Exclusive 2:1 molecular complexation of 2,3-dichloro-5,6-dicyanobenzoquinone and *para*-substituted *meso*-tetraphenylporphyrins: spectral analogues for diprotonated *meso*-tetraphenylporphyrin

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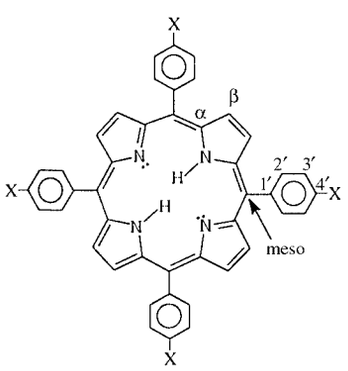
Various molar ratios of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and *para*-substituted *meso*-tetraphenylporphyrins ($H_2T(4\text{-}X)PP$, X = H, Cl, CH_3, $CH(CH_3)_2$, OCH_3) in dichloromethane at room temperature in several days always afforded $(DDQ)_2H_2T(4\text{-}X)PP$ molecular complexes as the sole products. The very close correspondence between the optical spectra of these 2:1 molecular complexes and their related diprotonated porphyrins, and particularly the remarkable agreement of their corresponding ^1H, ^{13}C NMR resonances with those of tetraphenylporphyrin dication, H_4TPP^{2+}, strongly suggest similar distorted porphyrin core structures in all these compounds. ^{13}C NMR and IR spectra of the complexed DDQs appear to be consistent with the interaction of one of their empty CN π* orbitals with a lone pair of a pyrrolenine nitrogen of the porphyrin. Also the loss of pyrrolic NH stretchings of the porphyrins in the IR spectrum of the molecular complexes indicates the occurrence of intramolecular H-bondings. It is proposed that coordination of DDQs in $(DDQ)_2H_2T(4\text{-}X)PP$ complexes occurs from above and below the "plane" of the porphyrins, and they occupy the same positions as HCls in the structure of $[H_4TPP]^{2+}$, $2Cl^-$ species.

Introduction

In contrast to the very extensive studies performed in varied aspects of porphyrin chemistry,[1] little attention has been paid to the nature of the interaction of neutral organic π acceptors with porphyrins. In a recent work on the complexation of *meso*-tetraphenylporphyrins with quinones in organic solvents it was suggested that van der Waals interactions were the main binding force and hydrogen bonding as well as charge-transfer interactions were scarcely involved in the complex formation.[2] We now report that interactions of various *para*-substituted *meso*-tetraphenylporphyrins (Fig. 1) and DDQ yield stable $(DDQ)_2H_2(4\text{-}X)PP$ complexes. To the best of our knowledge these species provide the first examples of 2:1 complexation of a quinone with porphyrins. The great similarities observed in the UV–VIS, ^1H and ^{13}C NMR data of the various $(DDQ)_2H_2T(4\text{-}X)PP$ compounds, and their remarkable correspondence with the known values of H_4TPP^{2+} acid dication [3–5] suggest analogous conformations for the porphyrin nucleus in these species, with two pyrrolenine nitrogen atoms (=N̈–) of the porphyrins acting as electron donors from above and below the mean plane of the porphyrins, forming σ→π* bonds with DDQs.



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

Experimental

Substituted benzaldehydes (4-Cl, 4-CH_3, 4-$CH(CH_3)_2$, 4-OCH_3) and benzaldehyde (Fluka, Merck, and B.D.H.) were used as received. Pyrrole (Fluka) was distilled before use. All the solvents employed for porphyrin synthesis and chromatography were obtained from Fluka, and used as received. Dichloromethane (Merck), which was used for synthesis of the 2:1 complexes, was purified by washing with 5 per cent aqueous sodium carbonate and water, followed by drying over anhydrous calcium chloride, and fractionated.[6] DDQ (Merck) was recrystallised twice from hot benzene–chloroform (2:3). The synthesis and purification of *para*-substituted tetraphenylporphyrins and H_2TPP employed in this study were carried out in general as reported previously.[7,8]

2:1 mixing of DDQ (0.2 mmol) and *meso*-tetraphenylporphyrins, $H_2T(4\text{-}X)PP$ (X = H, Cl, CH_3, $CH(CH_3)_2$, OCH_3) (0.1 mmol) in CH_2Cl_2 (60 ml) at room temperature (~25 °C) after 3–5 days, depending on the type of porphyrin, slowly produced green $(DDQ)_2H_2T(4\text{-}X)PP$ complex. The solid residue obtained after very slow evaporation (3–4 days) of the solvent contained no excess of either DDQ or $H_2T(4\text{-}X)PP$. These reactions led to the same green compounds in the dark or under Ar, and also in chloroform or benzene as solvents.

