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Preparation and Spectroscopic Characterization of 2 : 1 Molecular Complexes of Tetracyanoethylene and *meso*-Tetraphenylporphyrins

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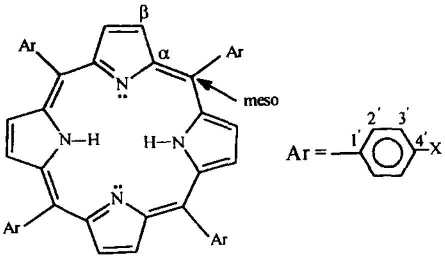
Different para-substituted *meso*-tetraphenylporphyrins ($H_2T(4\text{-}X)PP$, X = H, Cl, CH_3, $CH(CH_3)_2$, OCH_3) react with various molar ratios of tetracyanoethylene (TCNE) in dichloromethane or benzene and produce only the 1 : 2 molecular complex, $(TCNE)_2H_2T(4\text{-}X)PP$. The remarkable agreement between the corresponding ^1H, ^{13}C solution ($CDCl_3$) NMR resonances of the porphyrin moiety in these complexes with those of tetraphenylporphyrin dication, H_4TPP^{2+}, and also the strong resemblance between their UV-vis spectra and the spectra of the related diprotonated porphyrins indicates similar out-of-plane distorted porphyrin core structure in all of them. Based on these close spectral correspondences among the various molecular complexes and the related diprotonated porphyrins, and also consideration of the known structure of $H_4TPP^{2+}Cl_2^-$ species, it is proposed that the two TCNEs in $(TCNE)_2H_2T(4\text{-}X)PP$ complexes are bonded from above and below the mean porphyrin plane to the lone electron pairs of the pyrrolenine nitrogens of the porphyrins.Spectral data (^{13}C, IR) of the bonded TCNEs in the molecular complexes seem to be most consistent with the interaction of an acceptor π^* orbital centered at a CN group of the TCNEs with the porphyrin core nitrogen donors.

Aspects of TCNE chemistry, including charge-transfer intermolecular complexation with organic substrates, its coordination ability, and applications in organometallic chemistry have been studied and reviewed.[1—4] TCNE readily exhibits charge-transfer spectra when mixed with molecules possessing π-electrons or groups having atoms with an unshared electron pair.[5] To date, however, there has been only a single report on the 1 : 1 complexation of TCNE and *meso*-tetraphenylporphyrin.[6] In this work we present, for the first time, UV-vis, ^1H, and ^{13}C NMR evidence for exclusive 2 : 1 complexation of TCNE and various para-substituted *meso*-tetraphenylporphyrins ($H_2T(4\text{-}X)PP$, X = H, Cl, CH_3, $CH(CH_3)_2$, OCH_3) in dichloromethane or benzene, with no indication for the formation of a 1 : 1 adduct. The remarkable resemblance between the spectral data of the various $(TCNE)_2H_2T(4\text{-}X)$-PP complexes, and their close correspondence with those of $H_4T(4\text{-}X)PP^{2+}$ acid dications,[7,8] provide convincing evidence for analogous porphyrin core structures in these species, with pyrrole rings tilted up and down the porphyrin plane. This conformation leads to an appropriate orientation of the pyrrolenine nitrogen lone pairs and the pyrrole NH groups, for donation and hydrogen-bondings to TCNEs, respectively. Furthermore, it appears that the bonding of each TCNE occurs primarily through a π^* of one of its CN groups, and they are presumably located above and below the plane of the porphyrin core.



X = H, H_2TPP

X = Cl, $H_2T(4\text{-}Cl)PP$

X = CH_3, $H_2T(4\text{-}CH_3)PP$

X = $CH(CH_3)_2$, $H_2T(4\text{-}CH(CH_3)_2)PP$

X = OCH_3, $H_2T(4\text{-}OCH_3)PP$

Fig. 1.

Results and Discussion

Electronic Spectra. The UV-vis spectra for $CHCl_3$ solutions of five different para-substituted *meso*-tetraphenylporphyrins (Fig. 1) and their 2 : 1 TCNE molecular complexes are shown in Fig. 2. The spectra for the molecular complexes consist of two new intense absorption bands at 439.6—454.2 and 655.3—691.7 nm, which are completely different from those of the corresponding porphyrins. They closely resemble the spectra of the related diprotonated porphyrin dications[7a] (Table 1). This remarkable UV-vis spectral correlation between various $(TCNE)_2H_2T(4\text{-}X)PP$ complexes and $H_4T(4\text{-}X)PP^{2+}$ dications, and their relative independence from the nature of the electron acceptors, i.e. TCNE or H^+, clearly indicates that the spectra are essentially due to the electronic transitions within the porphyrin core, and they can be qualitatively explained in terms of the four orbital model of porphines.[7,9]

