

Theoretical Conformational Study of Carotenoporphyrins Related to Photophysical Properties

F. Vigné-Maeder*[†] and P. Claverie[‡]

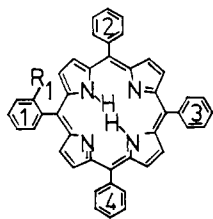
Contribution from the Laboratoire de Chimie Générale, Faculté de Pharmacie, 59045 Lille Cédex, France, and E. R. "Dynamique des Interactions Moléculaires", Université P. et M. Curie, Tour 22, 75005 Paris, France. Received March 24, 1986

Abstract: Photophysical properties of carotenoporphyrins (carotenoid polyene covalently linked to porphyrin) are known to depend on their molecular structure. Conformations of carotenoid-tetraphenylporphyrin-ortho ester and ortho ether are studied by a theoretical method and compared with NMR average solution conformations. Instantaneous geometries and related stabilities are obtained. The ortho ester conformations are compared with the simple association tetraphenylporphyrin- β -carotene.

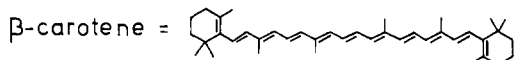
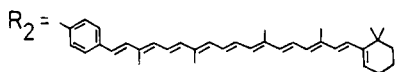
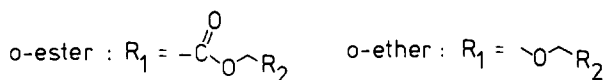
I. Introduction

The carotenoid pigments in photosynthetic organisms are known to have two functions related to energy exchange with chlorophyll. First, they absorb light and transfer excitation energy to chlorophyll (antenna function). Second, they protect from singlet oxygen damage by quenching chlorophyll triplet states which would otherwise sensitize $^1\text{O}_2$ production (photoprotection function). Through flash photolysis and pulse radiolysis experiments, Moore et al.,¹ Dirks et al.,² and Bensasson et al.³ have well-established that both functions can be mimicked by carotenoid polyenes covalently linked to porphyrins. The study by Gust et al.⁴ of a set of such molecules, called carotenoporphyrins, has displayed the importance of their static and dynamic structural properties. In these works, conformational information usually consists of time average solution conformations obtained with ^1H NMR spectroscopy.⁵

In the present work we use a theoretical method to investigate the static molecular conformation in vacuo of two representative carotenoporphyrins: the ortho ester as an example of a folded conformation and the ortho ether for a partly extended one. The main parts of these molecules, tetraphenylporphyrin (TPP) and carotenoid chain R_2 , are conjugated systems and can be considered as essentially rigid. The different conformations result then only



T.P.P. : $\text{R}_1 = \text{H}$



from torsions along the single bonds of the covalent linkage. Such an assumption was also made in the NMR study. The confor-

mational energy is computed as the interaction energy between the two parts: TPP and carotenoid. In the second section of this work, we compare the structure and the stability of the synthetic carotenoporphyrins with those of the simple association of TPP and β -carotene. These results, as well as those of a previous study on the porphyrin- β -carotene system⁸ can provide information concerning the arrangement of chlorophyll and carotenoids in photosynthetic systems.

II. Computational Procedure

The conformational energy is reduced to the interaction energy between the two rigid parts, treated as intermolecular interaction energy. This implies that the intramolecular energies within the covalent linkage and between it and the rigid parts are either small or nearly constant from one conformation to another. The interaction energy E is computed by means of an additive procedure developed by Gresh et al.⁶ and Langlet et al.⁷ It was shown to reproduce satisfactorily the results of ab initio SCF supermolecule computations as well as experimental results concerning essentially hydrogen-bonded complexes, where the electrostatic contribution to the interaction energy is dominant.^{6,7} With complexes such as those considered in the present work, namely TPP and carotenoids, the electrostatic term is rather weak, while the dispersion term becomes the main attractive contribution. Unfortunately, there is some lack of suitable (gas phase) experimental data as well as accurate computations (involving an evaluation of the dispersion term) for binary complexes involving stacked π -systems. This situation makes it somewhat difficult to assess the quality of our procedure for such complexes.

Before discussing this point further, let us first recall our expression of the interaction energy as a sum of four components

$$E = E_{\text{el}} + E_{\text{pol}} + E_{\text{rep}} + E_{\text{disp}}$$

where E_{el} is the electrostatic interaction energy computed between the multipole expansion of the charge distribution of each molecule, E_{pol} is the polarization energy computed accordingly by using the same multipole expansions to generate the electrostatic field and using experimental bond polarisabilities, and E_{rep} and E_{disp} are the repulsion and dispersion energies evaluated as a sum of

(1) Moore, A. L.; Dirks, G.; Gust, D. *Photochem. Photobiol.* **1980**, *32*, 691-695.

(2) Dirks, G.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **1980**, *32*, 277-280.

(3) Bensasson, R. V.; Land, E. J.; Moore, A. L.; Grouche, R. L.; Dirks, G.; Moore, T. A.; Gust, D. *Nature (London)* **1981**, *290*, 329-332.

