PAPER

NJC
www.rsc.org/njc

Unique 1 : 2 adduct formation of *meso*-tetraarylporphyrins and *meso*-tetraalkylporphyrins with BF_3: a spectroscopic and *ab initio* study

Daryoush Mohajer,*[a] Saeed Zakavi,[a] Saeed Rayati,[a] Mansour Zahedi,*[b] Nasser Safari,*[b] Hamid Reza Khavasi[b] and Shant Shahbazian[b]

[a] *Department of Chemistry, Shiraz University, Shiraz, 71454 Iran. E-mail: dmohajer@chem.susc.ac.ir; Fax: +98-711-2280926; Tel: +98-711-2284822*
[b] *Department of Chemistry, Shahid Beheshti University, Evin Tehran, P. O. 19397-4716 Iran*

Received (in Montpellier, France) 17th May 2004, Accepted 8th August 2004
First published as an Advance Article on the web 23rd November 2004

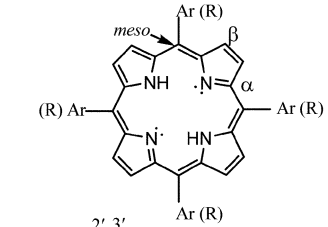
The interaction of a series of free base *meso*-tetraarylporphyrins (arylpor) and *meso*-tetraalkylporphyrins (alkylpor) with $BF_3 \cdot Et_2O$, with different molar ratios ($<1:1$ to $>1:2$) in chloroform, immediately and exclusively yielded the 1 : 2 adducts $(BF_3)_2$por. The close spectral correlation between the corresponding $(BF_3)_2$por and $(CF_3COOH)_2$por were suggestive of similar saddled porphyrin core structures with BF_3 molecules coordinated to the two pyrrolenine nitrogen donors, and simultaneously hydrogen bonded to the pyrrole NH groups of the porphyrin macrocycle from above and below the plane of the porphyrins. The complexation of various arylpor and alkylpor with BF_3 and their protonation with CF_3COOH caused red shifts of the Soret bands (3 to ~30 nm). The interaction of arylpor (except H_2tmp) and also H_2t(*tert*-Bu)p with $BF_3 \cdot OEt_2$ and CF_3COOH demonstrated red shifts of the Q(0,0) bands (5.4 to 40 nm). In contrast, reactions of the alkylpor (alkyl = Me, Et, *n*-Pr, *n*-Bu) and H_2tmp with BF_3 or CF_3COOH displayed blue shifts of the Q(0,0) bands (−13.5 to −31.8 nm). The observed differences in the Q(0,0) bands shifts for the complexation of arylpor *versus* alkylpor are presumably related to the relative co-planarity of the *meso*-aryl groups with the porphyrin core, and the possible π-interactions in the former. It is noteworthy that while the UV-vis spectrum of H_4t(*tert*-Bu)p^{2+} was very sensitive to excess amounts of CF_3COOH, the UV-vis spectrum of $(BF_3)_2H_2$t(*tert*-Bu)p showed no changes in the presence of additional $BF_3 \cdot Et_2O$. The ^{1}H and ^{13}C NMR spectra of the 1 : 2 adducts demonstrated a general correspondence with those of the related protonated porphyrins. However, the pyrrole NH signals of the $(BF_3)_2$por were upfield shifted to an unusual extent as compared to those of the diprotonated H_2por^{2+} species. This effect presumably is due to the weaker NH hydrogen bonding of the 1 : 2 molecular complexes compared to the protonated porphyrins. It was also observed that, in contrast to the gradual upfield shifts of the NH signals of H_2por^{2+} with increasing CF_3COOH concentration, the NH signals of $(BF_3)_2$por complexes remained fixed and independent of $BF_3 \cdot OEt_2$ concentration. ^{19}F and ^{11}B NMR spectra of various $(BF_3)_2$por showed upfield shifts of both ^{11}B and ^{19}F signals relative to those of $BF_3 \cdot OEt_2$. The observed larger upfield shifts of ^{11}B (−6.48 to −6.71 ppm) signals than those of ^{19}F (−3.53 to −4.20 ppm), apparently reflect direct coordination of the B atoms to the nitrogen donors and their closer proximity to the porphyrin core. The results of *ab initio* calculations illustrated that in $(BF_3)_2H_2$tpp the two BF_3 molecules are coordinated to the pyrrolenine nitrogen donors and are hydrogen-bonded to the pyrrole NH groups. Also calculations indicated that the addition of a BF_3 molecule to the 1 : 1 species, BF_3H_2tpp, is more favorable (2.4 kcal mol^{-1}) than its coordination to H_2tpp, and the 1 : 2 molecular complex is more stable (14.5 kcal mol^{-1}) than the 1 : 1 adduct. A mechanism is proposed to explain the absence of the 1 : 1 adduct and the observed symmetric NMR spectra of the pyrrole rings and fluorines in $(BF_3)_2$por.

DOI: 10.1039/b407529c

Introduction

The molecular interactions of free base porphyrins with neutral π-acceptors have been of interest to chemists.[1] In a recent development it has been shown that *meso*-tetraphenylporphyrins are capable of forming specific 1 : 2 molecular complexes with 2, 3-dichloro-5,6-dicyanobenzoquinone (DDQ),[1c] tetracyanoethylene (TCNE),[1d] and trialkylsilyl chlorides.[1e] The interaction of free base porphyrins with haloboranes has also been the subject of some investigations.[2] Recently, it has been demonstrated that the reaction of H_2tpp (Fig. 1) with $BF_3 \cdot Et_2O$ in *wet* chlorobenzene, after 12 h of stirring under an N_2 atmosphere, led to the formation of the B_2OF_2(tpp) complex. In this compound both hydrogen atoms of the central pyrrole NH groups of H_2tpp are lost, and each B atom is bonded to two adjacent pyrrole nitrogens.[2b]

In this report we present, for the first time, direct spectroscopic evidence for novel 1 : 2 molecular complexes of a series of arylporphyrins (arylpor; **1** to **5**) and alkylporphyrins (alkylpor; **6** to **10**), Fig. 1, with the strong, pure σ-acceptor BF_3 molecule. It was observed that the reaction of different molar ratios of these free base porphyrins with $BF_3 \cdot Et_2O$ in chloroform, as monitored by ^{1}H NMR and UV-vis spectroscopic methods, instantly produced the very stable green $(BF_3)_2$por adducts as the sole products. The remarkable correspondence of the UV-vis and ^{1}H NMR spectra of the resulting complexes with those of the related protonated porphyrins[3a–e] suggested similar saddled porphyrin core structures,[3d,f,h] with two BF_3



	Ar		R
1	4′ = H, H_2tpp	**6**	Methyl, H_2t(Me)p
2	4′ = Me, H_2t(4-Me)pp	**7**	Ethyl, H_2t(Et)p
3	4′ = Cl, H_2t(4-Cl)pp	**8**	n-Propyl, H_2t(n-Pr)p
4	4′ = OMe, H_2t(4-OMe)pp	**9**	n-Butyl, H_2t(n-Bu)p
5	2′,2′,4′ = Me, H_2tmp	**10**	*tert*-Butyl, H_2t(*tert*-Bu)p

Fig. 1 The free base porphyrins used in this study.

molecules bonded to the pyrrolenine nitrogen donors and simultaneously hydrogen bonded to the pyrrole NH groups of the porphyrin core, from above and below the porphyrin plane.