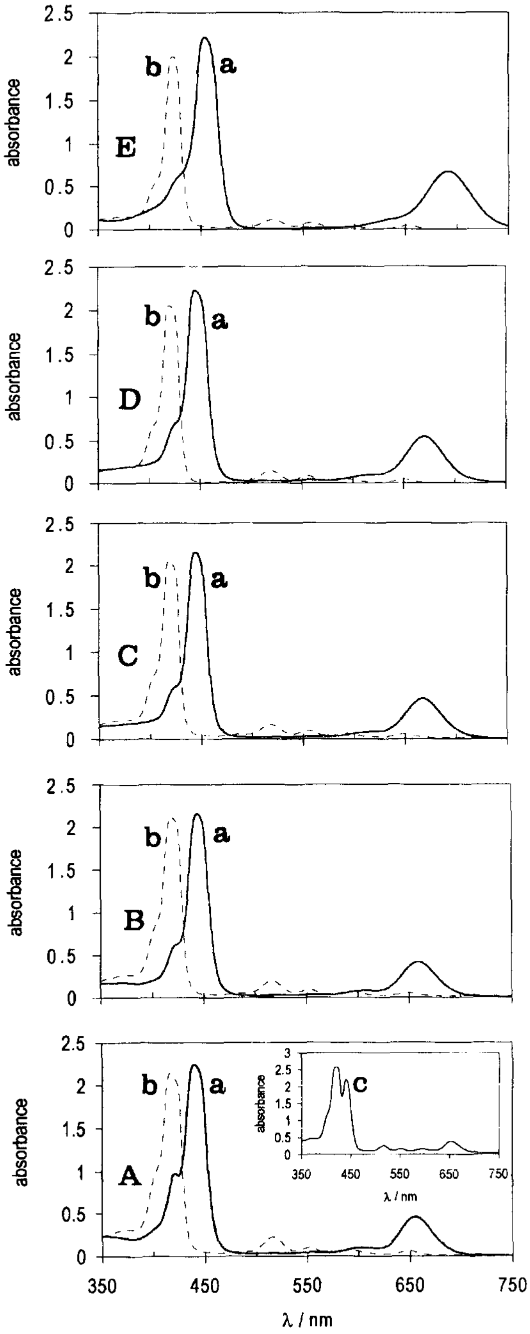


Fig. 2. UV-vis spectra of $CHCl_3$ solution (8.8×10^{-5} M) of $(TCNE)_2H_2TPP$ (Aa), H_2TPP (Ab); $(TCNE)_2H_2T(4\text{-}Cl)PP$ (Ba), $H_2T(4\text{-}Cl)PP$ (Bb); $(TCNE)_2H_2T(4\text{-}CH_3)PP$ (Ca), $H_2T(4\text{-}CH_3)PP$ (Cb); $(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$ (Da), $H_2T(4\text{-}CH(CH_3)_2)PP$ (Db); $(TCNE)_2H_2T(4\text{-}OCH_3)PP$ (Ea), $H_2T(4\text{-}OCH_3)PP$ (Eb) at 25 °C. The inset (Ac) is the spectrum of 1 : 1 TCNE–H_2TPP reaction mixture in $CHCl_3$ (8.8×10^{-5} M). TCNE has no absorption in this region.[3,10]

It is notable that parallel para-substituent effects are observed between the 2 : 1 TCNE complexes and their corresponding dications.[7a] Comparison of the shifts in the UV-vis spectra of various $(TCNE)_2H_2T(4\text{-}X)PP$ complexes, and $H_4T(4\text{-}X)PP^{2+}$ dications, relative to $(TCNE)_2H_2TPP$, and H_4TPP^{2+}, respectively, indicates that π-resonance rather than σ-induction effects are predominantly transmitted from para-substituents to the porphyrin nucleus in these species.[7a] The spectral red shift for $(TCNE)_2H_2T(4\text{-}OCH_3)PP$ (14.6, 36.4 nm), as compared to that of $(TCNE)_2H_2TPP$, is much greater than the shifts in the other $(TCNE)_2H_2T(4\text{-}X)PP$ complexes (4.4—6.0, 3.9—15.4 nm) (Table 1). This difference could be attributed to a better π-resonance-type interaction caused by the lone pairs of the 4-OCH_3 groups.

Our attempts at synthesis of 1 : 1 TCNE–porphyrin adducts from their 1 : 1 reaction mixtures were unsuccessful and only 2 : 1 complexes were formed. Figure 2Ac (inset) shows the spectrum of 1 : 1 TCNE–H_2TPP reaction system, which indeed corresponds to the superimposition of the spectra of H_2TPP and $(TCNE)_2H_2TPP$ complex, with no indication of the occurrence of a 1 : 1 intermediate adduct. It is noteworthy that very slow evaporation of the solvent (CH_2Cl_2) from a 1 : 1 mixture of TCNE and H_2TPP always resulted in the formation of separate pure crystals of H_2TPP and $(TCNE)_2H_2TPP$. An excess of TCNE beyond that required for the 2 : 1 complexation had no effect on the spectrum of $(TCNE)_2H_2TPP$. It is remarkable that these observations are in complete accordance with the results of protonation of H_2TPP[8C] in $CHCl_3$, producing only H_4TPP^{2+} dication, with no sign for the formation of a monoprotonated (H_3TPP^+) species.

