Spectroscopic Study of the Complexation of Meso-Tetraphenylporphyrin with π-Acceptors DDQ and TCNE in Chloroform Solution

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ABSTRACT: *Formation of the molecular complexes between meso-tetraphenylporphyrin (TPP) and the π-acceptors 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and tetracyanoethylene (TCNE) in chloroform solution was investigated spectrophotometrically. The formation constants of the resulting 1:1 molecular complexes were determined using the Benesi-Hildebrand and Nash methods. The TPP-DDQ proved to be more stable than TPP-TCNE complex. The resulting molecular complexes were isolated in crystalline form and characterized.*

KEY WORDS: *Molecular complexes, Stoichiometry, Stability, Spectrophotometry, IR, Tetraphenylporphyrin, DDQ , TCNE*

INTRODUCTION

The term "molecular complex" is used to describe a variety of association products of two or more molecules. A molecular complex between two molecules is an association, somewhat stronger than ordinary van der Waals association, of definite stoichiometry [1]. The partners are very often already of closed-shell (saturated valence) electronic structures. The tendency to form molecular complexes occurs when one partner is an electron donor (Lewis base, D) and the other is an electron acceptor (Lewis acid, A). The term donor-acceptor (DA) complex include all such associations [1-3]. Frequently, in such molecular complexes, transition of electron occurs from one atom or group in the molecule to another which is called a "charge-transfer" transition. Subsequently, very intense charge-transfer bands, usually in the visible spectral region, results in molar absorptivities of 10^4 or greater [4,5].

During the past few decades, molecular complexation between a wide variety of donor and acceptor molecules have been the subject of extensive research [1-3,6]. The chemical and industrial applications of many of these molecular complexes are also presented [7,8].

Porphyrins are a class of red pigmented compounds with a cyclic tetrapyrrolic structure, which

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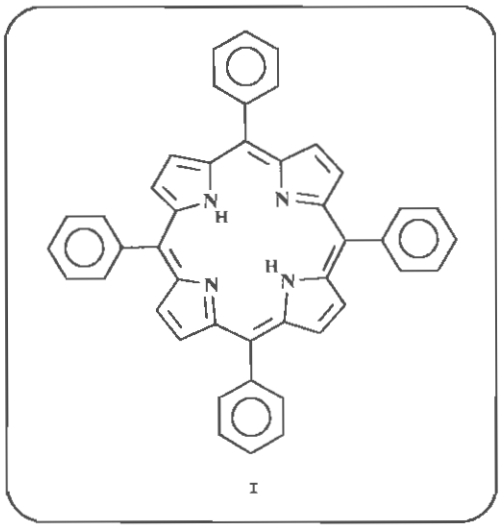
form part of the active nucleus of chlorophylls, hemoglobin, myoglobin, cytochromes and the enzymes catalyses and peroxidease [9,10]. Porphyrins readily enter complex formation with various metals, particularly iron, copper, nickel and manganese [9-15]. Metalloporphyrins are biologically assessable compounds whose function can be varied by changing the metal, its oxidation state, or the nature of the organic substituents on the porphyrin structure. However, in comparison with enormous studies on complexation of porphyrins and metal ions, much less attention has been paid to molecular complexation of porphyrins with neutral molecules [8,16-18].

In recent years we have been interested in spectroscopic investigation of molecular complexes of different macrocylic ligands with some neutral molecules [19-26]. In this paper we report the results of a spectrophotometric study of the complex formation between meso-tetraphenylporphyrin (TPP, I) and the π-acceptors 2,3- dichloro- 5,6- dicyanobenzoquinone (DDQ) and tetracyanoethylene (TCNE) in chloroform solution. Due to the participation of porphyrins and their metal derivatives in many reactions of chemical and biochemical interest [11], their molecular complexation with different organic molecules is of special interest [16-18,28]. In most of the resulting molecular complexes, porphyrins essentially act as electron donors. The extent of these donor-acceptor interactions depends on planarity and the size of participating molecules. In this work, we studied the donor-acceptor complexation of tetraphenylporphyrin with π-acceptors DDQ and TCNE in chloroform solution. To the best of our knowledge, there is no previous literature report on the systems studied.



I

EXPERIMENTAL

Reagent grade DDQ and TCNE (both from Merck) were used without any further purification except for vacuum drying over P_2O_5 . Meso-tetraphenylporphyrin (TPP) was synthesized and purified by the method described by *Adler* et al. [27]. HPLC grade chloroform (Merck) was used as received.

All electronic absorption spectra were recorded on a Philips PUB700 ratio recording spectrophotometer and the absorbance measurements were made with a Philips PU875 spectrophotometer at the desired temperature ±0.1°C. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer using KBr pellets. Melting points were measured by a Gallenkamp apparatus. Specific details are given in the Results and Discussion section.