(4) Gust, D.; Moore, T. A.; Bensasson, R. V.; Mathis, P.; Land, E. J.; Chachaty, C.; Moore, A. L.; Liddell, P. A.; Nemeth, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 3631-3640.

(5) Chachaty, C.; Gust, D.; Moore, T. A.; Nemeth, G. A.; Liddell, P. A.; Moore, A. L. *Org. Magn. Reson.* **1983**, *22*, 39-46.

(6) Gresh, N.; Claverie, P.; Pullman, A. *Int. J. Quantum Chem., Symp.* **1984**, *13*, 243-253.

(7) Langlet, J.; Claverie, P.; Caron, F.; Boeue, J. C. *Int. J. Quantum Chem.* **1981**, *20*, 299-338.

(8) Vigné-Maeder, F.; Claverie, P. *J. Mol. Struct., Theochem.* **1984**, *107*, 221-226.

* Address correspondence to this author at the Institut de Recherches sur la Catalyse, 2 av. Albert Einstein, 69626 Villeurbanne Cédex, France.

[†] Laboratoire de Chimie Générale.

[‡] Université P. et M. Curie.

atom-atom terms. For such nonpolar molecules as porphyrins and carotenoids, both last terms are the largest contributions to the interaction energy. For example, for the configuration (a) of ortho ester on Figure 3, the values are $E_{el} = -1.21$, $E_{pol} = -0.50$, $E_{rep} = 8.24$, $E_{disp} = -16.01$, $E = -9.49$ in kcal·mol⁻¹.

The dispersion and repulsion energies are expressed as

$$E_{disp} + E_{rep} = \sum_{\substack{i,j \\ \text{atoms}}} k_i k_j [-A_6(z^{-6} + C'_8 z^{-8} + C'_{10} z^{-10}) + CG_{ij} \exp(-\gamma z)]$$

with $z = r_{ij}/(4R_i R_j)^{1/2}$; R_i = atomic van der Waals radius, in Å; $R_H = 1.2$, $R_C = 1.7$ (carotene), 1.77 (TPP), $R_N = 1.6$; $G_{ij} = (1 - q_i/N_i)(1 - q_j/N_j)$; q_i = atomic net charge obtained from ab initio wave function calculation; N_i = number of valence electrons on atom i ; k_i = atomic parameters, $k_H = 1$, $k_C = 1$, $k_N = 1.18$; $A_6 = 0.143$ kcal·mol⁻¹; $C'_8 = 0.26626$, $C'_{10} = 0.095467$, $C = 90000$ kcal·mol⁻¹; $\gamma = 12.35$.

This formula is obtained from the one proposed by Kitaigorodskii.⁹ Successive modifications, which are described in ref 7, 10, and 11a, were made to the various parameters to correctly reproduce crystal energies¹⁰ or vaporization energies.⁹ An improvement that is not very important in the present work and is therefore not discussed in detail in the present article concerns the modification of the dispersion and repulsion parameters at short distances for hydrogen-bonded systems.^{11b}

Theoretical arguments support the procedure of evaluating the dispersion interaction in terms of contributions pertaining to interaction sites (bond and/or atoms), at least when dealing with nonconjugated molecules because it is possible in that case to express the molecular wave function in terms of well-located molecular orbitals.^{12,13} The situation is less simple from the theoretical point of view for conjugated systems, but some developments initiated recently^{14,15} offer promising prospects for dealing in a satisfactory way with this case, too. For the time being, a practical possibility consists of using for conjugated systems suitably modified values of the parameters involved in the site-site formulae. Thus, in the case of conjugated systems, the polarizability per atom is larger than that for saturated ones. Hence the dispersion energy will be larger, too, as would be implied by a London-type formula $E_{disp} \approx \alpha_1 \alpha_2 R^{-6} (b_1 + b_2)^{-1}$: this situation is reflected in our procedure by the use of larger van der Waals radii for carbon atoms in the conjugated case (note that, according to the formula above, the product $R_i R_j$ of van der Waals radii appears in the numerator of the dispersion terms z^{-6} , z^{-8} , z^{-10}).

With regard to the quality of the results for the interaction energy between molecules involving π -electron systems, we mention first that good values were obtained for the lattice (sublimation) energy of the crystals of benzene and nitrobenzene.¹⁰ In this work, the dispersion energy was calculated by using a R^{-6} term only (with a larger value of the A_6 coefficient), but the values obtained with the present formula (R^{-6} , R^{-8} , R^{-10}) are similar in the region of the van der Waals minimum. Admittedly, the molecules of benzene or nitrobenzene are not found in stacked configurations in their crystals, but these satisfactory results are nevertheless a

favorable indication as concerns the quality of the formulae when molecules involving π -systems are involved. The accuracy of the procedure was quite satisfactory, since the relative error with respect to experimental sublimation energies was about 10% (1.30/9.83 for benzene, 0.6/15.3 for nitrobenzene¹⁰).