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

^1H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX 250 MHz spectrometer. For good integration results, in addition to the correction of the spectrum base line, concentration of the molecular complexes should be 0.006 M. Deuteriochloroform was used as solvent in these experiments. The residual $CHCl_3$ in the conventional 99.8 atom% $CDCl_3$

Table 1 UV–VIS spectra of *meso*-tetraphenylporphyrins, and their 2:1 DDQ complexes in $CHCl_3$

Porphyrins	Free donor peaks (λ/nm) Soret	DDQ complexes peaks (λ/nm) Soret		Acid dication[a] peaks (λ/nm) Soret	
H_2TPP	416.7, 516.8, 551.5, 592.0, 648.0	443.3, 605.0, 658.1		441.7, 608.0, 658.8	
$H_2T(4\text{-Cl})PP$	418.0, 517.4, 551.4, 592.0, 648.8	446.5	662.9	443.6, 610.0, 661.0	
$H_2T(4\text{-CH}_3)PP$	418.3, 518.4, 554.0, 593.0, 649.0	446.1	669.6	445.6	671.9
$H_2T(4\text{-CH(CH}_3)_2)PP$	419.9, 519.2, 555.2, 594.4, 650.0	446.4	671.7	445.1	670.7
$H_2T(4\text{-OCH}_3)PP$	419.5, 520.5, 557.1, 596.0, 653.0	454.7	690.4	452.5	694.7

[a] Positions of the peaks correspond to those given in ref. 3(*a*) with DMF solvent.

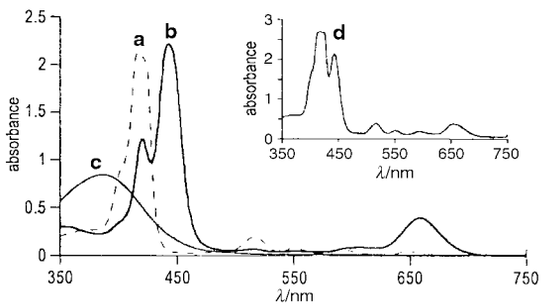


Fig. 2 UV–VIS spectra of (a) H_2TPP (1.33×10^{-4} M); (b) $(DDQ)_2$-H_2TPP (1.33×10^{-4} M); (c) DDQ (7.80×10^{-3} M) in $CHCl_3$ at 25 °C. Inset: (d) 1:1 DDQ–H_2TPP system (1.33×10^{-4} M).

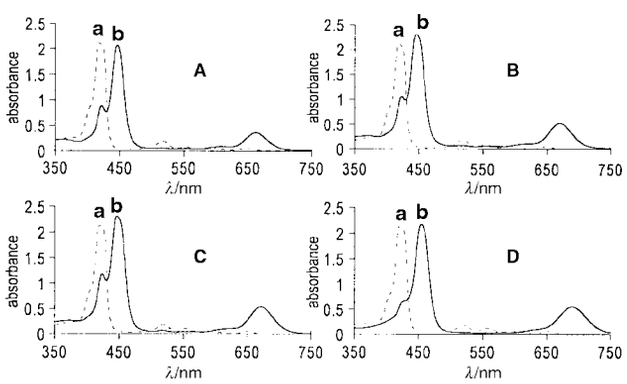


Fig. 3 UV–VIS spectra of $CHCl_3$ solutions (1.33×10^{-4} M) of H_2T-(4-Cl)PP (Aa), $(DDQ)_2H_2T(4\text{-Cl})PP$ (Ab); $H_2T(4\text{-CH}_3)PP$ (Ba), $(DDQ)_2H_2T(4\text{-CH}_3)PP$ (Bb); $H_2T(4\text{-CH(CH}_3)_2)PP$ (Ca), $(DDQ)_2H_2T$-$(4\text{-CH(CH}_3)_2)PP$ (Cb); $H_2T(4\text{-OCH}_3)PP$ (Da), $(DDQ)_2H_2T(4\text{-OCH}_3)PP$ (Db), at ~25 °C.

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-Elmer 781 spectrophotometer using KBr pellets.

Results and discussion

Electronic spectra

Fig. 2 shows the UV–VIS spectra of $CHCl_3$ solutions of H_2TPP, DDQ, $(DDQ)_2H_2TPP$ molecular complex, and also that of a $CHCl_3$ solution of the solid residue obtained (after several days) from the 1:1 DDQ–H_2TPP reaction system. The spectrum of the green $CHCl_3$ solution of $(DDQ)_2H_2TPP$ complex (Fig. 2b) with three new absorption bands at 443.3, 605.0, and 658.1 nm is quite different from the spectra of both H_2TPP (Fig. 2a) and DDQ (Fig. 2c). It appears that the ~420 nm band in Fig. 2b is due to the H_2TPP Soret absorption, produced by partial dissociation of the complex. It is observed that the relative intensity of this band is sensitive to the concentration of the complex, and increases by decreasing its concentration, indicating greater dissociation upon high dilution. The spectrum of the 1:1 DDQ–H_2TPP reaction mixture (Fig. 2d) clearly shows superimposition of H_2TPP and $(DDQ)_2H_2TPP$ spectra, with no indication for existence of a 1:1 adduct. It is noteworthy that our attempts to crystallise a 1:1 DDQ–H_2TPP complex, by very slow evaporation of the solvent from the corresponding 1:1 solution, always failed and led to the separation of pure crystals of $(DDQ)_2H_2TPP$ and H_2TPP. The use of an excess of DDQ beyond the 2:1 molar ratio in the synthesis caused no detectable changes in the spectrum of $(DDQ)_2$-H_2TPP complex. These observations are closely related to the spectral results for the protonation of H_2TPP (Table 1), which only yields H_4TPP^{2+} dication, with no evidence for the occurrence of a monoprotonated species.[3]

