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Replacement of all phenyl groups in *meso*-tetraphenylporphyrin, TPP, by [2.2]paracyclophane, PCP, enhances the increase of energy of the HOMO and HOMO-1 of porphine, P, already noticed for the mono-[2.2]paracyclophanyl-substituted TPP, and fills the energy gap by the occupied MOs of the PCP units. The first oxidation half-wave potential is respectively decreased to 0.52 V. The CNDO/S-CIS calculations agree with the experimental bathochromic shifts of all bands in the electronic spectra of the considered atropisomers of the title compound, TPCPP, as compared to TPP. In the excited B states the interactions between the PCP and porphine units are represented mainly by the charge transfer of 0.44 e from PCP to P, according to transition density matrix calculations. While electroreduction of the title compound results in a successive formation of the anion radical and dianion, oxidation represents a four-step process involving one electron transfer per step, and resulting in the oxidation of two PCP units. Formation of the conductive polymeric film on the electrode seems to be connected with the transient formation of a quinoid system of bonds.

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Introduction.

The successful synthesis in our laboratory of *meso*-[2.2]-paracyclophanyltriphenylporphyrin, PCPP, [1] as a representative of the novel class of compounds containing a direct link between paracyclophane and porphine drew our attention not only to conformational problems but also to the electronic structure and electrochemical behavior of this system [2]. Although mutual influence of the [2.2]paracyclophane and porphine components on the electronic structure of PCPP was considerable, the electronic structure was expected to be more substantially altered in the case of *meso*-tetrakis[2.2]paracyclophanylporphyrin, TPCPP, in which four [2.2]paracyclophane units, PCP, interact with the porphine core [3], Figure 1. Theoretical

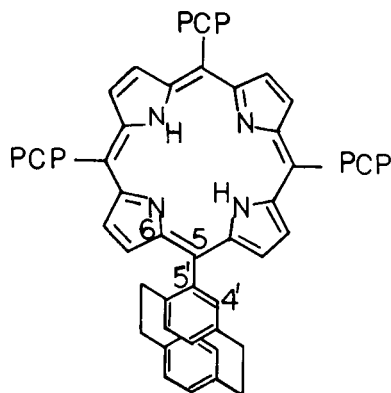


Figure 1. *meso*-Tetrakis[2.2]paracyclophanylporphyrin, TPCPP, under consideration. The [2.2]paracyclophanyl substituents, PCP, are attached either by C4' or C5' atoms which creates, respectively, the *S* or *R* centers.

treatment indicated the existence of four "narrow" classes of stereoisomers of TPCPP [4,5], each containing species of the same conformation ("up" or "down" location of the double-layered PCP substituents *vs* the porphyrin core denoted respectively U and D) but of different

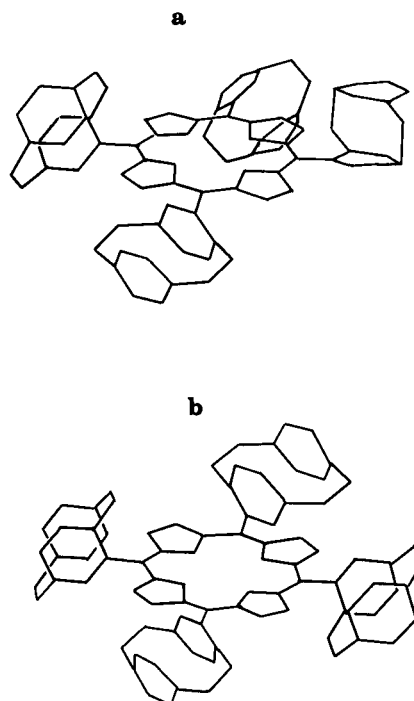


Figure 2. Structures of the two most stable conformers of TPCPP: (a) UDUD-(RRRR) and (b) UUDD-(SRRS) by the ORTEP program applied to the parameters obtained by geometry optimization.

configurations due to the *R* and *S* chirality centers created by the PCP-porphyrine links [5], see Figures 1 and 2. The experimental uv-visible spectra of two isolated classes of TPCPP stereoisomers differed in the positions of all five bands by only 0 to 2 nm and seemed to represent a good experimental basis for the theoretical treatment of the electronic structure of this unusual molecular system.