Results and discussion

UV-vis spectra

The interaction of $BF_3 \cdot OEt_2$ and H_2tpp at various molar ratios (from $<1:1$ to $>2:1$), in $CHCl_3$, immediately and exclusively produced $(BF_3)_2H_2$tpp compound (curve d in Fig. 2). The spectrum of $(BF_3)_2H_2$tpp with two new bands at 440 and 661 nm is quite different from that of H_2tpp (curve a in Fig. 2). The spectrum of the 1 : 1 $BF_3 \cdot OEt_2$–H_2tpp reaction mixture (Fig. 2, curve c) clearly demonstrates the superimposition of the H_2tpp and $(BF_3)_2H_2$tpp spectra, with no indication for the occurrence of a 1 : 1 adduct. The employment of an excess of $BF_3 \cdot OEt_2$ beyond the 2 : 1 molar ratio led to no detectable changes in the spectrum of the $(BF_3)_2H_2$tpp complex. The UV-vis spectra for H_2t(*n*-Pr)p and its 1 : 2 BF_3 complex in chloroform are displayed in Fig. 3. In a similar fashion the interaction of various arylpor and alkylpor with $BF_3 \cdot OEt_2$ in chloroform produced the corresponding $(BF_3)_2$por adducts. The UV-vis spectra of the complexes are closely related to the spectra of the protonated porphyrins, in $CHCl_3$ (Table 1). However, the Q(0,0) bands for $(BF_3)_2$arylpor as compared to those of $(BF_3)_2$alkylpor [except for $(BF_3)_2H_2$t(*tert*-Bu)p] demonstrate rather larger red shifts (4 to 9 nm) relative to the Q(0,0) bands of their corresponding $(CF_3COOH)_2$arylpor adducts.

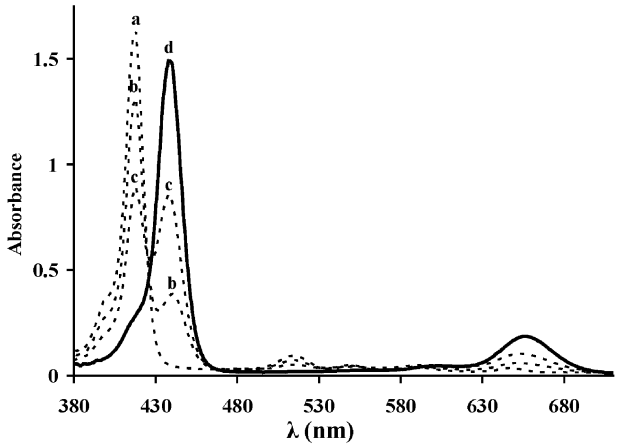


Fig. 2 UV-vis spectra for the titration of H_2tpp (3.5×10^{-5} M) (curve a) with: 0.5 (curve b), 1.0 (curve c), and 2.0 (curve d) equiv. of $BF_3 \cdot Et_2O$ in $CHCl_3$ (0.1 cm cell).

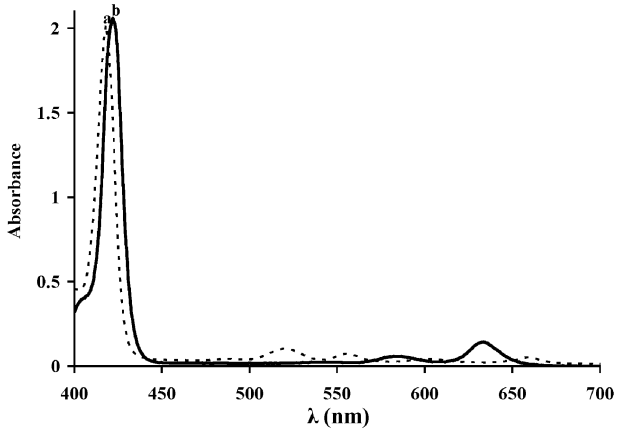


Fig. 3 UV-vis spectra for (curve a) H_2t(*n*-Pr)p (4.9×10^{-5} M) and (curve b) $(BF_3)_2H_2$t(*n*-Pr)p in $CHCl_3$ (0.1 cm cell).

The 1 : 2 adduct formation of arylpor and alkylpor with $BF_3 \cdot OEt_2$ and CF_3COOH led to Soret band red shifts (3 to ~30 nm). Also, the complexation and protonation of arylpor (except for H_2tmp) resulted in Q(0,0) band red shifts (5.4 to 40 nm). In contrast, the Q(0,0) band for both complexation and protonation of alkylpor [except for H_2t(*tert*-Bu)p] displayed a blue shift (−25 to −31.8 nm). The remarkable spectral correspondence between $(BF_3)_2$por and $(CF_3COOH)_2$por suggested analogous saddled porphyrin core structures[3d,f,g,h] and π-systems in these species. However, it is notable that while an excess of $BF_3 \cdot OEt_2$ had no effect on the UV-vis spectrum of $(BF_3)_2H_2$t(*tert*-Bu)p, the spectrum of H_4t(*tert*-Bu)p^{2+} was quite sensitive to additional amounts of CF_3COOH and demonstrated a large blue shift of the Q(0,0) band from 717 nm to 703 nm (with excess CF_3COOH), which is presumed to be due to the interactions of the *meso*-carbons with CF_3COOH.[4]

The free base arylpor and alkylpor with essentially planar cores (**1** to **9**),[3d,5] display similar Soret bands (λ_{max} = 416.7–422 nm), whereas the Q(0,0) band for the arylpor (λ_{max} = 643.5–650 nm) differ rather substantially from those of the alkylpor (λ_{max} = 659–661 nm). This seems to be related to the better σ-donor inductive effects of *meso*-alkyl groups (with sp^3 carbons) than *meso*-aryl groups (with sp^2 carbons). Complexation of arylpor with BF_3 leads to much larger red shifts of their Soret bands (15 to 30 nm) as compared to the complexation of alkylpor (3 to 5 nm). Also, the observed red shifts of the Q(0,0) bands for the complexation of arylpor (except for H_2tmp) contrast with the blue shifts of Q(0,0) bands for the complexation of alkylpor [excepting H_2t(*tert*-Bu)p]. The same trend has also been observed for the protonation of these porphyrins with CF_3COOH.

Consideration of the possible analogous saddling of the porphyrin cores in various protonated arylpor and alkylpor,[3d,f,g] and also the spectral similarities of the BF_3 and CF_3COOH porphyrin adducts, with presumably similar porphyrin macrocycle structures, suggest that the varied positions of the Soret and Q(0,0) bands in $(BF_3)_2$arylpor and $(BF_3)_2$alkylpor must primarily result from the different electronic nature of their *meso*-substituents.[3a,h,6] The relative co-planarity of the *meso*-aryl groups with porphyrin macrocycles,[3g,h] and their possible π-interactions in $(BF_3)_2$arylpor may account for the differences with $(BF_3)_2$alkylpor in the UV-vis spectra. The more pronounced UV-vis spectral shifts observed with the complexation of H_2t(4-OMe)pp compared to the complexation of **1**, **2**, and **3**, provide a clear evidence for the importance of π-donation by the 4-OMe groups. The smaller Soret band red shift for the complexation of the less flexible H_2tmp[3h] than for the complexation of the other arylpor, and also observation of a blue shift rather than a red shift for the Q(0,0) band, may indicate a lesser degree of co-planarity of the bulky mesityl groups with

Table 1 The UV-vis spectral data (in nm) of various arylpor and alkylpor and their 1 : 2 adducts with BF_3 and CF_3COOH adduct in $CHCl_3$ at room temperature[a]

	Porphyrin					BF_3 complex			Dication		
Porphyrin	Soret	IV	III	II	I	Soret	Q(1,0)	Q(0,0)	Soret	Q(1,0)	Q(0,0)
H_2tpp	416.7	513.8	548.1	589.8	646.6	440 (23.3)		661 (14.4)	436 (19.3)	600	652 (5.4)
H_2t(4-Me)pp	418.3	518.4	554	593	649	443 (24.7)		670 (21)	442 (22.7)		663 (14)
H_2t(4-Cl)pp	418	517.4	551.4	592	648.8	442 (24)		662 (13.2)	441 (23)	603	655 (6.2)
H_2t(4-OMe)pp	422	519	556	593	650	452 (30)		690 (40)	450 (28)		686 (36)
H_2tmp	418	512.5	545.5	586.5	643.5	433 (15)	580	630 (−13.5)	435 (17)	579	629 (−14.5)
H_2t(Me)p	416	520	557	602	661	419 (3)	582	633 (−28)	420 (4)	582.8	630.7(−30.3)
H_2t(Et)p[b]						420 (4)	582	632 (−29)	422 (6)	584	632 (−29)
H_2t(*n*-Pr)p[b]						421 (5)	585	633 (−28)	424 (8)	582.3	629.2 (−31.8)
H_2t(*n*-Bu)p	417	520	555	600	659	422 (5)	587	634 (−25)	424 (7)	582.8	630.5 (−28.5)
H_2t(*tert*-Bu)p	446	—	552	628	691	450 (4)		699 (8)	449 (3)		717(26)[c]

[a] The numbers in parentheses represent the band shifts relative to the corresponding bands of the free base porphyrins. [b] Indistinguishable from that of H_2t(Me)p. [c] Very broad peak.

the porphyrin core, and its less effective π-donation to the porphyrin macrocycle.

