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Molecular modelling of fullerene–porphyrin dyads

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Computational studies have been performed on a variety of C_{60}–porphyrin dyads, a class of donor–acceptor materials which have been a subject of considerable attention in recent years. Molecular modelling studies were carried out to clarify the relationship between molecular topology and experimentally determined rates of intramolecular electron and energy transfer in these systems. The systems studied include doubly linked cyclophane-like C_{60}–porphyrin dyads, where structural variations were made computationally on the porphyrin and linker portions, as well as dyads with flexible polyether and rigid steroid linkers. The molecular modelling studies involved building and minimising structures of the various fullerene–porphyrin dyads, followed by molecular dynamics to find the equilibrium and lowest energy conformations. The study confirmed that attractive van der Waals interactions between porphyrin and C_{60} moieties cause these dyads to adopt unusual conformations in which these groups are in close proximity, often in orientations which are not readily predictable from conventional structural representations. The implications of these computational data for the design of fullerene–porphyrin dyads with specific properties in the context of electron and energy transfer processes are discussed.

Introduction

Fullerene-C_{60} has three degenerate low-lying unoccupied molecular orbitals (LUMOs) making it a very good electron acceptor, particularly in photoinduced electron transfer processes.[1,2] The dynamics of electron transfer in a variety of donor–acceptor hybrids incorporating C_{60} has been the subject of intensive study in the past several years, with particular attention given to compounds in which porphyrin (P) and C_{60} moieties are connected by a variety of rigid, semirigid, and flexible linkers.[2–6] It has been found, not surprisingly, that the rates of forward and back electron transfer in such dyads are strongly sensitive to molecular topology, *i.e.*, the relative spatial orientation of the two chromophores.[7,8] Experimental evidence has been reported which points to strong attractive van der Waals interactions between P and C_{60} moieties in the ground state, which are expected to intensify when one or the other group is electronically excited. For example, it has been shown that a variety of porphyrins, both free base and metallo derivatives, form cocrystals with both C_{60} and C_{70}.[9,10] The X-ray crystal structures of these cocrystals show P–C_{60} contacts that are smaller than typical π–π interactions. Indeed, the interaction of the curved π-surface of the fullerene with the planar π-surface of the porphyrin has been concluded to represent a new type of recognition element in supramolecular chemistry.[9] While such electronic interactions between C_{60} and tetraarylporphyrins in solution are usually not strong enough to cause major perturbations in the UV-Vis absorption spectra of mixtures of these substances, small upfield shifts of selected nuclei in both ^{13}C and ^{1}H NMR spectra are indicative of intramolecular interactions in P–C_{60} dyads.[11,12] In covalently linked dyads in which π-stacking of the two chromophores is topologically possible, bathochromic shifts in the UV-Vis spectra are observed.[8] Upfield shifts in ^{3}He NMR spectra of some P–C_{60} dyads prepared from C_{60} containing endohedral ^{3}He,[13] indicative of ground state intramolecular electronic interactions, have also been observed.[14,15]

In the present study, we have computationally examined the nature and extent of *inter*molecular interactions of unlinked P and C_{60} moieties and *intra*molecular interactions of these same moieties in covalently linked dyads (see structures in Fig. 1) as a function of the nature of the linker. In all cases, the computed minimum energy conformations of these dyads are quite different from expectations based on standard structural depictions of these molecules, because of the strong intramolecular van der Waals attractive forces.

Using molecular dynamics, it was possible to obtain trajectories and energy barriers for conformational equilibration of some of the systems. The overall aims were (1) to better understand the factors which determine the lowest energy conformations of these dyads, (2) to attempt to correlate molecular topology and dynamics of electron and energy transfer processes, and (3) to identify those dyads which might be promising candidates for synthesis and photophysical studies.

Computational methods

General procedure:

Molecular models of the various C_{60}–porphyrin dyads were built and examined using the computer program Insight II (version 2000).[16] Initially, each molecule was roughly constructed based on its general atomic configuration. Forcefields used were ESFF[16] (extensible systematic forcefield), and CFF91[16] (consistent forcefield). The ESFF forcefield incorporates parameters for transition metals into its atom type set and is thus particularly well suited for computations on metalloporphyrin derivatives. CFF91 is a class II forcefield and is thus more advanced but less extensively tested and characterized.[16] Once the forcefield was chosen, minimum energy functions were then applied in order to set appropriate bond lengths and angles based on steric and electronic considerations. After the local minimum energy of each model was located, the corresponding structure was subjected to molecular dynamics for 100 000 femtoseconds. Snapshots, or frames, of the molecule were recorded during this process according to an