Similar results were obtained for the interaction of various *para*-substituted *meso*-tetraphenylporphyrins and DDQ. The UV–VIS spectra of four different *para*-substituted *meso*-tetraphenylporphyrins and their 2:1 DDQ complexes in $CHCl_3$ solutions are displayed in Fig. 3 (A–D). It is observed that the spectra of $(DDQ)_2H_2T(4\text{-X})PP$ complexes are distinctively different from those of the related free porphyrin bases. However, they nearly match with the spectra of their corresponding acid dications (Table 1),[3a] showing parallel substituent effects in all cases. Our attempts at making 1:1 DDQ adducts from 1:1 reaction mixtures were unsuccessful, and the sole products obtained were 2:1 DDQ–porphyrin compounds. It is noteworthy that whilst protonation of the bulky and less flexible tetramesitylporphyrin (H_2TMP), with large porphyrin–aryl dihedral angles,[4] instantly produced the corresponding green diprotonated species in CH_2Cl_2, it remained almost intact for several days in the presence of DDQ, under our experimental conditions. The absence of reaction between DDQ and H_2TMP clearly demonstrates the importance of steric effects of porphyrins in these complexation reactions.

UV–VIS spectral shifts upon complexation of various tetraphenylporphyrins with DDQ indicate that π-resonance rather than σ-induction effects are predominantly transmitted from *para*-phenyl substituents to the porphyrin core in these complexes, as has been observed for the related porphyrin acid dications and porphyrins themselves.[3a] It is notable that the spectral red shifts in $(DDQ)_2H_2T(4\text{-OCH}_3)PP$ (11.4, 32.3 nm), relative to $(DDQ)_2H_2TPP$, are much larger than the shifts corresponding to all the other $(DDQ)_2H_2T(4\text{-X})PP$ complexes (2.8–3.2, 4.8–13.6 nm) examined (Table 1). This effect may reflect a better resonance-type-interaction by π-electrons of 4-OCH_3 groups.

^{1}H NMR

Further evidence for spectral analogy between various $(DDQ)_2$-$H_2T(4\text{-X})PP$ complexes and H_4TPP^{2+} [ref. 5(*b*)] is obtained when their ^{1}H NMR data (Table 2) are compared. ^{1}H NMR spectra of H_2TPP in DDQ–H_2TPP reaction systems with 1:1 and 2:1 molar ratios are illustrated in Fig. 4. ^{1}H NMR spectra of different $H_2T(4\text{-X})PP$ and their corresponding 2:1 DDQ complexes are presented in Fig. 5 (A–D). It is observed that in the free base porphyrins the internal N–H protons are upfield (−2.74 to −2.86 ppm), and β-protons appear at 8.84–8.87 ppm.[9,10] The *meso*-phenyl protons consist of a doublet for the *ortho*-hydrogens (8.08 to 8.24 ppm) and another doublet (7.27 to 7.76 ppm) for the *meta*-protons. The *meta*- and *para*-

Table 2 ^{1}H NMR resonances of various *para*-substituted porphyrins and their 2:1 DDQ complexes[a]

Compounds	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
2:1 complex	−0.42	8.61	8.68	7.99	7.99
$\Delta\delta$	2.34	−0.26	0.47	0.24	0.24
H_2T(4-Cl)PP	−2.86	8.84	8.12, 8.15	7.73, 7.76	—
2:1 complex	−0.29	8.59	8.59	7.98, 8.01	—
$\Delta\delta$	2.57	−0.25	0.47	0.25	—
H_2T(4-CH_3)PP	−2.77	8.85	8.08, 8.11	7.54, 7.56	2.70
2:1 complex	−0.38	8.55	8.55	7.78, 7.81	2.77
$\Delta\delta$	2.39	−0.30	0.47	0.24	0.07
H_2T(4-$CH(CH_3)_2$)PP	−2.74	8.87	8.12, 8.15	7.59, 7.62	CH = 3.20–3.32, CH_3 = 1.56
2:1 complex	−0.32	8.56	8.56	7.84, 7.87	CH = 3.27–3.38, CH_3 = 1.58
$\Delta\delta$	2.42	−0.31	0.44	0.25	CH = 0.07, CH_3 = 0.02
H_2T(4-OCH_3)PP	−2.75	8.86	8.11, 8.14	7.27, 7.31	4.10
2:1 complex	−0.13	8.48	8.59, 8.62	7.50, 7.54	4.15
$\Delta\delta$	2.62	−0.38	0.48	0.23	0.05

[a] Chemical shifts in ppm from impurity of $CHCl_3$ (7.26 ppm) in $CDCl_3$ solvent. [b] The corresponding data are from ref. 5(*b*).

