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Synthesis and photophysical studies of a porphyrin–viologen dyad covalently linked by a flexible seven-atom chain

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Abstract

A dyad with terminal porphyrin (P) and viologen (MV^{2+}) chromophores covalently linked by a flexible seven-atom hexanoate chain has been synthesized. Ab initio and semi-empirical solvent continuum calculations suggest that the preference for 'extended' or 'folded' conformations of the dyad depend strongly on solvent. Fluorescence lifetime and transient absorption studies in acetonitrile indicate that approximately 80% of the dyad population are in a suitable conformation to undergo photoinduced electron transfer (PET) to produce P^{+}–MV^{+} with a rate of $5\times10^{8}\,s^{-1}$. A long-lived charge-separated state lifetime of 170 ns is observed. It is proposed that electrostatic repulsion between the positively charged end groups resulting from PET increases the average donor–acceptor separation thus retarding the charge recombination process. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrin; Viologen; Electron transfer; Fluorescence

1. Introduction

Rigid, covalently linked bichromophoric systems continue to provide valuable insight into fundamental aspects of long-range electron transfer (ET) processes, such as orientation and distance dependence of ET dynamics and the dependence of the strength of electronic coupling on the nature of the intervening medium (i.e. saturated hydrocarbon bridges, polypeptides, oligonucleotides) [1–14]. Increasing attention is being paid to the development of systems which display the desirable characteristics of undergoing efficient charge separation, combined with longevity of the resulting charge-separated state [15].

Multichromophoric systems offer considerable promise in this respect. One approach along this line is to connect a series of chromophores of graded redox characteristics in a chain using rigid saturated bridges [15–29]. We have been investigating this approach by applying our well known [1,30] strategy of using norbornylogous bridges to the construction of novel triads and tetrads which are already providing unusual yet insightful photophysical properties [24–29]. Of relevance to the work described in this paper are the photophysical studies on the supposedly rigid tetrad **1** (Fig. 1) in which the tetra-aryl zinc porphyrin (P), dimethoxynaphthalene (DMN), naphthoquinone (NQ) and viologen (MV^{2+}) are covalently linked by connecting norbornylogous bridges [28,29]. Rapid, photoinduced charge separation was observed to occur, leading to the formation of the giant charge-separated state **2** ($^{+}$P–DMN–NQ–MV^{+}) [28]. Convincing evidence has been amassed which strongly suggests that ET occurs directly between the locally excited porphyrin donor and the MV^{2+} acceptor, without involving either the DMN or NQ chromophores [28]. This direct ET mechanism in **1** is possible because of the structurally enforced propinquity of the terminal chromophores which, according to HF/3-21G calculations, results in the separation between the P and MV^{2+} groups being only about 4.1 Å (Fig. 1) [29,31]. At the AM1 level, the P–MV^{2+} separation is predicted to be about 5.3 Å. As a consequence, ET between the two terminal chromophores should easily occur, by either a through-space or a through-solvent mechanism. Both AM1 and HF/3-21G calculations indicate that the proximity of the P and MV^{2+} chromophores is largely due to the electrostatic attraction between these groups; in the absence of this stabi-