Since the σ-inductive effects of *meso*-alkyl substituents in the "planar" free base alkylpor (alkyl = Me, Et, *n*-Pr, *n*-Bu) and in the corresponding saddled BF_3 adducts are essentially the same, it appears that the observed blue shift of the Q(0,0) band for alkylpor complexation must be a consequence of a moderate saddling of the porphyrin macrocycle.[6] It should be noted, however, that the σ-acceptor properties of the coordinated BF_3 molecules can also contribute to the lowering of the a_{2u}[7] energy and the observation of a blue shift for the Q(0,0) band. The "unusual" red shift of the Q(0,0) band for the complexation and protonation of H_2t(*tert*-Bu)p is most likely related to a *high* degree of saddling of the porphyrin macrocycle in the corresponding adducts.[6]

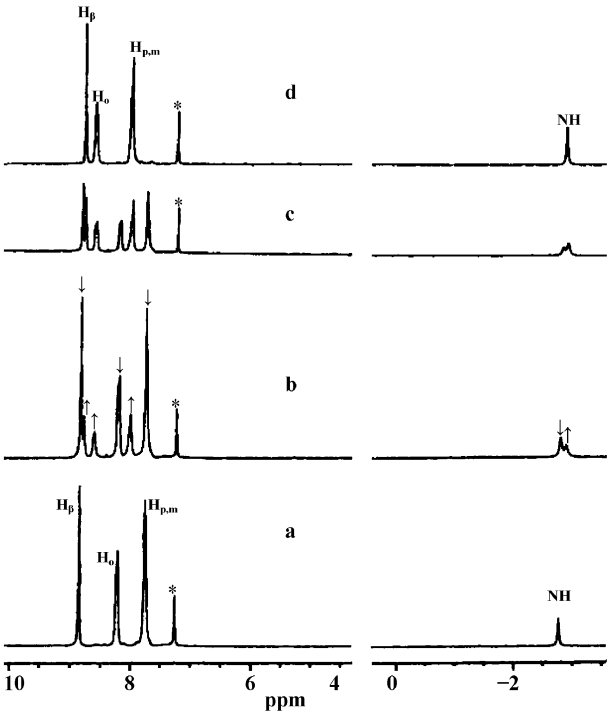


Fig. 4 ^{1}H NMR spectra for the titration of (a) H_2tpp (0.01 M) with (b) 0.5, (c) 1.0 and (d) 2.0 equiv. of $BF_3 \cdot Et_2O$ in $CDCl_3$, at 25 °C. On the left the chemical shifts of the aromatic proton signals are presented. On the right the chemical shifts of the NH proton lines are shown. The lines due to free Et_2O (1.18 and 3.45 ppm) are omitted for clarity. The $CHCl_3$ impurity (*, 7.26 ppm) in $CDCl_3$ was used for measuring the chemical shifts.

^{1}H NMR

The complete conversion of H_2tpp to $(BF_3)_2H_2$tpp and of H_2t(*n*-Pr)p to $(BF_3)_2H_2$t(*n*-Pr)p in $CDCl_3$, at room temperature, is presented in Figs. 4 and 5, respectively. The only product obtained at various molar ratios of $BF_3 \cdot Et_2O$: H_2tpp was the green $(BF_3)_2H_2$tpp compound (spectrum d in Fig. 4). Addition of a large excess of $BF_3 \cdot Et_2O$, had no effect on the ^{1}H NMR spectrum of the 1 : 2 complex. The NH signal showed an "unusual" upfield shift of −0.12 ppm upon complexation of H_2tpp. The ^{1}H NMR spectrum in the aromatic region afforded an upfield shift of the β-protons and a downfield shift of the phenyl proton signals relative to those of free base H_2tpp, analogous to the corresponding ^{1}H NMR shifts of $(DDQ)_2H_2$tpp,[1c] $(TCNE)_2H_2$tpp[1d] and $(Me_3SiCl)_2H_2$tpp[1e] molecular complexes and H_4tpp^{2+}.[3b] The *ortho*-phenyl and β-pyrrole hydrogens gave separate lines at 8.61–8.64 and at 8.80 ppm, respectively. The 12 *meta*- and *para*-hydrogens of $(BF_3)_2H_2$tpp produced a signal at 8.02–8.04 ppm.

The interaction of $BF_3 \cdot OEt_2$ with other arylpor and alkylpor under various molar ratios (from <1 : 1 to >2 : 1) immediately gave the ^{1}H NMR spectra of their corresponding 1 : 2 molecular complexes (Table 2).

NH signal. The "unusual" upfield shifts of the pyrrole NH resonances ($\Delta\delta$ = −0.01 to −1.92 ppm) for BF_3 adducts of

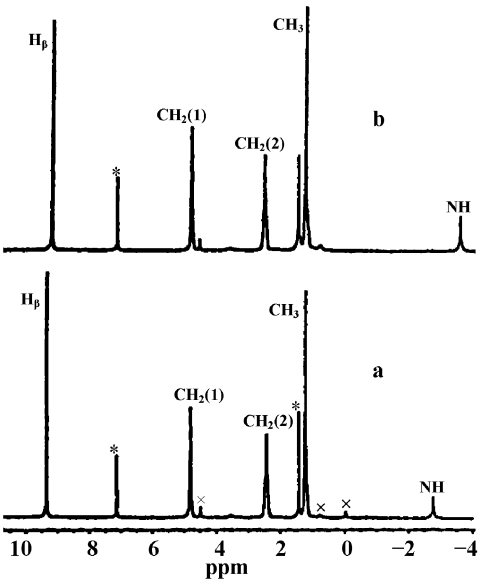


Fig. 5 ^{1}H NMR spectra of (a) H_2t(*n*-Pr)p, (b) $(BF_3)_2H_2$t(*n*-Pr)p in $CDCl_3$ at 25 °C. * and × are impurities of the solvent and the porphyrin, respectively.

Table 2 ^{1}H NMR resonances of free base arylpor, alkylpor and their BF_3 complexes as well as a number of dications[a,b]

