

FULL PAPER

## Artificial Photosynthetic Reaction Centers: A Semiempirical Conformation Analysis of Various Donor-Acceptor Systems

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**Abstract** The electronic ground states of five covalently linked electron donor acceptor systems have been investigated by semiempirical methods using the AM1 Hamiltonian. A tetraphenylporphyrine (TPP) unit serves as an electron donor with various electron acceptors. In the porphyrine-anthracene (P-A) dyad, both subunits are separated by a biphenyl-like spacer, in the free base porphyrine-flavine (P-F) and the zinc porphyrine-flavine ( $P_{Zn}$ -F) dyad by a terphenyl-like aromatic spacer. The components of the porphyrine-quinone (P-Q) dyad are separated by a peptide-methylene (-NHCO-CH<sub>2</sub>-) unit. A benzoquinone is chosen as acceptor, because it is a derivative of the acceptor in the natural photosynthetic reaction centre (PSRC). Addition of a carotenoid unit generates the carotenoid-porphyrine-quinone (C-P-Q) triad, which is an excellent model for artificial photosynthesis. Geometries, conformational energies and activation barriers for rotation about the single bonds connecting the various subunits are characterised for all five systems. A direct comparison of the geometry with experimental results corroborates the theoretical computations where available. The strong dependence of the electron transfer rate upon distance and orientation of both the donor and acceptor subunit is the main reason for the detailed study of the flexibility of conformational degrees of freedom. Solvent effects are included in the computations by using the self consistent reaction field (SCRF) approach.

**Keywords** Ground state, Semiempirical calculations, Artificial photosynthesis, Donor-Acceptor system, Electron transfer

### Introduction

Molecular systems consisting of electron donors and electron acceptors are of great importance for a wide range of chemical and biological processes. In natural photosynthe-

sis, a photoinduced charge separation takes place in the photosynthetic reaction centre, followed by an electron transfer reaction. The PSRC consists mainly of a complex system of electron donor and acceptor systems. Typical electron donors are free base and metallated porphyrine systems. Carotenoids act both as secondary electron donors and as effective quenchers of triplet states. The most common acceptor systems are found within the class of quinones [1-3].

Many questions of the fundamental processes in photosynthesis research remain unanswered, and several so-called artificial photosynthetic reaction centres have been devel-

Dedicated to Prof. Dr. Friedemann W. Schneider on the occasion of his 65th birthday

oped in the course of these investigations of photosynthesis. These relatively small organic electron donor-acceptor compounds mimic the charge separation function of photosynthetic proteins. The distance between donor and acceptor subunits can be controlled by selective chemical synthesis, and the desired geometrical arrangement of the subunits is fixed by rigid spacers [4-6].

Various porphyrine-quinone complexes, e.g. a simple donor-acceptor dyad with a porphyrine and a quinone subunit separated by a benzene unit, imitate the chlorophyll and quinone subunits of the PSRC. Numerous examples of experimental efforts have been made under this topic [4-6], but only very few theoretical investigations have been published. Only crude molecular-mechanics optimisations of the electronic ground state have been possible, and investigations of natural and artificial photosynthetic reaction centres in its excited states have been published only for the donor or acceptor components alone, or small and unsuitable artificial PSRC's [7-10].

The probability of electron transfer depends strongly on the distance and orientation between the donor and the acceptor, as well as on the dielectric properties of the environment [6]. According to the "through-bond" mechanism, a direct overlap of the donor, spacer, and the acceptor electronic wavefunction is necessary for the electron to be transferred from the donor to the acceptor subunit. This is only possible when a partial conjugation through the whole system between D and A exists, i.e. the dihedral angles between the single spacer units have to be significantly smaller than 90°. This electronic decoupling corresponds to orthogonal oriented subsystems. Therefore, the flexibility and rigidity of the spacer units becomes of major importance for the efficiency of an electron transfer. The so-called "superexchange" or "through-space" mechanism [11] for electron transfer does not require such a direct overlap of their respective wave functions. Several virtual states of the spacer unit or orbitals of the environment contribute to the overall electronic configuration of the donor-spacer-acceptor system. The relative orientation of the donor to the acceptor becomes of great importance, where complete decoupling (i.e. orthogonal subunits) of the spacer units is found. In the case of non-aromatic hydrocarbons as spacer units, the through-bond mechanism is also not possible.

In the present paper, five covalently linked donor acceptor systems are investigated by means of their ground state properties:

1) The P-A dyad, where a porphyrine system is linked to an anthracene unit by a spacer of two aromatic units. This relatively weak electron acceptor has been chosen because the system has been well investigated by various experimental methods. The possibility to donate an electron also makes this group of special interest, as an electron transfer can in principle take place in both directions.

2) In the P-F dyad, the porphyrine donor is separated by three aromatic moieties from a flavine acceptor system. The flavine unit is a well known prosthetic group in a number of natural occurring redox reactions, where both one and two electrons can be transferred. We, therefore, consider this ac-

ceptor moiety to be of potential interest for electron transfer reactions.

3) In the P<sub>Zn</sub>-F dyad a zinc atom is added to the P-F system. This addition strengthens the donor properties of the porphyrine system, and should therefore also enlarge the electron transfer rate of the complete dyad. These three systems have been synthesised and characterised by spectroscopical methods as described elsewhere (P-F dyad: reference [12]; P-A and P<sub>Zn</sub>-F dyads: reference [13]).

4) The P-Q dyad has been investigated because detailed spectroscopic data are known, and a highly efficient electron transfer has been reported. The porphyrine donor is attached by a peptide unit and a methylene group to a benzoquinone acceptor [14]. By rotation of the methylene group, various orientations of the donor relative to the acceptor are possible, which could have a significant influence on the electron transfer properties.

5) C-P-Q represents the first biomimetic triad consisting of a porphyrine donor covalently linked to both a benzoquinone-type electron acceptor and a carotenoid polyene donor. The carotenoid can be seen as a secondary electron donor in this system [15, 16]. This triad is of special interest because it represents an artificial photosynthetic reaction centre that has been used successfully for conversion of light energy to a proton potential when embedded in liposomes [17].

Due to numerous different geometrical relaxation modes within the dyads investigated, an analysis of the properties in their excited states is impossible without a detailed characterisation of the electronic ground state as presented in the current paper. The relative orientation and distance of the spacer phenylene/pyrimidine groups and the relative rotational modes of the electron donor and acceptor moieties have been studied in detail. The knowledge of the equilibrium geometries, rotational barriers and changes in dipole moment for different geometries will allow the characterisation of geometrical modes of interest for excited state relaxation in a forthcoming paper [12]. The influence of a polar environment is simulated by a solvent continuum model.

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## Computational methods

The semiempirical Hamiltonian AM1 [18] was used as implemented in the quantum mechanical program VAMP, version 6.1 [19]. The geometry optimisation of the ground states was carried out by the eigenvector following routine (EF) [20]. All geometries were completely optimised, i.e. no restrictions in geometry were assumed, and all degrees of freedom were optimised. First, the single subsystems, the tetraphenylporphyrine (TPP), the carotenoid unit, and all acceptor systems were optimised separately. After that, the complete system was generated by connection of the porphyrine to the spacer and acceptor units according to the following scheme: The P-A dyad by connection of the free base TPP (R'<sup>1</sup>=H, M=2H) with R<sub>1</sub>, P-F with R<sub>2</sub> (for P<sub>Zn</sub>-F with M=Zn), and P-Q with R<sub>3</sub> (Figure 1). The triad C-P-Q corresponds to the P-Q dyad where a further electron donor unit is added,

the carotenoid R' (see also Figure 1). After the construction of the covalently linked systems, a complete geometry optimisation was carried out. The total minimum of the dyads and the triad was located by optimising various starting geometries, which can lead to a conformation with a low total energy.

The characteristic angles of the five compounds are defined in Figure 1. All systems are characterised by the dihedral angle between the porphyrine unit and the four phenyl substituents. They are denoted as **A**, **B**, **C**, and **D**. The three dyads P-A, P-F and P<sub>Zn</sub>-F are further characterised by two and three rotation angles, **E** and **G** (P-A), and **E**, **F**, and **G** (P-F, P<sub>Zn</sub>-F) within the spacer unit. The donor of the P-Q dyad is linked to the acceptor moiety by a peptide (NHCO) and a methylene (CH<sub>2</sub>) unit.