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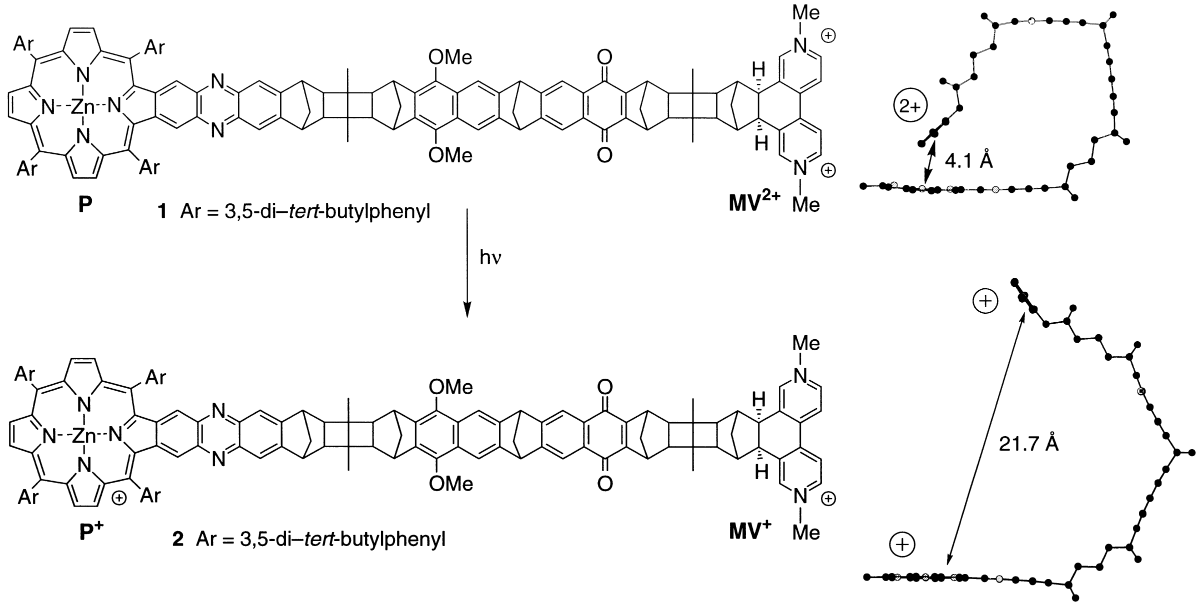


Fig. 1. The U-shaped tetrad **1** and its charge-separated state **2**. Also shown are the profiles of the gas phase geometry optimized structures: HF/3-21G for **1** and UHF/3-21G for the triplet charge-separated state **2**.

lizing interaction, the separation between the terminal chromophores in **1** is expected to be approximately 13.4 Å [29].

Intriguingly, the charge-separated state **2** has an unusually long lifetime, about 420 ns (in acetonitrile). This finding is surprising since it might be expected that through-space or solvent-mediated ET should be equally facile for both charge separation and charge recombination processes. However, both the HF/3-21G and AM1 level gas phase MO calculations predict that the distance between the terminal chromophores in **2** is about 17 Å greater than in **1**, and that this enormous increase in separation is caused by strong electrostatic repulsion between the positively charged P^+ and MV^+ groups which is relieved by out-of-plane bending of the DMN and NQ groups (Fig. 1). The large separation between the terminal chromophores in **3** now ensures that direct charge recombination is a slow process.

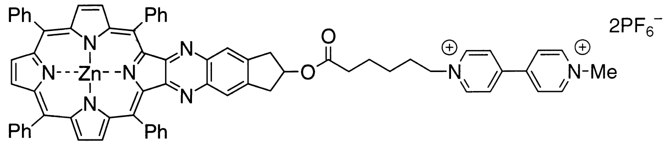
The finding that the dynamics of charge separation and charge recombination in **1**/**2** seem to be governed by electrostatically induced structural changes in the molecular framework suggests that this mechanism might have useful applications in the development of photovoltaic devices. However, for this approach to be viable, the ‘electrostatic’ mechanism needs to be shown to occur in systems which are structurally simpler and synthetically more accessible than **1**. A promising candidate is the novel dyad **3** (Fig. 2), in which the porphyrin and viologen chromophores are covalently linked by a single flexible, seven-atom hexanoate chain. The chain length is long enough to allow the viologen group to lie over the porphyrin ring in close proximity, if such a conformation were favoured by electrostatic interactions. Indeed, both ab initio and semi-empirical MO gas phase calculations (see further) suggest that the folded conformation is substantially more stable than any extended conformation and that in the former conformation the viologen and porphyrin groups are sufficiently close to each other that direct photoinduced charge separation should be facile (Fig. 2). Electrostatic repulsion in the resulting charge-separated state should induce a switch from the folded conformation to the extended conformation in which the two chromophores are much further apart (Fig. 2). Herein, we present the synthesis of **3** and the results of photophysical studies and computational investigations on this dyad.

2. Results and discussion

2.1. Synthesis

The synthesis of **3** was achieved using the reactions shown in Fig. 3 and full details are provided in Section 4.1.^{1}H NMR (nuclear magnetic resonance) spectroscopy was used to examine the conformation of **3**. If the folded conformation were dominant, then large upfield shifts in the viologen proton resonances of **3** should be observed since these protons lie within the shielding region of the porphyrin ring (see Fig. 2).