Compound	N–H	H_β	$H_o/CH_2(1)$	$H_m/CH_2(2)$	$H_p/CH_2(3)$	CH_3
H_2tpp	−2.77	8.84	8.21–8.24	7.75–7.77	7.75–7.77	—
1 : 2 complex	−2.89	8.79	8.61–8.64	8.02–8.04	8.02–8.04	—
$\Delta\delta_1$	−0.12	−0.05	0.40	0.27	0.27	—
H_4tpp^{2+}	0.35	8.58–8.61	8.58–8.61	7.99	7.99	—
$\Delta\delta_2$	3.08	∼ −0.25	0.37	0.24	0.24	—
H_2t(4-Me)pp	−2.77	8.85	8.08–8.11	7.54–7.56	—	2.70
1 : 2 complex	−2.78	8.73	8.52–8.49	7.82–7.85	—	2.79
$\Delta\delta_1$	−0.01	−0.12	0.42	0.29	—	0.09
H_2t(4-Cl)pp	−2.84	8.84	8.12–8.15	7.73–7.76	—	—
1 : 2 complex	−2.83	8.77	8.51–8.54	8.05–8.02	—	—
$\Delta\delta_1$	0.01	−0.07	0.39	0.29	—	—
H_2tmp	−2.48	8.63	—	7.26	—	1.87[c], 2.64[d]
1 : 2 complex	−3.14	8.72	—	7.36	—	1.94[c], 2.65[d]
$\Delta\delta_1$	−0.66	0.09	—	0.10	—	0.07, 0.01
H_4tmp^{2+}	−0.28	8.57	—	7.35	—	1.93[c], 2.65[d]
$\Delta\delta_2$	2.20	−0.06	—	0.09	—	0.06, 0.01
H_2t(Me)p	−2.39	9.47	—	—	—	4.59
1 : 2 complex	−3.48	9.36	—	—	—	4.65
$\Delta\delta_1$	−1.09	−0.11	—	—	—	0.06
H_4t(Me)p^{2+}	−0.25	9.18	—	—	—	4.58
$\Delta\delta_2$	2.14	−0.29	—	—	—	−0.01
H_2t(Et)p	−2.65	9.50	5.00	—	—	2.14
1 : 2 complex	−3.52	9.37	4.99	—	—	2.20
$\Delta\delta_1$	−0.87	−0.13	−0.01	—	—	0.06
H_4t(Et)p^{2+}	−0.32	9.16	4.93	—	—	2.14
$\Delta\delta_2$	2.33	−0.34	−0.07	—	—	0.00
H_2t(*n*-Pr)p	−2.65	9.48	4.93	2.54	—	1.37
1 : 2 complex	−3.47	9.31	4.90	2.62	—	1.37
$\Delta\delta_1$	−0.82	−0.17	−0.03	0.08	—	0.00
H_4t(*n*-Pr)p^{2+}	−0.21	9.10	4.84	2.48	—	1.32
$\Delta\delta_2$	2.44	−0.38	−0.09	−0.06	—	−0.05
H_2t(*n*-Bu)p	−2.63	9.47	4.95	2.51	1.84	1.14
1 : 2 complex	−3.47	9.30	4.91	2.56	1.87	1.20
$\Delta\delta_1$	−0.84	−0.17	−0.04	0.05	0.03	0.06
H_4t(*n*-Bu)p^{2+}	−0.23	9.10	4.86	2.47	1.78	1.15
$\Delta\delta_2$	2.40	−0.37	−0.09	−0.04	−0.06	0.01
H_2t(*tert*-Bu)p	1.52	9.08	—	—	—	2.01
1 : 2 complex	−0.40	8.14	—	—	—	2.15
$\Delta\delta_1$	−1.92	−0.94	—	—	—	0.14
H_4t(*tert*-Bu)p^{2+}[e]	0.79	8.00	—	—	—	2.08
$\Delta\delta_2$	−0.73	−1.08	—	—	—	0.07

[a] Chemical shifts in ppm relative to $CHCl_3$ (7.26 ppm) impurity in $CDCl_3$ solvent. [b] Since the dication NH and H_β signal positions are sensitive to an excess amount of CF_3COOH,[3b] the spectra were taken under a *strict* 2 : 1 molar ratio of CF_3COOH : por. [c] CH_3(*ortho*). [d] CH_3(*para*). [e] From ref. 3*d*.

arylpor and alkylpor, and also the very small downfield shift ($\Delta\delta$ = 0.01 ppm) of the NH signal for $(BF_3)_2H_2$t(4-Cl)pp (Table 2), compared to those of the parent free base porphyrins, are in complete contrast (Table 2) with the observed large downfield shifts of the NH signals for the 1 : 2 complexes of different *meso*-tetraphenylporphyrins with DDQ ($\Delta\delta$ = 2.34 to 2.62 ppm),[1c] TCNE ($\Delta\delta$ = 1.50 to 1.83 ppm),[1d] and trialkylsilyl chlorides (3.04 to 3.29 ppm),[1e] as well as diprotonation of the free base porphyrins ($\Delta\delta$ = 2.14 to 3.08 ppm).[3b] It should be also pointed out that, contrary to the observed gradual upfield shifts of the NH resonances of H_2por^{2+} with increasing CF_3COOH concentration,[3b] addition of $BF_3 \cdot OEt_2$ caused no changes at all in the positions of the $(BF_3)_2$por NH signals. This effect is presumably related to the possible formation of hydrogen bonds between the coordinated CF_3COOH in the $(CF_3COOH)_2$por adduct with the excess CF_3COOH in solution, as has been observed in the solid state.[3d] It is expected that such hydrogen bonding interactions lead to the weakening of the (N–H···CF_3COO^-) hydrogen bonds in the protonated porphyrins, hence causing an upfield shift of the NH signal.

It appears that the observed NH upfield shifts are inexplicable in terms of the possible saddled deformations of the porphyrin cores, caused by the complexation,[1c,d,e] and their subsequent influence on the porphyrin ring current effects. Apparently, nonplanar distortions of the porphyrin macrocycles are expected to lead to reductions of the ring currents, and cause downfield shifts of the NH proton signals.[3b,8]

We propose that the observed upfield shifts are presumably due to some weakening of the NH hydrogen bonding in the 1 : 2 complexes as compared to those of their corresponding free base porphyrins, and the related protonated porphyrins. Such a weakening of the hydrogen bonding would strengthen the N–H bonds and bring the NH protons closer to the porphyrin ring current, hence leading to an upfield shift of their signals. It is noteworthy that the downfield shift of the NH signal for the ruffled free base H_2t(*tert*-Bu)p (δ = 1.52), as compared to the NH signal of H_2t(*n*-Bu)p (δ = −2.63) with a planar core (Table 2), has also been rationalized in terms of an enhanced intramolecular hydrogen bonding of the NH protons in the former.[9]

Accordingly, the relative positions of the NH signals for $(BF_3)_2$arylpor (δ = −2.78 to −3.14 ppm) and $(BF_3)_2$alkylpor (δ = −3.47 to −3.52 ppm), with the exception of $(BF_3)_2H_2$t (*tert*-Bu)p (δ = −0.4 ppm), suggest stronger N–H···FBF_2

hydrogen bonding in the former compounds. Inversely, it may be concluded that the NH···N hydrogen bonds in the parent free base arylpor (δ = −2.77 to −2.84 ppm), except for H_2tmp (δ = −2.48 ppm), should be weaker than those of the alkylpor (δ = 1.52 to −2.65 ppm). This reversed relationship is presumably due to the relatively greater extent of co-planarity of the phenyl groups with the saddled porphyrin macrocycle in $(BF_3)_2$arylpor than in the related free base arylpor, which leads to a more efficient shift of π-electron density to the porphyrin core in the former.[3g,h] Thus, it seems that in the free base porphyrins σ-donation of the *meso*-alkyl substituents will take precedence over π-donation of the *meso*-aryl groups, causing the pyrrolenine nitrogen donors in the alkylpor to become more basic than those of the arylpor, and hence form stronger NH···N hydrogen bonds.

Consideration of the relative positions of the NH signals for $(BF_3)_2H_2$tmp and the other $(BF_3)_2$arylpor complexes and also for $(BF_3)_2H_2$t(*tert*-Bu)p *versus* the other $(BF_3)_2$alkylpor is interesting. The upfield shifts of the NH signal for $(BF_3)_2H_2$tmp (−0.25 to −0.35 ppm), as compared to the NH resonances of the other $(BF_3)_2$arylpor, may reflect weaker NH···FBF_2 hydrogen bonds in the former. It seems that the lesser flexibility of the bulky H_2tmp core[3h] hinders its possible core nonplanar deformations and effective coordination and hydrogen bonding of BF_3 to the porphyrin macrocycle. On the other hand, the large downfield shifts of the NH signal for $(BF_3)_2H_2$t(*tert*-Bu)p (3.07 to 3.12 ppm) relative to the NH signals for the other $(BF_3)_2$alkylpor may indicate formation of stronger NH···FBF_2 hydrogen bonds in the former. This seems to be consistent with the possible much greater saddling of the porphyrin core in $(BF_3)_2H_2$t(*tert*-Bu)p, as has been observed for the corresponding H_4t(*tert*-Bu)p^{2+} dication,[3d] leading to more effective interactions of BF_3 with the H_2t(*tert*-Bu)p nucleus.

The low temperature ^{1}H NMR spectrum of $(BF_3)_2H_2$tpp (at −78 °C, in CD_2Cl_2) was quite sharp, and showed virtually no changes with respect to that at room temperature (20 °C). However, it only displayed an upfield shift of the NH signal (−0.15 ppm). It may be that the lowering of temperature, which is expected to lead to a less flexible porphyrin core, can cause the NH protons to become less available for effective N–H···FBF_2 hydrogen bonding, and hence an upfield shift of the NH signal may result.