As mentioned above, checking the quality of our procedure for the dispersion term for stacked π -system is hard because benchmark experimental or theoretical results are rather scanty for complexes where this term plays a dominant role. We mention, however, a paper by Aida and Nagata¹⁶ where an ab initio evaluation of the interaction energy between two adenine molecules stacked in the B-DNA configuration is presented: for the dispersion term, these authors give the value -6.61 kcal·mol⁻¹. Good agreement with this value was obtained by using the above formula.^{11a,b} In a previous work,¹⁷ the less refined formula involving a z^{-6} term only was used and gave for the dispersion energy the value -8.8 kcal·mol⁻¹ (see Table VI of ref 17) for the optimized geometry of the stacked complex. This result remains reasonable since the B-DNA configuration is not optimal and is therefore expected to give a weaker interaction energy.

The accuracy of the procedure is more difficult to assess here than in the case of crystals, due to the lack of reliable experimental results for stacked complexes. The satisfactory results obtained for hydrogen-bonded complexes (absolute error ~ 1 kcal·mol⁻¹, relative error smaller than 10%)^{7,17} can indeed be considered as providing indirect evidence only. As discussed by Langlet et al.,¹⁷ the experimental results obtained by using field ionization mass spectrometry^{18,19} were biased to a variable extent (according to the complex under consideration) due to the perturbation exerted on the complex by the strong electric field used for producing the various ionized species. This effect was unfortunately found quite important (see section IV.C of ref 17) just for the stacked complexes considered by Verkin et al.,¹⁹ namely 1,3-dimethyluracile and 1,3-dimethylthymine. However, this theoretical study was able to give a value of -4.1 kcal·mol⁻¹ (for 1,3-dimethyluracile complex) in the presence of an electric field of $0.6 \text{ V} \cdot \text{Å}^{-1}$, which is in reasonable agreement with the value -3.56 kcal·mol⁻¹ reported by Verkin et al.¹⁹ (the actual value of the ionizing electric field in these experiments is not known with high accuracy, since it varies with distance to the electrode).

Thus, to the extent that some conclusion can be drawn from these few results, it would seem that our formula for the dispersion and repulsion terms gives reasonable values even in the case of stacked π -systems.

Multipole expansions for the large porphyrin and carotene molecule are built from ab initio wave functions of fragments, as described in a previous work.⁸ The addition of four phenyl groups to give TPP and the replacement of one terminal cyclohexene ring by a simple phenyl ring to give the carotenoid R_2 are accomplished by treating the phenyl ring as a fragment. The multipoles localized on the junction bonds with porphyrin or carotenoid conjugated chain are derived following the procedure described by Gresh et al.²⁰ for single bonds. It is not necessary here to improve this representation by taking into account the spreading of electronic conjugation over the junction bond in the carotenoid,²¹ since in any case the multipole expansions contribute to interaction energies through the small terms E_{el} and E_{pol} only. This question does not arise for the phenyl groups attached to the porphyrin because they are not allowed in its plane due to steric hindrance, and this limits the degree of conjugation.

The phenyl geometry is the standard one with bond lengths of 1.38 Å for C-C and 1.03 Å for C-H. The β -carotene and por-

(9) Huron, M. J.; Claverie, P. *J. Phys. Chem.* **1972**, *76*, 2123-2133.

(10) Cailliet, J.; Claverie, P. *Acta Crystallogr.* **1975**, *A31*, 448-461.

(11) (a) Caron, F. "Application de calculs théoriques d'interaction d'empilement entre paires de bases à l'étude de la structure des acides désoxyribonucléiques: une possibilité d'explication de la sélection des paires de bases constitutives du matériel génétique", Thèse de Doctorat de 3ème Cycle de Chimie Physique, Université Pierre et Marie Curie (Paris 6), 1983. (b) Caron, F.; Langlet, J.; Claverie, P. "Theoretical study of the stacking of purine and pyrimidine bases", revised preprint (1985), to be submitted to *Biopolymers*.

(12) Claverie, P. In *Intermolecular Interactions: from Diatomics to Biopolymers*; Pullman, B., Ed.; Wiley: New York, 1978; Chapter 2, pp 69-305.

(13) Amos, A. T.; Crispin, R. J. *Mol. Phys.* **1976**, *31*, (a) 147-158, (b) 159-176. (c) Amos, A. T.; Crispin, R. J. In *Theoretical Chemistry, Advances and Perspectives*; Eyring, H., Henderson, D., Eds.; Academic: New York, 1976; pp 1-66.

(14) (a) Claverie, P. *Int. J. Quantum Chem.* **1983**, *23*, 1687-1688. (b) Claverie, P. In *Structure and Dynamics of Molecular Systems*; Daudel, R., Korb, J. P., Lemaître, J. P., Maruani, J., Eds.; Reidel: Dordrecht, 1986; Vol. 2, pp 1-33.