^{1}H NMR. Figure 3 presents ^{1}H NMR spectra of various tetraphenylporphyrins and their 2 : 1 TCNE molecular complexes in $CDCl_3$ at 25 °C. In the free porphyrins the internal NH protons appear upfield (−2.74 to −2.86 ppm) and β-protons occur as a singlet in the range of 8.84 to 8.87 ppm (Table 2).[11] Resonances due to the *meso*-phenyl protons consist of two doublets, one for ortho (8.08 to 8.24 ppm) and another for meta hydrogens (7.27 to 7.76 ppm). In the case of H_2TPP, the meta and para hydrogens overlap and give a doublet (7.75, 7.77 ppm).[11]

Comparison of the related ^{1}H NMR data of $(TCNE)_2H_2T(4\text{-}X)PP$ complexes and H_4TPP^{2+} provides further evidence for spectral correspondence among these species. Formation of 2 : 1 TCNE–porphyrin adducts, similar to the diprotonation of H_2TPP,[8c] leads to a downfield shift of NH signals ($\Delta\delta$ = 1.50 to 1.83 ppm) and an upfield motion of β-protons ($\Delta\delta$ = −0.03 to −0.18 ppm), Table 2. The meta phenyl protons of TCNE complexes of the para-substituted *meso*-tetraphenylporphyrins, and the meta and para hydrogens of the H_2TPP complex give a signal in the 7.54 to 8.07 ppm region.

Figure 4 shows the ^{1}H NMR spectrum of 1 : 1 TCNE–H_2TPP reaction system, which is exactly related to the superimposition of the signals due to H_2TPP (Fig. 3Ab) and $(TCNE)_2H_2TPP$ (Fig. 3Aa), lacking any extra lines that could be related to a 1 : 1 adduct formation. This result is in complete agreement with ^{1}H NMR studies of protonation of H_2TPP in $CHCl_3$, in which no monoprotonated species (H_3TPP^+) has been detected.[8c] An excess of TCNE beyond that needed for 2 : 1 complexation of H_2TPP had no effect on ^{1}H NMR spectrum of the complex. Interactions of various para-substituted *meso*-tetraphenylporphyrins with TCNE

Table 1. UV-vis Spectral Data of Various $H_2T(4\text{-}X)PP$, $(TCNE)_2H_2(4\text{-}X)PP$ Complexes, and $H_4T(4\text{-}X)PP^{2+}$ Dications

$H_2T(4\text{-}X)PP$ and RS[a]	Porphyrins Peaks[b] (λ/nm)					TCNE complexes Peaks[b] (λ/nm)			Dications Peaks[c] (λ/nm)		
	Soret	IV	III	II	I	Soret	II	I	Soret	II	I
X = H	415.8,	516.6,	551.2,	592.0,	648.8	439.6,	605.0,	655.3	441.7,	608.0,	658.8
X = Cl	414.9,	517.1,	551.2,	592.0,	648.9	444.0		659.2	443.6,	610.0,	661.0
RS						4.4		3.9	1.9		2.2
$X = CH_3$	418.9,	518.5,	554.4,	593.6,	649.6	445.1		667.6	445.6		671.9
RS						5.5		12.3	3.9		13.1
$X = CH(CH_3)_2$	419.7,	519.2,	555.1,	594.4,	650.4	445.6		670.7	445.1		670.7
RS						6.0		15.4	3.4		11.9
$X = OCH_3$	422.9,	520.8,	558.4,	596.8,	652.9	454.2		691.7	452.5		694.7
RS						14.6		36.4	10.8		35.9

a) Red shifts (RS) are measured relative to $(TCNE)_2H_2TPP$ and H_4TPP^{2+}. b) In all cases the solvent is $CHCl_3$. c) The data are taken from Ref. 7a, with DMF as the solvent.