The spectroelectrochemical examination PCPP [1,2] pointed to some decrease of the first oxidation potential when compared to *meso*-tetraphenylporphyrin, TPP, and to the appearance of two electron transfers in both the reduction and oxidation processes. The oxidation processes were accompanied by remarkable uv-visible spectral changes and revealed a polymerization resulting in the formation of a conductive film on the electrode surface. According to our working hypothesis [1,2], the polymerization proceeds *via* a quinoid form of the paracyclophanylporphyrin. It seemed desirable to examine the behavior of TPCPP from the point of view of the above-listed phenomena in order to obtain better insight into the nature of the paracyclophanyl-porphyrin systems.

The thorough examination of the free-base TPCPP and several respective metallo-complexes [6] gains additional importance in light of the fact that the polymeric material obtained on the electrode from some of them, especially from the Ni(II) complex, reveals strong electrocatalytic activity in a number of processes [7].

EXPERIMENTAL

Materials.

Porphyrin under Investigation.

meso-Tetrakis[2.2]paracyclophanylporphyrin was obtained as a mixture of stereoisomers from (*R* + *S*)[2.2]paracyclophane-4-carbaldehyde [8] and pyrrole in chloroform solution at room temperature as described previously [5a] by following the method of Lindsey *et al.* [9]. The mixture of atropoisomers seen on tlc (1-bromobutane) as overlapping diffused bands within the range of *R_f* 0.2 to 0.6 was used in the electrochemical and spectroelectrochemical investigations, while the separated stereoisomeric classes, UDD and UDUD, were used for recording the uv-visible spectra. The first step in the separation of the latter atropoisomers was performed on a Florisil column, as described previously [5a]. The amount of 100 mg of the isomeric mixture gave 600 ml of eluent after washing with methylene chloride-ethyl acetate (200:1). Evaporation *in vacuo* left 53 mg of microcrystalline material with a metallic glare. The second step in the separation, not considered previously, was based on the following procedure: 53 mg of the preliminary separated fraction of mixed isomers was dissolved in 50 ml of methylene chloride, 5 g of Florisil was added, and the slurry was dried *in vacuo*. The resulting green material was placed on the top of a chromatography column packed with 30 g of Florisil. The developing was performed with methylene chloride until the green band reached the bottom of the column. The collected solvent containing small amounts of non-porphyrin products was discarded. Washing with methylene chloride

was continued until the first green band was eluted. After evaporation of the solvent, 7 mg of the purple glistening microcrystals of UDUD was obtained. Washing was now performed using a methylene chloride-ethyl acetate mixture (200:1), and 25 ml fractions were collected. The combined sixth and seventh fractions characterized by the highest optical density yielded after evaporation 21 mg of the purple crystalline UDD isomer (for the ¹H nmr, 300 MHz spectra see [5a]).

Chemicals for Electrochemical Use.

1,2-Dichloroethane was purchased from Fisher Scientific Company as hplc grade and was twice distilled from phosphorus pentoxide before use. The supporting electrolyte, tetrabutylammonium perchlorate, TBAP, obtained from Eastman was twice recrystallized from ethanol and dried *in vacuo* at 45°.

UV-Visible Spectroscopy.

The uv-visible spectra of TPCPP-UDUD were recorded in benzene on a Perkin-Elmer Lambda 4c uv-vis spectrophotometer C 688-0002 version. The uv-visible spectroelectrochemistry was performed in a bulk cell as well as in a thin-layer cell with a Tracor Northern multichannel analyzer composed of a Tracor Northern 6050 spectrometer containing a crossed Czerny-Turner spectrograph and a Tracor Northern 1710 multichannel analyzer. Spectra were recorded from 279 and 891 nm by a double-array detector. The wavelength values are accurate to ±0.2 nm, while ϵ values are good to ±2% of the absolute value presented. The thin-layer cell built according to Lin *et al.* [10] had a calculated path length of 0.5 mm and platinum mesh as a working electrode.

Electrochemical Methods.

Cyclic voltammetric and differential pulse voltammetric measurements were made with an IBM EC 225 voltammetric analyzer. An omnigraphic Houston 1000 X-Y recorder was used to record the current voltage output for sweep rates between 0.002 and 0.30 V/s. Current voltage curves taken at sweep rates between 0.40 and 10.0 V/s were collected on a digital storage oscilloscope with an X-Y recorder attached. The differential pulse voltammograms were obtained at a stationary platinum disk electrode in 1,2-dichloroethane containing 0.1 M TBAP. A saturated calomel electrode (SCE) was used as the reference electrode.

Theoretical Approach.

Good results achieved in the theoretical treatment of PCPP [2] and the cyclophanes [11a-e] have prompted us to apply a similar procedure to TPCPP. In all calculations the semiempirical quantum chemistry methods were applied in all-valence-electron approximation, AVE. The AVE method was chosen due to the substantial size of the molecule containing 158 atoms which had a basis set of 422 atomic orbitals. All calculations were performed on a Cray supercomputer. A FORTRAN program written by one of the authors (AKW) was used. The Householder-QR-Inverse-Iteration method [12] was modified by one of us (AKW) [13] and applied to matrix diagonalization.