(15) Stone, A. J. *Mol. Phys.* **1985**, *56*, 1065-1082.

(16) Aida, M.; Nagata, C. *Chem. Phys. Lett.* **1982**, *86*, 44-46.

(17) Langlet, J.; Claverie, P.; Caron, F. In *Intermolecular Forces*; Proceedings of the 14th Jerusalem Symposium on Quantum Chemistry and Biochemistry; Pullman, B., Ed.; Reidel: Dordrecht, 1981; pp 397-429.

(18) Yanson, I. K.; Teplitsky, A. B.; Sudhodub, L. F. *Biopolymers* **1979**, *18*, 1149-1170.

(19) Verkin, B. I.; Sukhodub, L. F.; Yanson, I. K. *Dokl. Biophys. (Proc. Acad. Sci. USSR, Biophys. Sect.)* **1979**, *245*, 76-80.

(20) Gresh, N.; Claverie, P.; Pullman, A. *Theor. Chim. Acta* **1979**, *66*, 1-20.

(21) Vigné, F. *Chem. Phys. Lett.*, submitted.

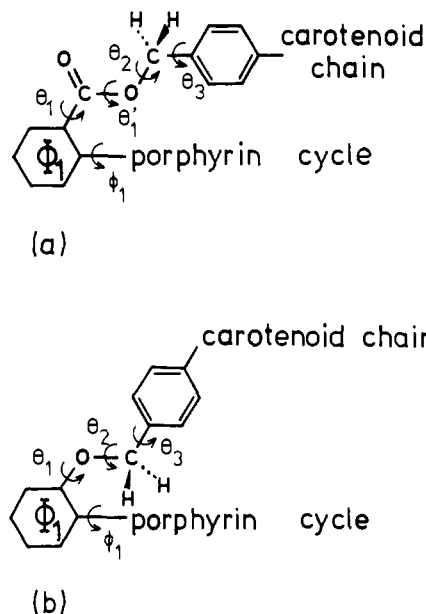
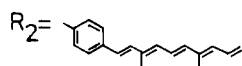


Figure 1. Definition of the torsion angles taken as variable in the interaction energy calculations: (a) ortho ester; (b) ortho ether.

pyrrole structures are taken from crystallographic data, leading to some deviations from standard geometry. In β -carotene, the polyene chain is curved, with the methyl groups on the convex side, as described by Stam²² for vitamin A. In TPP (Silvers and Tulinsky²³), the macrocycle is not rigorously planar. Some units are weakly inclined with respect to the mean plane: the pyrroles carrying the central hydrogen atoms ($\sim 6^\circ$) and the bonds joining the phenyl groups to the cycle ($\sim 9^\circ$), the dihedral angles ϕ_1 - ϕ_4 between the phenyl planes and the mean plane are $\sim \pm 60^\circ$ or $\sim \pm 80^\circ$ in the crystal,²⁴ but in solution NMR studies suggest smaller angles ($\sim 45^\circ$, Chachaty et al.⁵) or rotation of the phenyl rings (Eaton and Eaton²⁵). We have performed calculations with two values $\pm 45^\circ$ and $\pm 60^\circ$, which lead to the same preferred conformations, but with a somewhat better stability for 45° (energy differences of about 1 kcal·mol⁻¹).

For the carotenoporphyrins, bond lengths and angles of the covalent linkage are standard ones for sp^2 and sp^3 carbon and oxygen atoms: C-O = 1.4 Å, C-C = 1.5 Å, C-H = 1.1 Å. The interaction energy between the TPP and the carotenoid moieties is studied as a function of the torsion angles ϕ_1 and θ_2 - θ_3 (Figure 1). The angles ϕ_1 , θ_2 , and θ_3 are respectively varied in the intervals $[50^\circ, 90^\circ]$, $[-80^\circ, 80^\circ]$, and $[-180^\circ, 180^\circ]$ by 10° increments. For each pair ϕ_1 , θ_2 , we search for the θ_3 value giving the smallest interaction energy E_{\min} . The angles θ_1 , θ_1' are kept fixed to one reasonable value with respect to similar substituted aryl compounds. Results are given for ϕ_2 - $\phi_4 = \pm 45^\circ$. Two simplifications are introduced. First we do not consider the whole carotenoid part, because the nonlinked carotenoid end is expected to lie very far from the porphyrin cycle, whatever the conformation may be. As the intermolecular energy decreases with interatomic distances, we have verified on some configurations that energy values were not changed with a truncated carotenoid. Most calculations are thus done with only half the polyene chain. Second, before



performing interaction energy calculations, we eliminate unlikely conformations (E too large) by computing all interatomic distances between the two parts, TPP and carotenoid. We establish that any distances must not be lower than 2 Å and that at least about