**Figure 1** Definition of the systems investigated with the definition of the dihedral angles and bond lengths **A**, **B**, **C**, and **D** in the tetraphenylporphyrine subunit and the spacer units (**E**, **F**, and **G**)

P-A:  $R_n=R_1; R'=H; M=2H$

P-F:  $R_n=R_2; R'=H; M=2H$

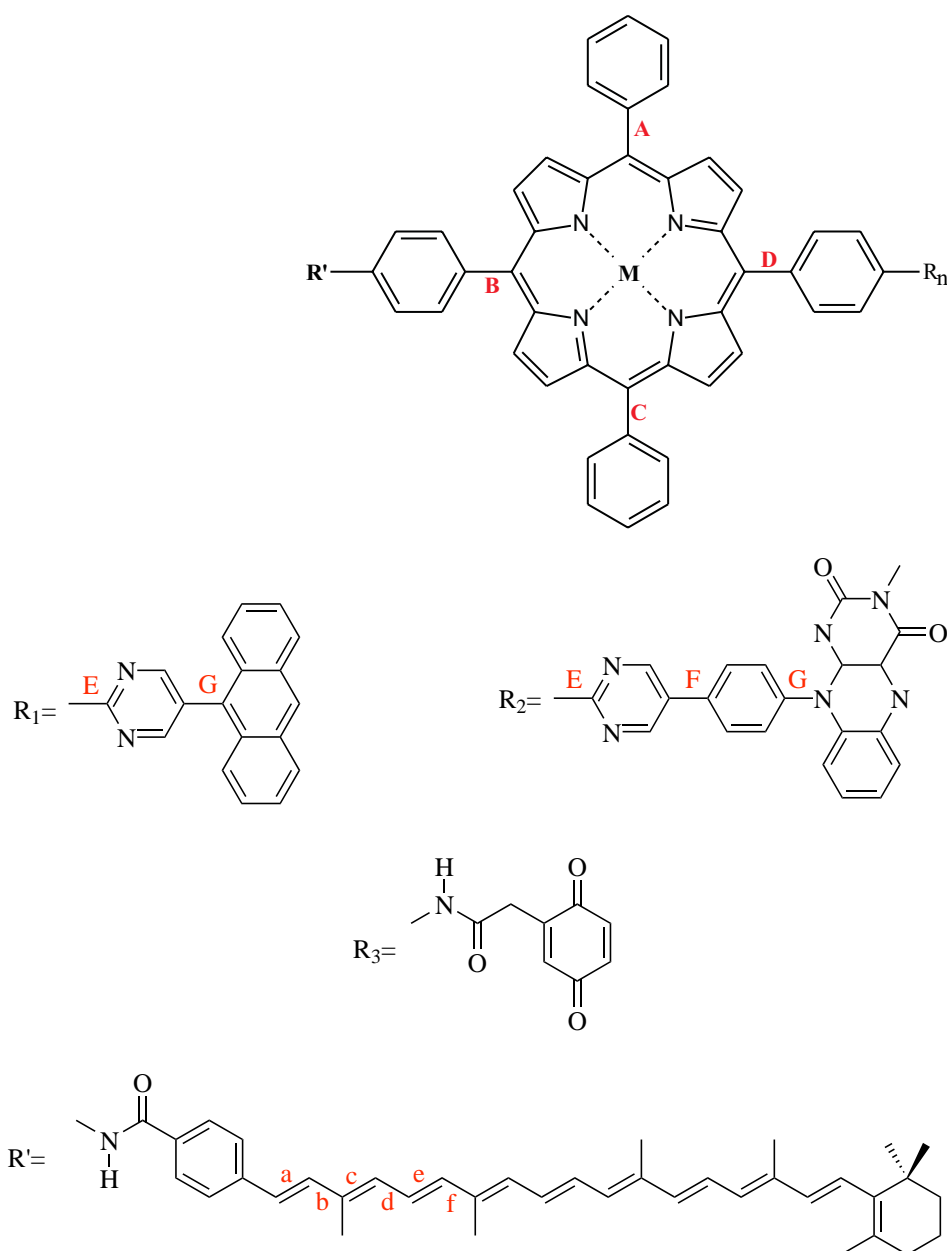
P<sub>Zn</sub>-F:  $R_n=R_2; R'=H; M=Zn$

P-Q:  $R_n=R_3; R'=H; M=2H$

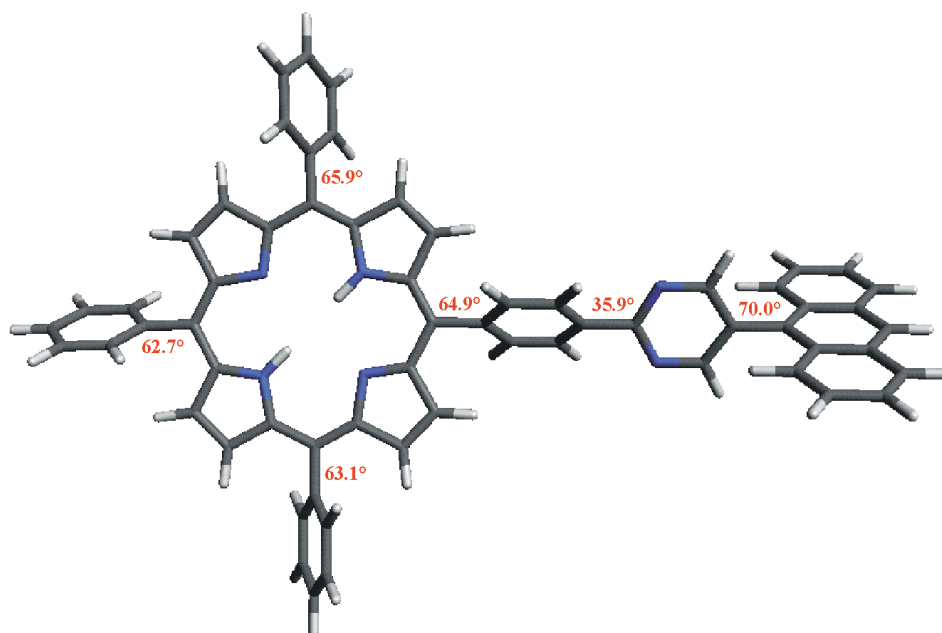
C-P-Q:  $R_n=R_3;$   
 $R'=\text{Carotenoid};$   
 $M=2H$

An estimation for the distance from the donor to the acceptor group is given by calculating the distance between the centre of the porphyrine ring, and that of the central 6-membered ring of the anthracene and flavin unit, and the centre of the 6-membered ring bearing the quinone moiety. For the carotenoid, the middle of the central double bond has been chosen.

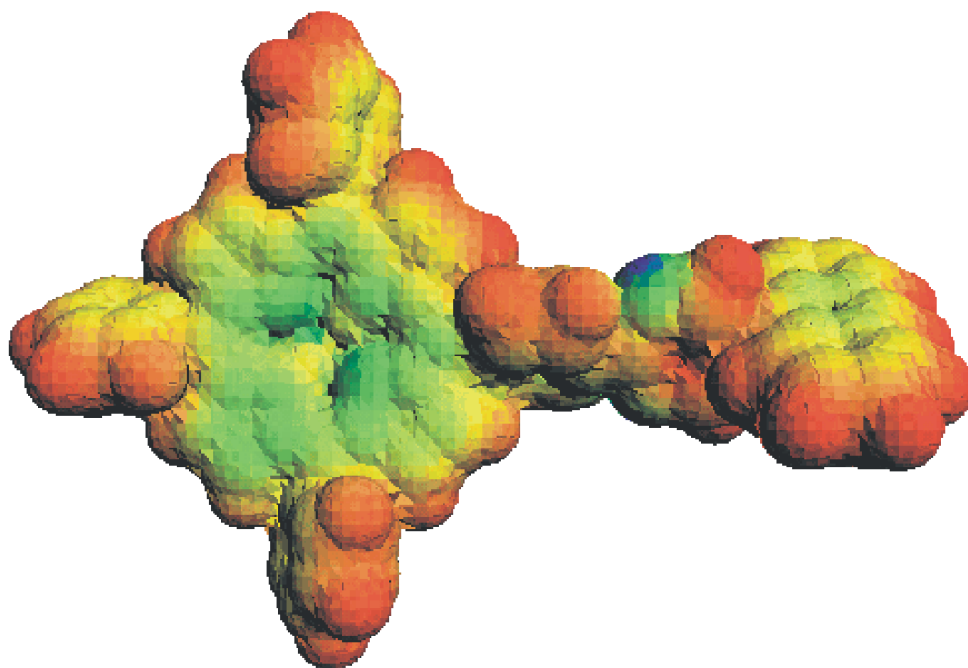
Solvent effects are taken into account by using the self consistent reaction field (SCRF) method [21]. This approach represents a continuum model with a solvent cage not depending on an arbitrarily chosen Onsager radius. The continuum is fitted to the shape of the molecule, and the calculations are carried out for the highly polar solvent acetonitrile. The properties of this environment are defined by its dielectric permittivity  $\epsilon$  and its refractive index  $n$ . Thereby, the rela-