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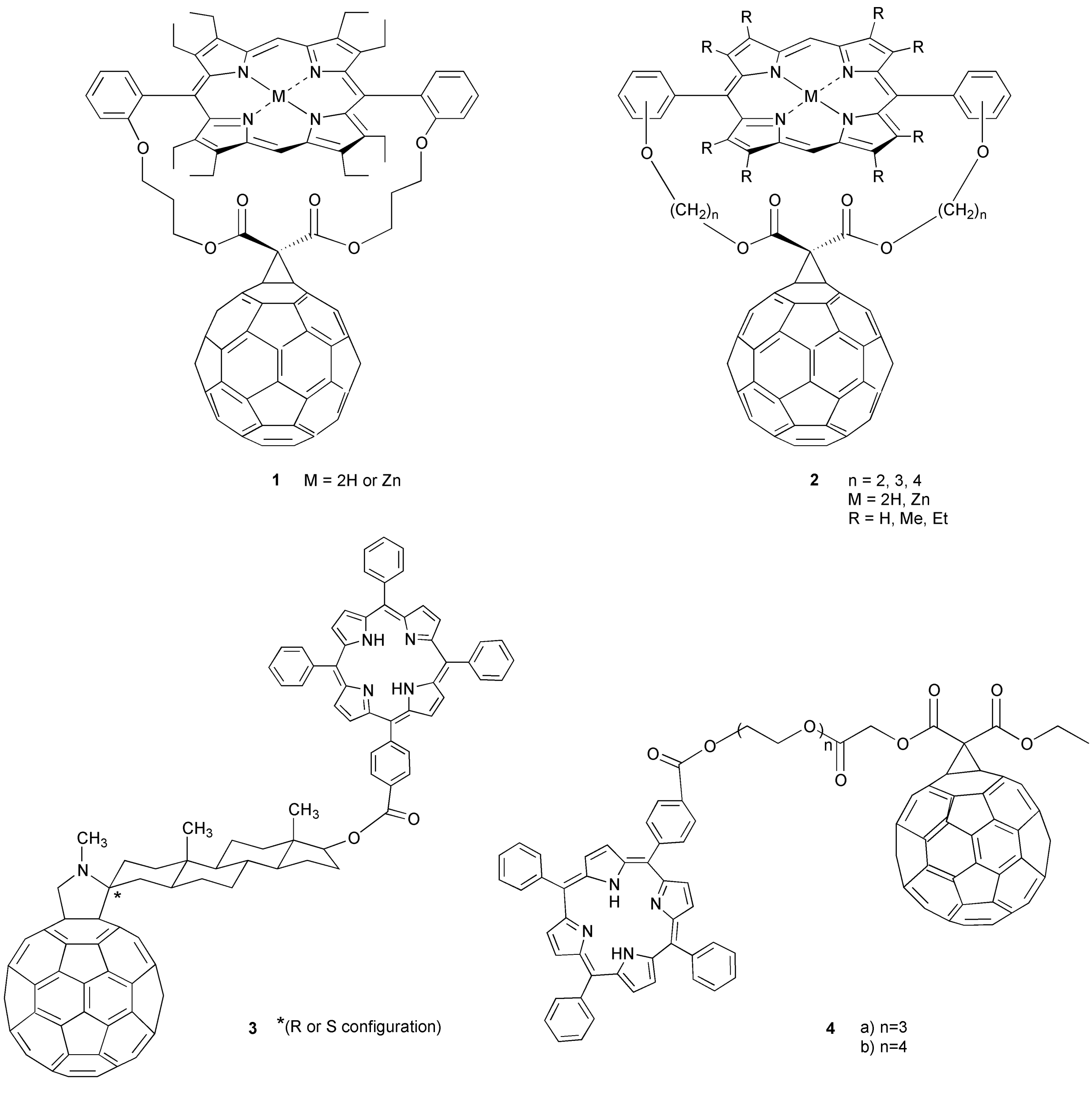

1 M = 2H or Zn

2 n = 2, 3, 4
M = 2H, Zn
R = H, Me, Et

3 *(R or S configuration)

4 a) n=3
b) n=4

Fig. 1 Structures of C_{60}–porphyrin dyads studied.

arbitrarily chosen time interval. Energy data were collected over this time period and represented graphically, and then the lowest energy conformation in each series was minimised using the same parameters as in the initial minimisation. To achieve consistency, this process was repeated using different starting geometries of the various model systems. Convergence to the presumed global minimum energy conformation from the above-mentioned variations was recognised when displacement of the atoms in successive structural iterations showed root mean square (RMS) deviations of less than 0.001 Å.

A key parameter in the lowest energy structure in each system is the centre-to-centre distance (D_{cc}), which corresponds to the distance from the geometric centre of the porphyrin ring system to the centre of the C_{60} fullerene sphere. Measurements were performed using Insight II, where selected atoms composed the set for which the geometric mean was calculated. For the porphyrin moiety, this set included the 36 atoms (35 for zinc-containing compounds) in the ring system, while the 60 carbon atoms of the fullerene were used to locate its centre. The centre-to-surface distances (D_{cs}) were measured from the centre of the porphyrin to the carbon atom on the fullerene that was closest to a line connecting both centres.