Conformation analysis was performed (MINDO/3 [14]) with the use of geometry optimization by the semiempirical force field method [15]. In all calculations, the porphine structure of D_{2h} symmetry was considered based on X-ray diffraction studies [16a-d]. Similarly, for the paracyclophane structural fragment, the geometry chosen was based on the crystallographic data of [2.2]paracyclophane [17].

The electronic spectra were calculated by the CNDO/S method [18] together with the interaction of singly excited configurations method, CIS. Calculations were performed for UDUD-(RRRR) and UDDD-(SRRS) stereoisomers of TPCPP [5] which represent the lowest energy [5b]. This approach improved the interpretation of the electronic spectra of not only porphine [19,20] and PCP [11], but also of the *meso*-tetraphenylporphyrin, TPP, and PCPP [2]. In this CIS method, 400 configurations were considered for TPCPP, for which the energetic criterion equaled 75000 cm^{-1} . The same criterion was accepted for TPP and PCPP [12]. In the framework of this criterion, one mixes the most important configurations of both the porphine and PCP. The values of oscillator strengths were calculated with the use of the dipole moment operator [18,21]. The transition density matrix method [22,23] was applied to the analysis of the excited states of TPCPP UDUD-(RRRR)]. Details concerning the latter method, as applied to the interpretation of the transannular interactions and the intramolecular charge transfer, can be found in the authors' previous publications [11a-e].

Results and Discussion.

Molecular Orbital Structure.

Conformational analysis showed that the [2.2]paracyclophane-porphine system can assume two energetically stable positions, appearing for the dihedral angles (PCP rotation) 141.8° and 321.8° , respectively [2,5b]. The dihedral angles are represented by C6-C5-C5'-C4' for the *R* mode and C6-C5-C4'-C5' for the *S* mode, Figure 1 (their values increase for the clockwise rotation when looking from C5 to C5' or C4'). As a result of this, the "down", D, and "up" U, conformations appear for each *R* and *S* configuration, and hence a variety of stereoisomers of TPCPP emerge [5a,b]. They are inconvertible due to the high barrier of rotation [5b].

The substitution of porphine in *meso* positions by the phenyl rings, as in the case of TPP, influences the MO energy levels of porphine only to a small degree. However, replacing even one phenyl by PCP demonstrates a substantial influence [2]. This is the reason why TPP represents the reference molecule in our consideration. In TPP the frontier MOs are porphine π -type orbitals. Both the two highest occupied orbitals, HOMO and HOMO-1, and the two lowest unoccupied orbitals, LUMO and LUMO + 1, are separated from the remaining MOs by a significantly large gap of energy. In PCPP the single PCP substituent alters the picture of the occupied orbitals, which is reflected by two effects: (1) increase of the energy of the HOMO and HOMO-1 of porphine and (2) filling the energy gap by the orbitals of PCP. Replacement of all phenyls by PCP substituents enhances both effects. When the most stable conformer of TPCPP is considered, UDUD-RRRR, one can find that further increase of the orbital energy of the HOMO and HOMO-1 or porphine takes place and the energy gap is filled by the occupied orbitals of the successive PCP units. The first effect is illustrated by the HOMO energy values which are -7.39 , -7.26 , and

-6.93 eV for TPP, PCPP, and TPCPP, respectively. According to Koopmans' theorem [24], TPCPP should have the smallest first ionization potential while TPP should have the highest. The above trend is observed during electrochemical oxidation. The first half-wave potentials for TPP and PCPP [1,2] are 1.05 and 0.98 V, respectively. For TPCPP this potential greatly decreases, down to 0.52 V.

The lack of separation of the HOMO and HOMO-1 of porphine from the occupied orbitals of PCP negates the validity of the four-orbital model of Gouterman and co-workers [25]. One can assume that the close vicinity of the highest occupied MOs of the PCPs and porphine in the case of TPCPP, results in the presence of singly excited configurations from the HOMO and HOMO-1 of the PCP substituents to the LUMO and LUMO + 1 or porphine in the well-known Q and B excited states. Similar results were also obtained by the MINDO/3 method.

Singlet Spectra.