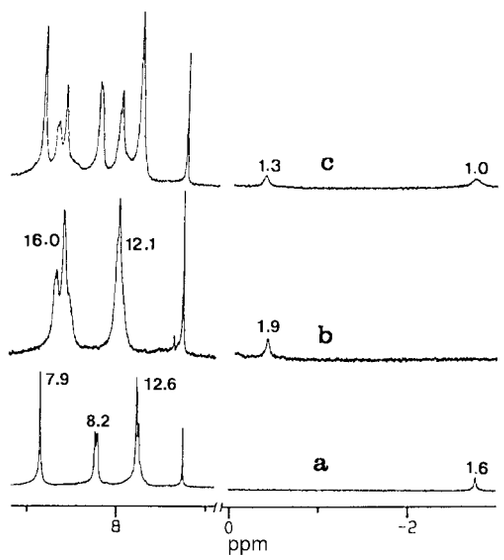


Fig. 4 ^{1}H NMR spectra (250 MHz) of (a) H_2TPP (0.006 M); (b) $(DDQ)_2H_2TPP$ (0.006 M); (c) 1:1 DDQ–H_2TPP (0.006 M) system in $CDCl_3$ at 25 °C. Integrals of the lines or multiplets, are given on their sides. The line at 7.26 ppm is related to $CHCl_3$ in the solvent. On the right are displayed chemical shifts for N–H proton lines. On the left the chemical shifts of aromatic proton lines are shown.

hydrogens of H_2TPP overlap and give a doublet (7.75–7.77 ppm).[9,10]

Complexation of porphyrins with DDQ, similar to the diprotonation of H_2TPP,[5b] affords a downfield motion of N–H signals ($\Delta\delta$ = 2.34 to 2.62 ppm) and an upfield shift of β-protons ($\Delta\delta$ = −0.25 to −0.38 ppm), Table 2. Both of these changes are in the direction to be expected if the ring current of the porphyrin core decreases on complexation.[5b] Also complexation of different H_2T(4-X)PPs with DDQ and diprotonation of H_2TPP lead to similar changes in the spectra for the corresponding protons of the *meso*-phenyl rings. All the phenyl ring protons show a downfield motion, and *ortho*-phenyl and β-pyrrole hydrogens overlap and result in a broad line at 8.55 to 8.68 ppm. However, in the case of $(DDQ)_2H_2T$(4-OCH_3)PP the *ortho*- and the β-proton resonances are separated (Fig. 5 Db). A slightly broad signal is also observed at 7.50–8.01 ppm which is assigned either to 8 *meta*-phenyl protons, or to 12 *meta*- and *para*-hydrogens in the case of the H_2TPP complex. It should be noted that the integration for pyrrolic NH hydrogens, which is critically concentration dependent, in all 0.006 M $CDCl_3$ solutions of the $(DDQ)_2$porphyrin complexes (Fig. 4, 5) is less than 2.5 in contrast to ~4 as is expected for a diprotonated porphyrin species.

The ^{1}H NMR spectrum of the 1:1 DDQ–H_2TPP reaction system (Fig. 4c) demonstrates superimposition of signals of both H_2TPP and $(DDQ)_2H_2TPP$ complex at their normal chemical shift values, with no line which could be assigned to the formation of a 1:1 intermediate adduct. Again this is in complete accord with the protonation of H_2TPP in $CHCl_3$ where no monoprotonated species H_3TPP^+ has been observed.[5b] When the relative amount of DDQ with respect to H_2TPP was increased beyond that required for $(DDQ)_2H_2TPP$ formation, no changes in the chemical shifts of ^{1}H NMR signals were observed. The same trend, with no sign of the formation of a 1:1 compound, has also been seen in the interaction of the other tetraphenylporphyrins with DDQ.

Consistent with the above experiment, ^{1}H NMR spectra for the titration of 0.2, 0.5, 1.0, 1.3, 1.6 equivalents of DDQ into a $CDCl_3$ solution of H_2TPP (0.006 M) and H_2T(4-OCH_3)PP (0.002 M) displayed only resonances of both free porphyrins and the corresponding 2:1 DDQ complexes. The ^{1}H NMR spectrum for the addition of 2 equivalents of DDQ into porphyrins exclusively showed the lines of $(DDQ)_2$porphyrin complexes. The relative integrations for combined β-pyrrole and the *ortho*-phenyl hydrogens of the free and the complexed porphyrins at the intermediate stoichiometries of DDQ also closely correlated with 2:1 rather than 1:1 complexation of DDQ with H_2TPP, and H_2T(4-OCH_3)PP. Since the reactions were slow the spectra were taken 1–3 days after the preparation of the NMR samples, to ensure complete complexation of DDQ and the porphyrins.