It is noteworthy that an alternative explanation may also be provided for these observations, which is based on the relative extent of nonplanar deformations of the porphyrin macrocycles in the complexes, and their resulting ring current effects. The relatively less nonplanar deformed porphyrin cores, with greater ring currents [*i.e.*, $(BF_3)_2H_2$tmp, and low temperature $(BF_3)_2H_2$tpp solution samples] are expected to give upfield-shifted NH signals. However, it appears that even a large out-of-plane deformation of the porphyrin macrocycles may lead to only a 5% change in the ring current.[8] Thus, it seems that the observed NH signal shifts cannot be solely related to the porphyrin ring current changes, and NH hydrogen bonding presumably plays a significant role.[9]

β-protons. The complexation of arylpor (except H_2tmp) and alkylpor with BF_3 leads to an upfield shift of the β-protons. While nonplanar deformations of the porphyrin cores, generated by the complexation, may reduce the porphyrin macrocycle ring current effects and bring about an upfield shift of the β-protons, the σ-acceptor inductive effects of the coordinated BF_3 molecules are expected to deshield the β-protons and cause a downfield shift of their signals. Therefore, the generally observed upfield shifts of the β-protons for $(BF_3)_2$por indicate that the reduction of the ring current effect upon complexation is more important than the σ-inductive effects of the complexed BF_3 molecules. In contrast, the downfield shift of the β-protons for $(BF_3)_2H_2$tmp suggests the greater importance of the BF_3 σ-inductive effect. This argument seems to be consistent with the lesser flexibility of the H_2tmp core[3h] and its relatively smaller nonplanar deformations upon complexation with BF_3.

Also, the protonation of the porphyrins, including H_2tmp, affords upfield shifts of the β-protons (Table 2). Interestingly, these upfield shifts are larger than those for the porphyrin complexes. These results imply either the occurrence of larger nonplanar deformations of the porphyrins macrocycles during their protonation than during complexation, or a smaller σ-inductive effect of CF_3COOH than BF_3. Very similar positions of the Soret bands for $(CF_3COOH)_2$por and $(BF_3)_2$por may suggest analogous porphyrin core structures in these species. Thus, it might be concluded that BF_3 is a stronger σ-acceptor than the coordinated CF_3COOH. Also, the larger downfield shifts of the *meso*-substituent protons in $(BF_3)_2$por than in $(CF_3COOH)_2$por (Table 2), seem to provide corroborative evidence for the greater σ-acceptor properties of BF_3 than CF_3COOH. High stability of $(BF_3)_2H_2$tpp in the presence of CF_3COOH is consistent with this view. Surprisingly, different molar ratios (1 : 1 to 8 : 1) of CF_3COOH and $(BF_3)_2H_2$tpp in $CDCl_3$, after several days, displayed virtually identical ^{1}H NMR spectra as the intact 1 : 2 adduct. In contrast, a 2 : 1 mixture of $BF_3 \cdot Et_2O$ and $[H_4tpp]^{2+}(CF_3COO)^{2-}$ immediately led to the complete displacement of CF_3COOH and the formation of $(BF_3)_2H_2$tpp.

^{13}C NMR

Table 3 presents ^{13}C NMR chemical shifts of six different arylpor and alkylpor and their BF_3 adducts, as well as H_4tpp^{2+} and H_4t(*n*-Pr)p^{2+}. The ^{13}C NMR spectrum of H_2tpp (Fig. 6, spectrum a) consists of a broad resonance and five sharp signals.[10a,b] The very broad C_α resonance (~145 ppm) is not observable. The complexation of H_2tpp with BF_3 sharpens both C_α (146.40 ppm) and C_β (130.17 ppm) signals (spectrum b in Fig. 6), and leads to small downfield shifts of C_{meso}, C_2', C_3', C_4' and upfield shifts of C_1' and C_β. Diprotonation of H_2tpp and its complexation with DDQ[1c] and TCNE,[1d] also leads to similar changes in the ^{13}C NMR spectrum. The ^{13}C NMR spectral assignment of the arylpor and their 1 : 2 adducts were performed by considering the ^{13}C NMR spectra of H_2tpp[10a,b] and the related $(DDQ)_2$arylpor[1c] and $(TCNE)_2$arylpor complexes.[1d]

Fig. 7 illustrates the ^{13}C NMR spectra of H_2t(*n*-Pr)p and $(BF_3)_2H_2$t(*n*-Pr)p. The positions of C_α, C_β, and C_{meso} signals for the porphyrin core in alkylpor and $(BF_3)_2$alkylpor are closely related to those of arylpor and $(BF_3)_2$arylpor, respectively (Table 3). The assignments of the *meso*-alkyl carbons in $(BF_3)_2$alkylpor were easily made from the ^{13}C NMR of the corresponding free base alkylpor,[10c,d] and on the basis of their relative distances from C_{meso}, while considering the positions and splitting patterns of their corresponding ^{1}H NMR spectra (Table 2). The C_1 and C_1' attached to C_{meso} showed upfield shifts during the complexation of the porphyrins, except for H_2t(*n*-Pr)p.

^{19}F and ^{11}B NMR

The ^{19}F NMR spectrum of $(BF_3)_2H_2$tpp, in $CDCl_3$ or CD_2Cl_2, appears as two sharp peaks with relative intensities approaching a 20 : 80 ratio, at −156.95 ppm ($^{10}BF_3$) and −157.01 ppm ($^{11}BF_3$), between 25 to −90 °C (Fig. 8). Similar ^{19}F NMR spectra were also obtained for the other $(BF_3)_2$por and the reference $BF_3 \cdot Et_2O$[11] in $CDCl_3$ (Table 4). $(BF_3)_2H_2$tmp displayed only a single rather broad ^{19}F NMR signal at −156.91 ppm, presumably consisting of both $^{10}BF_3$ and $^{11}BF_3$ peaks. The observation of a single ^{11}B NMR line (−6.48 to −6.71 ppm) for various $(BF_3)_2$por (Table 4), may indicate the

Table 3 ^{13}C NMR chemical shifts of some free base arylpor, alkylpor, and their BF_3 adducts as well as two porphyrin dications[a]

Compound	C_α[b]	C_β[b]	C_{meso}	C_1'/C_1	C_2'/C_2	C_3'/C_3	C_4'/C_4
H_2tpp	—	131.50	120.55	142.58	134.97	127.09	128.11
H_4tpp^{2+}	145.20	127.70	122.10	139.40	137.90	127.70	129.40
$\Delta\delta$	—	−3.80	1.55	−3.18	2.93	0.61	1.29
$(BF_3)_2H_2tpp$	146.40	130.17	123.80	139.73	139.07	128.95	130.91
$\Delta\delta$	—	−1.33	3.25	−2.85	4.10	1.86	2.80
H_2t(4-Me)pp	—	131.37	120.47	139.73	134.92	128.71	137.71
$(BF_3)_2H_2t$(4-Me)pp	146.48	129.80	123.48	137.32	139.15	129.80	141.42
$\Delta\delta$	—	−1.57	3.01	−2.41	4.23	1.09	3.71
H_2t(4-Cl)pp	—	131.64	119.38	140.75	135.89	127.45	134.79
$(BF_3)_2H_2t$(4-Cl)pp	146.49	130.23	120.95	138.55	139.86	129.56	138.07
$\Delta\delta$	—	−1.41	1.57	−2.20	3.97	2.11	3.28
H_2tmp	—	130.89	117.97	138.67	139.87	128.10	138.03
$(BF_3)_2H_2tmp$	146.06	129.82	121.03	135.27	140.84	128.99	140.84
$\Delta\delta$	—	−1.07	3.06	−3.40	0.97	0.89	2.81
H_2t(*n*-Pr)p	—	129.70	118.52	37.79	31.98	15.37	—
$(BF_3)_2H_2t$(*n*-Pr)p	145.06	127.22	122.21	38.69	31.49	15.16	—
$\Delta\delta$	—	−2.48	3.69	0.90	−0.47	−0.19	—
H_4t(*n*-Pr)p^{2+}	144.74	126.14	121.79	38.52	31.31	15.04	—
$\Delta\delta$	—	−3.55	3.67	0.73	−0.67	0.33	—
H_2t(*n*-Bu)p	—	128.59	118.74	41.18	35.64	24.08	14.62
$(BF_3)_2H_2t$(*n*-Bu)p	144.99	127.17	122.47	40.60	36.82	24.08	14.47
$\Delta\delta$	—	−1.42	3.75	−0.58	1.18	0.00	−0.15

