N-Methyltetraphenylporphyrin with an Inverted *N*-Methylpyrrole Ring: The First Isomer of *N*-Methyltetraphenylporphyrin

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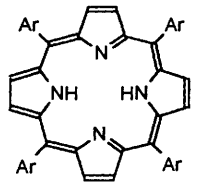
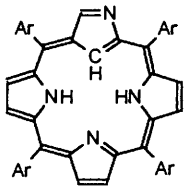
In the course of the mild methylation of 5,10,15,20-tetraphenyl-21-carbaporphyrin ($CTPPH_2$) a novel isomer of *N*-methyl-5,10,15,20-tetraphenylporphyrin with an inverted *N*-methylated pyrrole ring, *i.e.* 2-*N*-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin ($2\text{-}NCH_3TPPH$) has been synthesised. The protonation of $2\text{-}NCH_3CTPPH$ proceeds stepwise including mono- and two di-cationic species. $2\text{-}NCH_3CTPPH$ can be considered as a new anion-specific binding agent. The lability of the 21-CH proton afforded the easy insertion of nickel(II) to form a stable organometallic macrocyclic complex.

Since its synthesis by Rothemund,[1] 5,10,15,20-tetraphenylporphyrin and its substituted analogues are ubiquitous as models of co-ordination centres in biomimetic chemistry[2,3] and investigations on metalloporphyrin catalysed oxidation.†[4] In spite of extensive studies of tetraarylporphyrins (*e.g.* 5,10,15,20-tetra-*p*-tolylporphyrin, $TTPH_2$),[5] its isomeric form: 2-aza-21-carba-tetra-*p*-tolylporphyrin ($CTTPH_2$) has been only recently discovered.[6,7]



$TTPH_2$



$CTTPH_2$

Ar = *p*-tolyl

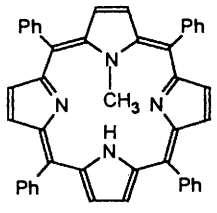
To the best of our knowledge only two other types of porphyrin isomers are known: [2.0.2.0] porphyrin (porphycene) and [2.1.0.1] porphyrin (corrphycene).[8-10]

With replacement of the pyrrolenine nitrogen by a methine group, the macrocycle retains co-ordination properties as demonstrated by the formation of the diamagnetic nickel(II) complex, $(CTTP)Ni^{II}$.[6] The unusual lability of the inner C–H bond is a prerequisite of the 21-carbaporphyrin co-ordination to produce the relatively robust $C\text{–}Ni^{II}$ bond.[6]

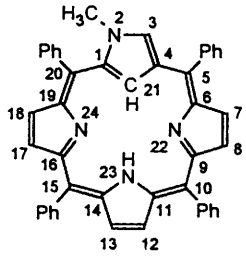
In this paper we present the synthesis and spectral characterisation of the outer *N*-methylated derivative, 2-methyl-2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin ($2\text{-}NCH_3CTPPH$), and its nickel(II) complex and comment on their relation to regular *N*-methylated counterparts (NCH_3TPPH).[11-16]

Despite the fact that $CTPPH_2$ is geometrically similar to the TPP dianion (P^{2-}),[6] it might differ in its net core charge as a ligand (P^{3-}) because it is capable of losing three inner protons (21-CH, 22-NH, 24-NH). Formally, the 21-carbaporphyrin

† Abbreviations: $2\text{-}NCH_3CTPP$ ($2\text{-}NCH_3CTPPH$) 2-methyl-2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin dianion; $2\text{-}NCH_3CTTP$ ($2\text{-}NCH_3CTTPH$) 2-methyl-2-aza-5,10,15,20-tetra(*p*-tolyl)-21-carbaporphyrin dianion; NCH_3TPP (NCH_3TPPH) *N*-methyl-5,10,15,20-tetraphenylporphyrin anion; CTPP ($CTPPH_2$) 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin dianion; CTTP ($CTTPH_2$) 2-aza-5,10,15,20-tetra-(*p*-tolyl)-21-carbaporphyrin dianion; TPP ($TPPH_2$) 5,10,15,20-tetraphenylporphyrin dianion; TTP ($TTPH_2$) 5,10,15,20-tetra-(*p*-tolyl)-porphyrin dianion; TFA (TFAH) anion of trifluoroacetic acid; DCA (DCAH) anion of dichloroacetic acid. The abbreviations for the neutral forms are given in parentheses.

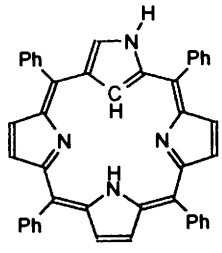


NCH_3TPPH



$2\text{-}NCH_3CTPPH$

ligand, as found for $(CTPP)Ni^{II}$, is structurally related to one of the feasible, although experimentally not encountered, tautomers of $CTPPH_2$, *i.e.* 2-NHCTPPH.