^{13}C NMR

^{13}C NMR spectra of H_2TPP, DDQ, and $(DDQ)_2H_2TPP$ are presented in Fig. 6. H_2TPP gives rise to six ^{13}C signals (Fig. 6a) and a very broad signal (at ~145 ppm, not observed) for α-carbons[9] (see Table 3, for the assignments).[5c] Complexation of H_2TPP with DDQ sharpens the α-carbon (145.96 ppm), and β-carbon (128.95 ppm) signals (Fig. 6b) and causes small downfield shifts in the NMR lines of C_{meso}, C_2', C_3', and C_4' and upfield shifts of C_1' and C_β of the porphyrin, Table 3. These changes are in the same directions as those observed for the corresponding carbons upon diprotonation of H_2TPP.[5c]

^{13}C NMR spectra of different *para*-substituted *meso*-tetraphenylporphyrins, and their DDQ complexes are presented in Fig. 7 (A–D). The ^{13}C assignments for H_2T(4-Cl)PP[9] (Fig. 7 Aa), H_2T(4-CH_3)PP[9] (Fig. 7 Ba), and H_2T(4-OCH_3)PP (Fig. 7 Da) are based on the known values for the corresponding

Table 3 ^{13}C NMR chemical shifts of some *para*-substituted porphyrins and their 2:1 DDQ complexes[a]

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
2:1 complex	145.96	128.95	123.44	139.89	138.87	128.73	130.51
H_2T(4-Cl)PP	—	131.64	119.38	140.75	135.89	127.45	134.79[c]
2:1 complex	145.87	128.91	122.39	137.87[d]	139.66	129.11	137.12[d]
H_2T(4-CH_3)PP	—	131.37	120.47	139.73	134.92	127.81	137.71[c]
2:1 complex	146.05	128.68	121.82	137.47	138.94	129.35	140.93
H_2T(4-$CH(CH_3)_2$)PP	—	131.44	120.46	140.01	135.12	125.13	148.56
2:1 complex	146.03	128.88	123.57	137.71	139.23	127.04	151.80
H_2T(4-OCH_3)PP	—	131.34	120.13	135.07[f]	135.99[f]	112.60[e]	159.80[e]
2:1 complex	146.36	128.53	123.01	133.44	140.46	114.50	162.11

[a] Chemical shifts in ppm downfield from $CDCl_3$ (76.90–77.92 ppm). [b] Chemical shifts, from ref. 5(*c*) with internal Me_4Si (±0.010). [c] Assignments of C_4' signals in H_2T(4-Cl)PP (134.79 ppm), and H_2T(4-CH_3)PP (137.71 ppm) are based on the resonances of the carbons attached to Cl in chlorobenzene (134.3 ppm)[12] and to CH_3 in toluene (137.7 ppm),[12] respectively. [d] May be interchanged. [e] For H_2T(4-OCH_3)PP the two signals at 112.60 and 159.80 ppm which are assigned to C_3' and C_4' are closely related to the corresponding ^{13}C resonances of anisole.[12] [f] The relative intensities ~(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-OCH_3)PP, respectively.

Table 4 ^{13}C NMR chemical shifts for free and porphyrin complexed DDQs

Porphyrins	C_1	C_4	C_2	C_3	C_5	C_6	C_7	C_8
Free DDQ	169.57		142.28		126.61		108.36	
H_2TPP	(171.81, 172.07)		143.33		135.39	87.99	165.43	112.23
H_2T(4-Cl)PP	(171.69, 172.07)		143.27		135.37	87.90	165.27	112.21
H_2T(4-CH_3)PP	(171.78, 171.95)		143.25		135.35	87.93	165.51	112.24
H_2T(4-$CH(CH_3)_2$)PP	(171.80, 172.10)		143.36		135.36	87.99	165.49	112.25
H_2T(4-OCH_3)PP	(171.89, 172.08)		143.38		135.42	87.98	165.69	112.40

