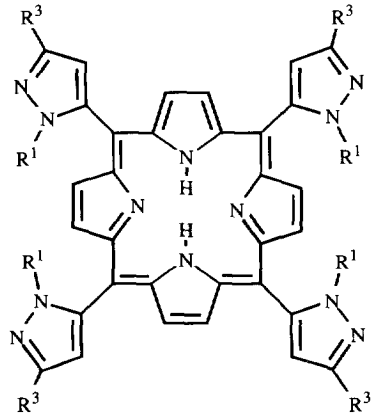
The present publication reports: i) the complexing properties of porphyrin **1**; ii) the X-ray structure at 200 K of *meso*-tetrakis{1-[2-(trimethylsilyl)ethoxymethyl]-5-methylpyrazol-3-yl}-porphyrin **2** (R^1 = SEM) whose synthesis was described in our previous paper [compound **8c** of reference 1]; iii) the synthesis of *meso*-tetrakis[1-benzyloxypyrazol-5-yl]-porphyrin **3** ($R^1 = OCH_2Ph$). Due to restricted rotation about the $C_{3(5)}$-C_{meso} bonds *meso*-tetrakisporphyrins exist as a mixture of the αααα, ααββ, αββα and αβαβ atropisomers which can be observed by NMR provided that the interconversion barriers are sufficiently high.



2, $R^1 = CH_2OCH_2CH_2SiMe_3$, $R^5 = CH_3$



3, $R^1 = OCH_2C_6H_5$, $R^3 = H$
4, $R^1 = CH_2C_6H_5$, $R^3 = CH_3$

Table 1. Selected geometrical parameters (Å,°) of porphyrin **2**. C(A) and C(B) are the centroids of the N101...C105 and N201....C205 rings

a) Porphyrin core	i=1	i=2		i=1	i=2
N(i01)-C(i02)	1.377(3)	1.370(4)	C(i05)-N(i01)	1.362(3)	1.382(3)
C(i02)-C(i03)	1.446(4)	1.431(3)	C(i05)-C(i06)	1.407(3)	1.402(4)
C(i03)-C(i04)	1.340(4)	1.354(4)	C(i06)-C(i07)	1.485(4)	1.488(3)
C(i04)-C(i05)	1.451(4)	1.425(4)	C(i06)-C(202/102')	1.395(4)	1.404(4)
C(i02)-N(i01)-C(i05)	105.0(2)	110.1(2)	N(i01)-C(i05)-C(i04)	110.9(2)	106.3(2)
N(i01)-C(i02)-C(i03)	110.7(2)	106.8(2)	C(i07)-C(i06)-C(202/102')	116.3(2)	118.9(2)
C(i02)-C(i03)-C(i04)	106.6(2)	108.0(2)	C(i05)-C(i06)-C(i07)	117.5(2)	115.9(2)
C(i03)-C(i04)-C(i05)	106.8(2)	108.7(2)	C(i05)-C(i06)-C(202/102')	126.1(2)	125.2(2)
b) Substituents					
C(i07)-N(i08)	1.337(4)	1.334(4)	C(i13)-O(i14)	1.399(3)	1.403(4)
C(i07)-C(i11)	1.407(4)	1.403(4)	O(i14)-C(i15)	1.433(5)	1.435(4)
N(i08)-N(i09)	1.369(3)	1.368(3)	C(i15)-C(i16)	1.511(6)	1.508(5)
N(i09)-C(i10)	1.355(4)	1.353(4)	C(i16)-Si(i17)	1.852(5)	1.881(4)
N(i09)-C(i13)	1.451(4)	1.447(4)	Si(i17)-C(i18)	1.846(7)	1.861(6)
C(i10)-C(i11)	1.365(4)	1.374(4)	Si(i17)-C(i19)	1.859(14)	1.859(6)
C(i10)-C(i12)	1.495(5)	1.494(4)	Si(i17)-C(i20)	1.902(11)	1.858(6)
C(i06)-C(i07)-N(i08)	118.7(2)	120.0(2)	N(i09)-C(i13)-O(i14)	113.9(3)	112.5(2)
C(i06)-C(i07)-C(i11)	129.9(3)	128.6(2)	C(i13)-O(i14)-C(i15)	112.7(3)	113.4(2)
N(i08)-C(i07)-C(i11)	111.4(2)	111.3(2)	O(i14)-C(i15)-C(i16)	108.0(3)	107.6(3)
C(i07)-N(i08)-N(i09)	103.9(2)	104.3(2)	C(i15)-C(i16)-Si(i17)	115.7(4)	114.5(3)
N(i08)-N(i09)-C(i10)	112.5(2)	112.4(2)	C(i16)-Si(i17)-C(i18)	112.3(3)	110.6(2)
N(i09)-C(i10)-C(i11)	106.5(2)	106.3(2)	C(i16)-Si(i17)-C(i19)	107.0(3)	109.0(2)
C(i07)-C(i11)-C(i10)	105.7(3)	105.7(3)	C(i16)-Si(i17)-C(i20)	106.0(4)	109.1(3)
C(i10)-N(i09)-C(i13)	128.7(3)	128.6(2)	C(i18)-Si(i17)-C(i19)	108.3(5)	110.1(3)
N(i08)-N(i09)-C(i13)	118.8(2)	118.9(2)	C(i18)-Si(i17)-C(i20)	107.6(4)	108.3(3)
N(i09)-C(i10)-C(i12)	122.3(3)	122.7(2)	C(i19)-Si(i17)-C(i20)	115.6(5)	109.8(3)
C(i11)-C(i10)-C(i12)	131.2(3)	131.0(3)			
C(i04)-C(i05)-C(i06)-C(i07)	11.8(4)	-6.7(4)	O(i14)-C(i15)-C(i16)-Si(i17)	-54.2(4)	63.9(3)
C(i05)-C(i06)-C(i07)-N(i08)	57.6(3)	126.9(3)	C(i15)-C(i16)-Si(i17)-C(i18)	73.9(4)	-78.1(4)
C(i10)-N(i09)-C(i13)-O(i14)	-84.1(4)	88.3(3)	C(i15)-C(i16)-Si(i17)-C(i19)	-44.8(5)	43.1(4)
N(i09)-C(i13)-O(i14)-C(i15)	-76.8(3)	85.5(3)	C(i15)-C(i16)-Si(i17)-C(i20)	-168.8(5)	162.9(3)
C(i13)-O(i14)-C(i15)-C(i16)	-177.0(3)	-170.4(3)			