Both porphyrin [25] and [2.2]paracyclophane [26] reveal interesting physicochemical properties. This is proven by the electronic spectra of these compounds which provide valuable information concerning the electronic structure, especially when the spectra are supplemented by their theoretical treatment. The latter is provided for the porphyrin mainly by Gouterman *et al.* [25] and for the cyclophanes by our previous publications [11a-e]. It is known that substitution of the porphyrin core in a *meso* position by a single PCP modifies the electronic structure of the porphyrin which results in PCPP acquiring new properties [2]. One can assume that the increase in the number of PCP substituents enhances this trend.

The uv-visible absorption spectra of TPP, PCPP and TPCPP show gradual bathochromic shifts of all absorption bands, see Figure 3. The magnitude of the shifts increases in the order of TPP < PCPP < TPCPP, and shows linear dependence on the number of PCP substituents [5a]. Changes in the intensities of bands also have similar characteristics. However, they are different depending on the type of band; for instance, for the Soret band (B), the intensity increases [5a].

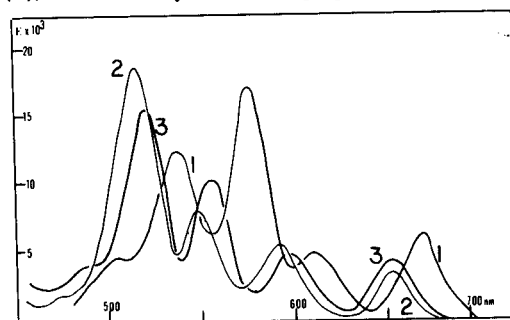


Figure 3. The visible region of the electronic spectra of: *meso*-tetrakis[2.2]paracyclophanylporphyrin, UDUD, **1**; *meso*-tetraphenylporphyrin, **2**; *meso*-[2.2]paracyclophanyltriphenylporphyrin, **3**.

Table 1

Calculated and Observed Electron Transitions of *meso*-Tetrakis[2.2]paracyclophanylporphyrin Compared with *meso*-Tetraphenylporphyrin and *meso*-[2.2]Paracyclophanyltriphenylporphyrin

State [a]	<i>meso</i> -Tetraphenylporphyrin		<i>meso</i> -[2.2]Paracyclophanyltriphenylporphyrin		<i>meso</i> -tetrakis[2.2]Paracyclophanylporphyrin		<i>meso</i> -tetrakis[2.2]Paracyclophanylporphyrin	
	Calcd. [b]	Obsd. [c]	Calcd. [b]	Obsd. [d]	Calcd. (RRRR)-UDUD	Calcd. (SRRS)-UDUD	Obsd. [e]	Obsd. [e]
	λ , nm	f [f]	λ , nm	f [f]	λ , nm	f [f]	λ , nm	f [f]
QX	708.3	0.017	647	0.019	721.5	0.008	652	0.025
QY	601.8	0.071	548	0.046	608.3	0.076	555	0.058
Bx	371.5	2.055			394.0	0.877		
					364.3	1.268		
By	361.0	3.147	419	2.630	385.9	1.351	424	2.339
					375.2	1.417		

[a] See Ref [25] for a discussion of the nomenclature. [b] Ref [2]. [c] In benzene, Ref [38]. [d] In benzene, Ref [2]. [e] In benzene, Ref [3, 5a]. [f] Calculated from $\log E = 5.25 + \log f$.

Table 2

Analysis of some Excited States of *meso*-Tetraphenylporphyrin, *meso*-[2.2]Paracyclophanyltriphenylporphyrin and *meso*-Tetrakis[2.2]paracyclophanylporphyrin by Transition Density Matrix Method

State	<i>meso</i> -Tetraphenylporphyrin [a]				<i>meso</i> -[2.2]Paracyclophanyltriphenylporphyrin [a]				<i>meso</i> -tetrakis[2.2]Paracyclophanylporphyrin, (RRRR)-UDUD				
	1B	1Ph	LE%	CT%	1B	1Ph	1PCP	CT%	1B	1PCP	LE%	CT%	
QX	3.7	0.0	17.1	43.0	4.0	82.9	3.2	0.0	0.1	16.8	40.8	2.3	4.7
QY	6.5	0.0	23.9	26.6	4.0	76.1	5.9	0.0	0.1	22.7	24.8	2.2	4.4
Bx	1.6	0.8	21.0	31.0	3.2	79.0	0.8	0.3	3.3	17.4	15.5	0.2	41.6 [b]
							1.5	0.5	0.5	21.4	22.3	1.3	12.9 [b]
By	10.9	2.0	25.1	34.2	5.6	74.9	3.8	0.4	5.0	20.5	15.4	1.0	39.6 [b]
							3.9	0.4	2.1	16.3	16.3	1.1	43.5 [b]

[a] From Ref [2]. [b] Denotes mainly the transfer from PCP of porphine, the reverse transfer being negligible.