**Figure 2a** Optimized Geometry of the P–A dyad with the dihedral angles given in [°]



**Figure 2b** Optimized Geometry of the P–A dyad with the electrostatic potential in the range from  $-70 \text{ kcal}\cdot\text{mol}^{-1}$  (blue) to  $+15 \text{ kcal}\cdot\text{mol}^{-1}$  (red)



**Table 1** Energy minimum and maximum conformations, energy barrier in kcal·mol<sup>-1</sup>, and Bond Length in [Å] of the P-A dyad for rotation about the dihedral angles **D**, **E**, and **G**

Bond	Minimum	Local Maximum	Rotation Barrier	Bond Length
D	65°	90°	0.7	1.4
E	35°	0° / 90°	0.5 / 1.4	1.48
G	70°	90°	0.1	1.46

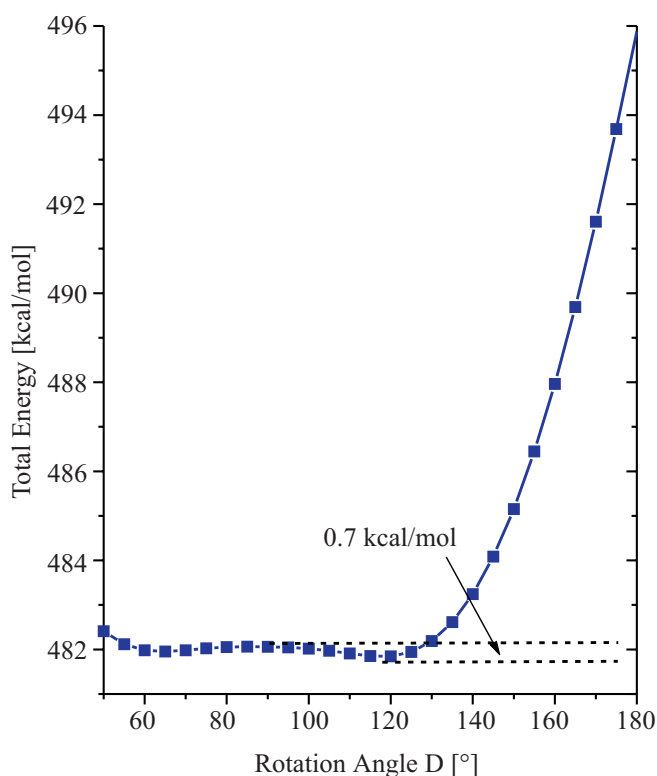
tive stabilisation energy can be estimated as well as its effect on the orientation and magnitude of the dipole moment. Differences in the electron distribution also yield a conclusion about the effect of a polar solvent. The complete C-P-Q triad is too large to compute solvent effects. In this case, only the gas phase results are presented. The electrostatic potentials are given in kcal·mol<sup>-1</sup> and visualized using the TRAMP program, version 1.1b [22].

## Results and discussion

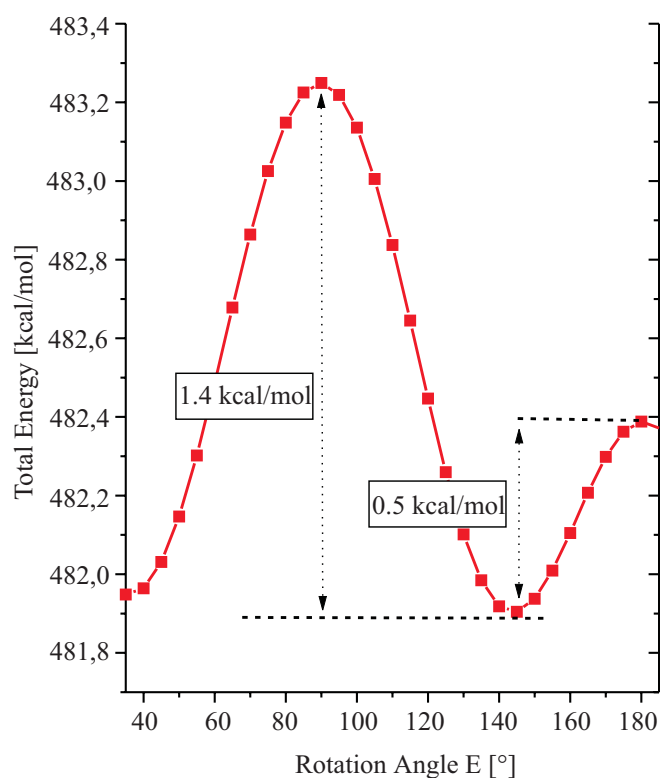
### Porphyrine-Anthracene dyad

The geometry optimisation of the P-A dyad results in the geometry presented in Figure 2a. The optimised dihedral angles (see Figure 1) are 65.9° (**A**), 62.7° (**B**), 63.1° (**C**), and 64.9° (**D**) with bond lengths typical for carbon-carbon single bonds: 1.468 Å (**A**), 1.473 Å (**B**), 1.473 Å (**C**), and 1.468 Å (**D**). The optimised dihedral angle **E** is computed to 35.9° and the benzene-anthracene dihedral angle **G** 70.0°. A distance of 14.9 Å is computed for the distance from the donor to the acceptor moiety. The total energy is computed to be 481.9 kcal·mol<sup>-1</sup>, and the dipole moment of 1.8 D is directed from the anthracene to the porphyrine unit along the molecular axis connecting the donor to the acceptor unit. A highly negative charged centre is located within the porphyrine unit (Figure 2b) and at the two nitrogens of the pyrimidinyl spacer group. The positive charge is mainly located at the four phenyl groups attached to the porphyrine system as well as in the anthracene unit. The SCRF calculation in the highly polar solvent acetonitrile yields a stabilisation in energy of 10 kcal·mol<sup>-1</sup> ( $H_f = 471.6$  kcal·mol<sup>-1</sup>) and an enlargement of the dipole moment to 2.2 D.

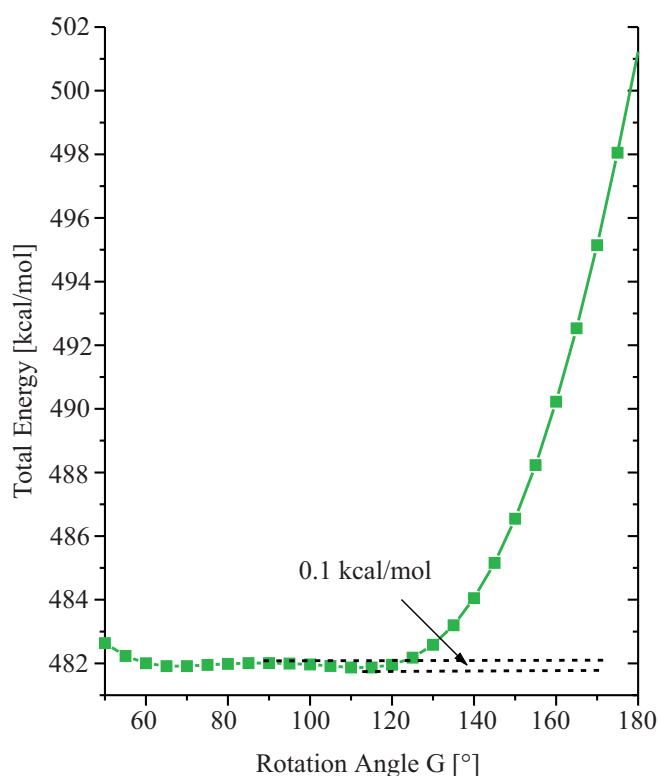
In Figure 3 the rotational coordinate of the three decisive dihedral angles **D**, **E**, and **G** of the spacer moiety connecting the porphyrine donor and the anthracene acceptor unit, is presented. In Table 1, the corresponding energy minimum and maximum conformations are summarised along with the rotational barriers and the bond length of the biphenyl-like bonds. The energy minimum of angle **D** at 65° is separated from its 115° counterpart by a small energy barrier of 0.7 kcal·mol<sup>-1</sup>, which is slightly above the energy available at