c) Hydrogen interactions

C-H···Centroid	C-H	C···Centr.	H···Centr.	C-H···Centr.
C(212)-H(2122)...**C(A)**(x,1-y,1/2+z)	0.95(6)	3.512(4)	2.66(6)	150(4)
Centroid···Centroid				
C(A)...**C(B)**(-x,-y,-z)		3.817(2)		
X-H...Y	X-H	X...Y	H...Y	X-H...Y
N(201)-H(201)...N(101)	0.85(3)	2.961(3)	2.47(3)	118(3)
N(201)-H(201)...N(101)(-x,1-y,-z)	0.85(3)	2.871(3)	2.30(4)	125(3)
C(104)-H(104)...N(108)	0.95(4)	3.058(3)	2.68(4)	105(3)
C(115)-H(1152)...N(108)	1.06(5)	3.295(5)	2.72(4)	114(3)
C(213)-H(2131)...N(108)(x,1-y,1/2+z)	0.94(4)	3.472(4)	2.61(3)	152(3)
C(215)-H(2151)...N(208)	1.04(3)	3.316(4)	2.63(4)	123(3)
C(103)-H(103)...N(208)(-x,1-y,-z)	0.95(4)	2.985(3)	2.51(3)	111(3)
C(118)-H(1181)...O(114)	0.99(12)	3.183(7)	2.68(11)	112(8)
C(218)-H(2183)...O(214)	1.01(11)	3.283(7)	2.65(10)	121(7)
C(113)-H(1132)...O(214)(x,1-y,z-1/2)	1.02(4)	3.548(4)	2.55(4)	167(3)

RESULTS AND DISCUSSION

X-Ray Crystallographic Study

The molecule of porphyrin **2** was located on a symmetry center and two views of its molecular structure are shown in Fig. 1. The two independent pyrazole rings are situated on the same side of the porphyrin plane so that **2** adopts (Table l) a global $\alpha\alpha\beta\beta$ conformation like tetrakis-(benzylpyrazol-4-yl)-porphyrin.[1] The porphyrin core of **2** is distorted from planarity (Fig. 1b). The angles between the pyrrole rings are 6.4(1)° and the angle between the pyrrole rings (i = 1,2) and the plane defined by the contiguous *meso* carbon atoms are 1.7(1), 11.2.(1)°, 7.3(1) and 5.0(1)°, respectively. This loss of planarity is greater in compound **2** than in compound **1**,[1] although they otherwise have similar bond distances and angles. The values of the angles at imino and amino nitrogen (Ni01, i = 1,2) of 105.2(2)° and 110.1(2) correspond to the absence of proton disorder.

The bond angles in the pyrazole rings agree with the values reported for pyrazole itself at low temperature.[2] In spite of the substantial elongation of the Ni08-Ni09 and Ni09-Ci10 bonds (Table 1) the Paul-Curtin's coordinates[3] of $\Delta A(N)$ = 8.1-8.6° and $\Delta R(NC)$ = (1.8-1.9) x 10^{-2} Å correspond to simple *N*-alkyl pyrazoles. That these rings are less perpendicular to the porphyrin core than in compound **1** [Ci05-Ci06-Ci07-Ci08 = 57.6(3), 126.9(3) *vs.* 83.6(4), -97.2(4)° respectively] may be due to the fact that compound **1** possesses CH groups adjacent to the *meso* bond while compound **2** possesses a CH group and a less bulky N-atom adjacent to the *meso* bond.[1] The trimethylsilylethoxymethyl substituents do not induce the *meso*-pyrazolyl substituents to adopt a helical conformation since the Ni08 (i = 1, 2) atoms are at similar distances of H103 and H104 atoms (Fig. 1a).