Results of the CNDO/S-CIS calculations obtained for the two most stable conformers of TPCPP, UDUD-(RRRR) and UDD-(SRRS) are shown in Table 1, which also contains our results for TPP and PCPP [2]. The data refer only to the excited Q and B states assigned to the proper absorption bands. One can see that all of the calculated electronic transitions in TPCPP take place at lower wavelengths than those in PCPP and much longer than those in TPP. Furthermore, these wavelengths agree with the observed spectral properties reflected in band locations. Calculated oscillator strength values increase for the particular excited states of TPCPP and parallel the excitation energies. This agrees with our previous experimental observations [3,5a]. The situation deteriorates, however, when the oscillator strengths of the three porphyrins under consideration are compared with the trend of changes observed in absorption band intensities which follow in the order TPP - PCPP - TPCPP. It is possible that when the values of oscillator strength are calculated by applying the gradient operator rather than by using the dipole moment operator, better quantitative results would be obtained [27].

In the case of PCPP [2], calculations suggested the split of the B_x and B_y excited states into two components (see Table 1). For TPCPP the same phenomenon takes place, however, only with regard to the B_x excited state. Together with the split of the mentioned states a decrease of approximately one-half of their oscillator strength takes place. Because both effects are absent in TPP, these changes are a consequence of the introduction of PCP as a substituent instead of phenyl. It is known that as a result of this change, the MO structure is altered, and in the excited states of TPCPP the singly excited configurations appear from the HOMO and HOMO-1 of PCP to the LUMO and LUMO+1 of porphine. This is confirmed by the analysis of the CI coefficients of the B_x and B_y excited states, where the weights of these configurations are approximately the same as those of the singly excited configurations from HOMO and HOMO-1 of porphine to its LUMO and LUMO+1.

Charge Transfer and Local Excitation Effects.

Further proof of the influence of PCP as the substituent, is provided by the analysis of the excited states by the transition density matrix method [23]. The corresponding results are shown in Table 2. Each molecule has been divided into a number of fragments. Four pyrrole rings (Py) and four methine bridges (B) are the structural fragments common for all three molecules considered. The additional fragments appearing in TPP are the phenyl rings (Ph), and in PCPP and TPCPP are the PCP substituents. The numbers l_{Py} , l_B , l_{Ph} and l_{PCP} , in %, give the measure of the local excitation of the respective structural fragments [see 11e]. The numbers l_{B-Py} , l_{Ph-Py} and l_{PCP-Py} , in

%, represent in turn, the extent of the electron interactions connected with the charge transfer between the respective molecular fragments [see 11e]. The LE% numbers give the weight of the states locally excited, while the CT% numbers give the weight of the states with the charge transfer occurring between the fragments. No substantial changes in LE% and CT% numbers have been noticed for any excited states except for the small increase of CT% numbers as a result of the decrease of LE% numbers in the order TPP - PCPP - TPCPP. This would point to the limited influence of the PCP substituents during excitation. This is not the case, however, as shown by the l'_{PCP-Py} numbers. The latter are particularly meaningful for the B_x and B_y excited states of PCPP and TPCPP where $l'_{PCP-Py} = ca. \frac{1}{2} CT\%$. The significance of the interaction between the porphine and the PCP is shown by the extent of the charge transferred from the PCP to porphine. This transfer for the split B_x excited state in TPCPP equals 0.44e, which is greater than in PCPP (0.38 e, [2]). This also demonstrates that the porphine-paracyclophane interactions are greater in TPCPP than in PCPP.

The data in Table 1 show that the calculations of the excited states of both conformers of TPCPP: UDUD-(RRRR) and UDD-(SRRS), give almost identical results. This agrees with the uv-visible spectra of the two separated groups of atropoisomers of TPCPP which are also nearly identical.

Cyclic Voltammetry and Spectroelectrochemistry.