RESULTS AND DISCUSSION

The electronic absorption spectra of TPP, TCNE and their mixture in chloroform solution, as well as the spectra of TPP in the presence of TCNE of varying concentration are given in Figs. 1 and 2, respectively. The corresponding spectra for the TPP-DDQ system revealed more or less similar spectra. The red solutions of TPP in chloroform turned green upon addition of the π-acceptors used, which was associated with a considerable change in the electronic absorption spectra. As seen, the visible absorption bands of TPP at about 515 and 550 nm disappear gradually and, simultaneously, the two weak absorptions of TPP at 590 and 645 nm are replaced by two intense bands at 600 and, especially, 665 nm, respectivley. Such a considerable change in TPP spectrum in the presence of TCNE (and DDQ) and observation of a very intense absorption band at 665 nm must be associated with a charge-transfer complex, since neither the donor nor the acceptor molecular absorb significantly in this spectra region.

The stoichiometry of the molecular complexes, determined by the continuous variation method [29],

was 1:1 in both cases. Moreover, the existence of well-defined isosbestic points in the spectra of TPP upon titration with the π-acceptors used (see Fig. 2) is a further evidence for a simple complexation equilibrium in solution. It should be noted that the formation of such 1:1 molecular complex between porphyrins and some quinones has already been reported in the literature [17, 18, 28].

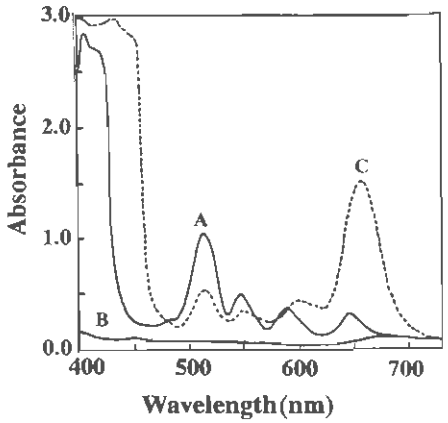


Fig. 1: Absorption spectra of TPP (A, 5.4×10^{-5}M), TCNE (B, 5.0×10^{-5}M) and their molecular complex (C, TPP=4.9 × 10^{-5}M + TCNE= 3.9×10^{-2}M) in chloroform.

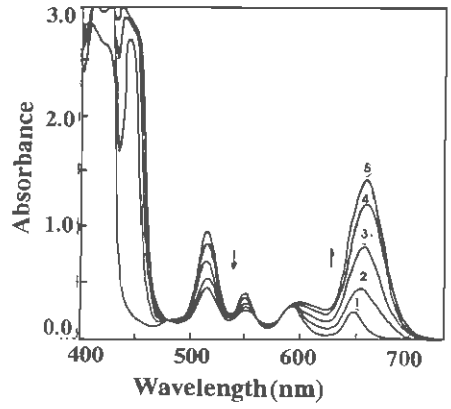


Fig. 2: Absorption spectra of 4.9×10^{-5}M TPP in the presence of varying concentration of TCNE: 1, 0.0 M; 2, 1.9×10^{-3}M; 3, 2.8×10^{-3}M; 4, 3.7×10^{-3}M; 5, 3.9×10^{-2}M.

It is interesting to note that, based on the spectrophotometric monitoring of the complexation reactions, the formation of the TPP-TCNE adduct was found to be a relatively slow process, while that of the TPP-DDQ adduct was fast. The time dependence of the absorption spectrum of a mixture of TPP-TCNE (115:1) is depicted in Fig. 3. The absorbance signal was found to reveal a uniform pseudo-first-order kinetics for the TPP-TCNE complex formation process in solution. The corresponding ln absorbance vs. time plot is rectilinear in the time period studied. The corresponding rate constant at 25°C was calculated as $k_{obs}= 1.1\times10^{-2}\,s^{-1}$.

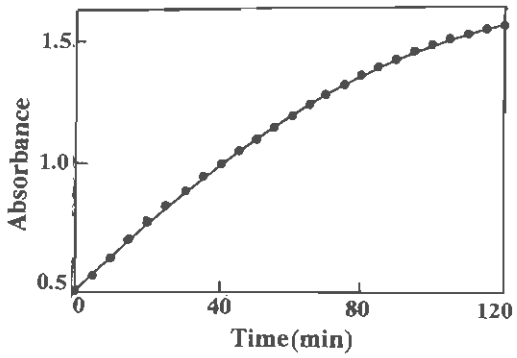


Fig. 3: Absorbance-time plot at 25°C and 665 nm for a 5.0×10^{-5}M of TPP solution in the presence of excess TCNE (i.e. [TCNE]/[TPP]= 115) in chloroform solution.