2-NHCTPPH

This tautomer presents strongly marked, pyrrolic nature of the inverted ring. In this form only two inner protons 21-CH and 23-NH are available for the inner dissociation to create a dianion. We have noticed that $2\text{-}NCH_3CTPPH$ would provide an analogous, conveniently preorganised structure for the similar co-ordination pattern.

Results and Discussion

Synthesis and Characterisation of N-*Methylcarbaporphyrin.*—2-*N*-methylcarbaporphyrin can be prepared in high yields by an adaptation of the methods routinely applied for *N*-methylated porphyrins.[11,14-17]

To achieve optimum selectivity for the 2-N position, we chose methyl iodide [eqn. (1)].

$$CTPPH_2 + CH_3I \longrightarrow 2\text{-}NCH_3CTPPH + HI \quad (1)$$

Although no effort was made to optimise the yield, the selectivity of this methylation was practically quantitative, determined by the ^1H NMR spectroscopy. The difference in the

reactivity between the inner and outer nitrogens is caused by (*a*) the steric protection provided by the porphyrin crevice, which restricts an access to the inner nitrogen and (*b*) the deformation of the porphyrin ring caused by methylation of the inner nitrogen.[11,12] In the studies on 21-carbaporphyrin protonation mechanism[6] we have demonstrated that the first step involves exclusively the outer nitrogen, confirming its more nucleophilic character.

An electronic spectrum of 2-NCH_3CTPPH is porphyrin-like with the most intense band around 450 nm corresponding to the Soret band of the regular porphyrin (Fig. 1). The most characteristic Q band is strongly red-shifted and located at 710 nm.

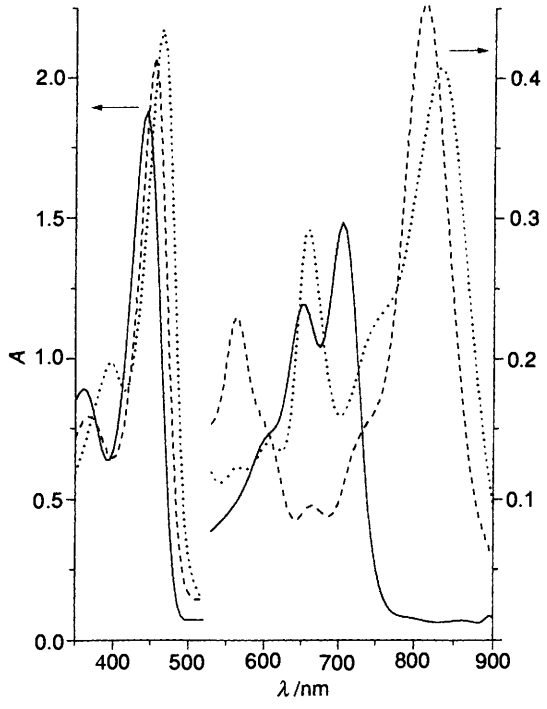


Fig. 1 Electronic spectra of dichloromethane solution obtained in the course of titration with TFAH at 293 K; solid line, 2-NCH_3CTPPH; dashed line, 2-$NCH_3CTPPH_2^+$; dotted line, 2-$NCH_3CTPPH_3^{2+}$

The ^{1}H NMR spectrum of 2-NCH_3CTTPH shows three AB patterns of regular pyrrole protons (Fig. 2, Table 1). The fourth inverted *N*-methyl pyrrole ring shows a 3-H doublet upfield of the typical porphyrin pyrrole position (7.270 ppm, CD_2Cl_2, 295 K). The resonance of 23-NH (the proton located on inner macrocycle perimeter) gave a broadened singlet at 3.074 ppm at 203 K. The definitive confirmation of the structure is provided by the unique inner 21-CH resonance (0.434 ppm, CD_2Cl_2) of the inverted *N*-methylated pyrrole ring. This and the outer 3-H protons are scalar coupled ($^4J_{HH}$ = 1.7 Hz). The 23-NH proton of 2-NCH_3CTPPH can be readily exchanged by deuterium of D_2O leaving only the 21-CH resonance of 2-NCH_3CTPPD in the upfield region. The methyl of the inverted *N*-methylated pyrrole ring gives the resonance at 3.434 ppm (CD_2Cl_2, 295 K), strongly downfield of the signal that regular *N*-substituted porphyrins usually exhibit (*e.g.* −4.322 ppm for NCH_3-TPPH).[11,12,17,18] One would expect a similar N–CH_3 peak position also in the case of carbaporphyrin, if the inner methylation took place. Thus, the chemical shift of the N-methyl of 2-NCH_3CTPPH is clearly associated with the location of the *N*-methyl group at the porphyrin periphery.

The 2-NCH_3CTPPH preserves the aromaticity. All outer pyrrole and phenyl resonances demonstrate downfield shifts due to the ring current effect. The remarkable shift difference of about 7 ppm between outer and inner pyrrolic resonances reflects their location in the deshielding or shielding zones of the aromatic macrocycle. However, we have noticed that the downfield shift of the regular pyrrole resonances and the upfield shifts of the 23-NH and 21-CH are less pronounced than those found for $CTPPH_2$ (Table 1). Evidently the *N*-methylated porphyrin is less aromatic than its parental macrocycle.