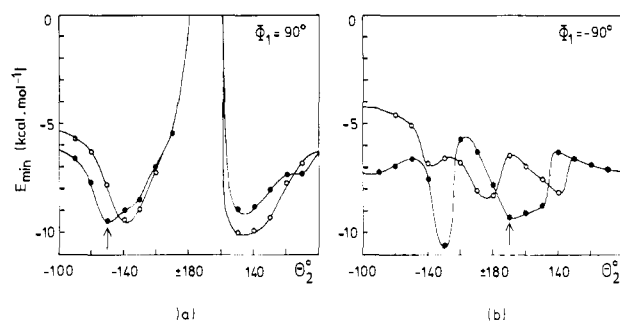


Figure 2. Ortho Ester: variation of the interaction energy between the TPP and carotenoid moieties. Each point corresponds to the optimized θ_3 value. The arrows designate the conformations represented in Figure 3. (a) $\phi_1 = 90^\circ$, $\theta_3 \sim 90^\circ$ for ● and $\sim -90^\circ$ for ○. (b) $\phi_1 = -90^\circ$, $\theta_3 \sim 140^\circ$ for ● and $\sim -140^\circ$ for ○.

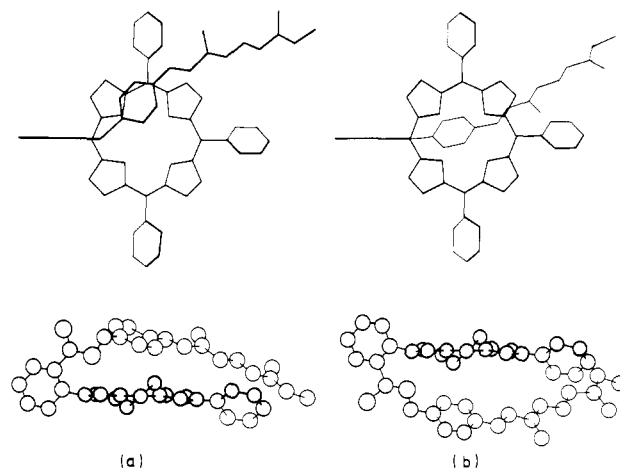


Figure 3. Ortho ester: conformations corresponding to the energy minima designated in Figure 2. (a) $\phi_1 = 90^\circ$, $\theta_2 = -130^\circ$, $\theta_3 = 100^\circ$, $E_{\min} = -9.49$ kcal·mol⁻¹, $z = 3.7$ Å. (b) $\phi_1 = -90^\circ$, $\theta_2 = 170^\circ$, $\theta_3 = 140^\circ$, $E_{\min} = -9.37$ kcal·mol⁻¹, $z = 4.2$ Å.

ten must be between 2 and 3 Å, otherwise respectively E_{rep} or E_{disp} will be too large.

For the association TPP- β -carotene, the mean planes of the molecules are assumed to be parallel. Results are given for ϕ_1 - $\phi_4 = \pm 60^\circ$. Geometry optimization starts from two reference conformations (A and B, see Figure 7), where the symmetry centers are superposed and which differ by the orientation of the polyene chain, either over or between porphyrin aryl groups, e.g., over (2),(4) for A, and between (2),(3) for B. Other nearly symmetrical orientations are equivalent, as shown in the previous study on the porphyrin- β -carotene association. From these arrangements (A and B), translations parallel (Δl_{\parallel}) or perpendicular (Δl_{\perp}) to the polyene chain are performed. The separation z between the planes is optimized for each displacement Δl_{\parallel} or Δl_{\perp} .

III. Results

1. Ortho Ester. A planar conformation, favored by conjugation effects, is assumed for the group Φ_1 -CO₂- and corresponds to $\theta_1 = 0^\circ$ and $\theta_1' = 180^\circ$ (in benzoic acid, rotational barriers for θ_1 and θ_1' through a variation of 90° are evaluated by Hehre et al.²⁶ as ~ 6 kcal·mol⁻¹). The other possible value, $\theta_1 = 180^\circ$, would give less stable extended conformations.

For $\phi_1 = 90^\circ$, the curve of E_{\min} vs. θ_2 (Figure 2a) indicates four preferred conformations at $-9 \sim -10$ kcal·mol⁻¹. The polyene chain is nearly parallel to the porphyrin plane with a separation of $z = 3.6$ Å (from the middle of the carotenoid aryl ring to the mean plane of the porphyrin) (Figure 3a). It lies over the spaces delimited by the phenyl groups (2),(3) (θ_2 negative) or (3),(4) (θ_2 positive), its methyl substituents being directed to one or the

(22) Stam, C. H. *Acta Crystallogr.* **1972**, *B28*, 2936-2945.

(23) Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331-3337.

(24) Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1938-1942.

(25) Eaton, S. S.; Eaton, G. R. *J. Chem. Soc., Chem. Commun.* **1974**, 576-576.

(26) Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496-1502.