Unfortunately, no strong evidence for the shielding of the viologen protons of **3** could be discerned from the NMR data in d_6-acetone. The most upfield of the aromatic signals in **3**, 8.34 ppm, is some 0.74 ppm more downfield than that observed in **1**, in which shielding of the viologen protons by the porphyrin is known to occur. The lack of anisotropic shielding in **3** is further supported by the significant 0.64 ppm upfield shift observed for the viologen methyl protons of **3** on going from d_6-acetone to the more polar d_3-acetonitrile solvent. Were shielding by the porphyrin important in **3**, a



3

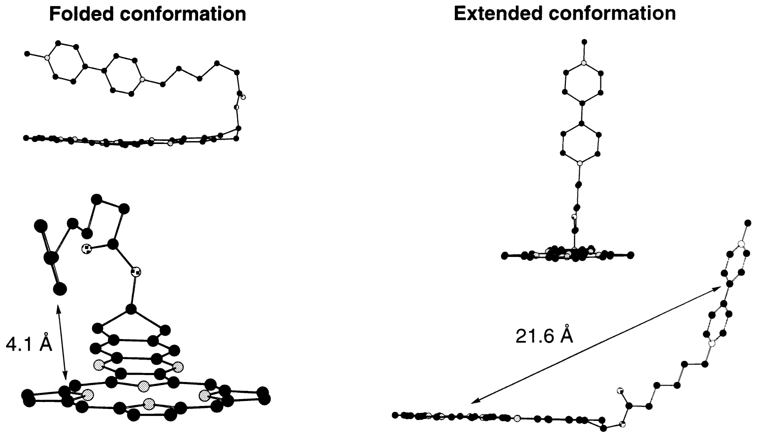


Fig. 2. Porphyrin–viologen dyad linked by a single seven-atom hexanoate chain. The HF/3-21G level gas phase optimized folded and extended conformations are shown.

move to lower field might be anticipated due to the stabilization of the positive charges by the more polar solvent, serving to reduce the contribution of any folded conformers. That only upfield shifts are observed seems consistent with simple charge dispersal.

In summary, the NMR data for **3** imply that, even if the folded conformation were dominant in the solvents studied (acetone and acetonitrile), then the distance between the porphyrin and viologen chromophores is much larger than that implied by the gas phase calculations (see further).

2.2. Photophysical studies

The absorption and fluorescence spectra of **3** in acetonitrile are shown in Fig. 4. The absorption spectrum of the dyad closely corresponds with the absorption spectrum of the model untethered porphyrin **9b** (Fig. 3), indicating that ground state electronic interactions between the porphyrin and viologen chromophores in **3** are minimal. Photophysical measurements were restricted to acetonitrile and acetone as there was evidence from absorption spectra for aggregation in less polar solvents. The steady state fluorescence of **3** was quenched by approximately 45% compared to the porphyrin model **9b**. The fluorescence decay profile of the porphyrin model **9b** could be well fitted (reduced chi-square 1.0, Durban–Watson fitting parameter 1.9) to a single exponential with a lifetime of 1.12 ns. However the porphyrin fluorescence decay in the dyad in acetonitrile solvent required a two exponential fit (reduced chi-square 1.05, Durban–Watson parameter 2.06) resulting in two lifetimes of 0.72 and 1.11 ns with a ratio of pre-exponential factors of 4.65:1. The minor longer-lived component has the same lifetime as the unquenched model and can be attributed to molecular conformations of the dyad which do not undergo a quenching process within the excited state lifetime. The major component with the quenched lifetime can be associated with molecules undergoing a competing non-radiative process with a rate constant of $5.0\times10^{8}\,s^{-1}$. Similar dual exponential fluorescence decay behaviour was observed for the dyad in acetone solvent with the ratio of the pre-exponential factors for the short (0.75 ns) and long (1.13 ns) lifetime components being 2.9:1.