The straightforward assignments of proton-bearing carbons have been carried out through the 2D ^{1}H-^{13}C correlation experiment (Table 2). The resonance of 21-C (106.0 ppm) is well separated from the cluster of the other aromatic carbon resonances and presents the unique spectroscopic feature for the identification of the carbaporphyrin macrocycle using ^{13}C NMR. In this specific case the position of the methyl resonance (38.8 ppm) is also crucial. The relevant ^{13}C NMR spectrum of

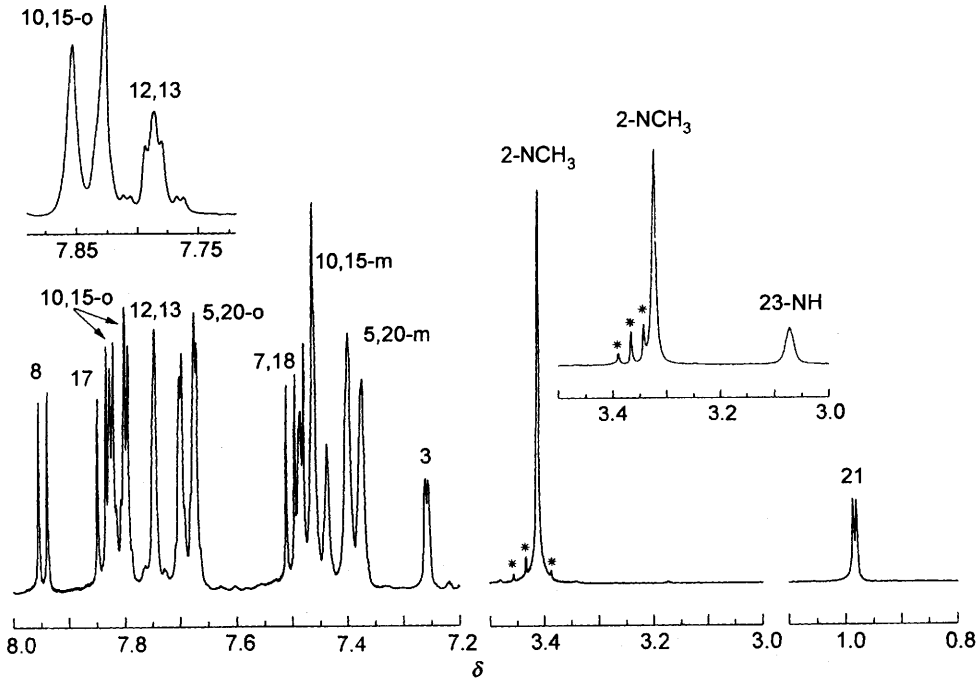


Fig. 2 The 300 MHz ^{1}H NMR spectrum of a [$^2H_2$]dichloromethane solution at 293 K of 2-NCH_3CTTPH. Two insets show fragments of the spectrum measured at 213 K. The complex pattern of 12,13-CH resonances reflects four-bond coupling to 23-NH. Peaks labels follow Scheme 1.

Table 1 ^{1}H NMR Data for the CD_2Cl_2 solutions of 2-NCH_3CTTPH, 2-NCH_3CTPPH, NCH_3TPPH and (2-NCH_3CTPP)Ni^{II} (*J* values given in Hz)

Compound (temperature)	2-CH_3	3	7	8	12	13	17	18	21	24	*p*-CH_3	*o*	*m*
2-NCH_3CTTPH (293 K)	3.434	7.270 d $^4J_{HH}$ 1.7	7.515 J_{AB} 4.7	7.958	7.768[a] J_{AB} 4.7	7.783[a]	7.853 J_{AB} 4.65	7.477	0.984 d	3.43[b]	2.577 2.554	(10,15) 7.833 m 7.812 m (5,20) 7.709 m 7.687 m	(10,15) 7.498 7.449 (5,20) 7.412 7.386
2-NCH_3CTTPH (213 K)	3.445	7.116	7.538 J_{AB} 4.7	8.026	7.779[a] J_{AB} 4.7 $^4J_{HH}$ 1.7	7.792[a]	7.909 J_{AB} 4.5	7.499	0.434 d $^4J_{HH}$ 1.7	3.074	2.542 2.329 2.510	(10,15) 7.857 7.830 (5,20) 7.694 7.672	(10,15) 7.491 7.468 (5,20) 7.399 7.373
2-NCH_3CTPPH (203 K)	3.311	7.206	7.57	8.054	7.80		7.996 J_{AB} 4.6	7.530	0.314	2.941	—	(10,15) 7.97 m (10,20) 7.83 m	7.68 m 7.66 m 7.57 m
NCH_3TPPH (223 K)	—	7.513	8.666[a] J_{AB} 4.5	8.470[a]	8.911		8.470[a]	8.666[a]	−4.332[c]	−2.55	—	(5,20) 8.65 8.23 (10,15) 8.28 8.24	(5,20) 7.91 m (10,15) 7.79 m
(2-NCH_3CTPP)Ni (293 K)	3.570	8.380	8.082 J_{AB} 5.0	7.81	7.946 J_{AB} 5.0	7.914	7.83 J_{AB} 5.0	7.771	—	—	—	7.84–7.80	7.64–7.58