[a] Chemical shifts (ppm) are downfield from $CDCl_3$ (76.90–77.92 ppm) at 25 °C. [b] For the free base porphyrins C_α is indistinguishable from the baseline noise and C_β gives a broad signal.

equivalence of the BF_3 in these 1 : 2 adducts. Coordination of BF_3 to the porphyrins caused upfield shifts of the ^{19}F [$\Delta\delta$ = −3.60 to −4.20 ppm ($^{10}BF_3$) and $\Delta\delta$ = −3.53 to −4.19 ($^{11}BF_3$)] and ^{11}B ($\Delta\delta$ = −6.48 to −6.71 ppm) signals relative to the corresponding signals of $BF_3 \cdot OEt_2$ (Table 4). The larger upfield shift of ^{11}B than of ^{19}F presumably reflects the shorter distance of the former from the nitrogen donor site and the greater influence of the porphyrin ring current.

Ab initio calculations

The results of *ab initio* calculations suggested that in $(BF_3)_2H_2tpp$ the two BF_3 molecules are coordinated from above and below the mean H_2tpp plane, and that the *cis*-$(BF_3)_2H_2tpp$ isomer is more stable (4.3 kcal mol^{-1}) than the *trans* one (Fig. 9). The porphyrin core in the *cis* isomer is

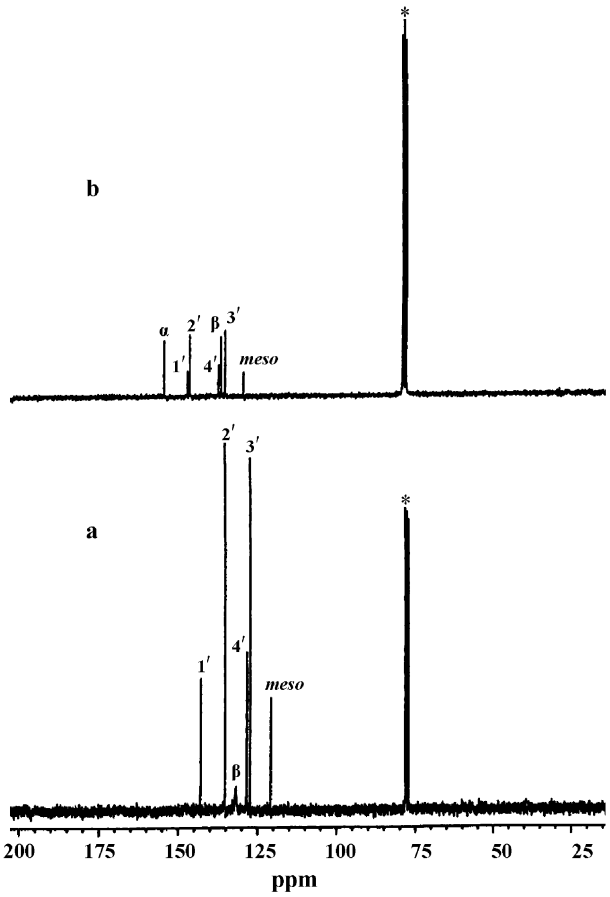


Fig. 6 ^{13}C NMR spectra of (a) H_2tpp and (b) $(BF_3)_2H_2tpp$ in $CDCl_3$, at 25 °C. * denotes solvent impurities.

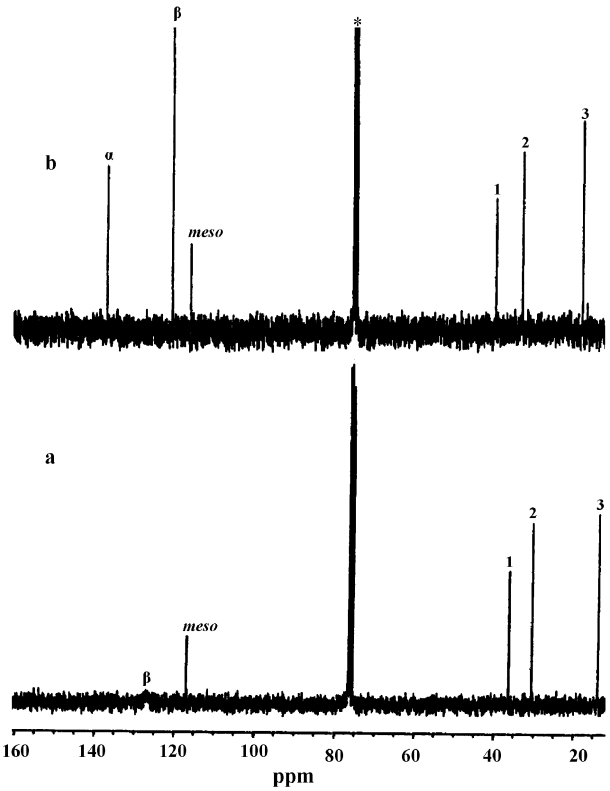


Fig. 7 ^{13}C NMR spectra of (a) H_2t(*n*-Pr)p and (b) $(BF_3)_2H_2t$(*n*-Pr)p in $CDCl_3$, at 25 °C. * denotes solvent impurities.

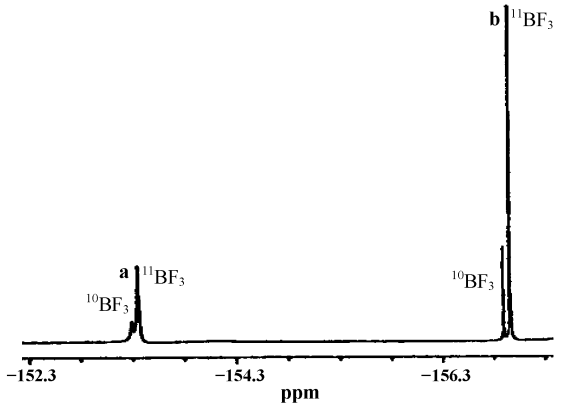


Fig. 8 ^{19}F NMR of $(BF_3)_2H_2tpp$ (b) in the presence of excess $BF_3 \cdot Et_2O$ (a) in $CDCl_3$ at 25 °C.

saddled with NH groups *cis* to one another, whereas in the *trans* isomer the two adjacent pyrroles are tilted upwards and the other two downwards, with the NH groups *trans*. On each face of H_2tpp one BF_3 molecule is σ-bonded to a pyrrolenine nitrogen donor through its B center, and is simultaneously hydrogen bonded through one of its fluorine atoms to a pyrrole NH group ($NH\cdots FBF_2$), located either on the opposite (*cis* isomer) or adjacent (*trans* isomer) site. An *ab initio* quantum mechanical calculation as well as a geometry optimization of H_2tpp for coordination with BF_3 were performed using the DFT method[12] (B3LYP/6-31g*). Full optimization of $(BF_3)H_2tpp$ and $(BF_3)_2H_2tpp$ donor-acceptor complexes showed that in both cases the B–N chemical bond, with an approximate length of 1.66 Å, and $F\cdots H$ intermolecular hydrogen bond of about 1.7 Å, are present. Calculations show that coordination of a BF_3 molecule to the 1 : 1 complex is more favorable (2.4 kcal mol^{-1}) than its addition to a free base H_2tpp, and the resulting 1 : 2 complex is more stable (14.5 kcal mol^{-1}) than the 1 : 1 adduct. This is in complete accord with our experimental results that only 1 : 2 molecular complexes are formed. The optimized geometries for both the *cis*- and *trans*-$(BF_3)_2H_2tpp$ structures are sketched in Fig. 9. The chemical bonds formed between B and N atoms and the intermolecular hydrogen bonds between two fluorines and the two pyrrole NH groups confirm strong interactions in $(BF_3)_2H_2tpp$, and explain the occurrence of a highly distorted porphyrin core in this adduct.