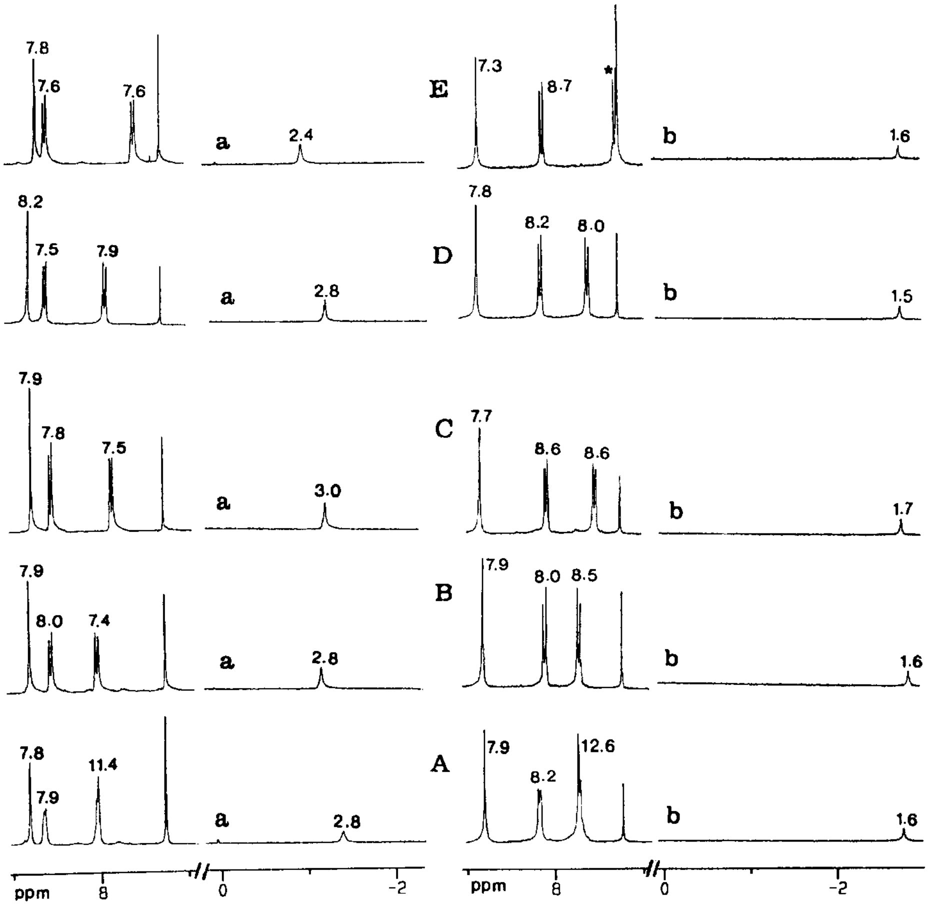


Fig. 3. ${}^{1}H$ NMR spectra (250 MHz) of $(TCNE)_2H_2TPP$ (Aa), H_2TPP (Ab); $(TCNE)_2H_2T(4\text{-}Cl)PP$ (Ba), $H_2T(4\text{-}Cl)PP$ (Bb); $(TCNE)_2H_2T(4\text{-}CH_3)PP$ (Ca), $H_2T(4\text{-}CH_3)PP$ (Cb); $(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$ (Da), $H_2T(4\text{-}CH(CH_3)_2)PP$ (Db); $(TCNE)_2H_2T\text{-}(4\text{-}OCH_3)PP$ (Ea), $H_2T(4\text{-}OCH_3)PP$ (Eb) in $CDCl_3$ at 25 °C. Concentration for all the species is 0.006 M. Integrals of the lines or multipletes, are given on their sides. The line at 7.26 ppm is due to $CHCl_3$ impurity in the solvent. On the left side of the spectra resonances of aromatic protons are shown, on the right the N–H proton lines are displayed. *The related integration cannot be measured precisely.

showed a similar trend, with no indication for the formation of a 1 : 1 species.

${}^{13}C$ NMR. ${}^{13}C$ NMR spectra of the various tetraphenylporphyrins and their 2 : 1 complexes in $CDCl_3$ solutions are illustrated in Fig. 5. Detailed assignments for the resonances are given in Table 3. Figure 5Ab shows ${}^{13}C$ NMR spectrum of H_2TPP, consisting of one broad (β-carbon) and five sharp signals.[8a] Resonance due to α-carbons (at ca. 145 ppm)[8a]

Table 2. ^{1}H NMR Data of Various $H_2T(4\text{-}X)PP$,[a] $(TCNE)_2H_2T(4\text{-}X)PP$[a] Complexes, and H_4TPP^{2+}

Compounds /$\Delta\delta$	N–H	H_β	H_o	H_m	H_p or H_x
H_4TPP^{2+} [b]	0.35	8.58	—	—	—
$\Delta\delta$[b]	3.08	−0.25	—	—	—
H_2TPP	−2.76	8.85	8.21, 8.24	7.75, 7.77	7.75, 7.77
TCNE complex	−1.26	8.81	8.64, 8.67	8.03, 8.07	8.03, 8.07
$\Delta\delta$	1.50	−0.04	0.43	0.28	0.28
$H_2T(4\text{-}Cl)PP$	−2.86	8.84	8.12, 8.15	7.73, 7.76	—
TCNE complex	−1.16	8.81	8.55, 8.58	8.03, 8.06	—
$\Delta\delta$	1.70	−0.03	0.43	0.30	—
$H_2T(4\text{-}CH_3)PP$	−2.77	8.85	8.08, 8.11	7.54, 7.56	2.70
TCNE complex	−1.20	8.76	8.51, 8.54	7.82, 7.85	2.80
$\Delta\delta$	1.57	−0.09	0.43	0.28	0.10
$H_2T(4\text{-}CH(CH_3)_2)PP$	−2.74	8.87	8.12, 8.15	7.59, 7.62	CH = 3.20—3.32, CH_3 = 1.54, 1.57
TCNE complex	−1.18	8.77	8.59	7.88, 7.91	CH = 3.30—3.41, CH_3 = 1.58, 1.60
$\Delta\delta$	1.56	−0.10	0.47	0.29	CH = 0.10, CH_3 = 0.04
$H_2T(4\text{-}OCH_3)PP$	−2.75	8.86	8.11, 8.14	7.27, 7.31	4.10
TCNE complex	−0.92	8.68	8.55, 8.59	7.54, 7.58	4.18
$\Delta\delta$	1.83	−0.18	0.44	0.27	0.08

a) Chemical shifts in ppm from impurity of $CHCl_3$ (7.26 ppm) in $CDCl_3$ solvent. b) The corresponding data are from Ref. 8c.