In the 2-trimethylsilylethoxymethyl chain, the differences observed in the bond distances and angles around the Si atom can be explained in terms of the high value of displacement parameters for i = 1, although a disorder model could not be established. The Oi14-Ci15 bonds are significantly longer than the Ci13-Oi14 bond as observed for the only previously reported structure of this chain.[4] The Oi14-Ci15 distances agree with the tabulated[5] value reported for the Csp^3-O-Csp^3 fragment of 1.426(19) Å. The puckering of these two independent chains allows the formation of weak intramolecular interactions (Table 1). Apart from the usual intramolecular N-H···N bond in the porphyrin core, the molecules are linked by C-H···N/O interactions along the **c** axis (Fig. 2a) and the pyrrole rings stack in pairs through symmetry centers (Table 1, Fig. 2b). The crystal is built up of alternate layers of porphyrin cores and 2-trimethylsilylethoxymethyl chains joined together by van der Waals interactions. This packing leaves prolate shaped cavities of 26.2 $Å^3$ which are clustered near the spherical tipped rod.[6] The center of the cavities are located between the C(120) and C(220) methyl groups separated 2.50 and 3.09 Å from the H(1203) and H(2203) hydrogen atoms. The total packing coefficient amounts to 0.64.

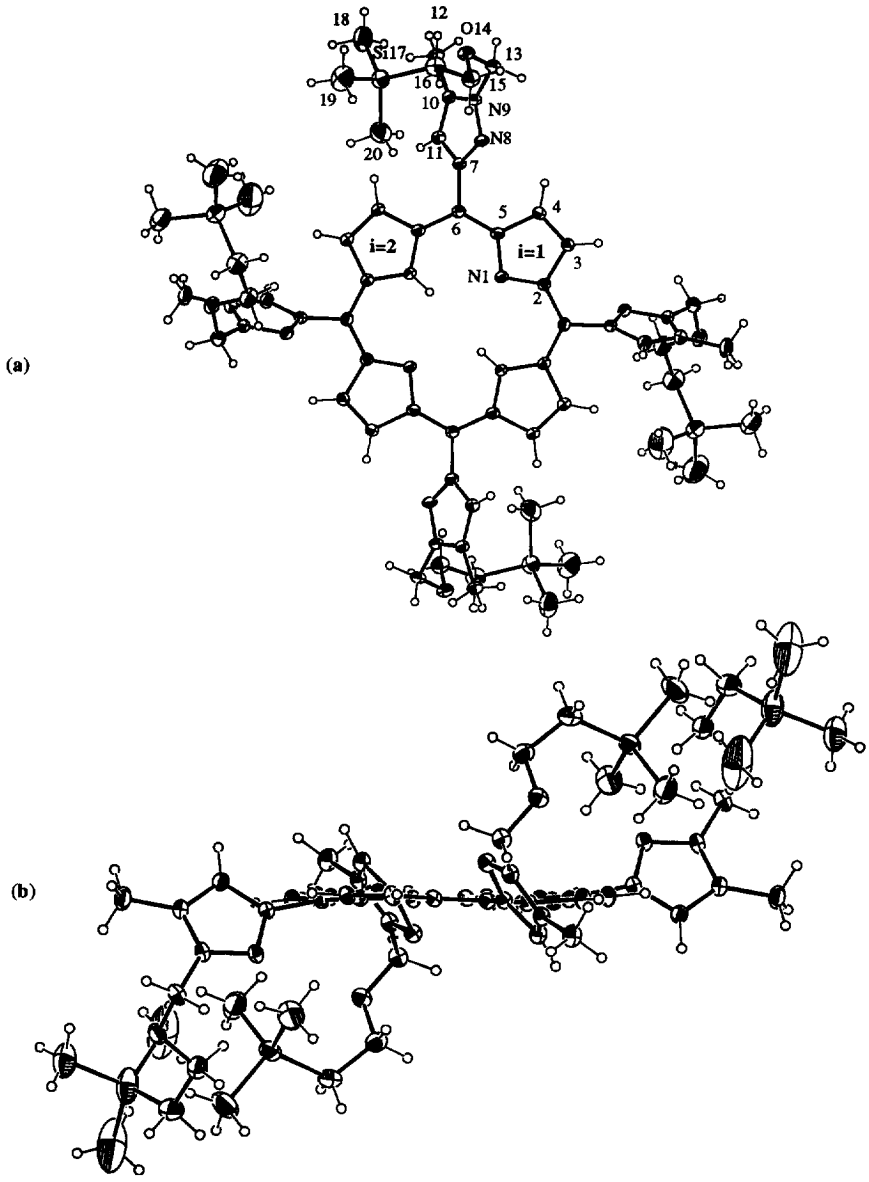


Fig.1 Two views of the molecular structure of the porphyrin, showing the atom labelling [i=1, N9 means N(i09) or N(109) in Tables 1 and 9]. The ellipsoids show 30% occupancy.