In **1** the quenching of fluorescence was accompanied by the appearance of new transient species associated with the formation of P^{+} and MV^{+} radical ions [28]. Similar transient absorption spectra were observed following laser flash photolysis of **3** (cf. Fig. 5). The transient spectrum exhibits narrow minima at 570 and 615 nm associated with photobleaching of ground state porphyrin absorption Q-bands. The major contribution to the strong new transient absorption in the region of 580–700 nm was identified as MV^{+} by comparison with the absorption spectrum of chemically reduced MV^{2+}. The transient kinetics at 640 nm are shown in Fig. 6 and can be modelled by a major species (MV^{+}) with a decay time of 170 ns and a much longer-lived minor component decaying over tens of microseconds. The absorption spectrum of the minor long-lived component recorded after a delay of 1 μs (Fig. 5) shows the same spectral features as obtained from flash photolysis of the model porphyrin

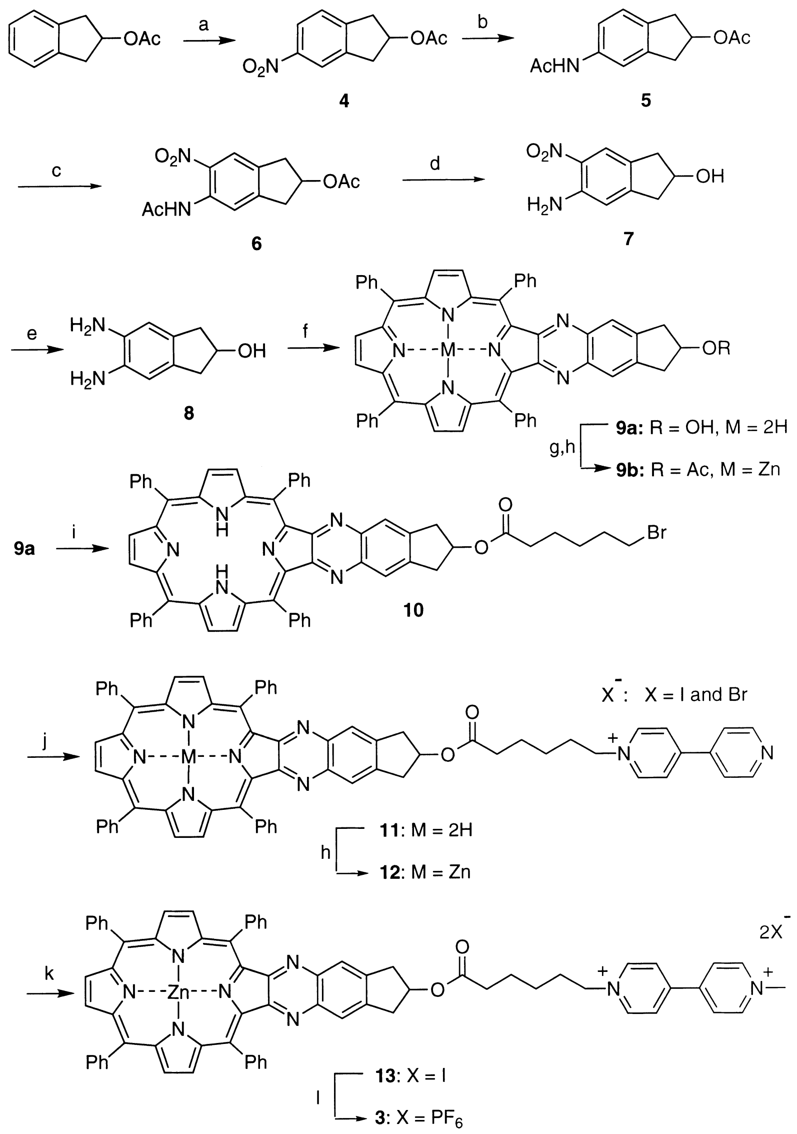


Fig. 3. Scheme for the synthesis of **3**. Reagents and conditions: (a) $Cu(NO_3)_2{\cdot}3H_2O$, Ac_2O; (b) Zn, Ac_2O; (c) HNO_3, Ac_2O; (d) HCl; (e) $H_2NNH_2{\cdot}H_2O$, Pd/C; (f) tetraphenylporphyrindione; (g) AcCl, C_5H_5N; (h) $Zn(OAc)_2{\cdot}H_2O$; (i) $ClCO(CH_2)_5Br$, C_5H_5N; (j) 4,4′-bipyridyl, NaI; (k) MeI; (l) NH_4PF_6, H_2O.