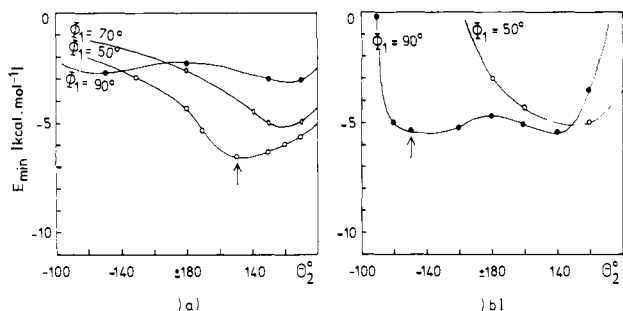


Figure 4. Ortho ether: variation of the interaction energy between the TPP and carotenoid moieties. The arrows designate the conformations represented in Figure 5. (a) $\theta_1 = 180^\circ$ (conformation I), optimized $\theta_3 \sim 180^\circ$. (b) $\theta_1 = 0^\circ$ (conformation II), optimized $\theta_3 \sim 0^\circ$.

other side (θ_3 positive or negative). The influence of the small distortion of the porphyrin macrocycle is shown on Figure 2b where the chain is linked at the other ortho position on the phenyl ring ($\phi_1 = -90^\circ$). The Φ_1 -axis being slightly inclined over the mean plane, the carotenoid moiety is slightly moved aside from the porphyrin. Four energy minima (-8 to -10 kcal·mol $^{-1}$) are therefore obtained, for which the larger distance ($z = 4.2$ Å) is compensated by a torsion of the chain (Figure 3b). These energetically stable conformations are thus less interesting for energy transfer that presumably requires some overlap of the π -electron systems.

Though the perpendicular arrangement of Φ_1 relative to the porphyrin plane can be expected to be favored, because of the large ortho substituent, energy minima of the same order are obtained from $\phi_1 = 90^\circ$ to $\phi_1 = 60^\circ$ with conformations where both moieties are still parallel to each other at a distance of ~ 3.5 Å.

In agreement with the NMR study, the stability of a tightly folded conformation for the ortho ester is confirmed by interaction energies on the order of -8 to -10 kcal·mol $^{-1}$. The conformation obtained and represented in ref [3 and 5], although folded, differs in some respects from our theoretical results. However, when one considers the approximations inherent in both methods and the fact that the conformation determined by NMR may be an average of several closely related conformers, the agreement is seen to be reasonable.

2. Ortho Ether. The interpretation of the NMR spectra of Chachaty et al.⁵ assumes an equilibrium between two conformations that differ in the θ_1 value (see Figure 1 for defining the torsion angles): 72% of conformer I ($\theta_1 = 180^\circ$) and 28% of conformer II ($\theta_1 = 0^\circ$). Energy computation results are given for these cases only (Figure 4), since more stable conformations do not appear with other θ_1 values. Energy minima are less deep than for the ortho ester, so that the linkage to the polyene chain is expected to be more flexible. The minima are of the same order (-5 to -6 kcal·mol $^{-1}$) for I and II, but for II they are independent of ϕ_1 , whereas the deepest minimum for I corresponds to the smallest ϕ_1 value. The curves are also very different: there is a barrier for II, when the polyene chain goes across the porphyrin cycle for small $|\theta_2|$, leading to very large repulsion terms, whereas the curve for I is smooth, without positive energy values, because the interacting parts become very distant by rotation around the O-CH $_2$ bond.

Both conformers thus have the same stability (we have verified that the repulsion owing to hydrogen atoms of O-CH $_2$ - in II is negligible), but the width of the energy minima is smaller for II than for I, and the probability of finding the second conformer is smaller. This could explain the percentage of I and II obtained by the NMR study. They are represented in the above-mentioned work of Chachaty et al.⁵ with $\phi_1 = 90^\circ$, $\theta_2 = 180^\circ$, $\theta_3 = 90^\circ$. As for the ortho ester, these angle values do not correspond to our energy minima but could be interpreted as an average of values pertaining to symmetrical preferred conformations. Alternatively, conformational interactions within the linkage may slightly shift our minima toward these values that correspond to the minimal conformational energy. Although the distance z is sufficiently small (3–5 Å) in the more stable arrangements, the π -electron

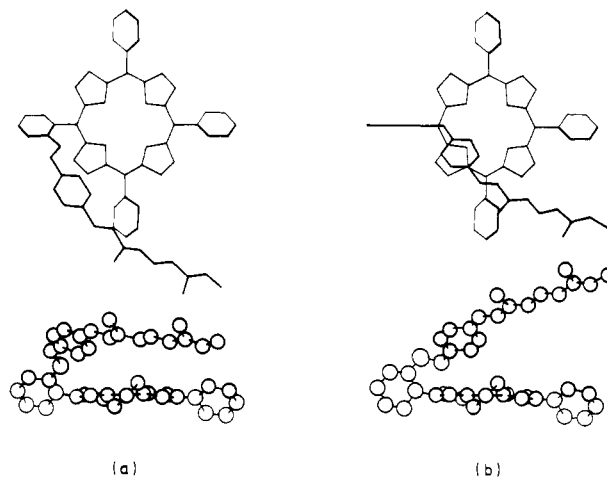


Figure 5. Ortho ether: conformations corresponding to the energy minima designated in Figure 4. (a) Conformation I, $\phi_1 = 50^\circ$, $\theta_1 = 180^\circ$, $\theta_2 = 150^\circ$, $\theta_3 = -170^\circ$, $E_{\min} = -6.47$ kcal·mol $^{-1}$, $z = 3.8$ Å. (b) Conformation II, $\phi_1 = 90^\circ$, $\theta_1 = 0^\circ$, $\theta_2 = -130^\circ$, $\theta_3 = 10^\circ$, $E_{\min} = -5.30$ kcal·mol $^{-1}$, $z = 3.9$ Å.