Results and discussion

5,10,15,20-Tetraphenylporphyrin and C_{60}

Boyd *et al.*[9] reported X-ray structures of naturally assembled cocrystallates of fullerenes (C_{60} and C_{70}) and porphyrins (free base and Zn complexes), formed by evaporation of 1 : 1 solutions of these compounds in toluene. These cocrystallates clearly indicate a special attraction between fullerene and P moieties, as also demonstrated in studies by Balch and co-workers.[10] The distances D_{cs} between the P plane and the closest atom in the fullerene range from 2.70 to 2.98 Å, which are shorter than expected for simple noncovalent interactions. For example, in fullerene–arene and porphyrin–arene systems, π–π interactions lead to separations in the range of 3.0–3.5 Å. In the tetraphenylporphine (H_2TPP)–C_{60} crystal, the electron-rich centre of H_2TPP was observed to be directly over a [6,6] bond, which is the bond between adjacent six-membered rings of the fullerene. This was attributed to electrostatic attraction between the electron-deficient centre of the porphyrin and the electron-rich olefinic [6,6] bond of the fullerene. The critical components of the interaction, however, were concluded to be van der Waals dispersion forces between the two systems. This was verified by molecular modelling studies of fullerene–porphyrin clusters, which gave the same kind of alternating H_2TPP–fullerene zigzag chains and intermolecular separations as observed in the X-ray structures. Significant interaction energies (28.0–33.6 kcal mol^{-1}) of H_2TPP with both C_{60} and C_{70} were calculated[9] using Universal[17] and PCFF[18] force fields. In all cases, the major contribution (80–95%) to the total binding energy is derived from the van der Waals terms of the forcefield.[9]

Since we were using different forcefields in our computations from those employed by Boyd, it was prudent to see if our computations could also reproduce the X-ray structural features of the C_{60}–H_2TPP cocrystallate.[9] This would provide a test of the accuracy of the method and lend credence to conclusions based on the subsequent computations on covalently linked P–C_{60} dyads. Using molecular mechanics with ESFF[16] and CFF91[16] forcefields, the H_2TPP–C_{60} crystal structure could be exactly reproduced (see Fig. 2). The distance D_{cs} was found to be essentially identical using both forcefields, 2.72 Å, well within the experimentally reported range. In the process of energy minimisation, the C_{60} molecules rotated so that a [6,6] bond was situated directly opposite the centre of the porphyrin, as was observed in the cocrystallate X-ray structure and in the earlier computations.[9,10] To our satisfaction, the zigzag pattern of the components observed in the crystal structure could also be reproduced computationally on more extended arrays (data not shown).

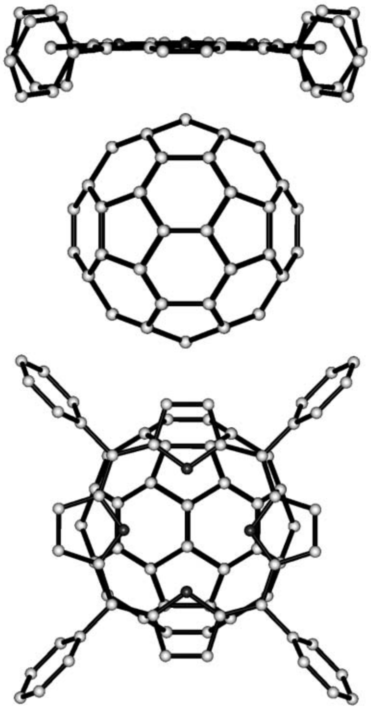

Fig. 2 Computed orientation of C_{60} and tetraphenylporphine in cocrystal using ESFF.

The success in reproducing the porphyrin–C_{60} cocrystallate X-ray structure provided validation of our computational method, and afforded confidence in results obtained using the same method pertaining to the lowest energy conformations and properties of covalently linked fullerene–porphyrin dyads. As will be seen, the unusual attraction between C_{60} and porphyrins demonstrated in the earlier study plays a significant role in our systems. We concur with the conclusion by Boyd *et al.*[9] that this interaction constitutes an important new structural motif in supramolecular chemistry.

Doubly linked porphyrin–C_{60} dyads ("Parachute" structures)

The doubly-linked C_{60}–porphyrin dyad **1** is a methanofullerene, which is linked to phenyl groups on opposite ends of the porphyrin. This compound, originally synthesised in our laboratory by Cheng,[15,19] is a derivative of 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-21*H*,23*H*-porphine, with a triethylene glycol linkage between the *ortho* carbons of the phenyl group and the two arms of the malonate moiety. The linkage to C_{60} was created by a Bingel–Hirsch reaction on the malonate.[20] Both the free base and the ZnP dyads were prepared, and photophysical studies on both these materials have been reported.[21]

Several variations on this so-called "parachute" structure were studied computationally. Structure **2** in Fig. 1 represents a generalised structure for this type of system. The first variant involves comparison of free base (P) and zinc-containing porphyrin (ZnP) dyads, since the oxidation potential of ZnP is significantly less than that of P.[22] Secondly, the effects of placing methyl and ethyl groups on the pyrroles in place of hydrogen were examined, since substituents on the pyrroles are often introduced to improve solubility in common organic solvents. It is recognised (and was indeed confirmed by computations) that such substituents can force the P ring system to become nonplanar. Thirdly, the position of attachment of the linker to the phenyl groups at the opposite *meso*-positions of the porphyrin ring was varied (*ortho*, *meta*, and *para*) to determine the effect of the linkage on the overall structural stability, molecular conformation, and electron donor properties of the system. Finally, the number of methylene groups in the chains connecting the phenyl groups to the ester groups of the malonate was varied from two to four. Not surprisingly, the length of the linker is crucial in determining the distances D_{cc} and D_{cs} as well as the overall molecular conformation.

An additional concern in these systems is the conformation of the carbonyl groups in the malonate moiety, which can exist in either *cis* or *trans* orientations, with the carbonyl oxygens pointing in the same or opposite directions, respectively. Since hydrogen bonding is not an issue here, the *cis–trans* preference is controlled entirely by neighbouring structural features.