TPCPP undergoes two reductions occurring at -1.27 and -1.65 V, shown in Figure 4 as waves I and II. They are characterized as having identical diffusion-limiting currents and have been analyzed as being reversible, one-electron transfer processes. This was confirmed by both coulometry and by the theoretically reversible 96 mV width of peaks at one-half peak current. As with other free base porphyrin systems, these reductions have been char-

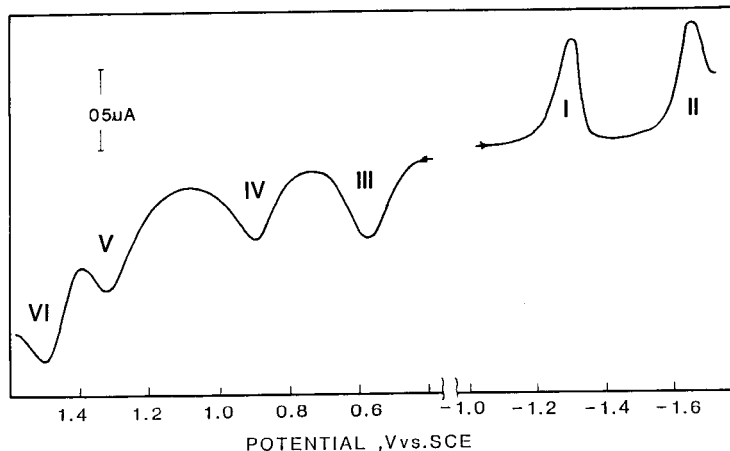


Figure 4. Differential pulse voltammogram of meso-tetrakis[2.2]paracyclophanylporphyrin in 1,2-dichloroethane, 0.1 M TBAP.

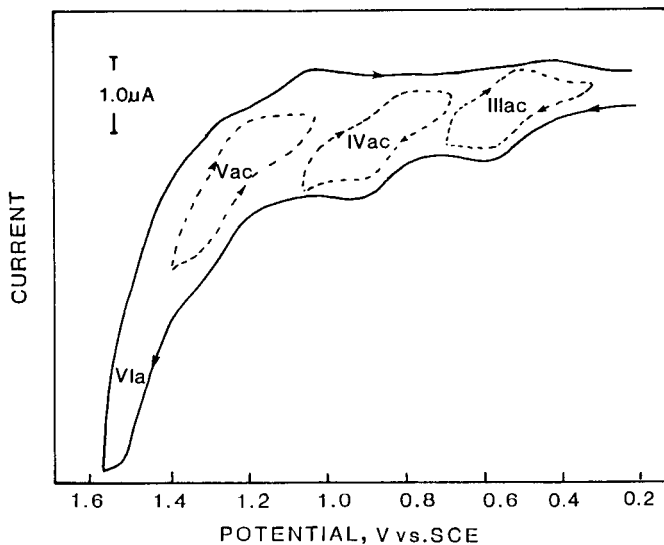


Figure 5. Continuous scan cyclic voltammogram (anodic scan) of *meso*-tetrakis[2.2]paracyclophanylporphyrin in 1,2-dichloroethane, 0.1 M TBAP.

acterized as due to the reduction of the π -ring system to yield the π -anion radical and dianion, TPCPP $^{\cdot -}$ and TPCPP $^{2-}$, respectively. When the potential is scanned from 0.0 to 1.65 V, four oxidation processes are observed. The formal potentials of these oxidation peaks are 0.52, 0.88, 1.30 and 1.46 V (peaks III, IV, V and VI in Figure 5, respectively). The limiting currents observed for each of the four oxidation peaks are approximately equal in magnitude, and controlled-potential electrolysis indicates that one electron was transformed in each oxidation step. Exhaustive electrolysis at 1.58 V confirmed that total of four Faradays were needed for oxidation.

In continuous and single scan cyclic voltammetry, the reversibility as well as the peak currents for those redox processes are strongly influenced by acid-base media. The first anodic process (peak IIIa) observed at 0.52 V occurs at potential about 600 mV more negative than that observed for first oxidation of TPP. This indicates facile oxidation of TPCPP which is demonstrated even at an open circuit in the presence of oxygen. Relatively low oxidation potentials have been observed, previously, only for tetraphenylporphyrins *para*-substituted with a strongly electron-donating substituent such as an *N,N*-diethylamino group [28]. The growth pattern for TPCPP in continuous scan cyclic voltammetry is shown in Figure 6a. In the range of potential between 0.0 and 1.8 V the original four oxidation peaks (IIIa to VIa) are clearly observed only in the first anodic scan. In the second and following scans these peaks gradually decrease and the formation of a new couple of peaks (VIIa and VIIc) is observed at 0.45 and 0.30 V, respectively. These peaks increase and reach a maximum after approximately 25 scans of the potential. The multiple scan voltammogram clearly indicates film

formation. If the potential is scanned further in the negative direction, another redox couple is perceived at -0.40 V (not shown in Figure 4). Both redox reactions (peak VII and peak at -0.40 V) are characteristic for the reduction and oxidation of compounds with a quinoid system of bonds [29]. It is characteristic in the cyclic voltammetry of quinones and hydroquinones, even though they show a strong dependence of $E_{1/2}$ values on the pH of solution, that the first redox couples appear in the range from 0.2 and 0.4 V [30], while the redox potentials for the polyquinonocycloalkanes containing the conjugated C=O and C=C bonds are found between 0.2 and 0.3 V [31].