**Figure 3a** Total Energy in kcal/mol of the P-A Dyad as a Function of the Dihedral Angle **D** in [°]



**Figure 3b** Total Energy in kcal/mol of the P-A Dyad as a Function of the Dihedral Angle **E** in [°]



**Figure 3c** Total Energy in kcal/mol of the P-A Dyad as a Function of the Dihedral Angle  $G$  in [°]

room temperature. In contrast, the rotation to more planar geometries becomes strongly disfavoured in energy, and the energy at a planarisation to  $30^\circ$  is more than  $5 \text{ kcal}\cdot\text{mol}^{-1}$  higher than for the perpendicular conformation. The local minimum is the result of two counteracting effects: On one hand delocalisation stabilises a coplanar orientation of the subunits whereas mutual steric effects, resulting from neighbouring free electron pairs, favour a perpendicular conformation. This results in an intermediate twist angle. According to X-ray analysis (triclinic crystals) data of free tetraphenylporphyrine [23,24], a rotation of  $62^\circ$  out of planarity is found, which is in good agreement with the calculated data. Another X-ray investigation of TPP in its tetragonal form [25] yields a dihedral angle of  $81^\circ$ . This experimental results of two different dihedral angles is corroborated in our calculations by the low energy barrier that separates the two minima. Also the experimental porphyrine-phenyl bond length of approximately  $1.5 \text{ \AA}$  [24] is characteristic for a typical single bond without any significant  $\pi$ -character, which fits excellently to our bond length of approximately  $1.47 \text{ \AA}$ .

In Figure 3b, the energy of the P-A dyad is shown as a function of the dihedral angle  $E$  between the phenyl and pyrimidine ring. The coordinate shows two symmetrically situated minima at  $35^\circ$  and  $145^\circ$  which are separated from each other by an energy barrier of  $0.5 \text{ kcal}\cdot\text{mol}^{-1}$  (via the planar transition state), and  $1.4 \text{ kcal}\cdot\text{mol}^{-1}$  (via the perpendicular transition state). A free rotation of the pyrimidine unit along

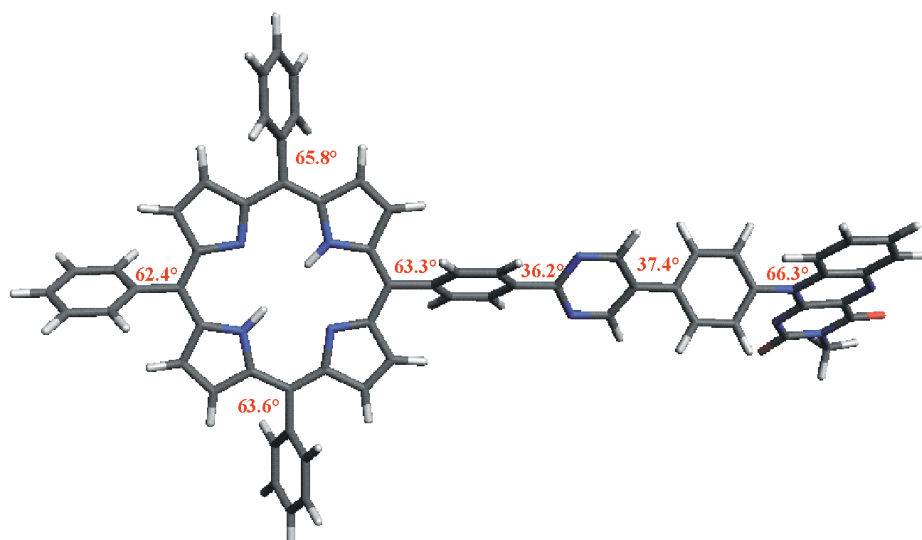
the single bond  $E$  is found because the barrier of  $0.5 \text{ kcal}\cdot\text{mol}^{-1}$  can be overcome easily at ambient temperature. This phenomenon of a free rotation can also be seen by experimental results. For similar compounds with a single bond connecting a biphenyl and a pyrimidine unit, a dihedral angle in the range between  $7.5^\circ$  and  $17^\circ$  is found by analysis of X-ray data [26, 27]. The difference between calculation and experiment results from crystal effects. These effects as present in an X-ray structure diminish the rotational angles in comparison to the gas phase computations. The large variety in experimental angles is a further hint at the very flat reaction coordinate for this rotation. At the first view, the larger barrier for rotation via the perpendicular transition state is quite surprising. This phenomenon becomes quite clear, when the electronic structure of the pyrimidine system is taken into account. The phenyl hydrogen in *ortho* position to the connecting single bond are positively polarized, thus attracting the free electron pairs at both pyrimidine nitrogens. At  $0^\circ$ , no significant barrier is detected, because no hydrogens in *ortho* position are present and the sterical hindrance is less marked than for a biphenyl-like rotation.

Finally, the rotation of the anthracene unit round the phenyl unit has been investigated. The results are presented in Figure 3c. The energy minimum conformation of about  $70^\circ$  is more or less isoenergetic to the slight maximum at  $90^\circ$ . The difference in energy is computed to be less than  $0.1 \text{ kcal}\cdot\text{mol}^{-1}$ . Between  $50^\circ$  and  $130^\circ$ , no notable barrier is obtained by the calculations. For rotation to smaller dihedral angles, a significant barrier arises. At  $165^\circ$  (and  $15^\circ$ ) the computed total energy is more than  $10 \text{ kcal}\cdot\text{mol}^{-1}$  higher than that conformation of the geometrical minimum. A direct comparison to experimental dihedral angle between an anthracene and a phenyl unit results in an angle of  $66^\circ$  [28], which is within the range of the computed flat minimum energy. The energy also has been calculated in the polar solvent acetonitrile. This low energy motion is even more significant in polar environment. The SCRf calculation in the polar solvent acetonitrile yields in a difference in energy of less than  $0.01 \text{ kcal}\cdot\text{mol}^{-1}$  when varying the dihedral angle  $G$  in the range between  $60^\circ$  and  $120^\circ$ .

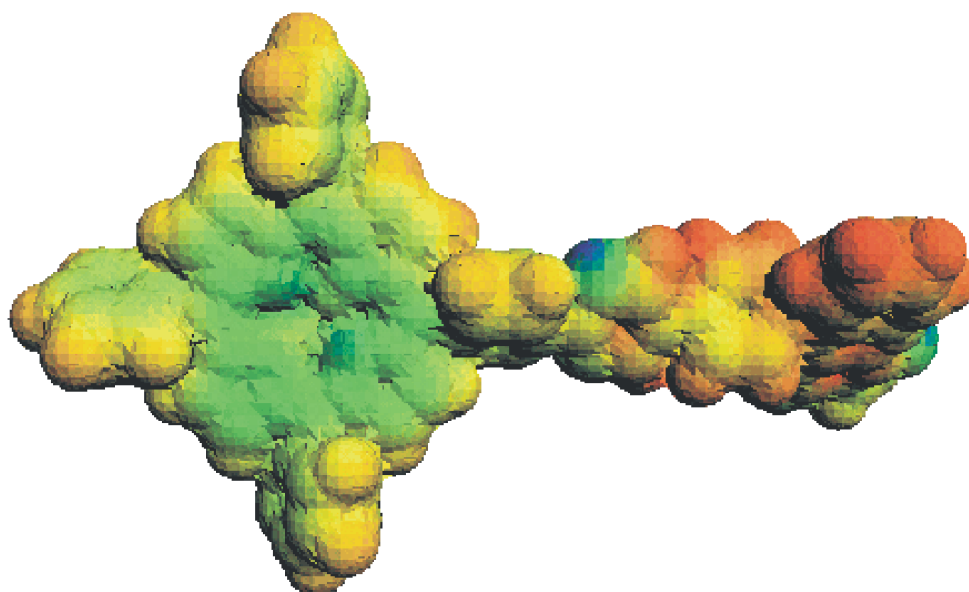
#### Porphyrine-Flavine dyad

The free base porphyrine-flavine P-F dyad has been investigated by semiempirical methods. The optimised geometry is presented in Figure 4. The total energy is computed to be  $489.6 \text{ kcal}\cdot\text{mol}^{-1}$  in gas phase and  $469.4 \text{ kcal}\cdot\text{mol}^{-1}$  in acetonitrile. The dipole moment increases from  $6.4 \text{ D}$  to  $9.1 \text{ D}$ , when the results in acetonitrile are compared to those *in vacuo*. The dipole moment is oriented parallel to the flavine unit in the centre of the spacer bridge, directing from the homoaromatic subunits towards the heteroaromatic moiety within the flavine unit. The distribution of the electron density is quite irregular due to the donor-acceptor character within the flavine subunit. In general, a high electron density is observed in the porphyrine subunit as well as in the heterocyclic part of the flavine. On the contrary, the positive