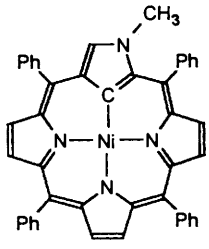
[a] The unequivocal signal assignment to the particular position could not be accomplished due to the overlap or broadness of the *ortho* resonances of neighbouring *meso* phenyls. [b] The signal is hidden under the 2-NCH_3 resonance and its position has been identified on the basis of the COSY cross peak showing scalar coupling with β-pyrrole protons in the positions 12 and 13. [c] *N*-methyl protons.

Table 2 Selected ^{13}C NMR data for 2-NCH_3CTPPH, NCH_3TPPH and CTPPH in $CDCl_3$ solutions at 293 K

	δ		
	2-NCH_3CTPP	$CTPPH_2$	NCH_3TPPH
C-3	136.2	156.0	118.3
C-7	130.4	128.3	132.6
C-8	134.8	126.4	133.9
C-12/13	129.3, 129.0	134.6	128.2
C-17	133.5	125.5	133.9
C-18	130.8	128.0	132.6
C-21	106.0	99.2	—
2-NCH_3	38.8	—	31.6
o	(10, 15) 135.0, 134.6 (5, 20) 133.4	136.9, 135.0	135.6, 134.1
m, p	128.3, 127.9 127.7, 127.2 126.7	128.1, 127.8 127.6, 127.4 127.0	127.9, 127.5 127.1, 126.7

NCH_3TPPH shows the inner N-CH_3 resonance at 31.6 ppm. The comparison of the inverted pyrrole (*N*-methylpyrrole) and its regular counterpart offers an analytically useful criterion. The established differences of the ^{13}C chemical shifts for β-carbons of *N*-methylated pyrrole ring ($CH_{ext.}$ − $CH_{int.}$) and methyl resonances ($NCH_{3ext.}$ − $NCH_{3int.}$) are equal to 12.3 and 7.2 ppm respectively. These changes arise mostly from the ring current effect. The ^{13}C NMR spectrum reflects also the effect of the pronounced reduction of the aromaticity of 2-NCH_3-CTPPH when compared with that of $CTPPH_2$ (Table 2). The signal of the inner C-21 is shifted about 7 ppm downfield while the position of the resonance of the outer carbon of the inverted pyrrole, *i.e.* C-3 is shifted 20 ppm upfield, with respect to the appropriate carbon resonances of $CTPPH_2$.

Formation of Nickel(II) *Complex*.—The double dissociation of the 2-NCH_3CTPPH inner 21-CH and 23-NH protons would result in the dianionic ligand resembling structurally 2-NH-CTPP and TPP dianions. We have found, that insertion of nickel(II) in this preorganised macrocycle can be readily achieved to produce (2-NCH_3CTPP)Ni^{II}.



(2-NCH_3CTPP)Ni^{II}

The electronic absorption spectrum of (2-NCH_3CTPP)Ni^{II} preserves features observed for metalloporphyrins and (CTPP)-Ni^{II}. Thus the intense feature at 429 nm corresponds to the porphyrin Soret band and the weaker features in the visible region are related to the Q bands. The ^{1}H NMR spectrum of (2-NCH_3CTPP)Ni^{II}, corresponding to a diamagnetic species, is similar to (CTTP)Ni^{II} (Table 1). The most notable feature of the nickel(II) complex is co-ordination through unprotonated β-carbon in the equatorial plane since the 21-CH resonance disappeared in the ^{1}H NMR spectrum. In spite of the formed Ni^{II}–carbon bond the (2-NCH_3CTPP)Ni^{II} complex is stable toward oxygen for several days both in solution and in the solid state.

Protonation of 2-N-*Methyl*-21-*carbaporphyrin*.—Titration of 2-NCH_3CTPPH with TFAH, followed by electronic spectroscopy in dichloromethane, is presented in Fig. 1. Both mono- and di-cation species have been obtained and well-defined isosbestic points have been found for the separate processes. The ^{1}H NMR spectroscopic titration, carried out for 2-