It is notable, however, that a very recent theoretical study on the complexation of porphine with BF_3 has demonstrated that *trans*-$(BF_3)_2$porphine is the most stable species.[13] Apparently, the *meso*-phenyl substituents in $(BF_3)_2H_2tpp$ have a definite effect on the preference for a *cis*-$(BF_3)_2H_2tpp$ structure over the *trans* one.

Postulated mechanism

The formation of the $(BF_3)_2$por adduct must pass through the 1 : 1 intermediate complex. However, the absence of UV-vis and NMR spectral evidence for such species, similar to the absence of a 1 : 1 adduct in the protonation of porphyrins,[3f,g] may reflect a very short lifetime and low concentration of the 1 : 1 complex. It is also observed that in a highly diluted solution ($<10^{-7}$ M), $(BF_3)_2$por is partially dissociated and the UV-vis bands of the corresponding free base porphyrins start to grow in upon further dilution, with no sign of occurrence of the 1 : 1 complex.

Table 4 ^{19}F and ^{11}B NMR spectral data for $(BF_3)_2$arylpor and $(BF_3)_2H_2$(*n*-Pr)p

Compound	^{11}B NMR	^{19}F NMR
$BF_3 \cdot Et_2O$	0.00	−153.31[a], −153.38[b]
$(BF_3)_2H_2tpp$	−6.48	−156.95[a], −157.01[b]
Δδ		−3.64[a], −3.63[b]
$(BF_3)_2H_2tmp$	−6.54	−156.91
Δδ		∼ −3.60[a], ∼ −3.53[b]
$(BF_3)_2H_2t$(4-Cl)pp	−6.71	156.96[a], −157.02[b]
Δδ		−3.65[a], −3.64[b]
$(BF_3)_2H_2t$(*n*-Pr)p	−6.61	−157.51[a], −157.57[b]
Δδ		−4.20[a], −4.19[b]

[a] $^{10}BF_3$ fluorines. [b] $^{11}BF_3$ fluorines.

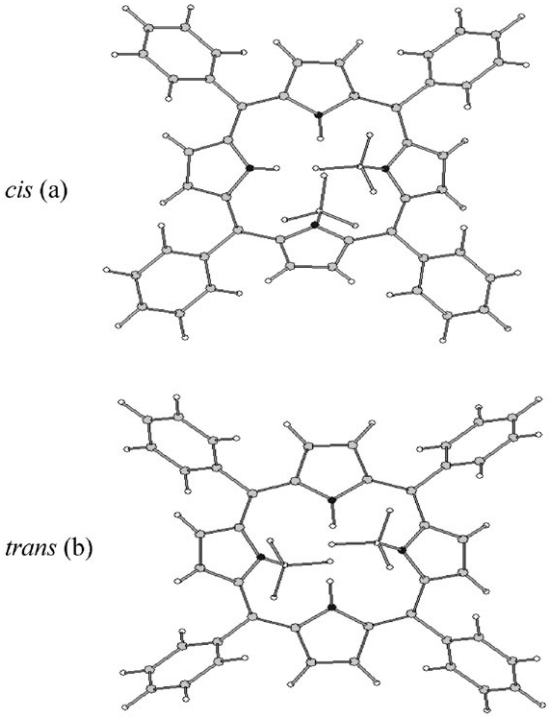


Fig. 9 Possible structures of *cis*- and *trans*-$(BF_3)_2H_2tpp$.

In the "planar" free base porphyrins, the pyrrolenine nitrogen donors are directed towards the center of the macrocycle and are strongly hydrogen bonded to the pyrrole NH groups.[9,14] The interaction of a free base porphyrin with a single BF_3 molecule and the formation of a 1 : 1 adduct apparently requires a relatively important nonplanar deformation of the porphyrin core and substantial perturbation of the intramolecular hydrogen bonds. Thus, the 1 : 1 complexation process should be associated with a high energy barrier and be rather slow.[3f,g] This step presumably will make the other pyrrolenine nitrogen donor and pyrrole NH group, on the open face of the porphyrin macrocycle, more accessible for interaction with an incoming BF_3. Hence, addition of a second BF_3 to the 1 : 1 adduct is greatly facilitated and should be much faster than the 1 : 1 complexation process. On the other hand, the observed "direct" partial dissociation of $(BF_3)_2$por into the free base porphyrin and BF_3, under very high dilution, indicates that the rather energetic 1 : 1 intermediate adduct, in the absence of a sufficient concentration of BF_3 in its immediate surroundings, easily collapses into its molecular components. Accordingly, the following equilibrium system is proposed for the complexation reaction:

$$\text{por} \underset{\text{fast}}{\overset{BF_3,\ \text{slow}}{\rightleftharpoons}} BF_3\text{por} \underset{\text{slow}}{\overset{BF_3,\ \text{fast}}{\rightleftharpoons}} (BF_3)_2\text{por}$$

Possible rapid proton exchange among the four central nitrogens in the free base porphyrins, and/or between the pyrrole and pyrrolenine nitrogens on the open face of the 1 : 1 intermediate adduct, followed by a rapid re-association of BF_3 with a new nitrogen donor site, may provide plausible pathways for the observation of the symmetric NMR spectra

for the pyrrole rings and for the fluorines of the coordinated BF_3 molecules in $(BF_3)_2$por.

The observation of separate sharp and distinct ^{19}F NMR signals for the coordinated BF_3 molecules in CD_2Cl_2 solution of $(BF_3)_2H_2$tpp (−156.95, −157.01 ppm) and $BF_3 \cdot OEt_2$ (−153.31, −153.38 ppm), between −90 to 25 °C, Fig. 8, implies that within this temperature range (i) there is no exchange of BF_3 between $BF_3 \cdot OEt_2$ and $(BF_3)_2H_2$tpp species in the solution, on the NMR time scale, (ii) the dissociation of $(BF_3)_2H_2$tpp into BF_3, BF_3H_2tpp, and H_2tpp components is followed by a very fast re-formation of $(BF_3)_2H_2$tpp within the solvent cage, and (iii) the concentrations of free BF_3 and BF_3H_2tpp in the solvent cage are too small to be detected by NMR.

Conclusions

Reaction of arylpor and alkylpor with $BF_3 \cdot OEt_2$ in chloroform immediately and exclusively produce highly stable $(BF_3)_2$por adducts. The spectral properties of $(BF_3)_2$por, seconded by results of *ab initio* calculations, indicate that BF_3 molecules are located above and below the plane of a saddled porphyrin core; each BF_3 is coordinated to a pyrrolenine nitrogen donor and simultaneously hydrogen bonded to an opposite pyrrole NH group of the porphyrin. The observed "unusual" upfield shifts of the NH signal in the $(BF_3)_2$por complexes relative to those of the corresponding free base porphyrins and $(CF_3COOH)_2$por species are suggestive of weaker hydrogen bonds with the NH groups in the BF_3 complexes. Rapid reaction of $BF_3 \cdot OEt_2$ with $(CF_3COOH)_2$por and formation of $(BF_3)_2$por complexes in chloroform indicate a much stronger bonding ability of BF_3 than CF_3COOH to free base porphyrins.

Experimental

The synthesis and purification of H_2t(4-Me)pp,[15a] H_2t(4-OMe)pp,[15a] H_2tpp,[15b] H_2t(4-Cl)pp,[15b] H_2tmp,[15c] H_2t(Me)p,[15d] H_2t(Et)p,[15d] H_2t(*n*-Pr)p,[15d] H_2t(*n*-Bu)p,[15e] and H_2t(*tert*-Bu)p[5e] were carried out following literature methods. Acetaldehyde, benzaldehyde, substituted benzaldehyde (4-Cl, 4-Me, 2,4,6-triMe), propionaldehyde, butyraldehyde, *n*-valeraldehyde (Merck, Fluka) and pivaldehyde (Aldrich) were used as received. Pyrrole (Fluka) was distilled before use. Trifluroacetic acid ($\geq$ 98%, Fluka) and $BF_3 \cdot OEt_2$ (for synthesis, Merck) were used as received. Dichloromethane, which was used for the synthesis of the 1 : 2 complexes, was washed with 5% aqueous sodium carbonate and water,[16] then dried over anhydrous calcium chloride and distilled over CaH_2.