**Figure 4a** Optimized geometry of the P-F dyad with the dihedral angles given in [°]

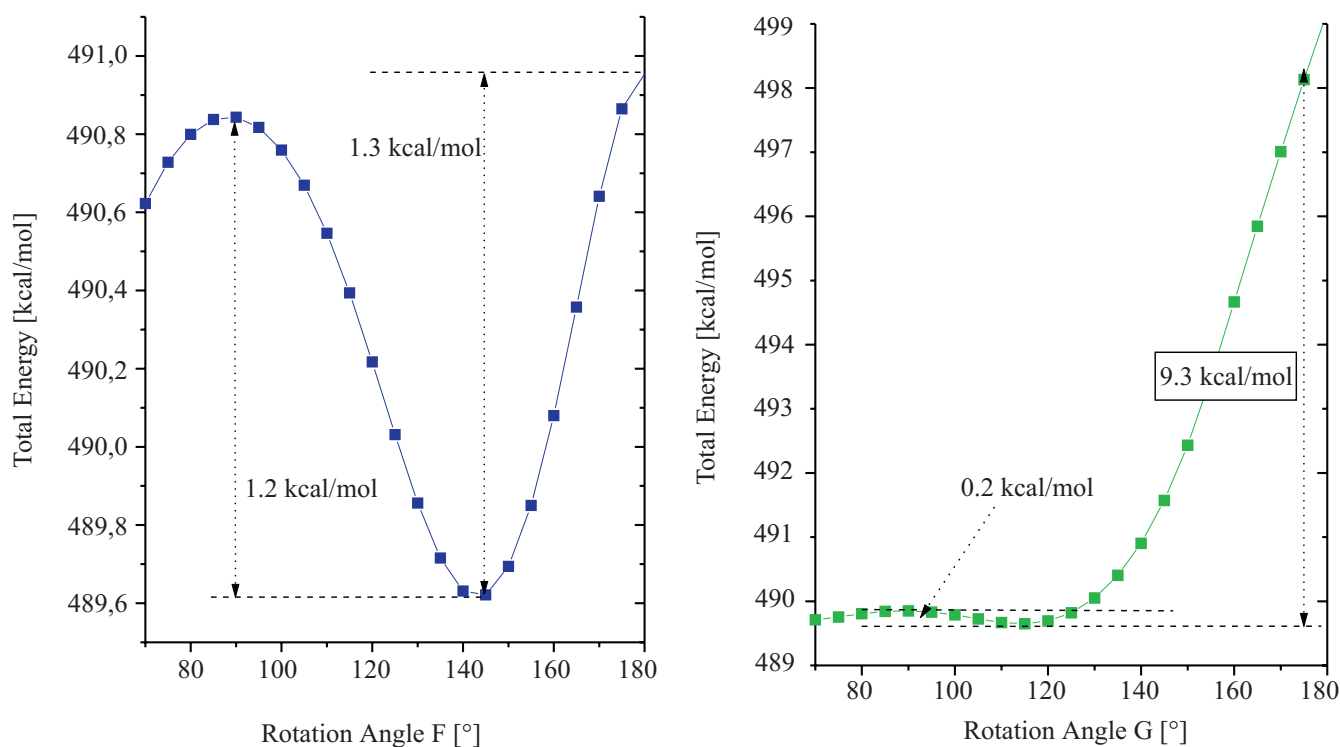


**Figure 4b** Optimized geometry of the P-F dyad with the electrostatic potential in the range from  $-70 \text{ kcal}\cdot\text{mol}^{-1}$  (blue) to  $+30 \text{ kcal}\cdot\text{mol}^{-1}$  (red)



charge is found both along the spacer chain (again, with the exception of the pyrimidyl nitrogen atoms) and on the carbon-rich side of the flavine (Figure 4b). The difference in the electrostatic potential in comparison to the P-A dyad is more marked in the P-F dyad, ranging from  $-70$  to  $+30 \text{ kcal}\cdot\text{mol}^{-1}$  (P-A: from  $-70$  to  $+15 \text{ kcal}\cdot\text{mol}^{-1}$ ). This illustrates the enhanced electron acceptor character of the flavine compound. The four dihedral angles and bond lengths **A**, **B**, **C**, and **D** (see Figure 1) differ by less than  $1^\circ$  and  $0.005 \text{ \AA}$ , respectively, to that of the P-A dyad. The tetraphenylporphyrine system is connected to the flavine acceptor by three aromatic spacer units, of the pattern phenyl-pyrimidine-phenyl. The

distance from the donor to the acceptor subunit is about  $19.1 \text{ \AA}$  and thus more than  $4 \text{ \AA}$  larger than that for the P-A dyad caused by the additional phenyl ring system. The first dihedral angle between the phenyl and the pyrimidine **E** is characterised in analogy to the P-A dyad with an optimised angle of  $36.2^\circ$ . The biphenyl-like dihedral angle **F** is computed to be  $37.4^\circ$  which agrees quite well with the experimental gas phase number of approximately  $40^\circ$  [29]. The angle between the flavine and the phenyl subunits is computed to be  $66.3^\circ$ . This also corresponds fairly well with the experimental X-ray angle of  $77.6^\circ$  for a comparable molecule [30].



**Figure 5** Total energy in kcal·mol<sup>-1</sup> of the P-F dyad as a function of the dihedral angle **F** (top) and **G** (bottom) in [°]

The variation of the dihedral angles **D** and **E** results in the same trend as for the P-A dyad, the energies for rotation differ by less than 0.1 kcal·mol<sup>-1</sup>. Thereby only the rotational coordinates for the variation of the differing dihedral angles **F** and **G** are presented (Figure 5). The barrier for rotation of the biphenyl-like single bond is quite independent of the direction of rotation chosen. For the path over the perpendicular transition state (**F**= 90°), a barrier of 1.2 kcal·mol<sup>-1</sup> is computed, whereas the planar conformation (**F**= 0°) is 1.3 kcal·mol<sup>-1</sup> higher in total energy than the minimum energy conformation. At room temperature, the region ±20° apart from the most stable conformation can be reached by thermal energy. The two aromatic spacer subunits are oriented to each other in a position where an effective conjugation of both the pyrimidine and the phenyl ring is possible. For more decoupled systems, i.e. larger dihedral angles **F**, an energy that is not available at standard conditions is necessary.

Finally, the phenyl-flavine rotation motion **G** was investigated. Although the flavine system is not comparable to the anthracene system in its electronic and structural properties, the rotational coordinate **G** is quite similar to that of the P-A dyad. Shallow minima at 65° and 115° are separated by a transition state, only 0.2 kcal·mol<sup>-1</sup> higher in energy. This is in good agreement to the experimental number of 71.3° of a comparable phenyl-flavine bond [31]. At room temperature, an equal distribution of all conformations between 40° and 140° is assumed, because the energy difference is always below the available thermal energy at room temperature, approximately 0.5 kcal·mol<sup>-1</sup>. The increase in energy for a more decoupled conformation is even less significant than for the

P-A dyad. The energy for the perpendicular transition state is less than 10 kcal·mol<sup>-1</sup> higher in energy, about twice of this energy is found for the rotation of the anthracene unit. The threefold-annulated aromatic system accounts for a similar description of the rotational coordinate in comparison to the P-A dyad.