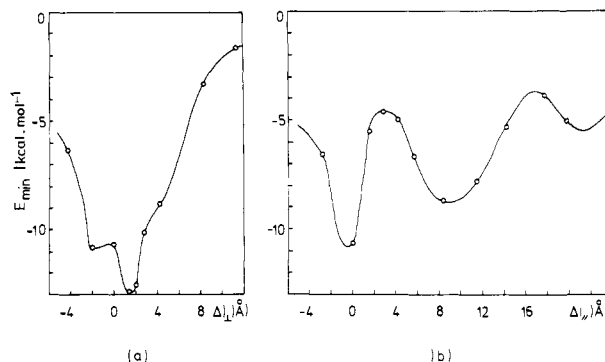


Figure 6. Association of TPP- β -carotene: variation of the interaction energy for the reference conformation (B). The displacements Δl_{\parallel} and Δl_{\perp} are respectively parallel and perpendicular to the β -carotene chain. ϕ_1 to $\phi_4 = \pm 60^\circ$.

system overlap is rather poor because the two parts are not parallel (Figure 5b) or the chain lies only over the edge of the porphyrin cycle (Figure 5a).

3. Association of TPP- β -Carotene. Energy minima, reported in Figure 6 for B, indicate a larger stability, of about 4 kcal·mol $^{-1}$, for the nonlinked molecules, as compared with the carotenoporphyrins. This proceeds from a better superposition of the two molecules, the superposition in the ortho ester being restricted to half the porphyrin cycle. The separation between the two planes (~ 3.9 Å) is of the same order of magnitude as for the ortho ester. Its slightly larger value can be attributed to the phenyl groups that occupy more space out of the porphyrin plane for $\phi_1 - \phi_4 = \pm 60^\circ$ than for $\pm 45^\circ$.

With respect to the porphyrin- β -carotene system, the interaction with the TPP phenyl groups stabilizes more definite arrangements (Figure 7). The dispersion term is enhanced by the proximity of the polyene chain with these phenyl groups, so that they try to be as close as permitted by the repulsion term. Displacements of 1 Å in the plane are allowed without large variations of the interaction energy, instead of 4 Å for the former system. The plane separation is somewhat larger (3.8–3.9 Å instead of 3.4–3.6 Å) owing to the volume occupied by the phenyl groups.

IV. Discussion

The present results are in agreement with the average conformations in solution as obtained by NMR. Our goal is to yield information concerning the instantaneous conformations and their related stabilities. The correlation of the NMR results with the triplet energy transfer rates for carotenoporphyrins provided several pathways for such energy transfer.⁴ Introducing our results into

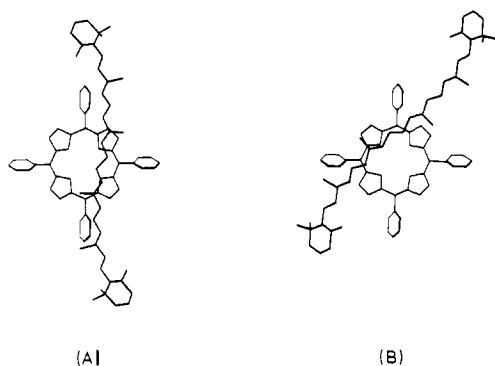


Figure 7. Association of TPP- β -carotene: preferred conformations of type A and B. For A, $\Delta l_{\perp} = 0$, $\Delta l_{\parallel} = 2 \text{ \AA}$, $E_{\min} = -13.8 \text{ kcal}\cdot\text{mol}^{-1}$, $z = 3.6 \text{ \AA}$. For B, $\Delta l_{\perp} = 2 \text{ \AA}$, $\Delta l_{\parallel} = 2 \text{ \AA}$, $E_{\min} = -12.9 \text{ kcal}\cdot\text{mol}^{-1}$, $z = 4.2 \text{ \AA}$.

this study can contribute to the interpretation of some details.

Although the ortho ester molecule is not perfectly rigid the mean conformation is tightly folded with porphyrin and carotenoid planes parallel and separated by 3.6–4 \AA . This is related to the large energy transfer rate constant, similar in polystyrene matrix ($k \geq 1.3 \times 10^8 \text{ s}^{-1}$) and in solution ($k \geq 2 \times 10^8 \text{ s}^{-1}$).