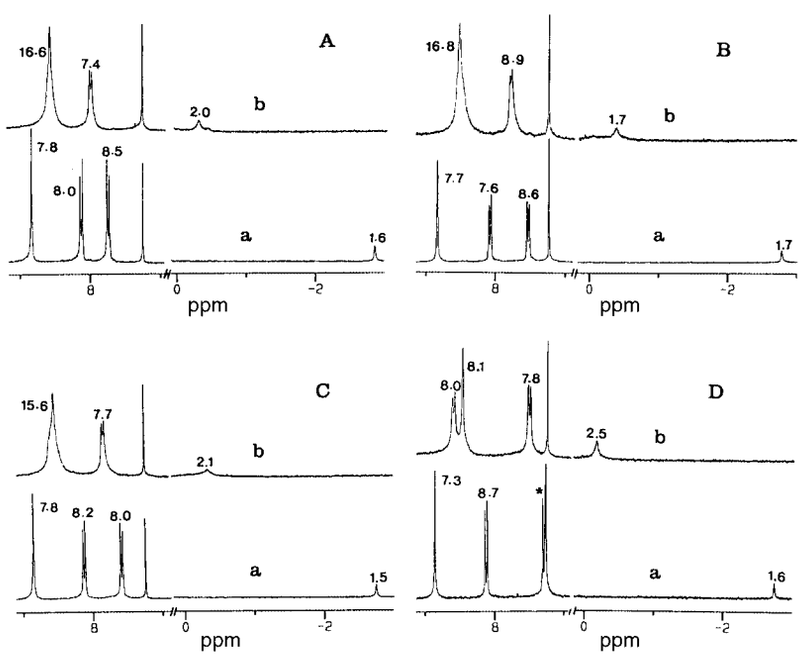


Fig. 5 ^1H NMR spectra (250 MHz) of H_2T(4-Cl)PP (Aa), $(DDQ)_2H_2T$(4-Cl)PP (Ab); H_2T(4-CH_3)PP (Ba), $(DDQ)_2H_2T$(4-CH_3)PP (Bb); H_2T(4-$CH(CH_3)_2$)PP (Ca), $(DDQ)_2H_2T$(4-$CH(CH_3)_2$)PP (Cb); H_2T(4-OCH_3)PP (Da), $(DDQ)_2H_2T$(4-OCH_3)PP (Db) in $CDCl_3$ at 25 °C. The concentrations of all species are 0.006 M. The corresponding integration for the peak marked * cannot be determined precisely.

carbons in H_2TPP,[5c,9] H_2T(4-$CH(CH_3)_2$)PP[11] and by considering ^{13}C shifts of the related carbons in chlorobenzene,[12] toluene[12] and anisole,[12] Table 3. Complexation of various tetraphenylporphyrins with DDQ, leading to the formation of 2:1 compounds, results in very similar changes in their ^{13}C resonances as compared with those observed for the corresponding carbons in the conversion of H_2TPP to H_4TPP^{2+} [ref. 5(*c*)] (Table 3).

The remarkable correspondence between UV–VIS, ^1H and ^{13}C NMR spectral data of H_4TPP^{2+} and various $(DDQ)_2H_2T$-(4-X)PP complexes leads to the presumption of a similar structure for their porphyrin skeletons in all these species, with noncoplanar pyrrole rings tilted alternately up and down.[13] The proposed conformation makes the lone electron pairs of the two pyrrolenine nitrogens more accessible for donation to π* acceptor orbitals of DDQs, possibly located above and below the mean plane of the porphyrin (Fig. 8a), similar to the electron donation to the protons in H_4TPP^{2+} acid dication.[13] The structure in Fig. 8a requires that N–H protons be on adjacent nitrogens, which is not normal for H_2TPP.[13] However, it should be noted that the proposed tilting of the pyrroles in the complexes minimizes the van der Waals repulsion of the inner N–H hydrogens in such a conformation.[13]

The rather large broadening of ^1H NMR signals of porphy-

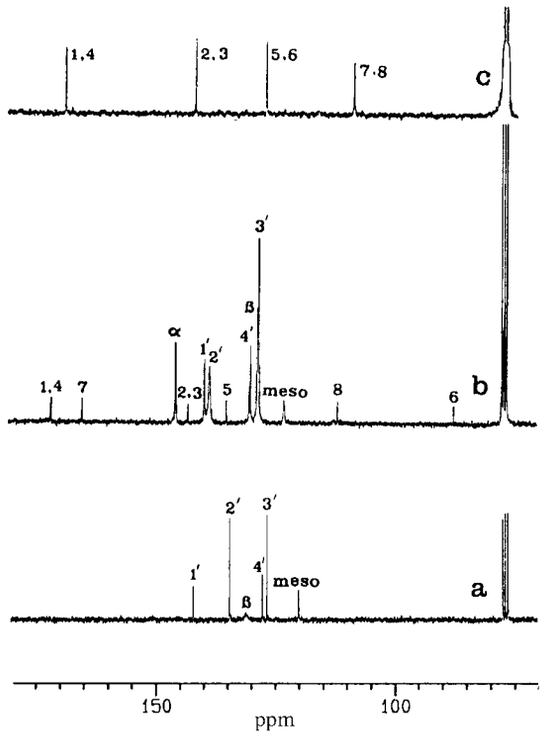


Fig. 6 ^{13}C NMR spectra of (a) H_2TPP (b) $(DDQ)_2H_2TPP$ (c) DDQ in $CDCl_3$ at 25 °C.

rins (Fig. 4b, 5b), caused by their complexation with DDQs, may reflect the occurrence of an asymmetry or some dynamic processes in these systems. The specific two-point coordination of porphyrins to DDQs (Fig. 8a) seems to be consistent with asymmetrical pyrrole rings being present in the porphyrin structure. In accordance with this some resonances of ^{13}C of the complexed porphyrins are also slightly broad.

One might, however, assume another possibility for the structure of $(DDQ)_2H_2(4\text{-}X)PP$ complexes, in which both inner hydrogens are on one side of the tilted porphyrin core and bonded to the opposite nitrogens. This structure requires that the two rather bulky DDQs be located on the other side of the porphyrin plane, and bonded to the two pyrrolenine nitrogens, Fig. 8b. It appears that the relatively larger steric demands, and the absence of any possibility for intramolecular H-bondings for such a structure, may make it less favorable than Fig. 8a.