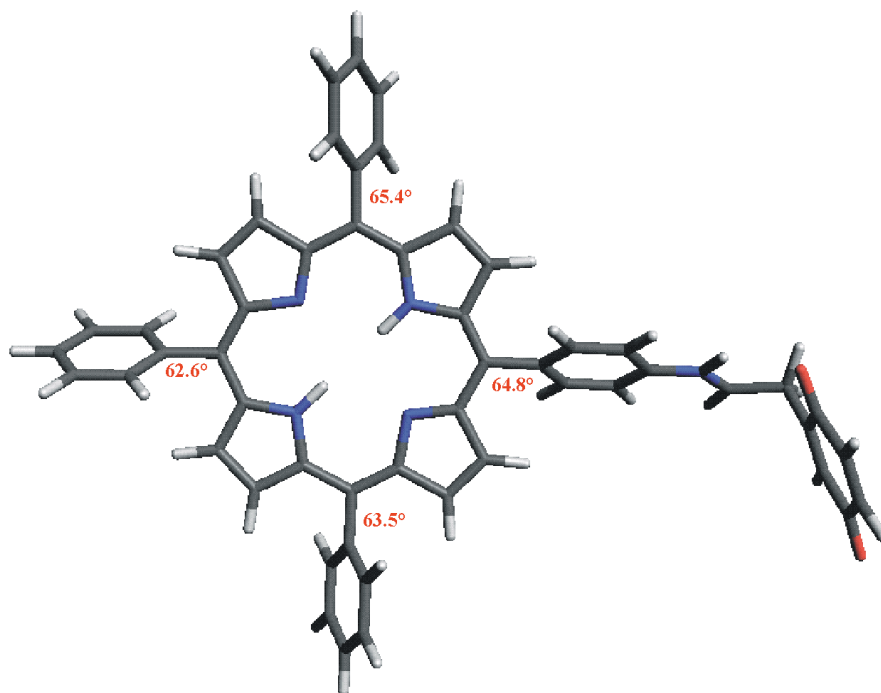
#### Metallated Porphyrine-Flavine dyad

The donor properties of the porphyrine moiety are significantly enhanced by substitution of the two nitrogen bonded hydrogens by a zinc atom [32-34]. The photophysical properties of a P<sub>Zn</sub>-F dyad are thus expected to be different to that of the free base P-F dyad; in addition, several experimental studies have shown that the charge separated state in metallated dyads is also energetically more stabilised [4-6]. It is not known if the ground state properties of a metallated artificial PSRC also differ in comparison to the free base counterpart. Therefore, the ground state properties of P<sub>Zn</sub>-F were computed by means of a direct comparison with the P-F system.

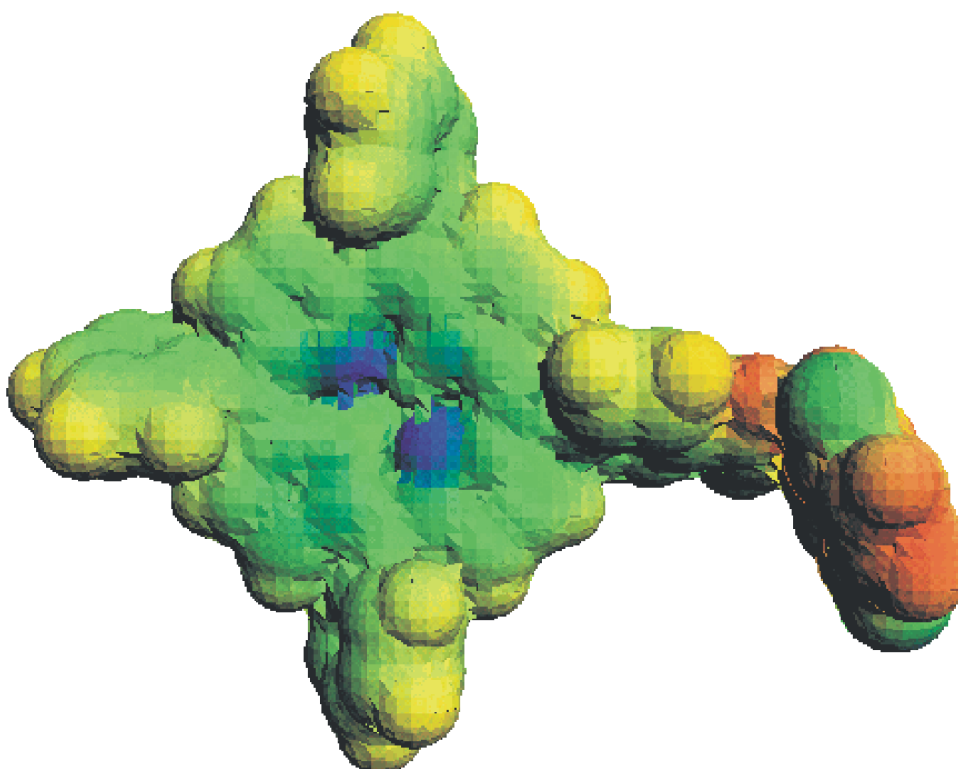
The results differ only marginally from those of the free base system. The dihedral angles vary by less than 0.5° and the bond lengths by less than 0.01 Å. The zinc atom is located in the plane of the porphyrine moiety with a distance of 2.04 Å to all four nitrogen atoms. The stabilisation of 21.2 kcal·mol<sup>-1</sup> by the polar environment of acetonitrile is also quite similar to that of P-F (20.2 kcal·mol<sup>-1</sup>): The standard enthalpy is computed to be 519.1 kcal·mol<sup>-1</sup> *in vacuo* and

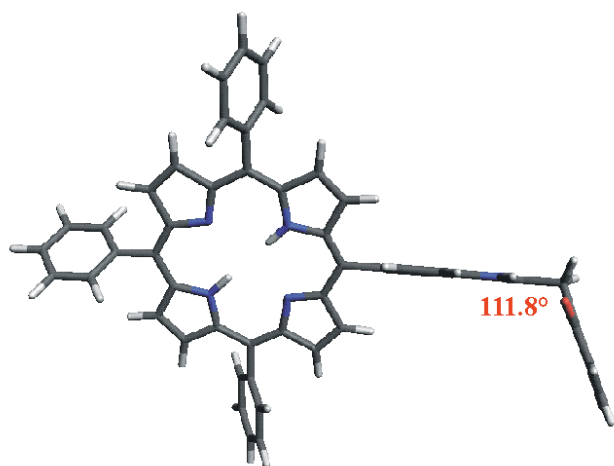


**Figure 6a** Optimized geometry of the P-Q dyad with the dihedral angles given in [°]



**Figure 6b** Optimized geometry of the P-Q dyad with the electrostatic potential in the range from  $-55 \text{ kcal}\cdot\text{mol}^{-1}$  (blue) to  $+30 \text{ kcal}\cdot\text{mol}^{-1}$  (red)



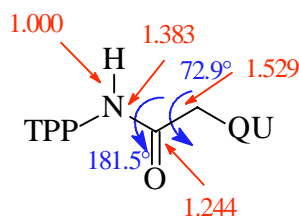


**Figure 6c** Optimized geometry of the P-Q dyad with the bending angle [ $^{\circ}$ ]

497.9 kcal·mol<sup>-1</sup> in acetonitrile. The electron density and the magnitude and orientation of the dipole moment are almost identical in comparison to the P-F dyad: 6.4 D in gas phase and 9.0 D in acetonitrile. In addition, the barrier for rotation about both dihedral angles **F** and **G** were computed. They turned out to be of approximately of the same amount (1.4 kcal·mol<sup>-1</sup> for **F** and 0.3 kcal·mol<sup>-1</sup> for **G**) as for the non-metallated system. Summarizing, the ground state properties of P<sub>Zn</sub>-F dyad do not differ in any way from the P-F dyad. Therefore, none of the differing properties between the two molecules can be attributed to structural or electronic differences in their electronic ground states but rather to differences in their excited state properties.