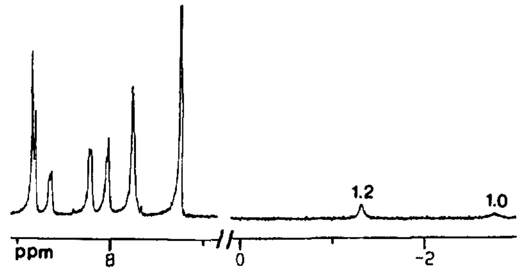


Fig. 4. ^{1}H NMR spectrum of 1 : 1 TCNE–H_2TPP (0.002 M) reaction system in $CDCl_3$ at 25 °C.

would be very broad and is not observed.[11b] Formation of $(TCNE)_2H_2TPP$ complex sharpens signals of both α-carbons (145.84 ppm), β-carbons (129.98 ppm) (Fig. 5Aa), and leads to a small downfield motion in the NMR lines of C_{meso}, C_2', C_3', C_4' (see Fig. 1 for the numbering), and upfield shifts of C_2' and C_β (Table 3). Diprotonation of H_2TPP also causes similar shifts in the corresponding ^{13}C resonances.[8a]

The ^{13}C assignments for the spectra of $H_2T(4\text{-}X)PP$ ($X = Cl, CH_3, OCH_3$) were made on the basis of the known shifts of the corresponding carbons in H_2TPP,[8a,11b] $H_2T(4\text{-}CH(CH_3)_2)PP$,[13] and also by taking into account the ^{13}C lines of the related carbons[12] in chlorobenzene, toluene, and anisole. Complexation of TCNE with various para-substituted *meso*-tetraphenylporphyrins and diprotonation of H_2TPP led to very similar changes in their corresponding ^{13}C resonances (Table 3).

The very close agreement between UV-vis, ^{1}H, and ^{13}C NMR spectral data of H_4TPP^{2+} acid dication and those of the different $(TCNE)_2H_2T(4\text{-}X)PP$ complexes suggests the occurrence of a similar porphyrin core structure in these species. Thus, a series of noncoplanar porphyrin pyrrole rings tilted alternately up and down, analogous to the structure of H_4TPP^{2+},[14] is assumed to exist in the 2 : 1 TCNE molecular complexes. Such a conformation better exposes the two pyrrolenine nitrogen electron pairs for binding with an empty π^* orbital of TCNEs, probably from above and below the "plane" of the porphyrin (Fig. 6), resembling the interaction of acids with porphyrin nucleus in H_4TPP^{2+}.[14] In the proposed conformation (Fig. 6) the NH protons are adjacent, which is not consistent with the normal structure of H_2TPP.[14] It appears, however, that in this conformation the tetrahedrally tilted pyrrole rings would minimize the van der Waals repulsion between the NH hydrogens.[14]

Observation of five ^{13}C resonances for a complexed TCNE (Fig. 5) rather than two for a free TCNE[3,15] at 108.25 and 112.31 ppm (Fig. 5F), suggests a loss of symmetry upon its coordination with various $H_2T(4\text{-}X)PP$ molecules. The proposed binding of each TCNE through an empty CN π^* orbital with an electron pair of a pyrrolenine nitrogen (Fig. 6), and also the suggested π-conjugation in the bonded TCNE (Fig. 6) seems to be in good agreement with the ^{13}C NMR assignments of the coordinated TCNEs. It appears that the ^{13}C resonance due to the unique interaction site (C_3) should be accompanied with the greatest downfield motion (153.40—153.76 ppm), and the nearest neighboring carbon atom to this site (C_1) should show the largest upfield shift (60.28—60.87 ppm), relative to the corresponding carbons in the free TCNE, Table 4. Such an assignment for the acceptor site, with a quasi allene-type $C_1{=}C_3{=}N$ resonance form, is consistent with the trend in ^{13}C line positions in allene[16] itself. In accordance with this analogy, C_4 and C_5 atoms in the two rather distant CN groups with a pseudo allene structure, must also resonate downfield in the region 112.36 to 113.07 ppm. The shifts for C_2 (109.85 to 110.09 ppm) and C_6 (110.39 to 110.63 ppm) can be interchanged; in either case C_6 is upfield, since it is not involved in the π-conjugation system.