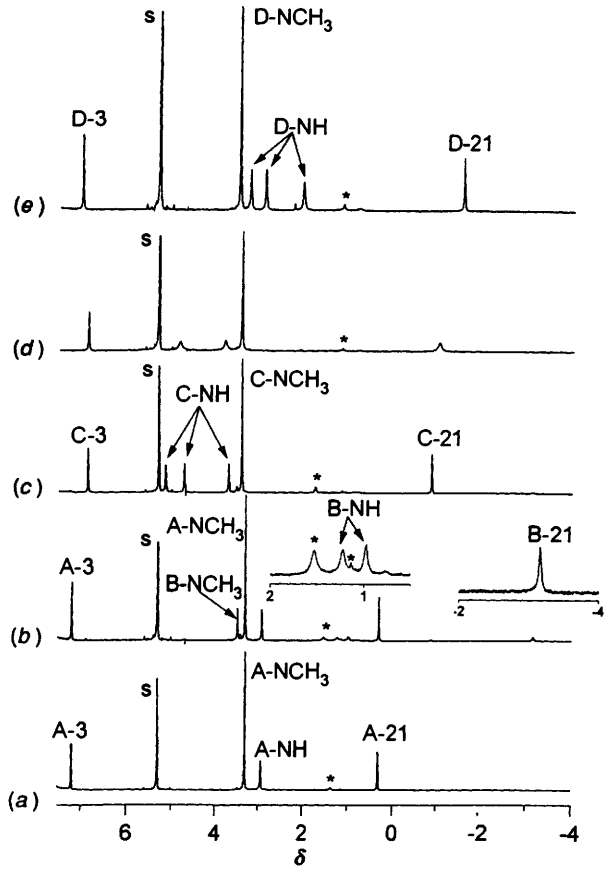


Fig. 3 ^{1}H NMR spectra of 2-NCH_3CTPPH in [$^2H_2$]dichloromethane at 203 K: (*a*) Spectrum of 2-NCH_3CTPPH alone; (*b*) spectrum after addition of 0.3 equiv. of TFAH; (*c*) spectrum after addition of 1.5 equiv. of TFAH; (*d*) spectrum after addition of 3 equiv. of TFAH; (*e*) spectrum after addition of 6 equiv. of TFAH. Resonances are assigned to the following species: A, neutral form, B, monocation; C and D dications. * Solvent and solvent impurities.

NCH_3CTPPH by addition of TFA to solution of the free base in [$^2H_2$]dichloromethane at 203 K, is shown in Fig. 3. The individual resonances of neutral 2-NCH_3CTPPH (A), monocationic 2-$NCH_3CTPPH_2^+$ (B) and two dicationic species 2-$NCH_3CTPPH_3^{2+}$ (C and D) have been concurrently identified in the course of the titration. This fact has been attributed to a slow proton exchange among ionic forms in the system in the conditions of our experiment. The protonation mechanism has been analysed based upon the well-separated set of singlets in the 7 to −5 ppm spectral region. The pyrrole and phenyl resonances at the 9–7.3 ppm region overlap substantially preventing further analysis. Generally, the upfield increase of 21-CH and NH chemical shifts has been determined in the monocationic species in comparison with neutral and dicationic ones (Fig. 3 and Table 3). The number of resonances, contained in individual sets of 3-H, 21-CH and 2-NCH_3 protons, indicate unambiguously the number of the species formed in the particular stage of the titration. In addition, the neutral, monocationic and dicationic forms present one, two or three NH resonances, respectively. Their multiplicity could be discussed in structural terms. We have already shown that the neutral form is protonated at the 23-N position (2.95 ppm). One can predict the formation of three tautomers at a monocationic level (Scheme 1): (22-NH, 23-N, 24-NH); (22-NH, 23-NH, 24-N); (22-N, 23-NH, 24-NH). However, only a single monocationic species [Fig. 3(*b*)] has been identified at 203 K. Presumably, in the monocationic form the two inner protons are on 22-N, 24-N nitrogens flanking the 21-CH proton. This structure resembles that one established for the 21-carbaporphyrin monocation[6] with the methyl group replacing 2-NH proton. The dissociation scheme is presented in Scheme 1.

The formation of the monocation is accompanied by an appearance of the dication (C) pattern which shows three narrow NH resonances. This dication becomes a major species at the 1:1.5 macrocycle to TFAH molar ratio. The marked broadening of all NH resonances has been determined in the further course of titration, *i.e.* in the range of 1:2 to 1:4 molar ratio [Fig. 3(*d*)]. At higher TFAH concentration we have detected the second, strongly upfield shifted set of three NH singlets. Their chemical shifts continuously depend on the TFAH concentration. Their presence indicates the unexpected formation of the new ionic species (D). The spectral pattern, seen in Fig. 3(*e*) corresponds to the dication because the protonation status of the inner nitrogens remained intact. It is important to realise that the observed spectral changes require at least two different dications in an equilibrium. We suggest that the following equilibrium between two tight ionic aggregates is maintained:

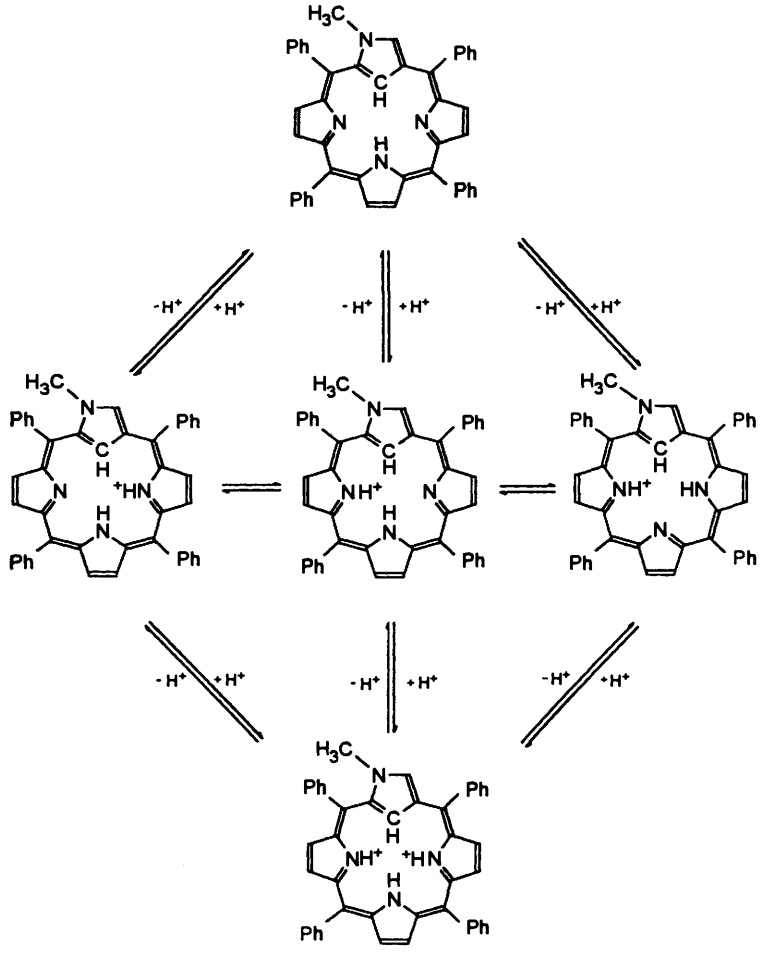
$$[(2\text{-}NCH_3CTPPH_3)TFA]^+ + TFA \longrightarrow [(2\text{-}NCH_3CTPPH_3)(TFA)_2]$$

The considerable difference of the NH shifts for two dications results probably from the steric requirements imposed by mono-coordinate (one TFA ligand bound above the porphyrin plane) and bis-coordinate (two TFA ligands on the opposite side of the porphyrin plane) structures. The bis-coordinate species locates the NH protons in the porphyrin plane as demonstrated by the upfield contribution to their chemical shifts. The additional equilibrium which is reflected by the smooth change of chemical shifts for the second dication, suggests also the independent interaction of this ionic aggregate with the bulk of TFAH through a network of the hydrogen bonds.

We have tested this model in the parallel titration of 2-NCH_3CTPPH with DCAH which is a weaker acid. The dichloromethyl group of DCA allowed the structure of cationic forms to be investigated by using the anion resonance(s) as an independent spectroscopic probe. The general scheme of the protonation by DCAH resembles one of the 2-NCH_3CTPPH–TFAH system. Both monocationic and dicationic forms showed the separate spectra. The essential differences of the chemical shifts and spectral patterns reflect immediately the different properties of two counter anions. This observation points out for the anion influence on the structure of ionic aggregates (Fig. 4, Table 3), particularly for the dication identified in the lowest concentration of the added acids. The C*H*Cl_2 resonance of a bonded DCA anion has been identified at 3.715 ppm for the first dication (C). The upfield change of the chemical shift of the bonded anion with respect to non-bonded DCAH (6.060 ppm, in [$^2H_2$]dichloromethane, 203 K) reflected its location in the deshielding zone of the dication ring current, due to formation of the tight ionic pair.

A comparison of the ^{1}H NMR spectra of [2-NCH_3-$CTPPH_3^{2+}$][DCA] and Sn^{IV}(TPP)$(DCA)_2$ reveals that the C*H*Cl_2 resonances occur in similar regions for both species, *i.e.* 3.715 and 2.88 ppm respectively, in spite of the different nature of the DCA binding. In these two systems the chemical shifts of C*H*Cl_2 are directly related to the geometry dependent ring current effect. Thus, we conclude that the ^{1}H NMR data for [2-$NCH_3CTPPH_3^{2+}$][DCA] are consistent with the localisation of the DCA anion over the centre of dication in an analogous manner as DCA is placed above Sn^{IV} in the Sn^{IV}(TPP)$(DCA)_2$ complex.[19]

In the further steps of the titration the resonance of the



Scheme 1

Table 3 Selected ^{1}H NMR data for the protonated cationic and dicationic forms of 2-NCH_3CTPPH in [$^2H_2$]dichloromethane solutions at 203 K