DDQ interaction site

The next question to be addressed now concerns the nature of the acceptor orbital of DDQ. Observation of seven ^{13}C signals for a complexed DDQ (Fig. 6, 7), in contrast to only four signals for a free DDQ[14] (Fig. 6c), clearly indicates a great loss in the symmetry of DDQ upon its reaction with $H_2T(4\text{-}X)PP$. The suggested resonance form for the interaction of a π^* orbital, centered at a –C≡N group, accepting an electron pair from a pyrrolenine nitrogen (Fig. 8a) appears to be most consistent with the ^{13}C NMR assignments of a complexed DDQ. As far as

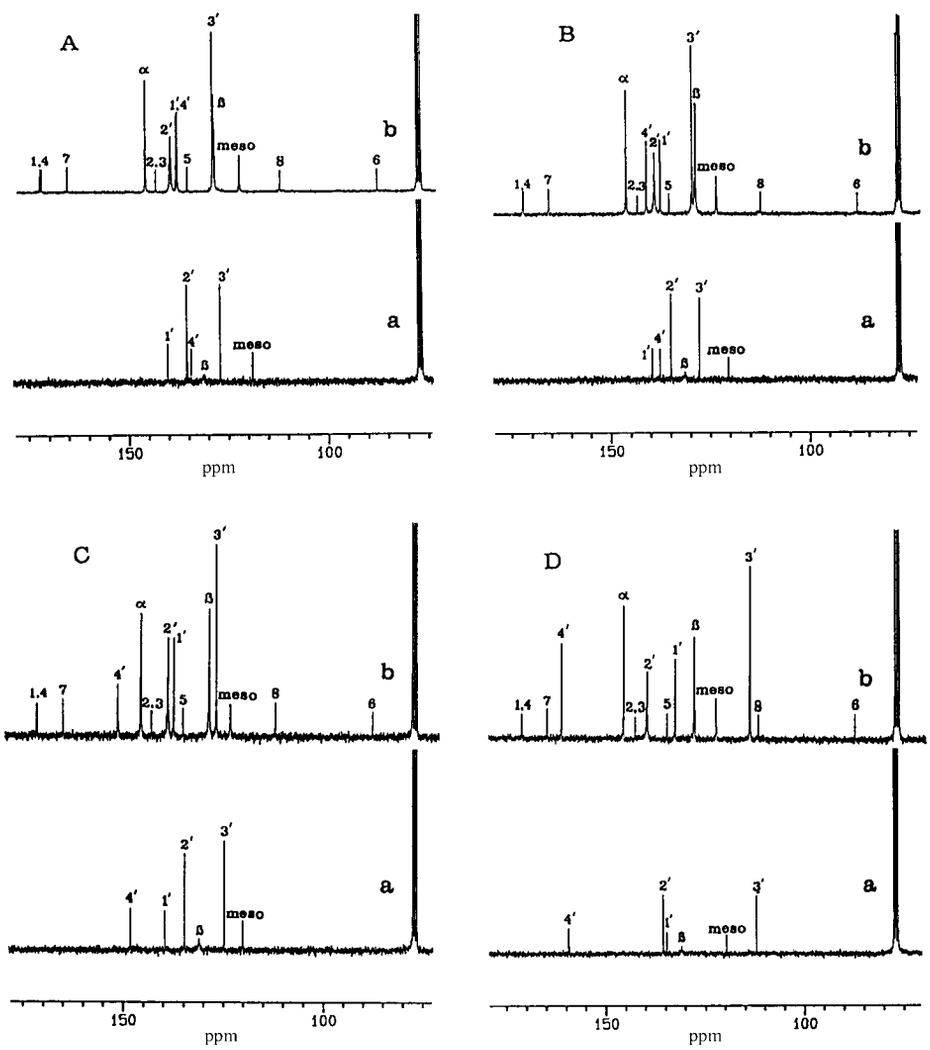


Fig. 7 ^{13}C NMR spectra of (Aa) $H_2T(4\text{-}Cl)PP$, (Ab) $(DDQ)_2H_2T(4\text{-}Cl)PP$; (Ba) $H_2T(4\text{-}CH_3)PP$, (Bb) $(DDQ)_2H_2T(4\text{-}CH_3)PP$; (Ca) $H_2T(4\text{-}CH(CH_3)_2)PP$, (Cb) $(DDQ)_2H_2T(4\text{-}CH(CH_3)_2)PP$; (Da) $H_2T(4\text{-}OCH_3)PP$, (Db) $(DDQ)_2H_2T(4\text{-}OCH_3)PP$ in $CDCl_3$ at 25 °C.