Two different spectrophotometric methods were employed to calculate the molecular complex formation constants, K_f . The first method was based on the use of the *Benesi-Hildebrand* [30] equation for a donor-acceptor complexation equilibrium:

$$D + A \overset{K_f}{\rightleftharpoons} DA$$

$$\frac{[D]_\circ}{Abs} = \frac{1}{K_f \varepsilon b} \cdot \frac{1}{[A]_\circ} + \frac{1}{\varepsilon b} \qquad (1)$$

where $[A]_\circ$, $[D]_\circ$, Abs, b and ε are the initial concentration of acceptor, donor, solution absorbance, cell thickness and molar absorptivity, respectively. Eq. (1) is applicable under conditions $[A]_\circ >> [D]_\circ$. A second method by *Nash* [31] was also used to estimate the K_f values under the same conditions:

$$\frac{1}{[A]_\circ} = \frac{1}{1\text{-}Abs/Abs_\circ}\,(K_f - K_f \varepsilon_{DA}/\varepsilon_D)\text{-}K_f \qquad (2)$$

where $[A]_\circ$, $Abs_\circ$, ε_{DA} and ε_D are the initial concentration of acceptor, initial absorbance of solution and molar absorptivities of the complex and donor.

Typical Benesi-Hildebrand (A) Nash (B) plots for TPP-DDQ system are shown in Fig. 4 and all calculated K_f values are summarized in Table 1. The linearity of the plots shown in Fig. 4 is a further evidence

for the 1:1 stoichiometry of the molecular complexes, under the experimental conditions used. The data given in Table 1 clearly show excellent agreement between the K_f values obtained by the two different methods. It is also interesting to note that the K_f values for TPP complexes increase with the rise of the electron affinity of the π-acceptors from TCNE to DDQ. These observations agree well with the previously reported results for their complexes with macrocyclic ligands [19, 32, 33]. Noteworthy, due to the planar rigid structure of TPP and the existence of enough donating nitrogen atoms in the porphyrin cavity, there exists the possibility for the approach of two π-acceptor molecules, to the porphyrin ring, presumably one from the top and one the bottom of its rigid plane, to form a 1:2 DA_2 complex. However, under the experimental conditions employed, and because

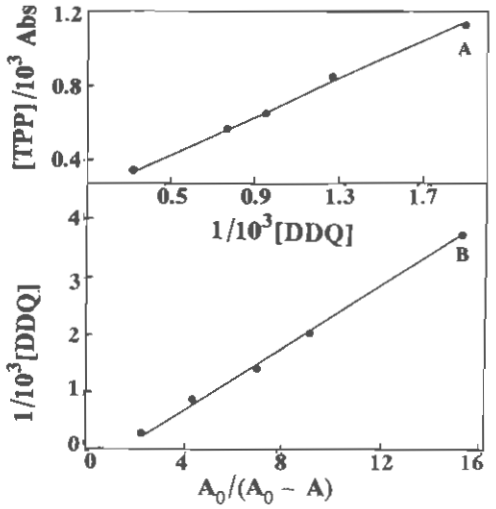


Fig. 4: Benesi-Hildebrand (A) and Nash (B) plots for a 4.9×10^{-5}M solution of TPP in the presence of excess amounts of DDQ in chloroform at 655 and 25°C.

Table 1: Formation constants of the molecular complexes between TPP and DDQ and TCNE in chloroform solution at 25°C

Complex	log K_f*	
	Benesi-Hildebrand	Nash
TPP-DDQ	2.56±0.07	2.53±0.08
TPP-TCNE	2.25±0.05	2.23±0.07

** Average of three replicate measurements*

of the low stability of the resulting complex, the value of K_2 cannot be evaluated by the methods used.

In order to prepare the molecular complex of TPP with DDQ and TCNE in crystalline form, 10 mL of solutions containing 15 mg of TPP and an appropriate amount of the π-acceptor were prepared in chloroform. After filtration, solutions were allowed to evaporate in a time period of about 48 h. The resulting crystals were collected and dried under vacuum for 10 h. The melting points as well as the IR spectral data of the complexes are compared in Table 2.

As it is seen from Table 2, the CN stretching of TCNE and CO stretching of DDQ show a considerable shift to lower and higher frequencies, respectively, upon molecular complex formation with TPP. These shifts are indicative of a higher charge density on the cyano and lower charge density on the carbonyl groups of the π-acceptors TCNE and DDQ, respectively [19,33], as a result of charge transfer from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the π-acceptor.