All combinations of these individual variations on structure **2** were examined computationally. Energy minimisations were carried out as described above. As with most molecular modelling studies, calculated energy values generally do not correlate absolutely with experimental data, but comparisons of data for the same compound in different conformations, or data for closely related compounds, can be meaningful. Such comparisons are most revealing for models that have nearly identical or at least very similar structures. Relevant characteristics of dyads possessing *ortho*-, *meta*, and *para*-linked phenols with otherwise identical numbers of linker atoms are compared in Table I. Several interesting trends are revealed. For example, the calculated heats of formation for the *ortho*- and *meta*-linked dyads are in all cases lower than for the corresponding *para*-linked compounds, which are invariably more strained. The extent of the strain not surprisingly decreases as the linker length is increased.

In *all* cases, the minimum energy structure is clearly not the one in which the P ring sits symmetrically above the fullerene sphere, in a parachute-like conformation with C_{2v} symmetry (Fig. 3b), but rather structures in which P has shifted position to the side of the fullerene (Fig. 3a). Table 1 contains values of D_{cc} and D_{cs} for a large number of free base dyads corresponding to structure **2** in the unsymmetrical conformation. These unsymmetrical conformations all have significantly smaller values of D_{cc} and D_{cs} than the analogous C_{2v} structures ($\sim$6.5 and $\sim$10 Å, respectively), and are computed to be significantly more stable. Molecular dynamics indicates that the P ring moves back and forth from one side of the C_{60} sphere to the other passing through the C_{2v} structure, since the energy barrier is not large enough to lock it in position at ambient temperatures. If this is indeed the case, conformational equilibration must be fast on the NMR timescale at room

Table 1 Computed energies and distances of minimum energy conformations for free-base porphyrin–C_{60} dyads of **2**

R-group	n	Phenol linkage	Total energy/kcal mol^{-1}	D_{cc}/Å	D_{cs}/Å
H	2	*ortho*	962.128	8.07	4.68
		meta	975.375	7.28	3.87
		para	993.933	8.05	4.66
	3	*ortho*	959.003	7.01	3.54
		meta	954.826	6.61	3.10
		para	977.710	8.05	4.78
	4	*ortho*	946.888	6.88	3.42
		meta	944.007	6.30	2.91
		para	957.822	7.55	4.22
CH_3	2	*ortho*	905.159	7.35	3.87
		meta	911.160	7.32	3.78
		para	937.696	7.95	4.52
	3	*ortho*	898.866	7.09	3.55
		meta	898.145	7.18	3.73
		para	924.795	8.22	4.89
	4	*ortho*	885.903	6.68	3.12
		meta	898.754	6.60	3.14
		para	913.365	7.55	4.11
CH_2CH_3	2	*ortho*	870.999	7.67	4.20
		meta	891.285	7.41	3.96
		para	901.504	8.08	4.53
	3	*ortho*	863.013	7.75	4.23
		meta	880.804	6.82	3.50
		para	887.572	7.78	4.31
	4	*ortho*	849.418	7.12	3.69
		meta	867.148	6.66	3.19
		para	877.818	7.83	4.29

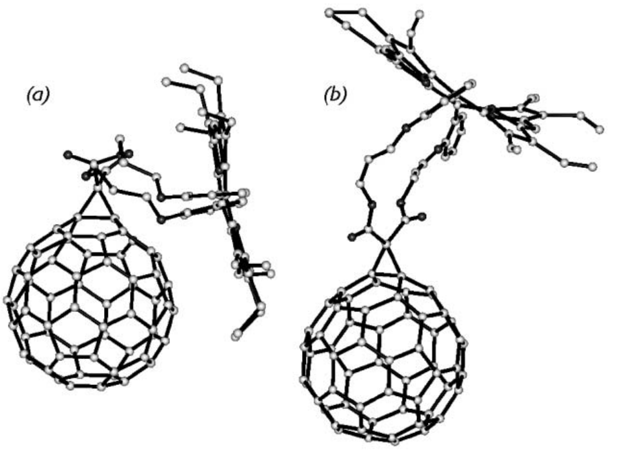

Fig. 3 a) Computed minimum energy conformation of free base dyad **1**; b) high energy conformation of free base dyad **1**.

temperature since the ^1H NMR spectrum of dyad **1** corresponds to the structure with C_{2v} symmetry.[15] Thus, our original depiction of these types of dyads as parachute-shaped structures with C_{2v} symmetry[19] is in error, because we underestimated the strength of the attractive forces between the P and C_{60} moieties which cause these dyads to adopt what at first glance appear to be strained unsymmetrical geometries. It would obviously be of interest to examine the ^1H and ^3He NMR spectra of **1** and related "parachute" dyads at low temperatures in attempts to directly detect the unsymmetrical structure.

A significant finding is that the zinc-containing C_{60}–ZnP dyads in this series had both lower heats of formation and smaller dipole moments than their free base counterparts.