The mass spectrum of $(BF_3)_2H_2$tpp (MW = 750.36) showed a peak at m/z 750.62 (M^+). The results of elemental analyses for $(BF_3)_2H_2$tpp and $(BF_3)_2H_2$t(*n*-Pr)p complexes, which were prepared in CH_2Cl_2 and dried under dynamic vacuum for 24 h, were consistent with $C_{44}H_{30}N_4B_2F_6 \cdot CH_2Cl_2$: calcd C, 64.70; H, 3.86; N, 6.70 (found: C, 64.74; H, 4.39; N, 6.85), and $C_{32}H_{38}N_4B_2F_6 \cdot 0.5\ CH_2Cl_2$: calcd C, 59.44; H, 5.98; N, 8.53 (found: C, 58.61; H, 6.17 N, 8.50), respectively.

^1H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX 250 MHz spectrometer. ^{19}F NMR, and ^{11}B NMR were recorded on a Bruker Avance DRX 500 MHz spectrometer in $CDCl_3$ or CD_2Cl_2. Mass spectra of H_2tpp$(BF_3)_2$ was recorded in a Kratos Kompact MALDI III. Elemental analyses were performed with a CHN-O-Rapid Foss-Heraeus analyzer. The electronic absorption spectra were recorded in chloroform solutions utilizing a Multispect-1501 Shimadzu within the wavelength range of 350 to 750 nm.

Acknowledgements

This work was supported by the Shiraz University Research Council under project 79-SC-1370-C 123.

References

1 (*a*) Y. Aoyama, M. Asakawa, Y. Matsui and H. Ogoshi, *J. Am. Chem. Soc.*, 1991, **113**, 6233; (*b*) T. Hayashi and H. Ogoshi, *Chem. Soc. Rev.*, 1997, **26**, 355; (*c*) D. Mohajer and H. Dehghani, *J. Chem. Soc., Perkin Trans. 2*, 2000, 199; (*d*) D. Mohajer and H. Dehghani, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1477; (*e*) D. Mohajer and S. Rayati, *New J. Chem.*, 2003, **27**, 242; (*f*) K. Kano, T. Hayakawa and S. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 778; (*g*) V. G. Maslov, T. P. Prokofeva and A. N. Sidorov, *Zh. Fiz. Khim.*, 1984, **58**, 381.

2 (*a*) C. J. Carrano and M. Tsutsui, *J. Coord. Chem.*, 1977, **7**, 125; (*b*) W. J. Belcher, P. D. W. Boyd, P. J. Brothers, M. J. Liddell and C. E. F. Rickard, *J. Am. Chem. Soc.*, 1994, **116**, 8416; (*c*) W. J. Belcher, M. Breede, P. J. Brothers and C. E. F. Rickard, *Angew. Chem., Int. Ed.*, 1998, **37**, 1112; (*d*) A. Weiss, H. Pritzkow, P. J. Brothers and W. Siebert, *Angew. Chem., Int. Ed.*, 2001, **40**, 4182; (*e*) T. Kohler, M. C. Hodgson, D. Seidel, J. M. Veauthier, S. Meyer, V. Lynch, P. D. W. Boyd, P. J. Brothers and J. L. Sessler, *Chem. Commun.*, 2004, 1060.

3 (*a*) M. Meot-Ner and A. D Adler, *J. Am. Chem. Soc.*, 1975, **97**, 5107; (*b*) R. I. Walter, E. C. A. Ojadi and H. Linschitz, *J. Phys. Chem.*, 1993, **97**, 13308; (*c*) E. C. A. Ojadi, H. Linschitz, M. Gouterman, R. I. Walter, J. S. Lindsey, R. W. Wagner, P. R. Droupadi and W. Wang, *J. Phys. Chem.*, 1993, **97**, 13192; (*d*) M. O. Senge, *Z. Naturforsch., B: Chem. Sci.*, 2000, **55**, 336; (*e*) A. Rosa, G. Ricciardi, E. J. Baerends, A. Romeo and L. M. Scolaro, *J. Phys. Chem. A*, 2003, **107**, 11468; (*f*) E. B. Fleischer and A. L. Stone, *J. Chem. Soc., Chem. Commun.*, 1967, 332; (*g*) A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735; (*h*) B. Chenge, O. Q. Munro, H. M. Marques and R. Scheidt, *J. Am. Chem. Soc.*, 1997, **119**, 10732.

4 T. Ema, M. O. Senge, N. Y. Nelson, H. Ogoshi and K. M. Smith, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1879.

5 (*a*) M. Ravikanth and T. K. Chandrashkar, *Struct. Bonding*, 1995, **82**, 105; (*b*) J. Takeda, T. Ohaya and M. Sato, *Chem. Phys. Lett.*, 1991, **183**, 384; (*c*) J. L. Retsek, S. Gentemann, C. J. Medforth, K. M. Smith, V. S. Chirvony, J. Fajer and D. Holten, *J. Phys. Chem. B*, 2000, **104**, 6690; (*d*) S. Gentemann, C. J. Medforth, T. P. Forsyth, D. J. Nurco, K. M. Smith, J. Fajer and D. Holten, *J. Am. Chem. Soc.*, 1994, **116**, 7363; (*e*) M. O. Senge, I. Bischoff, N. Y. Nelson and K. M. Smith, *J. Porphyrins Phthalocyanines*, 1999 **3**, 99.

6 S. G. Dimagno, A. K. Wertsching and C. R. Ross, *J. Am. Chem. Soc.*, 1995, **117**, 8279.

7 M. Gouterman, *J. Mol. Spectrosc.*, 1961, **6**, 138.

8 C. J. Medforth, C. M. Muzzi, K. M. Shea, K. M. Smith, R. J. Abraham, S. Jia and J. A. Shelnutt, *J. Chem. Soc., Perkin Trans. 2*, 1997, 839.

9 M. S. Somma, C. J. Medforth, N. Y. Nelson, M. M. Olmstead, R. G. Khoury and K. M. Smith, *Chem. Commun.*, 1999, 1221.

10 (*a*) R. J. Abraham, G. E. Hawkes, M. F. Hudson and K. M. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1975, 204; (*b*) A. Gradillas, C. del Campo, J. V. Sinisterrra and E. F. Llama, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2611; (*c*) L. Frydman, A. C. Olivieri, L. E. Diaz, B. Frydman, F. G. Morin, C. L. Mayne, D. M. Grant and A. D. Adler, *J. Am. Chem. Soc.*, 1988, **110**, 336; (*d*) L. Frydman, A. C. Olivieri, L. E. Diaz, A. Valasinas and B. Frydman, *J. Am. Chem. Soc.*, 1988, **110**, 5651.

11 R. S. Drago, *Physical Methods for Chemists*, Saunders College Publishing, Philadelphia, 2nd edn., 1992, p. 235.

12 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

13 H. R. Khavasi, M. Zahedi, S. Shahbazian, N. Safari, S. Weng Ng and D. Mohajer, *Chem. Phys.*, 2004, **301**, 1.

14 E. B. Fleischer, *Acc. Chem. Res.*, 1970, **3**, 105.

15 (*a*) A. M. d'A. Rocha Gonsaves, J. M. T. B. Varejao and M. M. Pereira, *J. Heterocycl. Chem.*, 1991, **28**, 635; (*b*) A. D. Adler, *J. Org. Chem.*, 1967, **32**, 476; (*c*) P. Hoffmann, A. Robert and B. Meunier, *Bull. Soc. Chem. Fr.*, 1992, **129**, 85; (*d*) S. Neya and N. Funasaki, *J. Heterocycl. Chem.*, 1997, **34**, 689.

16 A. I. Vogel, *Textbook of Practical Organic Chemistry*, Longman, London, 3rd edn., 1957, p. 174.