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Table 2: Melting points, colours and IR spectral data of TCNE and DDQ and their molecular complexes with TPP

Compound	TPP	DDQ	TCNE	TPP-DDQ	TPP-TCNE
Melting point(°C)	>300	212-215	198-200	135-140 (decomposed)	120-125 (decomposed)
Colour	purple	yellow	white	green	green
$\nu_{CO}(cm^{-1})$	—	1673	—	1700	—
$\nu_{CN}(cm^{-1})$	—	2215	2228	2210	2218
			2261		2260

REFERENCES

[1] Mulliken, R. S. and Person, W. B., "Molecular Complexes", Wiley, New York (1969).
[2] Foster, R., "Organic Charge Transfer Complexes", Academic Press, London (1969).
[3] Andrews, L. J. and Keefer, R. M., "Molecular Complexes in Organic Chemistry", Holden-Day, New York (1964).
[4] Mulliken, R. S., Rec. Trav. Chim., **75,** 845(1956).
[5] Drago, R. S., "Physical Methods in Chemistry", Saunders College Publishing, New York (1977).
[6] Tamres, M. and Yarwood, J., "Spectroscopy and Structure of Molecular Complexes", Plenum, New York (1974).
[7] Bryce, M. R. and Murphy, I. C., *Nature,* **309,** 119 (1984).
[8] Izatt, R. M., Bradshaw, J. S., Pawlak, K., Bruening, R. L. and Tarbet, B. J., *Chem. Rev.,* **92,** 1261 (1992).
[9] Falk, J. E., "Porphyrins and Metalloporphyrins", Elsevier, Amsterdam (1964).
[10] Owens, J. W. and O'Connor, *Coord. Chem. Rev.,* **84,** 1(1988).
[11] Alston, K. and Storm, C. B., *Biochemistry,* **18,** 4299(1979).
[12] Hughes, M. N., "The Inorganic Chemistry of Biological Processes", Wiley, New York(1981).
[13] Barkigia, K. M., Chantranupong, L., Smith, K. M. and Fajer, J., *J. Am. Chem. Soc.,* **110,** 7566(1988).
[14] Edwards, S. L. and Poulos, T. L., *J. Biol. Chem.,* **265,** 2588(1990).
[15] D'Souza, F., Hsieh, Y. Y. and Deviprasad, G. R., *J. Electroanal. Chem.,* **426,** 17(1997), and references therein.
[16] Slifkin, M. A., "Charge Transfer Interaction of Biomolecules", Academic Press, New York(1971).
[17] Chardrashekar, T. K. and Krishnan, V., *Can. J. Chem.,* **62,** 475(1984).
[18] Kano, K., Hayakawa, T. and Hashimoto, S., *Bull. Chem. Soc. Jpn.,* **64,** 778(1991).
[19] Semnani, A. and Shamsipur, M., *Spectrochim. Acta,* **44A,** 1277(1988).
[20] Semnani, A. and Shamsipur, M., *J. Incl. Phenom.,* **22,** 99(1995).
[21] Semnani, A. and Shamsipur, M., *J. Chem. Soc., Dalton Trans.,* 2215(1996).
[22] Rouhollahi, A., Kakanejadifard, A., Farnia, S. M. F. and Shamsipur, M., *Polish J. Chem.,* **71,** 731 (1997).
[23] Hasani, M. and Shamsipur, M., *J. Incl. Phenom.,* **28,** 39(1997).
[24] Sadeghi, S., Shamsipur, M. and Elahi, M., *Polish J. Chem.,* **71,** 1594(1997).
[25] Shamsipur, M. and Hasani, M., *Can. J. Anal. Sci. Spectrosc.,* **42,** 185(1997).
[26] Hasani, M. and Shamsipur, M., *J. Chem. Soc., Perkin Trans.,* **2,** 1277(1998).
[27] Adler, A., Long, F. K., Finarelli, J. D., Goldmacher, J., Assour, J. and Korsakoff, J., *J. Org. Chem.,* **32,** 476(1976).
[28] Kano, T., Nakajima, T. and Hashimoto, S., *J. Phys. Chem.,* **91,** 6614(1987).
[29] Likussar, W. and Boltz, D. F., *Anal. Chem.,* **43,** 1262(1971).
[30] Benesi, H. A. and Hildebrand, J. H., *J. Am. Chem. Soc.,* **71,** 2703(1949).
[31] Nash, C. J., *J. Phys. Chem.,* **64,** 50(1960).
[32] Campbell, M., Demetriou, B. and Jones, R., *J. Chem. Soc., Perkin trans.,* **2,** 917(1983).
[33] Nour El-Din, A. M., *Spectrochim. Acta,* **42A,** 637 (1986).