Steroid linked porphyrin–C_{60} dyads

A rigid steroid linker (androstane) was introduced in an attempt to force the porphyrin and fullerene moieties far apart, as illustrated by dyad **3** in Fig. 1.[23] It was of interest to see which process would dominate in this system, photoinduced electron transfer or energy transfer. The first step in the synthesis of this type of dyad involved formation of a steroidal fulleropyrrolidine by a Prato reaction,[24] involving 1,3-dipolar cycloaddition to C_{60} of an azomethine ylide prepared from 17-hydroxyandrostan-3-one and sarcosine (*N*-methylglycine). Since this reaction is stereochemically nonselective, two diastereomers of **3** should be formed, with *R* and *S* configurations at the spiro carbon atom (*). These *R* and *S* epimers differ with respect to the orientation of the angular methyl groups of the steroid relative to the fullerene moiety, *i.e., anti* (*S*) or *cis* (*R*). In addition, the ester used to link the steroid to the porphyrin can exist in the s-*trans* (*Z*) or s-*cis* (*E*) conformation, using the nomenclature of Eliel and Wilen.[25] Usually, esters exist overwhelmingly in the thermodynamically more stable (5–6 kcal mol^{-1}) s-*trans* (*Z*) conformation, with a rotational barrier on the order of 11 kcal mol^{-1}.[25]

Computational examination of the steroid-linked dyads **3** followed the general procedure outlined earlier. Both the ESFF and CFF91 forcefields were used in all determinations, except for the torsional rotor calculations, which could only be performed using CFF91 in the Discover module using the "torsion force" function.[16] Both forcefields were found to yield nearly identical results. Total energy values for these forcefields reflect differences in the energies assigned to the various elements that go into the computation. Energy minimisation and identification of the lowest energy conformation was performed as described above.

The structure of the *S* isomer in the extended conformation shown in Fig. 4a has a D_{cc} value of 21.63 Å, after initial minimisation (ESFF).[26] Due to this large separation, it was originally assumed that there would be limited interaction between the P and C_{60} moieties in this system.[3,23] The computations, however, indicated the existence of a lower energy compact conformer of the *S* diastereomer with the ester in the s-*cis* (*E*) conformation, shown in Fig. 5a. In this structure, the H_2TPP and C_{60} moieties are within 6.13 Å (D_{cc}) of each other, and D_{cs} is only 2.63 Å. The calculated barrier to rotation around the dihedral angle defined by the C(=O)–O–C ester unit in (*S*)-**3** indicates that the two conformers most likely do not readily interconvert This is shown in the potential energy diagram (see Fig. 6b) created using the parameters of the

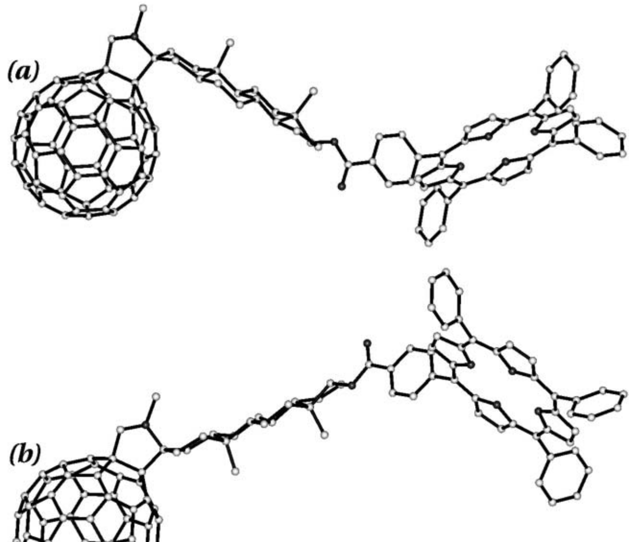

Fig. 4 a) *S*-Epimer of steroid-linked dyad **3** in the extended conformation; b) *R*-epimer of steroid-linked dyad **3** in the low energy extended conformation.

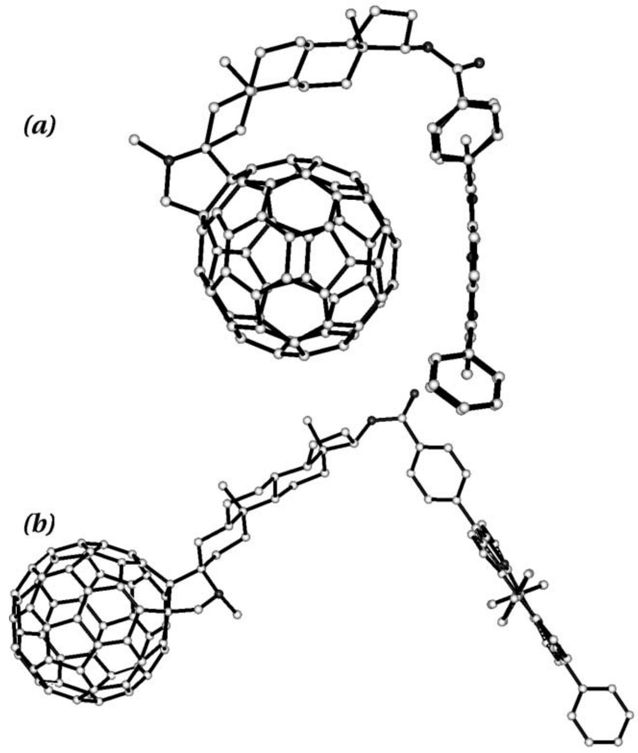

Fig. 5 a) *S*-Epimer of steroid-linked dyad **3** in the low energy compact conformation; b) *R*-epimer of steroid-linked dyad **3** in the high energy compact conformation.