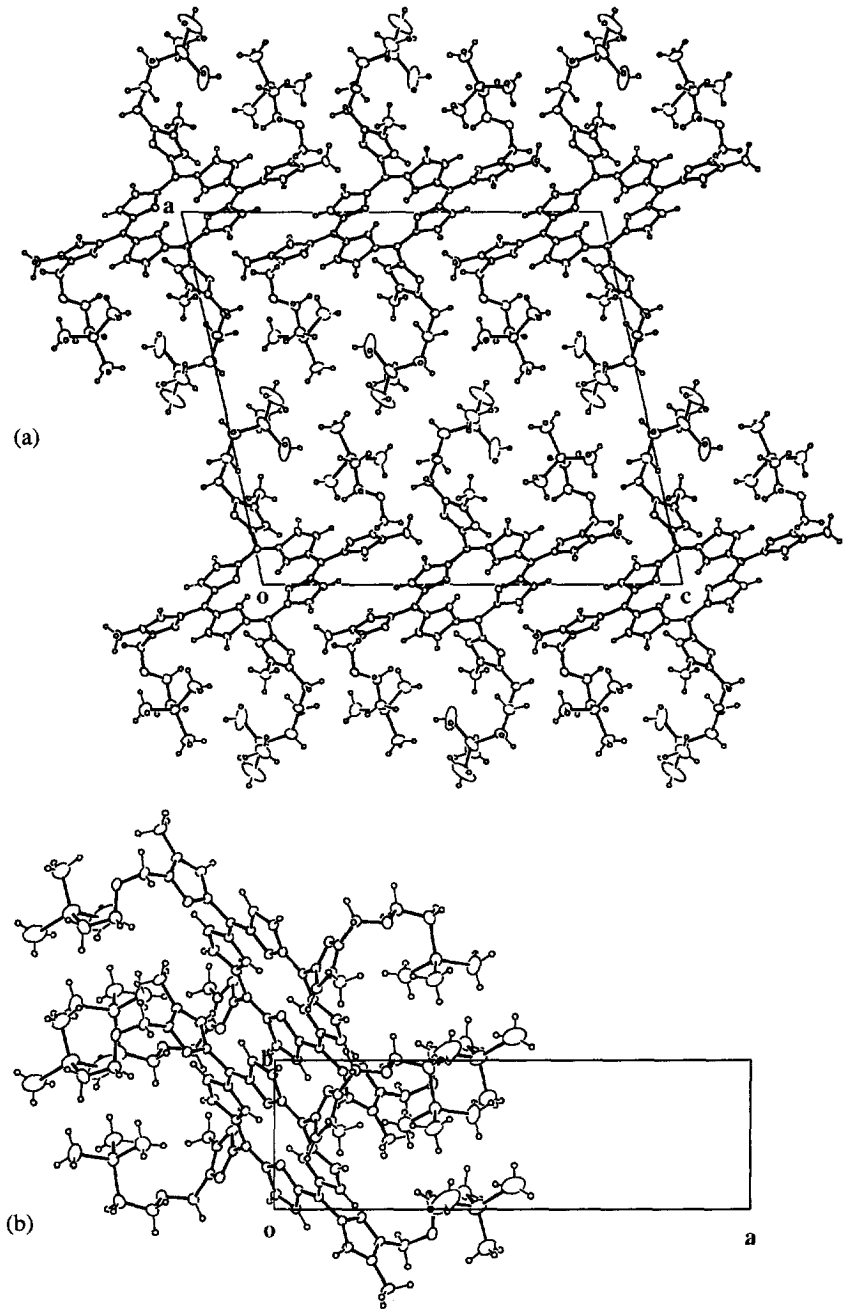
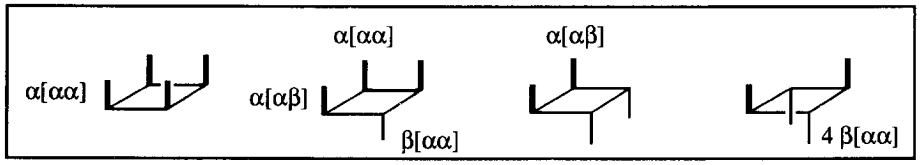


Fig. 2 (a) Crystal packing viewed down b axis. (b) Same along the c axes showing the partial overlapping of the pyrrole rings. Thermal ellipsoids are plotted at 30% probability level.

NMR Study of the Atropisomerism of Porphyrins 3 and 4

Aryl *meso*-substituted porphyrins can exist in four atropisomers designated αααα, ααaβ, ααββ and αβαβ.[1,7,8] Considering only the two neighbouring substituents, these four atropisomers correspond to three situations : α[αα], α[αβ] and α[ββ] (identical to β[αα]).[1]



αααα
4 α[αα]

ααaβ
2 α[αβ]
1 α[αα]
1 β[αα]

ααββ
4 α[αβ]

αβαβ
4 β[αα]

According to the X-ray structure, the porphyrins **1** and **2** adopt the ααββ conformation in the solid state. Unfortunately, good crystals of porphyrin **3** could not be prepared. We will discuss here the problem of atropisomerism present in porphyrin **3** and its relationship with porphyrin **4** (compound **7b** of reference 1). Compounds **3** and **4** are both 5-pyrazolyl derivatives whose barriers depends on the substituents on C_4 (H in both compounds) and N_1 (CH_2Ph in **4** and OCH_2Ph in **3**) but not on C_3.