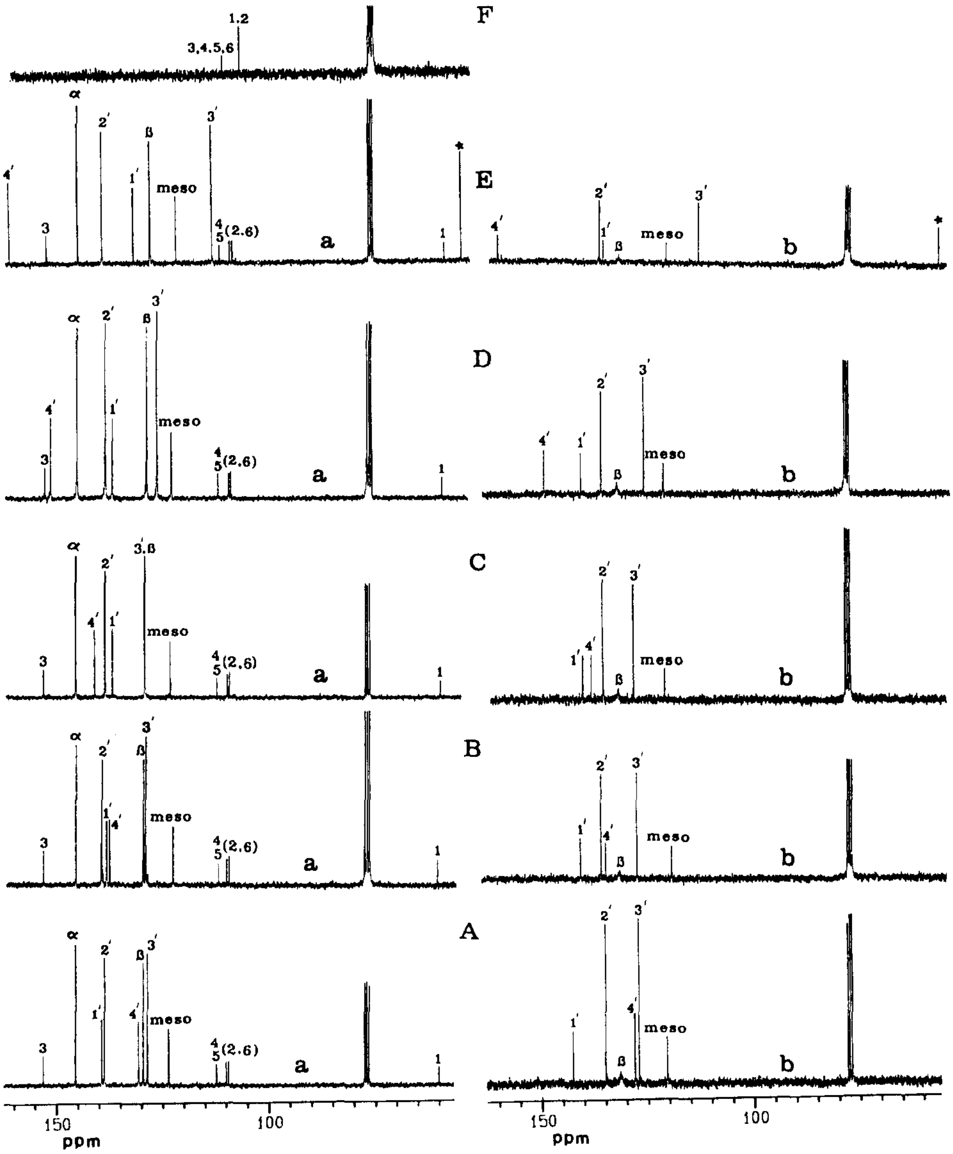


Fig. 5. ^{13}C NMR spectra of $(TCNE)_2H_2TPP$ (Aa), H_2TPP (Ab); $(TCNE)_2H_2T(4\text{-}Cl)PP$ (Ba), $H_2T(4\text{-}Cl)PP$ (Bb); $(TCNE)_2H_2T(4\text{-}CH_3)PP$ (Ca), $H_2T(4\text{-}CH_3)PP$ (Cb); $(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$ (Da), $H_2T(4\text{-}CH(CH_3)_2)PP$ (Db); $(TCNE)_2H_2T(4\text{-}OCH_3)PP$ (Ea), $H_2T(4\text{-}OCH_3)PP$ (Eb); TCNE (F) in $CDCl_3$ at 25 °C. *Corresponds to 4-OCH_3 groups.

Another possibility that can be considered for the bonding of TCNEs is through their olefinic carbons. Symmetrical interaction of both olefinic carbons or bonding of a single olefinic carbon of TCNE with the pyrrolenine nitrogen donors of the porphyrins, should lead to two or four ^{13}C resonance, respectively. which are not consistent with the observed five ^{13}C lines of a complexed TCNE. However, it appears that these types of interactions are sterically more demanding than the complexation through a CN π^* of TCNE. Thus, it is believed that coordination through a CN site is probably more plausible than the bonding of the olefinic carbon atoms.

Figure 7 shows a representative IR spectrum (3500—2000 cm^{-1} region) for the complexation of TCNE with para-substituted tetraphenylporphyrins. Free TCNE gives two CN stretching bands (2255, 2220 cm^{-1})[17] in the IR spectrum. Upon complexation of TCNE with the various tetraphenylporphyrins, these bands are shifted to lower frequencies and appear at 2210 to 2215, and at 2190 cm^{-1}, respectively. These changes are expected if TCNE acts as an electron acceptor[17a,17b] through its π^*, causing a weakening of CN bonds. The IR spectrum of tetraphenylporphyrins shows a band at 3310—3320 cm^{-1} which is due to their NH stretching modes.[18] In $(TCNE)_2H_2T(4\text{-}X)PP$ complexes this band is completely lost (Fig. 7c). This effect may indicate the occurrence of intramolecular hydrogen-bonding[19] between the pyrrolic hydrogens and the complexed TCNEs. Such interactions should lead to further stabilization of the molecular complexes. The proposed out-of-plane conformation of the porphyrin pyrrole rings (Fig. 6) seems to provide a better orientation of NH groups for hydrogen-bonding.

The exclusive 2 : 1 interaction of TCNE with tetraphenylporphyrins and the absence of any evidence for their monocomplexation implies that the intermediate 1 : 1 adducts are

Table 3. ^{13}C NMR Data of Various $H_2T(4\text{-}X)PP$,[a] $(TCNE)_2H_2T(4\text{-}X)PP$[a] Complexes, and H_4TPP^{2+}