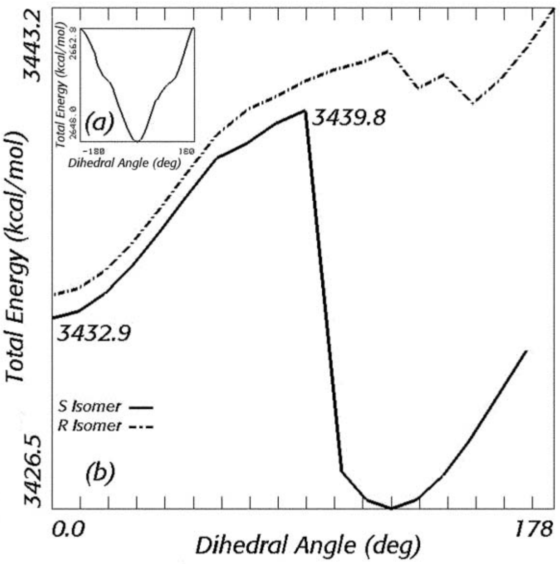

Fig. 6 Potential energy diagrams computed with CFF91 forcefield for rotation about the ester linkage for a) C_{60}–steroid–ester–phenyl control; b) *R* and *S* epimers of steroid-linked dyad **3**.

CFF91 forcefield. The dihedral angle was adjusted in increments of 10° in the range from 0° to 180°, with minimisation at each increment with a maximum of 3000 iterations, until an RMS deviation of 0.001 Å was reached using the conjugate minimisation method. Each of the angles was held in place using a force constant setting of 200 in the program.[16] An angle of 0° refers to the (*Z*) conformer of the ester while angles near 180° refer to the (*E*) conformation.

The situation is quite different for the *R*-epimer of **3**, for which the extended topology with the ester in the *Z* conformation was calculated to be much more stable than the compact structure with the ester in the *E* conformation. In the dynamic calculations, if the molecule was initially forced to adopt the compact conformation, it always isomerized (at 500 K) to the extended structure. The (*R*)-**3** epimer is configured such that P cannot interact with the C_{60} surface nearly as efficiently as in the *S* epimer (Fig. 5a). Thus, rotation in (*R*)-**3** about the dihedral angle in the ester does not lead to significant van der Waals attractive forces between the P and C_{60} moieties. While these forces were the decisive factor in determining conformer stability in the *S*-epimer, in the *R*-epimer the extended topology is preferred.

A control model system (C_{60}–steroid–phenyl), in which a phenyl group replaced the porphyrin, was subjected to the torsion force function using the same parameter set and minimisation method as above. The results are shown in Fig. 6a. This surface clearly indicates that in the absence of the porphyrin moiety, the potential energy increases as the structure is rotated around the dihedral angle of the ester as defined above, into the compact (*E*) conformation. The calculated energy difference between the two conformations in this control system is ~14 kcal mol^{-1}. Thus, given that the calculated energy difference between the compact *vs.* extended conformations of (*S*)-**3** is ~6 kcal mol^{-1} (Fig. 6b), favouring the compact structure, we conclude that the stabilisation of the compact form of (*S*)-**3** is directly ascribable to van der Waals attraction between P and C_{60}. The magnitude of this attraction can be estimated to be in the order of 20 kcal mol^{-1}, from the change in energies of (*S*)-**3** *vs.* the model system upon rotation from s-*trans* (*Z*) to s-*cis* (*E*) ester conformations. This value is about four times the energy of a standard hydrogen bond, *i.e.*, OH···O or NH···N,[27] which is striking. In any event, the attractive force is clearly sufficient in (*S*)-**3** to overcome the natural bias against the s-*cis* (*E*) ester conformation. Van der Waals energies generated by both forcefields for the minimum energy structures of (*S*)-**3** (Fig. 5a) and (*R*)-**3** (Fig. 4b) are shown in Table 2. The difference in these terms, ranging from 23.4–24.5 kcal mol^{-1}, corresponds to the van der Waals attractive force, and is in excellent agreement with the estimate made from comparison of (*S*)-**3** with the control system containing a phenyl group in place of the porphyrin. It is also in agreement with the interaction energy in the porphyrin–C_{60} cocrystallates calculated by Boyd *et al.*[9] Thus it is clear that the van der Waals term is the dominating force controlling molecular conformation in these systems. Computations performed by Maggini *et al.*[28] on structurally related steroid-linked dyads, with tris(2,2′-bipyridine)–Ru^{2+} as the donor in place of TPP, indicate negligible difference in this case in edge-to-edge distances in the corresponding *R*- and *S*-epimers. This suggests

Table 2 Distance and energy values for minimum energy conformations of dyads **3** and **4**

	ESSF Forcefield				CFF91 Forcefield			
Compound	D_{cc}/Å	D_{cs}/Å	Total energy/ kcal mol	van der Waals energy/ kcal mol^{-1}	D_{cc}/Å	D_{cs}/Å	Total energy/ kcal mol^{-1}	van der Waals energy/ kcal mol^{-1}
(*S*)-**3** (see Fig. 5a)	6.13	2.63	1195.78	52.66	6.15	2.81	3425.01	78.51
(*R*)-**3** (see Fig. 4b)	23.78	20.26	1204.32	77.05	23.7	20.29	3433.62	101.95
4a	6.15	2.64	1035.29	40.57	6.07	2.74	3710.53	54.83
4b	6.02	2.76	1033.14	37.59	5.91	3.06	3698.56	50.52

that the attractive forces discussed above are restricted to systems in which C_{60} interacts either inter- or intra-molecularly with porphyrins or porphyrin-like donor moieties.