According to NMR spectra the porphyrins **3** and **4** exist as a statistical mixture of the four atropisomers in solution which contains 1/8 of the αααα, 1/8 of the αβαβ, 1/4 of the ααββ and 1/2 of the ααaβ form. Two CH_2 signals are characteristic of the ααββ and ααaβ atropisomers since, due to symmetry reasons, they appear as AB systems. In the porphyrin **3** the H-4 proton appears (Fig. 3) as a series of doublets (J_{34} = 2.1 Hz) reflecting the statistical distribution. The H-3 protons (assigned through a COSY experiment) show the same pattern but significantly compressed. The aromatic protons appear between 6.1 and 6.7 ppm and the multiplet of β-pyrrole protons at 8.8-8.9 ppm.

Table 2. ^{1}H NMR data of porphyrin **3**

Atropisomer	Methylene	H-4	H-3	Relative intensity
αααα (α[αα])	5.101	7.339	7.925	1
ααaβ (α[αα])	5.110	7.313	7.920	1
ααaβ (α[αβ])	5.200[a]	7.255	7.910	2
ααββ (α[αβ])	5.203[b]	7.228	7.906	2
ααaβ (β[αα])	5.278	7.165	7.896	1
αβαβ (β[αα])	5.285	7.141	7.891	1

[a]Δν = 0.019 ppm, J_{AB} = 16 Hz; [b]Δν = 0.001 ppm.

The chemical shifts of the CH_2 and H-4 signals of porphyrins **3** and **4** are linearly related:

$\delta(CH_2\text{-}\mathbf{3}) = -1.65\pm0.20 + 1.34\pm0.04\ \delta(CH_2\text{-}\mathbf{4})$, n = 6, $r^2 = 0.997$

$\delta(\text{H-4-}\mathbf{3}) = -1.83\pm0.36 + 1.30\pm0.05\ \delta(\text{H-4-}\mathbf{4})$, n = 6, $r^2 = 0.994$

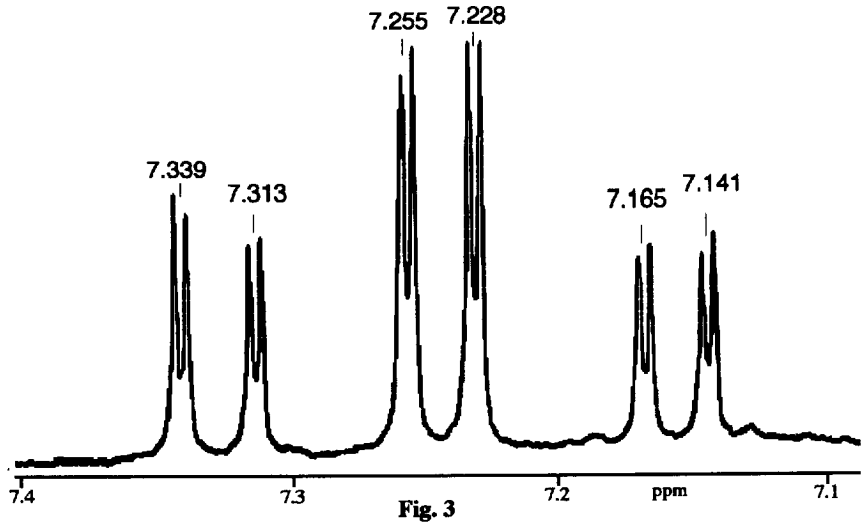


Fig. 3

The ^{13}C chemical shifts (the assignments of Table 3 were made through HETCOR experiments) confirm the presence of the four atropisomers. However, only the α[αα], α[αβ] and α[ββ] situations in a 1:2:1 ratio were observed and not the instead of six situations observed by ^{1}H NMR (see Fig. 3 and Table 2). The pyrrole signals are very broad due to the tautomerism of the porphyrin inner protons and only one C_β signal at 129.5 ppm and one C_α-signal at 140 ppm is observed for all atropisomers.

Table 3. ^{13}C NMR chemical shifts of porpnyrin **3**

	CH_2	C_{meso}	C-3	C-4	C-5	C_{ipso}	C_o	C_m	C_p
α[αα]	80.87	107.17	133.15	111.81[a]	134.26	135.73	129.68	128.59	129.44[b]
α[αβ]	80.70	107.13	133.10	111.92	134.29	135.73	129.61	128.50	129.32
α[ββ]	80.50	107.09	133.07	111.97	134.29	135.73	129.55	128.41	129.20[c]

[a]A second signal at 111.84 ppm; [b]A second signal at 129.37 ppm; [c]A second signal at 129.25 ppm.

Complexing Properties of Porphyrin 1

Complexes of porphyrin **1** with Zn(II) and Co(III) were identified by the characteristic pattern of Zn and Co isotopomers in the mass spectra (Table 4).