Compound (acid, quantity)	2-CH_3	3	21	NH	C*H*Cl_2
2-$NCH_3CTPPH_2^+$ (TFAH, 0.3 equiv.)	3.494	7.523	−3.161	1.221 0.975	—
2-$NCH_3CTPPH_3^{2+}$ (TFAH, 1.5 equiv.)	3.419	6.877	−0.876	5.155 4.730 3.725	—
2-$NCH_3CTPPH_3^{2+}$ (TFAH, 6 equiv.)	3.494	7.028	−1.576	3.252 2.909 2.053	—
2-$NCH_3CTPPH_2^+$ (DCAH, 0.7 equiv.)	3.519	7.52[a]	−3.101	1.283 0.976	
2-$NCH_3CTPPH_3^{2+}$ (DCAH, 0.7 equiv.)	3.404	6.857	−0.774	5.727 5.211 3.980	3.715
2-$NCH_3CTPPH_3^{2+}$ (DCAH, 4 equiv.)	3.469	6.977	−1.230	3.956 3.437 2.987	5.219

[a] Signal obscured by strong resonances of neutral form.

co-ordinated DCA broadens. Finally the single averaged resonance of C*H*Cl_2, corresponding to the fast exchange between co-ordinated and non-co-ordinated DCA molecules, has been observed. This resonance moved gradually downfield, *i.e.* in the direction of the free acid position as the molar ratio 2-NCH_3CTPPH to DCAH increased [Fig. 4(*c*)–(*e*)]. Its permanently upfield position with respect to free DCAH reflects plainly the contribution of the ring current shielding effect in the averaged shift of DCA.

Titration of NCH_3TPPH, *i.e.* the isomeric form of 2-NCH_3CTPPH has been previously investigated in [^{2}H]-chloroform by Al-Hazimi *et al.*[17] Both monocationic (two protons flanking NCH_3 nitrogen) and dicationic forms were identified. We have reinvestigated the titration of NCH_3TPPH to follow its acid–base chemistry in [$^2H_2$]dichloromethane. The replacement of [^{2}H]chloroform by [$^2H_2$]dichloromethane did not change the protonation pattern. In particular we have confirmed an existence of a single dication in the NCH_3TPPH–TFA system. Thus 2-NCH_3CTPPH presents unique properties in the studied series $TPPH_2$, NCH_3TPPH, $CTPPH_2$ and 2-NCH_3CTPPH in its ability to form a variety of ionic aggregates. We attribute this fact to the lowest aromaticity of the 2-NCH_3CTPPH in the investigated series. The lowering of aromaticity localises the positive charge on the protonated nitrogens on the inner perimeter of 2-$NCH_3CTPPH_3^{2+}$. It is important to note that such concentration of the electrostatic charge can increase direct electrostatic interaction of the dication with counter anion(s). Dication of 2-NCH_3CTPPH behaves as other polyprotonated macrocyclic cationic ligands which are known for their selective interactions with inorganic and organic anions.[20] It was also demonstrated that the dication of *meso*-tetra-(4-pyridyl)porphyrin ($[TPyPH_4]^{2+}$) binds the chloride counter anion *via* hydrogen bonds.[21] Recently sapphyrins ('expanded porphyrins') were characterised as a new type of anion-specific binding agent showing the impressive selectivity for the fluoride anion.[22]

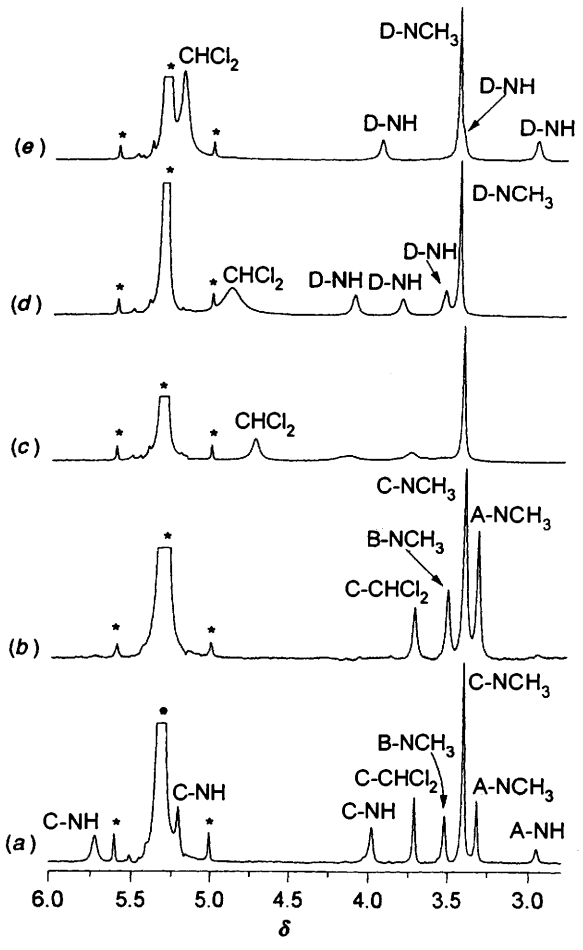


Fig. 4 ^{1}H NMR spectra of 2-NCH_3CTPPH in [$^2H_2$]dichloromethane at 203 K: (*a*) Spectrum of 2-NCH_3CTPPH after addition of 0.9 equiv. of DCAH; (*b*) spectrum after addition of 1 equiv. of DCAD (resonances of exchangeable NH protons disappeared); (*c*) spectrum after addition of 1.7 equiv. of DCAH; (*d*) spectrum after addition of 2.5 equiv. of DCAH; (*e*) spectrum after addition of 4 equiv. of DCAH. Resonances are assigned to the following species. A, neutral form, B, monocation, C and D, dications. The DCA resonance is labelled as $CHCl_2$. * Solvent and solvent impurities.