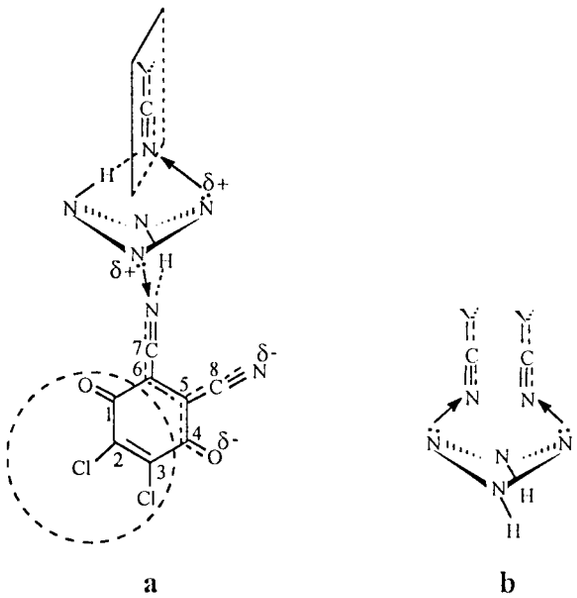


Fig. 8 (a) Schematic representation of the proposed structure and bonding interactions for a $(DDQ)_2H_2T(4\text{-}X)PP$ complex. In the middle the nitrogens of the tilted pyrroles of a porphyrin core are shown. Below the mean plane of the porphyrin a CN bonded DDQ and its possible π-resonance structure are illustrated. Above the "plane" another CN bonded DDQ is only partially drawn. The dashed circle separates C_1, C_2, and C_3 of the coordinated DDQ from the rest of the molecule indicating that they are out of the conjugation system. (b) Presents a less probable general scheme for the complexes, with two DDQs on one side of the porphyrin.

chemical shifts of ^{13}C signals in the complexed DDQ are concerned (Table 4), the expectation is that the largest shifts, relative to the corresponding values for the free DDQ, would be due to the carbon atoms that are either closest to the acceptor site or related to the ones that are involved in the conjugation system. Thus, the ^{13}C NMR line assignments for the acceptor site, C_6=C_7=N (C_6 = 87.90–87.99 ppm, and C_7 = 165.27–165.69 ppm), while displaying greatest shifts (38.71–38.80 upfield, and 56.91–57.33 ppm downfield, respectively), also compare well with the ^{13}C line positions in allene.[15] In contrast carbon atoms attached to the chlorins in DDQ (C_2, C_3), both being furthest away from the donor–acceptor interaction site and not participating in the conjugation, therefore have identical line positions in different complexes with only 0.97–1.10 ppm shifts compared to the free DDQ values. The two very close signals at 171.69–171.89, and at 171.95–172.10 ppm (Fig. 6b, 7b), are attributed to the two C=O groups in the complexed DDQs, and show very small shifts (2.12–2.53 ppm) relative to DDQ itself. Based on the π-resonance form presented in Fig. 8a, we may argue that C_1, although rather close to the interaction site, is not involved in the conjugation system and consequently is only slightly affected by the complexation, and has its ^{13}C NMR line relatively unchanged. On the other hand C_4, while participating in the π-resonance, is quite remote from the coordination site, and consequently its ^{13}C NMR resonance is expected to show very little shift upon the complexation. Assignment of the lines at 112.21–112.40 ppm to C_8 of the second –C≡N group (3.85–4.04 ppm shift) and the line at 135.35–135.42 ppm to C_5 (8.74–8.81 ppm shift) seems reasonable, and consistent with their relative distances from the interaction site.

The IR spectrum of free DDQ shows a C=O stretching (1675 cm^{-1}) and a –C≡N stretching (2233 cm^{-1}) band.[16] Complexation of DDQ with various $H_2T(4\text{-}X)PP$ results in two carbonyl stretching bands, tentatively assigned to C_1=O (~1695 cm^{-1}), which is not involved in the conjugation, and C_4=O (~1640 cm^{-1}), and a broad band (~2210 cm^{-1}) corresponding to both C_7N and C_8N stretchings. These results appear to relate reasonably well with the π-resonance form given for the complexed DDQ in Fig. 8a. Complete disappearance of the N–H stretching band of tetraphenylporphyrins (~3320 cm^{-1})[17] in the spectrum of $(DDQ)_2$porphyrin adducts suggests the formation of an intramolecular hydrogen-bonding between pyrrolic hydrogens of the porphyrins and DDQs.[18] Actually the deformation of the porphyrin core (Fig. 8a) seems to facilitate such interactions, through providing better orientations for the related sites.

Finally the absence of conclusive evidence for monocomplexation of porphyrins with DDQs is of interest. An explanation may be that the lone electron pairs of pyrrolenic nitrogens in the relatively planar free tetraphenylporphyrins are directed towards the center of the ring, and are not readily available for complexation.[13] Thus addition of the first DDQ, which probably leads to a major out of plane deformation of the flexible porphyrin core and tilting of the pyrrole rings as shown in Fig. 8a, is rather difficult and has a greater energy barrier than that for the addition of the second one.[13] This argument about the relative instability of the monocomplexes also explains why the abstraction of the second DDQ in the dissociation of $(DDQ)_2H_2T(4\text{-}X)PP$ complexes should also be easier than the first one, because it is associated with the relaxation of a distorted porphyrin skeleton in a 1:1 adduct to the "planar" free porphyrin. The bulk of our experimental results suggests the occurrence of equilibrium (1) for the complexation

$$2DDQ + H_2T(4\text{-}X)PP \rightleftharpoons (DDQ)_2H_2T(4\text{-}X)PP \quad (1)$$

reactions, which is again consistent with the diprotonation of porphyrins.[5b,13]

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