EPR SPECTRA OF STRUCTURALLY MODIFIED ROOFLIKE FOLDED HEMINS: AXIAL LIGAND-INDUCED RHOMBICITY

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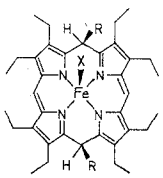

1: R = Me

Me = CH_3

2: R = CMe_3

Iron porphodimethenes 1 are hemins that have a roof-like folded porphyrin core due to the α,γ-addition of methyl groups [1]. The t-butyl groups in 2 impose a sterical hindrance to the axial ligands X, thus allowing the isolation of 2b, a momonuclear hydroxoiron(III)complex [2]. The EPR spectra [3] give the following results: The largest rhombicity is caused by methoxide (1b, 2c), followed by phenoxide and azide (1c, 2e). Lack of rhombicity in 2b or 2d is explained by the mobility of the OH proton or a special orientation of the PhO group due to sterical hindrance. The folding of the macrocycle does not cause rhombicity (1a, 2a).

TABLE: EPR parameters of various porphodimethene hemins 1 and 2 (frozen in toluene, T = 77K, Bruker B-ER 420, X-band)

No.	X	g_{xx}	$g_{\perp}$	g_{yy}	$g_{zz}(g_{\parallel})$	Rh[%][a]	Notes
1a	Cl		5,91		1,99	0	
1b	OMe	6,39		5,56	1,99	5,19	3% MeOH added
1c	OPh	6,27		5,70	1,99	3,56	Ph = C_6H_5
2a	Cl		5,83		2,00	0	
2b	OH		5,84		2,00	0	
2c	OMe	6,26		5,67	1,99	5,56	3% MeOH added
2d	OPh		5,70		2,00	0	Ph = C_6H_5
2e	N_3	6,19		5,64	2,00	3,44	Taken at 3,6K

a) Rhombicity: $Rh = [(g_{xx}-g_{yy})/16]. 100 [\%]$.

[1] J.W. Buchler and K.L. Lay, Z.Naturforsch. 30b, 385 (1975).
[2] J.W. Buchler, Angew. Chem. 90, 425 (1978).
[3] J. Billecke, Dissertation, Technische Hochschule Aachen 1980.