Table 4. Isotope patterns of porphyrins **1-Zn** and **1-Co** in the EI mass spectrum

Molecular formula	m/z (theoretical abundance)	m/z (experimental abundance)
$C_{60}H_{44}N_{12}Zn$	996 (100)	996 (100)
	997 (67.3)	997 (72.5)
1-Zn	998 (79.6)	998 (77.1)
	999 (51.9)	999 (56.5)
	1000 (57.8)	1000 (61.1)
	1001 (30.7)	1001 (33.6)
	1002 (9.5)	1002 (12.2)
	1003 (1.9)	1003 (3.4)

$C_{60}H_{44}N_{12}Co$	991 (100) 992 (67.2)	991 (100) 992 (50.4)
1-CoCl	993 (22.2) 994 (4.8)	993 (13.7) 994 (3.8)

The electronic spectra of **1-Zn** and **1-CoCl** (Table 5) belong to the 'normal spectrum' type.[9-11] In the case of **1-Co** the band at 549 nm is closer to that expected for Co(III) (548 nm)[12] than for Co(II) (554 nm).[11]

Table 5. Optical absorption spectra of porphyrins **H_2TPP, ZnTPP, CoTPP, 1, 1-Zn** and **1-Co**

Porphyrin	Absorption band				
	Soret	IV-Q_y	III-Q_x (β)	II-Q_x	I-Q_x (α)
H_2TPP	418 (5.64)	515 (4.17)	550 (3.80)	590 (3.65)	648 (3.62)
ZnTPP	421 (5.77)		549 (4.21)	591 (3.59)	
CoBrTPP	439 (5.23)		556 (3.91)	594 (3.70)[12]	
1 (CH_2Cl_2)[1]	422 (5.28)	522 (3.92)	564 (3.96)	596 (3.50)	660 (3.56)
1-Zn[a]	429 (5.34)		564 (3.95)	607 (3.93)	
1-CoCl[b]	432 (4.91)		549 (3.98)	590 (3.86)	

[a]CH_2Cl_2 + 1% DMF, [b]CH_3OH.

^1H and ^{13}C NMR spectroscopic data on **1, 1-Zn** and **1-CoCl** are given in Tables 6 and 7. The spectra of compound **1-CoCl** show narrow signals and weak effects on the chemical shifts. This indicates that the complex is diamagnetic and hence it is a Co(III) complex. In contrast, paramagnetic Co(II) complexes both of porphyrins[13] and of pyrazoles[14] are characterized by very broad signals and large contact shifts. It is well documented that porphyrins and $CoCl_2$ in the presence of air produce Co(III) complexes.[15] The nature of the axial ligand **L** of CoL(**1**) (**L** = Cl) has been deduced from the elemental analysis.[16]

Table 6. ^1H NMR chemical shifts of porphyrin **1** and its Zn(II) and Co(III) complexes

Solvent	Pyrrole-Hβ	Pz-H_3	Pz-H_5	CH_2	Phenyl
1, $CDCl_3$	9.05[a]	8.38	8.17	5.70	7.40-7.55
1, DMSO-d_6	9.12	8.83	8.38	5.76	7.30-7.58
1-Zn, DMSO-d_6	9.07	8.71	8.28	5.76	7.27-7.58
1-CoCl, CD_3OD	9.59	8.67	8.42	5.80	7.20-7.60
1-CoCl, DMSO-d_6					

[a]NH: -2.70 ppm.

Table 7. ^{13}C NMR chemical shifts of porphyrin **1** and its Zn(II) and Co(III) complexes

Solvent	Porphyrin-C_{meso}	Pyrrole-Cα	Pyrrole-Cβ	Pz-C_3	Pz-C_4	Pz-C_5
1, $CDCl_3$	110.35	136.60	130.86	143.96	123.09	133.38
1-Zn, DMSO-d_6	110.85	134.06	131.40	149.72	122.74	138.08
1-CoCl, CD_3OD	111.70	136.22	135.40	146.06	n.o.	138.49
Solvent	CH_2	Phenyl-C_i	Phenyl-C_o	Phenyl-C_m		Phenyl-C_p
1, $CDCl_3$	56.56	N.o.	127.87	129.11		128.35
1-Zn, DMSO-d_6	55.13	143.42	127.57	128.76		127.73
1-CoCl, CD_3OD	57.15	144.53	128.91	130.07		129.33

EXPERIMENTAL SECTION

Synthesis.- UV absorption spectra were recorded with a Shimadzu UV-160 spectrophotometer. The concentration of porphyrins used ranged from 10^{-5} M (Soret bands) to 10^{-4} M (Q bands). IR spectra were recorded with a Perkin-Elmer 681 spectrometer. Mass spectra of the intermediate compounds were determined on a VG2-250 quadrupole mass spectrometer (electron impact) while those of the porphyrins were obtained on a Kratos Concept 32S (electron impact or FAB). Elemental analyses were carried out with a Fisons EA-1108 apparatus. Column chromatography was performed using silica gel Merck 60 (230-400 mesh) or neutral aluminium oxide (Merck 100-125 mesh). Pyrrole was distilled from calcium hydride and stored at -17°C over calcium hydride. Dichloromethane was Merck p.a. quality and stored over 4 Å molecular sieves.