The heats of formation data and D_{cc}/D_{cs} distances for the two epimers of dyad **3** are summarised in Table 2.

Glycol ether-linked porphyrin–C_{60} dyads

The third type of hybrid studied employs a flexible polyethylene glycol linker between the C_{60} carboxylic acid synthon and H_2TPP, illustrated by dyads **4a** and **4b**, with $n = 3$ and 4, respectively (see Fig. 1).[29,30] In this system, it is expected that the C_{60} and P moieties will adopt conformations in which their D_{cc} and D_{cs} values are quite small. Indeed, the computations gave minimum energy structures with $D_{cc} = 6.15$ and 6.02 Å and $D_{cs} = 2.64$ and 2.76 Å for **4a** and **4b**, respectively. Once again, the general computational procedure was followed, and dynamics were run at 500 K for 100 000 fs. Relevant data are given in Table 2. Note that in these systems D_{cc} and D_{cs} values depend upon the orientation of the porphyrin relative to the [6,6] bond of the fullerene. It is evident from the minimum energy conformations of **4a** and **4b** (see Fig. 7), that the more conformational freedom one lends to the C_{60} and H_2TTP moieties, *i.e.* the longer the linker, the more readily a conformation is adopted in which the H_2TTP lies directly over the [6,6] bond of C_{60}, as in the C_{60}–porphyrin cocrystallates.

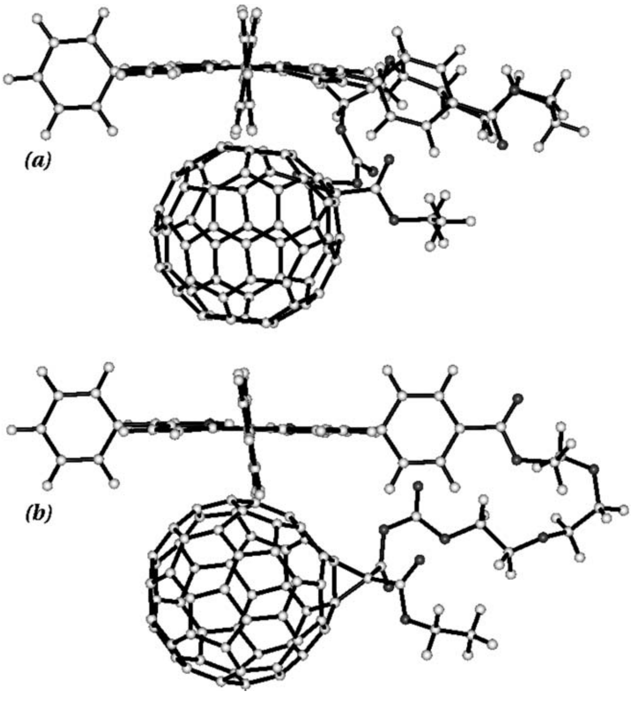

Fig. 7 Computed minimum energy conformations of flexibly-linked dyads a) **4a** and b) **4b**.

Relation of the computed conformations of P–C_{60} dyads to photoinduced electron transfer processes

These computational results have ramifications in the photophysics of these systems. Implicit in this conclusion is the assumption that photoinduced electron transfer occurs preferentially, if not exclusively, in the lowest energy conformations of these dyads. This is in accord with the Born–Oppenheimer approximation,[31] which is particularly applicable in the present situation, since the photophysical data for these and other P–C_{60} dyads show that the lifetime of the initially generated photoexcited state is typically in the order of a few picoseconds. Thus, there is not enough time for the systems to change their geometry appreciably before electron or energy transfer occurs. In all the systems studied, it was found that the highest occupied molecular orbital (HOMO) is located primarily on the fullerene moiety and the lowest unoccupied molecular orbital (LUMO) is on the porphyrin, with a dipole directed from the porphyrin toward the fullerene (data not shown). The dipole moments in the most favourable cases, *i.e.*, where the two chromophores are closest, range from 2–3 Debye units.

Thus, for the doubly-linked "parachute" dyad **1**, the extremely rapid rate of photoinduced electron transfer (PET) in polar as well as nonpolar solvents, is close to 10^{11} s^{-1}.[21] This rapid rate for PET is difficult to reconcile with the symmetrical (C_{2v}) structure in which D_{cc} is ~10 Å, but makes much better sense in terms of the unsymmetrical conformation shown in Fig. 3a, in which D_{cc} is only 6.5 Å. Even though there must be an energy barrier for flipping from one such conformation to its equivalent on the opposite side of the C_{60} sphere through the high energy C_{2v} conformation, this motion must occur rapidly at ambient temperatures, based upon the ^{1}H NMR spectrum of **1**.[32] Furthermore, our computations predict that D_{cc} should be even smaller, and PET consequently even faster, in the analogous *meta*-linked dyads, particularly using a linker with four methylene groups. Synthesis of such hybrids is currently underway.