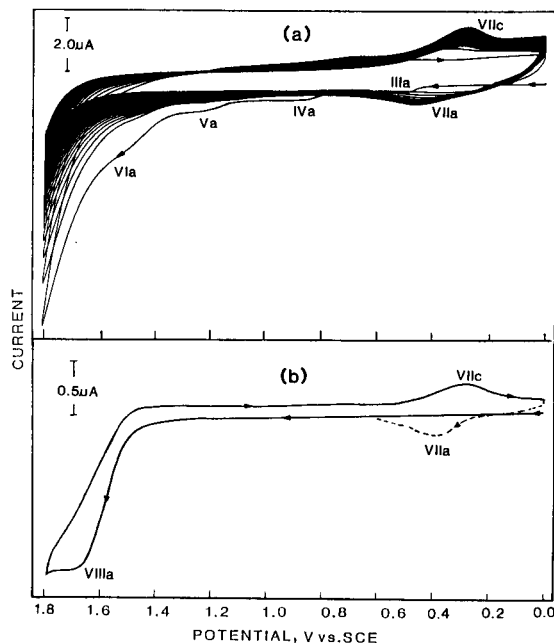


Figure 6. (a) Multiple scan (100 mV/s) cyclic voltammogram, at a Pt electrode, of the solution of *meso*-tetrakis[2.2]paracyclophanylporphyrin in 1,2-dichloroethane, 0.1 M TBAP. (c) Cyclic voltammogram, at a Pt electrode, of the solution of [2.2]paracyclophane in 1,2-dichloroethane, 0.1 M TBAP.

The oxidation of [2.2]paracyclophane itself occurs at a peak potential $E_{pa} = 1.63$ V (peak VIIIa in Figure 6b; compare also [32]), and is irreversible, *i.e.*, not coupled to a reverse reduction process. Both the shape of this peak and the current dependence on scan rate suggest that the electrochemical step is followed by a fast irreversible chemical reaction (an electrochemical EC mechanism). The reversal of the potential scan between 1.55 and 1.80 V yields a new redox couple (Figure 6b, peaks VIIc and VIIa) at $E_{pc} = 0.33$ V and $E_{pa} = 0.39$ V. These values correlate with the 0.2 to 0.4 range for the quinoid compounds mentioned above. It is of particular importance that the potentials of these two peaks are similar to those observed as being formed after a number of scans in the voltammetry of TPCPP, Figure 6a. This porphyrin was later found to form a polymeric film. The separation between these peaks is

larger due to the resistance of the films, but formal potentials are almost identical (0.36 V for [2.2]paracyclophane and 0.37 V for TPCPP).

Analysis of the cyclic voltammograms at different potential scan rates indicates that each of the oxidation steps may be followed by a chemical reaction. This chemical reaction involves proton detachment and, therefore, is expected to be more significant in the presence of OH⁻ ions. The thin-layer uv-visible spectroelectrochemistry shows the spectral changes for each of the four oxidation processes, Figure 7. This includes a decrease of the Soret band at 439.6 nm, the appearance and gradual increase of a new Soret band at 478.7 nm, and a new band at 706.2 nm. The final spectrum obtained after the fourth oxidation process reveals only two major bands at 478.7 and 706.2 nm.

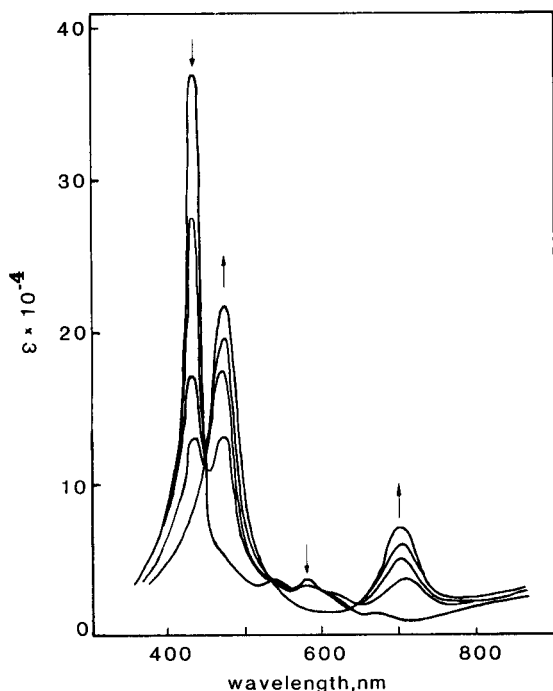


Figure 7. Thin-layer uv-visible spectroelectrochemistry of meso-tetrakis[2.2]paracyclophanylporphyrin in 1,2-dichloroethane, 0.1 M TBAP, during controlled-potential electrooxidation at 1.6 V.