X-ray Analysis.- A summary of data collection and refinement process is given in Table 8. Data were collected at 200K using an Oxford Cryostream device and checking the temperature continuously during data collection. Semi-empirical Ψ-scan absorption correction was applied.[17] The structure was solved by direct methods (SIR92)[18] and refined by least-squares procedures on Fo. All hydrogen atoms were obtained from difference Fourier synthesis and included and refined isotropically in the last cycles but some of their displacement parameters were kept fixed. The scattering factors were taken from the *International Tables for X-Ray Crystallography.*[19] Table 9 list the final atomic coordinates and equivalent thermal factors for non-hydrogen atoms. The calculations were carried out with the XTAL,[7] PESOS[20] and PARST[21] set of programs running on a VAX6410 computer.

NMR Spectroscopy.- Most spectra were recorded on a Varian Geminy 300 spectrometer. For the particular study of porphyrin **3** the spectra were determined on a Varian Unity 500 working at 499.84 MHz for proton and 125.70 MHz for carbon 13.

Meso-*tetrakis-1-(benzyloxypyrazol-5-yl)porphyrin (3).*

A procedure (Lindsey's 'mild' method) similar to that described in ref. 1 was used. A three-necked round-bottomed flask fitted with a reflux condenser and a nitrogen inlet port was filled with 200 mL pure dry dichloromethane and 1.5 mL (0.75 %) dry methanol. A sample of 1-benzyloxy-5-formylpyrazole (**5**)[21] (0.404 g, 2 mmol) and pyrrole (0.142 mL, 2 mmol) was added. The solution was purged with nitrogen for about 5 min, then a 2.5 M solution of boron trifluoride etherate ((0.246 mL, 0.66 mmol) was added *via* syringe and the reaction vessel was shielded from light. After stirring at room temperature for 2 h, *p*-chloranil (0.368 g, 1.5 mmol, *i.e.* 3 equivalents *per* porphyrinogen) was added in powder form and the reaction mixture was heated at reflux for 1 h. The reaction mixture was cooled to room temperature and 1 equivalent of triethylamine (0.1 mL, 0.66 mmol) was added to neutralize the excess acid. Repeated column chromatographies first on silica gel (petroleum ether-ethyl acetate 7:3 and ethyl acetate gradient), then on neutral alumina (dichloromethane) and finally on silica gel (dichloromethane-ethyl acetate 9:1) afforded 15 mg (3%) of pure **3** ($C_{60}H_{46}N_{12}O_4$) The synthesis was repeated several times to obtain enough product for essays of crystalization. The yields oscillated between 1 and 3%. MS (EI) m/z 998 (M). UV (CH_2Cl_2) λ_{max} nm (log ε) 420 (5.25), 515 (4.09), 548 (3.45), 590 (3.62), 644 (2.76). Anal. calcd for $C_{60}H_{46}N_{12}O_4$: C, 72.13%; H, 4.64%, N, 16.82%. Found: C, 71.87%; H, 4.91%, N, 16.42%.

Zinc(II)-meso-*tetrakis-(1-benzylpyrazol-4-yl)-porphyrin (1-Zn).*

Metal insertion was carried out following a procedure similar to that described by Shinkai.[23] A mixture of porphyrin **1** (0.03 g, 0.032 mmol) and zinc acetate dihydrate (0.01 g, 0.048 mmol) in dry DMF (3 mL) was

Table 8. Crystal analysis parameters at 200K.

Crystal data

Chemical formula	$C_{60}H_{86}N_{12}O_4Si_4$	Crystal system	Monoclinic
Mr	1151.761	Space group	*P2/c*
a (Å)	21.4615(31)	α (°)	90
b (Å)	6.6073(3)	β (°)	102.49(1)
c (Å)	23.5019(32)	γ (°)	90
Z	2	*Dx* (gr/cm³)	1.18
V (Å³)	3253.8(7)	Radiation	CuKα
Wavelength (Å)	1.5418	No. of reflections for	
θ range for lattice parameters (°)	2-45	lattice parameters:	63
Absorption coefficient (cm^{-1})	12.68	Temperature (K)	200
Crystal colour	Deep red	Crystal description	Plate
Crystal size (mm)	0.43 x 0.20 x 0.05		

Data collection

Diffractometer type	Philips PW1100, four circle. Graphite oriented monochromator.		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θ_{max} (°)	65
No. of standard reflections (interval)	2 (90 min.). No variation	Scan width (°)	1.5
No. of independent reflections	5556	No. of observed reflections, I>2σ(I)	4078

Refinement

Treatment of hydrogen atoms	See experimental part	Refinement: Least-Squares on *Fo*. Full matrix	
Secondary extinction correction (10^4)	0.44(6)		
R	0.052	No. of parameters refined	511
wR	0.060	Degrees of freedom	3567
$(\Delta\rho)_{max}$ (e/Å³)	0.47(near the Si atom)	Ratio of freedom	8.0
<Shift/error>	0.006	Max.thermalvalue(Å²)	U11[C(119)]=0.31(1)

Weighting scheme: Empirical as to give no trends in $<\omega\Delta^2F>$ vs. <|Fobs|> and $<\sin\theta/\lambda>$.