It has become increasingly clear that charge recombination (CR) in these and related P–C_{60} is in the Marcus inverted region.[2,21,33–35] That is, k_{CR} is inversely related to the thermodynamic driving force for the process, $-\Delta G^\circ_{CR}$. Thus, the charge-separated radical ion pair for **1** is longer-lived in nonpolar than in polar solvents,[36] a phenomenon which has been seen in several other systems.[8,37–39] The dependence of k_{CR} to changes in the molecular topology of P–C_{60} dyads, triads and larger assemblies has yet to be fully explored. From recent studies of a structurally related pair of doubly-linked dyads, when P and C_{60} moieties are forced into a face-to-face alignment, k_{CR} is significantly more rapid than it is in a dyad in which there is an edge-to-face topological relationship.[8] Photophysical studies of a series of dyads of general structure **2** (see Table 1) should help to clarify this issue.

Recent spectroscopic studies[36] show that the fluorescence decay of the electronically excited P moiety in steroid-linked dyad **3** (employing a mixture of the *R*- and *S*-epimers) is non-linear, corresponding to lifetimes of 0.64–0.68 and 5.2–5.7 ns, respectively. Transient absorption studies[36] indicate that a CS state is generated in polar solvents (THF, benzonitrile) while energy transfer dominates in toluene.

The principal mode of decay of the CS states is to form fullerene triplet states, since the efficiency of sensitisation of $^1O_2$ formation is high in polar as well as nonpolar solvents.[40] On the basis of the computations, it is tempting to interpret the fluorescence lifetime data for **3** in terms of contributions from two distinct species, namely the *S*-epimer in the compact conformation (short-lived component) and the *R*-epimer in the extended conformation (long-lived component). In order to test the validity of this proposal, it will be necessary to at least partially separate the two diasteromers, probably by HPLC, and determine their individual photophysical properties. This is currently in progress. Two stereoisomers of the same P–C_{60} dyad possessing vastly different photophysical properties is totally unprecedented.

As for the dyads **4a** and **4b**, photophysical studies[36] show that PET rates are again very fast, consistent with the close proximity of the two chromophores predicted by the computations. These rates increase as a function of solvent polarity, from 5×10^9 s^{-1} in toluene to 10^{10} s^{-1} in DMF. Charge recombination is significantly slower, and again appears to occur in the Marcus inverted region, as shown by the solvent dependence of k_{CR}.

Conclusions

Computations of the preferred conformations of hybrids of porphyrins and C_{60} as described in this paper confirm the importance of van der Waals attractive forces, which pull these two chromophores together into close proximity in these systems. This was originally demonstrated in a striking manner by the X-ray crystal by Boyd *et al.*,[9] and confirmed in this work. Strong supramolecular interactions between the planar porphyrin and the spherical fullerene surfaces control the topology of these systems in the ground and electronically excited states. As previously recognised, this has strong implications with respect to the properties of these types of systems, in particular to the rates of photoinduced electron and energy transfer.[2] A possible criticism of the present study is that these computations, as well as those previously reported, were all done *in vacuo*, *i.e.*, excluding the solvent. In addition to the fact that the already lengthy computations would have become even more involved if solvent were included, the decision to explicitly exclude the solvent can be justified on the basis that solvent polarity has been shown to have only a small effect on the rates of photoinduced electron transfer in these systems. This in turn implies that the topology of these covalently linked P–C_{60} dyads is not sensitive to solvent polarity. Thus, in the case of **1**, the rate of charge separation k_{CS} is almost the same in benzene and in THF. For the free base, k_{CS} is $(14\ \text{ps})^{-1}$ and $(23\ \text{ps})^{-1}$, respectively, while for the ZnP dyad, k_{CS} is $(9\ \text{ps})^{-1}$ and $(13\ \text{ps})^{-1}$, respectively.[21] For the steroid-linked dyad **3**, there is no significant difference in the rate of photoinduced charge separation in toluene, THF and benzonitrile, while for dyads **4a** and **4b**, these rates differ by at most a factor of two in five solvents ranging in polarity from DMF to toluene.[36] Finally, Guldi and co-workers find only minor variations in rates of photoinduced electron transfer in two rigid dyads in which face-to-face and edge-to-edge alignment of the P and C_{60} moieties is enforced by *trans-2* and equatorial bis-attachment of the porphyrin moiety to the fullerene sphere, respectively.[8]

The most stable molecular topologies predicted computationally for these dyads are unanticipated based on customary structural considerations. The role of unusual geometries of P–C_{60} dyads in photoinduced electron transfer (PET) processes has been suggested previously,[2–5,7,8,11] and is confirmed and extended by the present study. In particular, the computationally predicted dependence of molecular topology on the nature of the linker as well as stereochemical factors in these hybrids correlates very well with rates of PET for hybrid systems already studied, and allows predictions of the behaviour of dyads and larger molecular assemblies incorporating porphyrins and fullerenes yet to be prepared. Since synthesis of P–C_{60} dyads is inevitably a tedious process, these much less time-consuming computations allow identification of hybrids which would be the best targets for photophysical studies based on their predicted molecular topologies.

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