#### Porphyrine-Quinone dyad

The optimised geometry of the P-Q dyad, which consists of a tetraphenylporphyrine donor, a peptide-methylene NHCO-CH<sub>2</sub>-spacer unit and a benzoquinone acceptor, is presented in Figure 6. The total energy is computed to be 302.7 kcal·mol<sup>-1</sup> *in vacuo*, and 287.8 kcal·mol<sup>-1</sup> in acetonitrile, corresponding to a stabilisation energy in polar solvents of al-

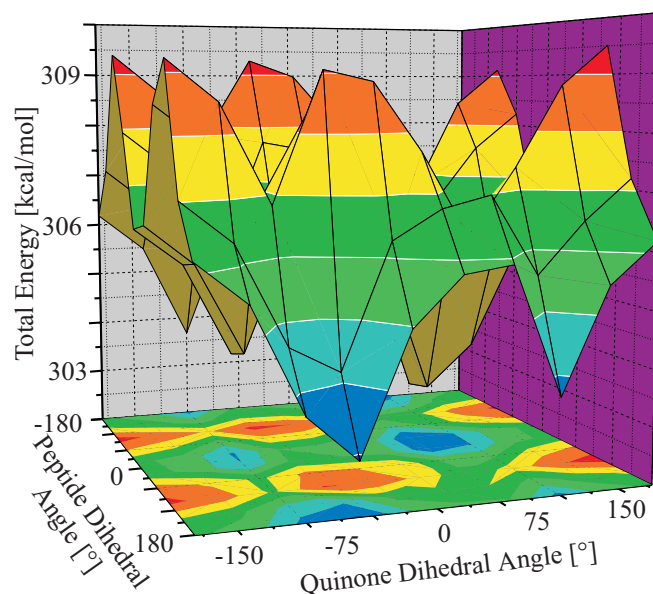


**Figure 7** Decisive bond lengths (red, in Å) and dihedral angles (blue) at the connection points of the P-Q dyad. TPP = tetraphenylporphyrine; QU = quinone (R<sub>3</sub>)

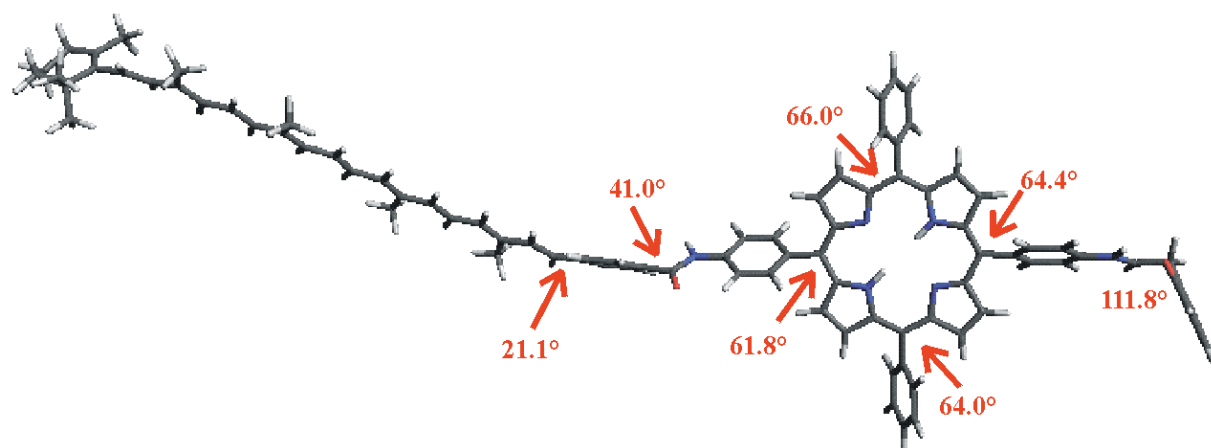
most 15 kcal·mol<sup>-1</sup>. The gas phase dipole moment of 3.6 D points from the quinone unit to the porphyrine unit and is enlarged to 4.2 D in polar environment. The electron density is as expected for this kind of system. A highly negatively charged part is observed within the porphyrine whereas the benzoquinone moiety is positively charged. The bending angle of the CH<sub>2</sub> group is widened slightly to 111.8 $^{\circ}$  in comparison to a pure sp<sup>3</sup> hybridization (Figure 6c). The four dihedral angles **A** to **D** are also of about the same number as in the two dyads discussed before. The most important dihedral angles and bond lengths at the connecting point between the donor and the acceptor of the P-Q dyad are summarised in Figure 7.

The structure of the peptide group is similar to that of a single, unconnected NHCO moiety, as a comparative semi-empirical study has shown. Both the bond lengths and dihedral angles of a C<sub>6</sub>H<sub>6</sub>-NH-CO-CH<sub>3</sub> molecule differ from those of the complete P-Q dyad by less than 0.005 Å and 1 $^{\circ}$ , respectively. The strong conjugation between the carbonyl group to the free electron pair of the peptide amino nitrogen results in a planar unit (see Figure 7). The quinone group is oriented about 73 $^{\circ}$  relative to the planar peptide group. The rotation of this dihedral angle strongly effects the relative orientation of the donor moiety to the acceptor subgroup and is thus considered more in detail.

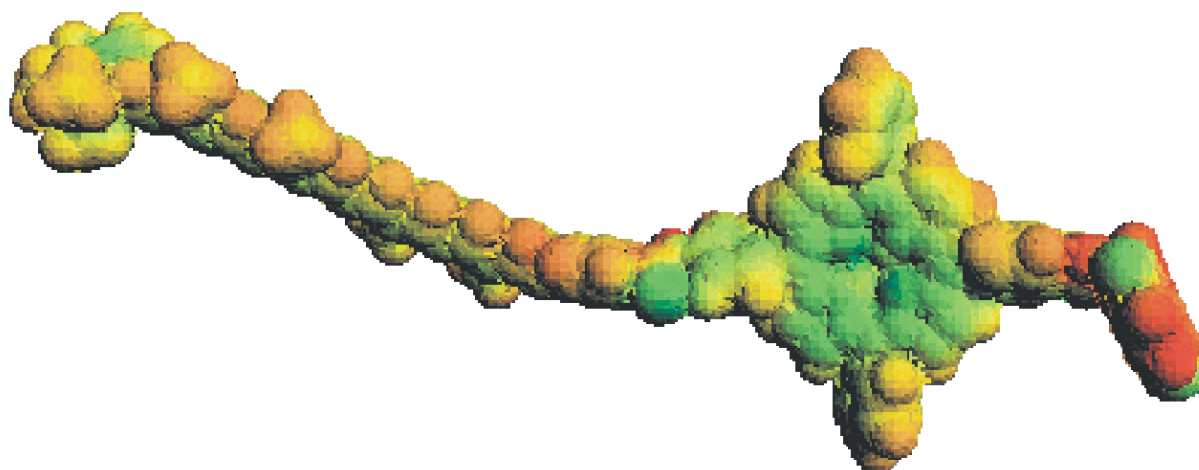
In Figure 8 the energy hypersurface of the P-Q dyad is shown as a function of the peptide dihedral angle and the orientation of the benzoquinone moiety. For the conformation of the total energy minimum, the quinone group is oriented approximately perpendicular ( $\pm 73^{\circ}$ ) relative to the -CH<sub>2</sub>-(C=O)-atoms. Energy maxima are observed for the planar (0 $^{\circ}$ ) conformation, i.e. with the quinone group and NH part pointing in the same (0 $^{\circ}$ ) and in opposite (180 $^{\circ}$ ) direc-



**Figure 8** Energy of the P-Q dyad as a function of both the peptide and quinone dihedral angle in [ $^{\circ}$ ]



**Figure 9a** Optimized geometry of the C-P-Q triad with the dihedral angles given in [°]



**Figure 9b** Optimized geometry of the C-P-Q triad with the electrostatic potential in the range from  $-70 \text{ kcal}\cdot\text{mol}^{-1}$  (blue) to  $+30 \text{ kcal}\cdot\text{mol}^{-1}$  (red)

tions. The conformations with the quinone group oriented parallel to the peptide moiety are  $3 \text{ kcal}\cdot\text{mol}^{-1}$  ( $0^\circ$ ) and  $3.5 \text{ kcal}\cdot\text{mol}^{-1}$  ( $180^\circ$ ) higher in energy than the conjugationally decoupled ( $73^\circ$ ) conformation. The calculations show, that the rotation of the quinone group about the C-C single bond towards the spacer unit is not completely free. The barrier for rotation about the single bond connecting the peptide group and the TPP-phenyl moiety are even higher in total energy - approximately  $4 \text{ kcal}\cdot\text{mol}^{-1}$ . This significant barrier still makes the large flexibility of all subunits feasible.