Owing to the rather broad energy minima, the ortho ester conformations range from folded to partly extended. In solution the carotenoid chain can move over the porphyrin cycle, but the π -orbital overlap is less efficient than for the ortho ester, leading to a slightly smaller rate constant (10^8 s^{-1}). The probability of stacked conformations can be estimated from the energy curves (Figure 5) as ~ 400 times smaller than for the ortho ester (the probability is proportional to $\Delta q \exp(-U/RT)$ where Δq and U are the width and the depth of the energy minimum). This is consistent with the slow decay rate ($k = 4.4 \times 10^6 \text{ s}^{-1}$) obtained in a plastic matrix which prevents any molecular motion. The energy transfer therefore has been assumed to occur across the covalent linkage.

The geometrical constraints of the covalent linkage in the ortho ester lead to very efficient conformations for both triplet and singlet energy transfer. It is noteworthy that their characteristics (distance of the parallel planes, stability) are very similar to those of the free association porphyrin- β -carotene or TPP- β -carotene which depend only on the interaction between the two parts. Such arrangements associate photophysical properties and stability; they can also be expected in photosynthetic membranes for chlorophyll and carotenoid pigments, which lack covalent linkages, although these molecules are submitted to other constraints by their environment. Recently²⁷ a non-covalently linked stacked dimer of two bacteriochlorophyll *b* (distance $\sim 3 \text{ \AA}$) has been found in the photosynthetic reaction center of a purple bacterium.

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Registry No. TPP, 917-23-7; TPP-*o*-CO₂CH₂-*p*-C₆H₄CH=CHC(CH₃)=CHCH=CHCH(CH₃)=CHCH=CHCH=C(CH₃)CH=CHCH=C(CH₃)CH=CHC(Me)(CH₂)₃C(Me)₂, 105230-66-8; TPP-*o*-CH₂-*p*-C₆H₄CH=CHC(CH₃)=CHCH=CHCH(CH₃)=CHCH=CHCH=C(CH₃)CH=CHCH=C(CH₃)CH=CHC(Me)(CH₂)₃C(Me)₂, 105230-67-9; TPP-*o*-CO₂CH₂-*p*-C₆H₄CH=CHC(CH₃)=CHCH=CHC(CH₃)=CHCH=CH₂, 105230-68-0; TPP-*o*-OCH₂-*p*-C₆H₄CH=CHC(CH₃)=CHCH=CHC(CH₃)=CHCH=CH₂, 105230-69-1; β -carotene, 7235-40-7.

(27) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* 1984, 180, 385-398.

Substituent Conformational Effects in the Magnetic Circular Dichroism and Absorption Spectra of Free-Base Carbonyl Porphyrins¹

Robert A. Goldbeck,* Bo-Ragnar Tolf,^{2a} Edward Bunnenberg,^{2b} and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received June 23, 1986

Abstract: Our previous MCD and absorption spectral studies of monosubstituted free-base alkylporphyrins found evidence in the sign and magnitude of visible-band MCD for out-of-plane conformers of π substituents, as well as effects due to the electronic influence of alkyl groups and the equilibrium of central-proton tautomers. The present study examines the MCD and absorption spectra of a series of acetylheptaalkylporphyrin free bases with various alkyl groups adjacent to the acetyl, as well as a fused-ring ketocyclohexenoporphyrin. Out-of-plane rotation angles of approximately 85, 65, and 35° for the acetyl moiety of the *tert*-butyl-, isopropyl-, and ethyl-substituted porphyrins, respectively, are deduced from variations in the observed MCD of the Q_y² band. INDO calculations of *B* terms for acetylporphyrin free base are found to reproduce the angle dependence observed for the MCD.

The occurrence of sign inversion in the magnetic circular dichroism (MCD) spectroscopy of two series of monosubstituted free-base porphyrins was recently studied.^{3,4} The structures of

these two series, **1** and **2**, are quite similar. As shown in Figure 1, series **2** is formally obtained from **1** by removal of the methyl adjacent to the π substituent, yet their MCD showed significant

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(2) (a) Present address: Pharmacia AB, S-751 82 Uppsala, Sweden. (b) Deceased December 8, 1984.

(3) Lu, Y.; Shu, A. Y. L.; Knierzinger, A.; Clezy, P. S.; Bunnenberg, E.; Djerassi, C. *Tetrahedron Lett.* 1983, 24, 2433.

(4) (a) Djerassi, C.; Lu, Y.; Waleh, A.; Shu, A. Y. L.; Goldbeck, R. A.; Kehres, L. A.; Crandell, C. W.; Wee, A. G. H.; Knierzinger, A.; Gaete-Holmes, R.; Loew, G. H.; Clezy, P. S.; Bunnenberg, E. *J. Am. Chem. Soc.* 1984, 106, 4241-4258. (b) Goldbeck, R. A.; Tolf, B.-R.; Wee, A. G. H.; Shu, A. Y. L.; Bunnenberg, E.; Djerassi, C. *Ibid.*, in press.