Compounds	C_α	C_β	C_{meso}	C_1'	C_2'	C_3'	C_4'
H_4TPP^{2+} [b]	145.2	127.7	122.1	139.4	137.9	127.7	129.4
H_2TPP	—	131.50	120.55	142.58	134.97	127.09	128.11
TCNE complex	145.84	129.98[c]	123.95	139.70	139.07	129.00[c]	131.03
$H_2T(4\text{-}Cl)PP$	—	131.64	119.38	140.75	135.89	127.45	134.79[d]
TCNE complex	145.89	130.01[e]	122.95	138.66[f]	139.81	129.52[e]	138.01[f]
$H_2T(4\text{-}CH_3)PP$	—	131.37	120.47	139.73	134.92	127.81	137.71[d]
TCNE complex	145.96	129.69[g]	123.83	137.36	139.11	129.82[g]	141.59
$H_2T(4\text{-}CH(CH_3)_2)PP$	—	131.44	120.46	140.02	135.12	125.13	148.56
TCNE complex	146.01	129.69	123.87	137.68	139.37	127.27	152.28
$H_2T(4\text{-}OCH_3)PP$	—	131.34	120.13	135.07[l]	135.99[l]	112.60[h]	159.80[h]
TCNE complex	146.30	129.45	123.33	133.35	140.60	114.81	162.52

a) Chemical shifts (ppm) are downfield from $CDCl_3$ (76.90—77.92 ppm). b) Chemical shifts are taken from Ref. 8a with internal Me_4Si (±0.010). c) May be interchanged. d) Assignments of C_4' signals in $H_2T(4\text{-}Cl)PP$ (134.79 ppm), and $H_2T(4\text{-}CH_3)PP$ (137.71 ppm) are made on the bases of the resonances of the carbon atoms attached to Cl in chlorobenzene (134.3 ppm)[12] and to CH_3 in toluene (137.7 ppm),[12] respectively. e) May be interchanged. f) May be interchanged. g) May be interchanged. h) For $H_2T(4\text{-}OCH_3)PP$ the two signals at 112.60 and 159.80 ppm are assigned to C_3' and C_4' and closely correspond to the related ^{13}C resonances of anisole.[12] l) The relative intensities ca. (1 : 2) of the signals at 135.07 and 135.99 ppm lead to their assignments to C_1' and C_2' of $H_2T(4\text{-}OCH_3)PP$, respectively. Such an intensity correlation is known in the spectra of tetraphenylporphyrins.[8a,13]

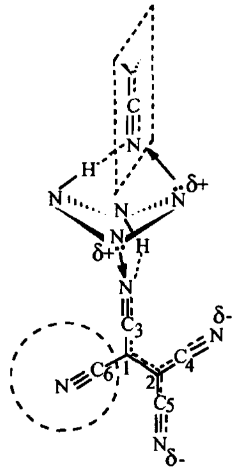


Fig. 6. Diagrammatic illustration of the proposed structure and bonding interactions for a $(TCNE)_2H_2T(4\text{-}X)PP$ complex. In the middle the tetrahedrally titled pyrrole nitrogens of a porphyrin core are shown. Below the mean porphyrin plane a CN bonded TCNE and its possible π-conjugation is illustrated. Another CN bonded TCNE, from above the plane, is only partially depicted. The dashed circle shows the C_6N group that is not involved in the π-resonance.

Table 4. ^{13}C NMR Shifts for TCNE in Free Form, and in $(TCNE)_2H_2T(4\text{-}X)PP$ Complexes

Porphyrins	C_1	C_2	C_3	C_4[a] C_5[a]	C_6
X = 0[b]	108.25			112.31	
X = H	60.54	109.85	153.45	(112.75)	110.39
X = Cl	60.87	109.87	153.40	(112.36)	110.39
X = CH_3	60.36	109.91	153.56	(112.92)	110.46
X = $CH(CH_3)_2$	60.33	110.01	153.64	(113.01)	110.53
X = OCH_3	60.28	110.09	153.76	(113.07)	110.63

a) Numbers in parentheses are assigned to both C_4 and C_5 chemical shifts in the complexed TCNE. b) Free TCNE.

much more reactive than the free porphyrins, and they react immediately with another TCNE molecule, after their formation. In accordance with the general arguments presented for the diprotonation of porphyrins,[8c,14] we suggest that the monocomplexation may lead to a substantial distortion in the porphyrin nucleus structure, and the tilting of the pyrrole rings in the manner shown in Fig. 6. This step, which requires a high energy barrier, makes the lone electron pairs of the pyrrolenine nitrogens and the pyrrole NH bonds more accessible for interactions with TCNE, thus facilitating the addition of a second TCNE to the porphyrin core, and achieving the final 2 : 1 complex. Hence, the following reaction scheme is believed to be operative in the complexation of TCNE and tetraphenylporphyrins.

$$\mathrm{TCNE} + H_2T(4\text{-}X)PP \xrightleftharpoons{\text{slow}} \mathrm{TCNE}\cdot H_2T(4\text{-}X)PP + \mathrm{TCNE} \xrightleftharpoons{\text{very fast}} (\mathrm{TCNE})_2H_2T(4\text{-}X)PP$$

Experimental

Benzaldehyde and various para-substituted benzaldehydes (4-Cl, 4-CH_3, 4-$CH(CH_3)_2$, 4-OCH_3) were obtained from Fluka, Merck, and B. D. H. and were used as received. Pyrrole (Fluka) was distilled before use. All the solvents that were employed for the synthesis of the porphyrins and chromatography were obtained from Fluka, and were used as received. Dichloromethane (Merck), for the preparation of the TCNE–porphyrin complexes, was purified by washing with 5 per cent aqueous sodium carbonate and water, followed by drying over anhydrous calcium chloride; then the material was fractionated.[20] TCNE (Merck) was vacuum sublimed. The