Conclusion

In the course of the mild methylation of 21-carbaporphyrin we have obtained the inverted isomer of *N*-methyl-5,10,15,20-tetraphenylporphyrin *i.e.* 2-*N*-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin. Formally a single inversion of the *N*-methylated pyrrole relates both isomers.[23] 2-NCH_3CTPPH is the second identified member of the inverted porphyrin family. Although the 2-NCH_3CTPPH is an isomeric form of NCH_3-TPPH, their physicochemical and chemical properties are markedly different. *N*-methylation at the 2-N position lowers the aromatic nature of the macrocycle as compared with NCH_3TPPH and $CTPPH_2$. This is clearly demonstrated by the smaller ring current shifts of all resonances.

The protonation of 2-NCH_3CTPPH proceeds stepwise including mono- and di-cationic species. The capability to form a variety of tight ionic aggregates with TFA anion seems to be the unique property of 2-NCH_3CTPPH. The lability of the 21-CH moiety facilitated the insertion of the stable nickel(II) organometallic macrocyclic complexes which is diamagnetic as usual for the four-coordinate planar nickel(II) structure. On the other hand its isomeric counterpart [$(NCH_3TPP)Ni^{II}$]$^+$ is five-coordinate and paramagnetic.[15]

This new example of carbaporphyrin offers the convenient route *via* *N*-substitution to control its remarkable ability to act as a tetradentate ligand to form a metal–carbon bond. Spectral properties of 2-NCH_3CTPPH highlight its potential application in photodynamic therapy.

Experimental

Solvents and Reagents.—[^{2}H]Chloroform and [$^2H_2$]dichloromethane (Aldrich) were dried by passing through a column of activated basic alumina. TFAH (Aldrich), DCAH (Ubichem) were used as received.

Preparation of compounds. $CTPPH_2$ and NCH_3TPPH were synthesised as previously described.[6,15]

2-NCH$_3$CTPPH. CH_3I (1 cm^3) was added to a solution of CTPPH (61 mg; 0.1 mmol) in dichloromethane. The reaction mixture was stirred at 20 °C for 24 h. After the reaction was completed the mixture was taken to dryness under reduced pressure. The product was dissolved in dichloromethane and chromatographed on a basic alumina column with CH_2Cl_2 as an eluent. The fastest moving green band was collected. The product was precipitated by addition of ethanol and reduction of the solution volume. Yield: 50 mg (80%). λ_{max}/nm (CH_2Cl_2) 450 (log ε 4.94, Soret), 660 (4.01), 710 (4.11) (Calcd. for $C_{45}H_{32}N_4$: C, 85.96; H, 5.13; N, 8.91. Found: C, 85.5; H, 5.2; N, 8.7%); *m*/*z* (EI) 628 (M^+, 100%).

The same synthetic procedure was applied in the case of 2-methyl-2-aza-21-carba-5,10,15,20-tetra(*p*-tolyl)porphyrin (2-NCH_3CTTP) which has been used in the selected ^{1}H NMR experiments.

(2-NCH$_3$CTPP)Ni^{II}. A solution of nickel acetate tetrahydrate (100 mg) in methanol (5 cm^3) was added to a solution of N-methyl-21-carbaporphyrin (25 mg) in dichloromethane (40 cm^3). The solution was stirred at room temperature for 1 h and then the solvent was removed under reduced pressure. The solid residue was extracted with dichloromethane. To the dichloromethane solution (20 cm^3) methanol (about 30 cm^3) was added and the solution was allowed to stand overnight. The fine black crystals which appeared after that time were collected by filtration and dried in air (20 mg; 75%). λ_{max}/nm 365 (log ε 3.87), 430 (4.12, Soret), 464 (sh), 563 (3.44), 660 (3.87), 712 (3.13), 776 (3.14) Calcd. for $C_{45}H_{30}N_4Ni{\cdot}CH_3OH$: C, 77.10; H, 4.75; N, 7.82. Found: C, 77.2; H 4.4; N 7.8); *m*/*z* (EI) 684 (M^+, 100%).

Instrumentation.—^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 300 AMX spectrometer operating in quadrature detection mode. The residual ^{1}H NMR spectra of the deuteriated solvents were used as secondary references. The assignments of the proton and carbon resonances have been obtained by ^{1}H COSY, ^{1}H NOESY and ^{1}H–^{13}C heteronuclear correlated shift experiments. Absorption spectra were recorded on a Specord M-42 spectrometer and a diode array Beckman 7500 spectrometer. Mass spectra were recorded on a ADM-604 spectrometer using the electron impact mass spectrometry technique.

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