Table 9. Final atomic coordinates and $Ueq=(1/3)\Sigma[Uij\cdot a_i^*\cdot a_j^*\cdot a_i\cdot a_j\cdot\cos(a_i,a_j)]\times10^3$

Atom	x	y	z	Ueq	Atom	x	y	z	Ueq
N(101)	0.0130(1)	0.2931(3)	-0.0598(1)	27(1)	N(201)	0.0610(1)	0.3420(3)	0.0674(1)	27(1)
C(102)	-0.0159(1)	0.2785(4)	-0.1180(1)	28(1)	C(202)	0.0970(1)	0.1799(4)	0.0574(1)	28(1)
C(103)	0.0048(1)	0.0977(4)	-0.1433(1)	32(1)	C(203)	0.1397(1)	0.1340(5)	0.1116(1)	34(1)
C(104)	0.0468(1)	0.0055(4)	-0.1007(1)	31(1)	C(204)	0.1289(1)	0.2686(4)	0.1519(1)	34(1)
C(105)	0.0523(1)	0.1294(4)	-0.0489(1)	27(1)	C(205)	0.0800(1)	0.4048(4)	0.1246(1)	29(1)
C(106)	0.0943(1)	0.0826(4)	0.0043(1)	27(1)	C(206)	0.0588(1)	0.5790(4)	0.1488(1)	28(1)
C(107)	0.1429(1)	-0.0767(4)	0.0035(1)	28(1)	C(207)	0.0861(1)	0.6134(4)	0.2118(1)	29(1)
N(108)	0.1837(1)	-0.0531(4)	-0.0316(1)	31(1)	N(208)	0.1136(1)	0.7899(4)	0.2298(1)	32(1)
N(109)	0.2222(1)	-0.2199(4)	-0.0207(1)	32(1)	N(209)	0.1335(1)	0.7678(4)	0.2888(1)	31(1)
C(110)	0.2065(1)	-0.3429(4)	0.0201(1)	34(1)	C(210)	0.1193(1)	0.5831(4)	0.3074(1)	32(1)
C(111)	0.1556(1)	-0.2551(4)	0.0367(1)	36(1)	C(211)	0.0885(1)	0.4799(5)	0.2586(1)	34(1)
C(112)	0.2414(2)	-0.5358(6)	0.0388(2)	52(1)	C(212)	0.1369(2)	0.5206(6)	0.3699(1)	43(1)
C(113)	0.2739(1)	-0.2415(6)	-0.0512(1)	42(1)	C(213)	0.1686(1)	0.9312(5)	0.3223(1)	37(1)
O(114)	0.3324(1)	-0.1662(4)	-0.0203(1)	46(1)	O(214)	0.2345(1)	0.9172(3)	0.3259(1)	40(1)
C(115)	0.3358(2)	0.0503(6)	-0.0220(2)	59(1)	C(215)	0.2545(2)	1.0074(6)	0.2772(1)	49(1)
C(116)	0.4019(2)	0.1132(8)	0.0097(2)	70(2)	C(216)	0.3235(2)	0.9505(6)	0.2815(2)	55(1)
Si(117)	0.4281(1)	0.0152(2)	0.0849(1)	91(1)	Si(217)	0.3378(1)	0.6716(2)	0.2747(1)	50(1)
C(118)	0.4483(4)	-0.2566(10)	0.0864(3)	100(3)	C(218)	0.3361(3)	0.5390(9)	0.3442(3)	83(2)
C(119)	0.3602(7)	0.0494(18)	0.1215(3)	195(6)	C(219)	0.2752(3)	0.5667(10)	0.2145(3)	83(2)
C(120)	0.5038(6)	0.1593(15)	0.1185(6)	200(6)	C(220)	0.4178(2)	0.6331(12)	0.2581(3)	91(2)

stirred at room temperature overnight. Metal insertion was monitored spectrophotometrically as well as by TLC. The solvent was evaporated to dryness and the residue was washed with water to eliminate the excess of zinc acetate. **1-Zn** ($C_{60}H_{44}N_{12}Zn$), yield 0.031 g (97%). MS (EI) m/z 996 (M), MS (FAB^+) m/z 998 (M+2). UV (CH_2Cl_2 + 1% DMF) λ_{max} nm (log ε) 429 (5.34), 564 (3.95), 607 (3.93). Anal. calcd for $C_{60}H_{44}N_{12}Zn$: C, 72.18%; H, 4.44%, N, 16.83%. Found: C, 71.63%; H, 4.85%, N, 16.37%.

Chloro cobalt(III)-meso-*tetrakis-(1-benzylpyrazol-4-yl)-porphyrin (1-CoCl).*

The corresponding cobalt derivative was prepared in a similar way starting from cobalt dichloride (0.006 g, 0.048 mmol, 1.5 equivalents). The solvent was evaporated to dryness and the residue was washed with water to eliminate the excess of $CoCl_2$. **1-CoCl** ($C_{60}H_{44}N_{12}CoCl$), yield 0.032 g (95%). MS (EI) m/z 991 (M), MS (FAB^+) 992 (M+1). UV (CH_3OH) λ_{max} nm (log ε) 432 (4.91), 550 (3.98), 590 (3.86).Anal. calcd for $C_{60}H_{44}N_{12}CoCl$: C, 70.14%; H, 4.32%, N, 16.36%; Cl, 3.45%. Found: C, 69.98 %; H, 4.67%, N, 15.95%; Cl, 3.62%.

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