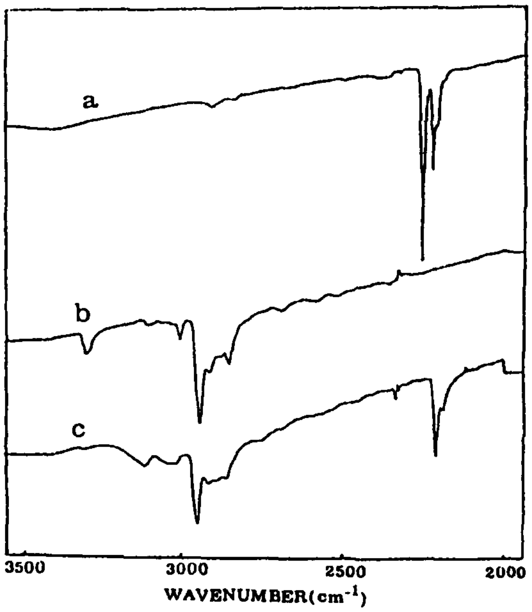


Fig. 7. IR spectra of TCNE (a), $H_2T(4\text{-}CH(CH_3)_2)PP$ (b), $(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$ (c).

synthesis of all the tetraphenylporphyrins employed in this work and their purification were generally performed in accordance with the reported procedures.[21,22]

$(TCNE)_2H_2TPP$: A 2 : 1 mixture of *meso*-tetraphenylporphyrin, H_2TPP (0.1 mmol) and TCNE (0.2 mmol) in CH_2Cl_2 (30 ml) led quantitatively to the production of a green $(TCNE)_2H_2TPP$ complex after 5 d, at room temperature (ca. 25 °C). Very slow evaporation (3—4 d) of the solvent resulted in a solid that contained no excess of either TCNE or H_2TPP.

$(TCNE)_2H_2T(4\text{-}Cl)PP$: $H_2T(4\text{-}Cl)PP$ (0.1 mmol in 40 ml CH_2Cl_2) was mixed with TCNE (0.2 mmol in 30 ml CH_2Cl_2) and this mixture was stirred for 8—9 d at room temperature. Slow evaporation (5—6 d) of the solvent resulted in a green solid, which was then dissolved in a minimum amount of boiling chlorobenzene. Gradual removal of the solvent (7—8 d) at room temperature led to dark green needle crystals of $(TCNE)_2H_2T(4\text{-}Cl)PP$.

$(TCNE)_2H_2T(4\text{-}CH_3)PP$: This complex was obtained by mixing of $H_2T(4\text{-}CH_3)PP$ (0.1 mmol) and TCNE (0.2 mmol) in CH_2Cl_2 (25 ml) at room temperature after 48 h. The solid residue obtained after slow evaporation (3 d) of the solvent, at room temperature, was dissolved in a minimum volume of hot benzene. Slow evaporation (4—5 d) of benzene at room temperature resulted in dark green crystals of the complex.

$(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$: To a solution of $H_2T(4\text{-}CH(CH_3)_2)PP$ (0.2 mmol) in boiling benzene (25 ml), a solution of TCNE (0.4 mmol) in hot benzene (5 ml) was added. The resulting solution was first heated until the total volume reduced to 15 ml and then cooled and kept at room temperature for 20 h. Slow evaporation (4—5 d) of the solvent at ambient temperature resulted in dark green needle crystals of $(TCNE)_2H_2T(4\text{-}CH(CH_3)_2)PP$ complex. In a slightly modified approach to the above procedure, $H_2T(4\text{-}CH(CH_3)_2)PP$ (0.1 mmol) and TCNE (0.2 mmol) were mixed in boiling benzene (20 ml). The solution turned green after cooling and stirring for 20 h at room temperature. Slow evaporation of the solvent (4—5 d) produced dark green crystals of $(TCNE)_2H_2T(4CH(CH_3)_2)PP$. This reaction is not complete in CH_2Cl_2 as solvent.

$(TCNE)_2H_2T(4\text{-}OCH_3)PP$: Mixing of $H_2T(4\text{-}OCH_3)PP$ (0.1 mmol) and TCNE (0.2 mmol) in CH_2Cl_2 (40 ml) resulted in a green solution after 24 h. The solvent was slowly (3 d) removed at room temperature and the solid residue was dissolved in a minimum amount of boiling benzene. Slow evaporation (4—5 d) of the benzene produced dark green crystals of $(TCNE)_2H_2T(4\text{-}OCH_3)PP$.

The electronic absorption spectra were recorded in chloroform solutions on a Philips PUB 700 spectrophotometer. The cell had an optical path length of 1 mm.

NMR spectra (^1H, ^{13}C) were recorded on a Bruker Avance DPX 250 MHz spectrometer in $CDCl_3$. To obtain good integration results, in addition to the correction of the spectrum base line, concentration of the molecular complexes was 0.006 M (1 M = 1 mol dm^{-3}). The residual $CHCl_3$ in the conventional 99.8 atom% $CDCl_3$ gives a signal at $\delta = 7.26$ ppm, which was used for calibration of the chemical shift scale.

IR spectra were recorded on a Perkin Elemer 781 spectrophotometer using KBr pellets.

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