Based on voltammetric, coulometric and spectroelectrochemical data, as well as on previous studies of PCPP [1,2], the first two reactions (waves III and IV in Figure 5) can be assigned to two one-electron oxidations of one of the paracyclophanyl substituents. We can assume that the following reactions (peaks V and VII) are also due to two one-electron oxidations, but of the second paracyclophanyl unit. Oxidation of the first substituent is followed by polymerization and formation of a conductive film on the surface of the electrode. Oxidation of the second substituent increases the rate of polymerization and formation of the

film which becomes more passivating for electrochemical reactions which are followed by chemical steps. However, it does not mean that the film is nonconductive; other reactions, *i.e.*, the reduction and oxidation of quinoid system may occur. All these new data are in agreement with the authors' working hypothesis (see also [2]) suggesting the role of the formation of the quinoid system of bonds in the electro-oxidation of TPCPP, in spite of the obvious strain [33] appearing in the PCP unit(s) containing the *ortho*- or *para*-quinoid system of bonds in one of two benzene rings forming the [2.2]paracyclophanyl substituent. Comparison of the uv-visible spectra of TPCPP and PCPP shows the remarkable decrease of the Soret band absorption connected with its bathochromic shift and the formation of a new longest wavelength band in the region near *ca.* 700 nm. The latter band is shifted bathochromically by 23 nm more for TPCPP than for PCPP. The intensity of this band for TPCPP becomes one-third of the Soret band intensity, while for PCPP the intensity is greater than that of the Soret band. The presence in TPCPP of two PCP units located in *meso* positions 10 and 20 gives a chance for formation of the extended quinoid system of bonds, involving both pyrrole NH centers, not just one, as in the case of PCPP. The shift calculated for such a quinoid TPCPP gave a value of 717.0 nm for the position of the longest wavelength band, as compared to the experimental 706.2 nm. Also a decrease of this band intensity has been revealed. At the present state of research, only the phenomenon of the decrease of the first oxidation potential of TPCPP can be substantiated (see the paragraph on MO Structure), while other phenomena can be approached from the working hypotheses. Although the suggested formation of the quinoid system of bonds during the electro-oxidation of PCPP [2] seems to be consistent with the observations concerning TPCPP, one cannot disregard the possibility of involvement of the initially formed cation radical in the process of polymerization: $\text{TPCPP}^+ + \text{TPCPP} \rightarrow [(\text{TPCPP})_2]^+$, proceeding to $[(\text{TPCPP})_n]^+$. This might be analogous to the formation of the dimeric species of 4,5,7,8-tetramethyl[2.2]paracyclophane [34] or the trimer of coronene [35], the idea which inspired the investigation of cation radical formation in quadruple-layered paracyclophane [36].

The hypothesis of quinoid intermediates gains further support in the case of TPCPP by the presence, in the cyclic voltammograms, of the new redox couple (VIIa, VIIc) discussed above. Also, the results from calculations showed that for the quinoid form of TPCPP in which two oppositely located PCP substituents denoted as PCP_q have single *o*-quinoid rings conjugated across the porphyrin core, diPCP(P)diPCP_q, the bathochromic shift of the longest wavelength band should be greater than that for PCPP. In the latter case, the quinoid system, because of the presence of a single PCP substituent, is able to be spread over

only a fragment of the porphyrin core. This happens because one of two detached protons and electrons are removed from the pyrrole NH center, making the extension of conjugation much more limited. These transient quinoid systems can be responsible for polymerization [37a] resulting in formation of the conductive film on electrode [37b].

Conclusions.

Replacement of all four phenyl groups in TPP by [2.2]paracyclophane units results in the enhancement of electronic effects noticed previously for the *meso*-[2.2]-paracyclophanyltriphenylporphyrin. The most remarkable are: the decrease of the first oxidation potential to 0.52 V, the strong charge transfer from the PCP substituents to the porphine core (0.44 e calculated for the Soret transitions), and the appearance of the four-electron transfer processes during electrode oxidation which involve the [2.2]paracyclophane units. All this allows us to expect interesting properties from the metallo complexes of TPCPP, especially in the field of electrochemistry.

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