The distance between the donor and the acceptor subunit becomes larger by  $1 \text{ \AA}$  when the conformation of the geometrical minimum ( $12.9 \text{ \AA}$ ) to the parallel orientation ( $0^\circ$ ) is compared ( $13.9 \text{ \AA}$ ).

#### Carotene-Porphyrine-Quinone triad

Finally, the C-P-Q triad was investigated. This triad is of special interest because it has been shown that this system has

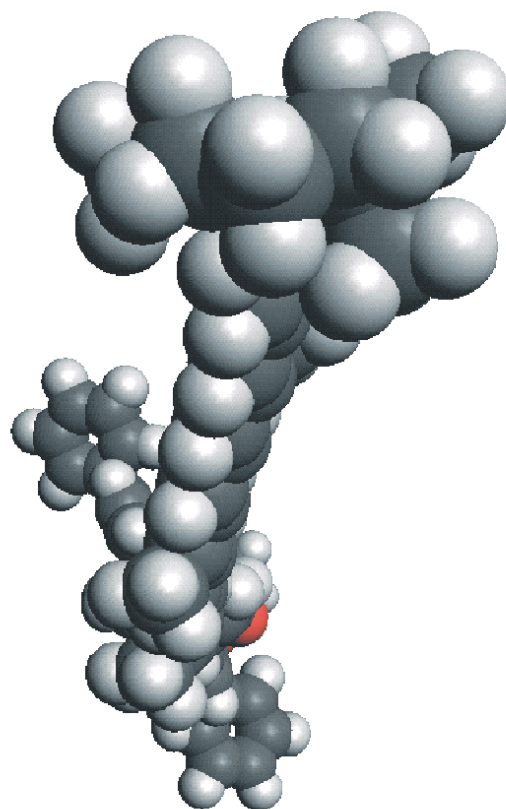
photophysical properties similar to natural PSRC. It has been incorporated into a membrane in order to mimic the primary processes of the photosynthetic reaction centre (PSRC) [17]. In order to explain the properties of this system, the electronic ground state has to be investigated prior to the study of its excited state properties. The standard enthalpy of this system is calculated as  $379.4 \text{ kcal}\cdot\text{mol}^{-1}$  and a dipole moment of  $3.7 \text{ D}$  is found pointing from the carotenoid to the porphyrine moiety. The distance between the secondary electron donor and the benzoquinone acceptor moiety has been computed as  $25.1 \text{ \AA}$ . The bond lengths and dihedral angles of the quinone acceptor moiety are equivalent to those of the P-Q dyad. Some selected twisted geometries were also optimised, and it is found that the energy barrier for rotation about the peptide and methylene single bond of the triad is also comparable to that of the corresponding dyad. The dihedral angle **D** (as defined in Figure 1) is  $61.8^\circ$ , just a few degrees smaller than for the P-Q dyad. The peptide group is also almost planar, with a dihedral angle H-N-C-O of  $182.0^\circ$ , slightly larger than for the P-Q dyad. The spacer phenyl group between the peptide and the carotenoid units slightly twisted out of planarity:  $41.0^\circ$  between the CO and the phenyl, and  $21.1^\circ$  between the phenyl and the carotenoid moieties, respectively.

The bond lengths within the carotenoid system show a marked bond length alternation similar to the free carotene. The double bonds **a**, **c**, **e**, ... (Figure 1) are of double bond character varying from  $1.34 \text{ \AA}$  to  $1.35 \text{ \AA}$ , whereas the bonds **b**, **d**, **f**, ... (Figure 1) are of single bond character with bond lengths from  $1.44 \text{ \AA}$  to  $1.46 \text{ \AA}$ . This effect can also be seen by the almost planar orientation between the C=C moieties (varying from  $179.4^\circ$  to  $181.4^\circ$ ) and the slightly distorted orientation within the C-C single bond connected units (varying from  $175.8^\circ$  to  $185.8^\circ$ ). The overall orientation thus results in an almost planar carotenoid unit, which shows a bending caused by the alternation of the orientation of the methyl groups between position **b-c**, **f-g**, **k-l**, and **o-p**. The terminating cyclohexenyl group is twisted significantly out of the polyene chain by  $153.8^\circ$ , corresponding to a twist of about  $25^\circ$  out of the polyene "plane".

The investigation of the electron density shows a deficiency of electron density at the quinone subunit and both the porphyrine and the carotenoid unit are highly negatively charged in their electronic ground states. The most positive net charge ( $+0.233$  electrons) is located at the hydrogen atom of the peptide group between the porphyrine and the carotenoid systems.

### Summary and conclusion

The three dyads P-A, P-F, and  $P_{Zn}$ -F are characterised by a rigid spacer connecting the TPP donor to the acceptor moiety. The distance between D and A is determined by the number of the aromatic spacer units. No significant change in this distance is possible by any rotational motions. The P-A dyad with two spacer units is characterised by a distance of  $14.9 \text{ \AA}$ , the two P-F dyads with three spacer units by a



**Figure 9c** side view of the optimized geometry of the C-P-Q triad

distance of  $19.1 \text{ \AA}$ . The anthracene moiety is a weaker electron donor, as can be seen by a less marked difference in the electron density between donor and acceptor and the smaller stabilisation energy in a polar solvent (P-A:  $10.3 \text{ kcal}\cdot\text{mol}^{-1}$ , P-F:  $20.2 \text{ kcal}\cdot\text{mol}^{-1}$ ). A deviation of the ground state properties is observed for P-F and  $P_{Zn}$ -F in comparison to all other systems. The ground state dipole moment is not oriented from the donor to the acceptor moiety along the axis of the spacer subunits but parallel to the flavine system. This deviation is explained by the highly polarisable electronic structure of flavine present in addition to the P-F-donor-acceptor pattern. The inhomogeneous structure of the flavine causes a large Stokes shift by a shift in electron density within the flavine subunit for its excited states. A different photophysical behaviour of these dyads is thus possible in comparison to both the P-A and the P-Q dyad.

The relative orientation of the donor, single spacer units and acceptor to each other is also quite similar within these three dyads. The biphenyl-like single bonds are twisted about  $60^\circ$  to  $70^\circ$  out of mutual planar orientation. But even under gas phase condition, a free rotation by approximately  $20^\circ$  is possible. Thus, a partial conjugation between the subunits is obtained. In addition, the phenyl-pyrimidyl connecting sin-

gle bond has an energetic minimum dihedral angle of approximately  $30^\circ$  and due to the lack of *ortho* positioned hydrogen atoms, a complete free rotation becomes possible. It is thus concluded that a partial conjugation is available between the TPP donor and the flavine and anthracene acceptor moiety, respectively. A possible electron transfer takes thus place via the through-bond mechanism. On one hand, this fact is quite surprising at first glance, because the phenyl-anthracene moieties are oriented nearly orthogonal to each other in the ground state minimum conformation, and the bond lengths are of typical single bond character. On the other hand, this rotational motion has shown to be even more flexible in polar solvents in comparison to the gas phase. Planarised geometries become more likely and a partial conjugation with shortened bond lengths is assumed in solution, thus favouring the through-bond mechanism for electron transfer.

The situation is different in the case of the benzoquinone dyad and triad, where no complete conjugation is present. The methylene unit causes an interruption of the continuous conjugation and a possible electron transfer must thus take place via a superexchange mechanism. For this through-space mechanism, the relative orientation and distance of D and A becomes of major importance. The distance between the electron donor and acceptor moiety can also only be varied over a range of approximately  $1 \text{ \AA}$  by rotation of the methylene unit. A complete rotation is not energetically possible, but a relatively large range of more than  $50^\circ$  around the total energy minimum are described by a very flat energy valley. In gas phase, the energy necessary for rotation about this single bond is about  $3 \text{ kcal}\cdot\text{mol}^{-1}$  to  $4 \text{ kcal}\cdot\text{mol}^{-1}$ , representing a significant barrier. The molecular triad C-P-Q shows for the P-Q part of the compound similar properties as the P-Q dyad. The additional carotenoid donor moiety causes an enlarged distance between the secondary electron donor C and the benzoquinone electron acceptor of  $48.0 \text{ \AA}$ . Although partial rotation is possible between the porphyrine and the carotenoid units, the rigid system of the polyene chain keeps both parts always at about the same distance and orientation. Thenon linear alignment of the polyene chain caused by the alternating methylgroups of the carotenoid system causes only small changes in the distance cyclohexenyl-porphyrine. Therefore, this effect can be neglected in all further studies.

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