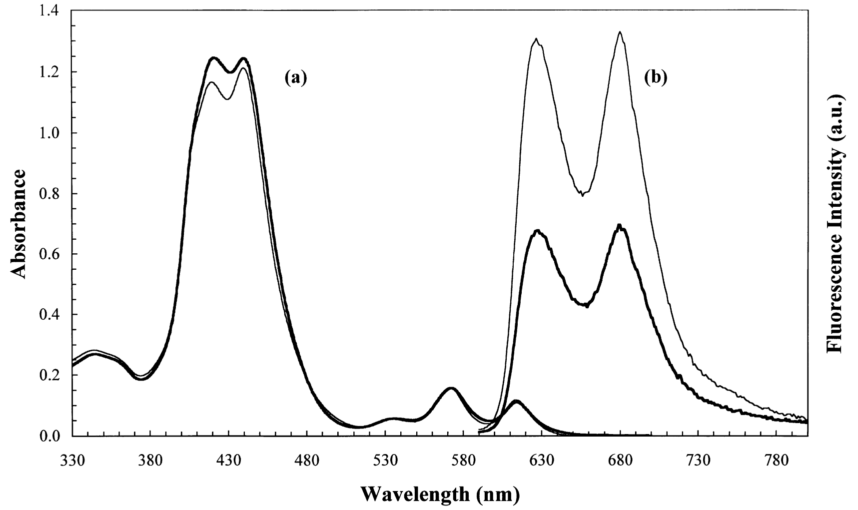


Fig. 4. (a) Absorption spectra and (b) corrected fluorescence spectra (ex. @ 572 nm) of the porphyrin model **9b** (—) and **3** (━━) in acetonitrile.

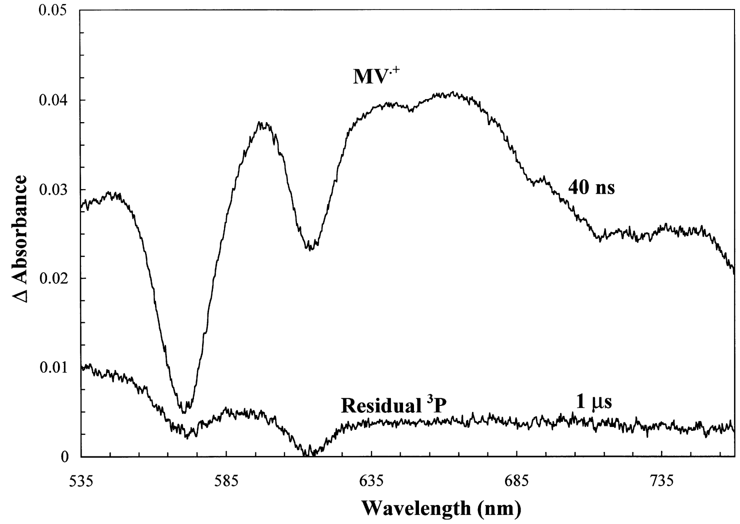


Fig. 5. Transient absorption spectra for **3** in acetonitrile recorded 40 ns and 1 μs after the 572 nm excitation pulse.

compound **9b** and can be attributed to residual porphyrin triplet state.

The energetics of photoinduced electron transfer (PET) in **3** can be discussed using the electrochemical data for the donor and acceptor and the excited state energies. The oxidation potential of the donor porphyrin (E^{ox}(D)) and reduction potential of the viologen acceptor (E^{red}(A)) have been determined previously in acetonitrile as 1.11 and −0.42 V, respectively [28]. The singlet state energy of the porphyrin is 2.01 eV [28] while the triplet state energy of zinc tetraphenylporphyrin is reported as 1.59 eV [32]. Ignoring any coulombic effects in the dyad that differ from those affecting the individual ions, the free energy change for ET from the porphyrin singlet and triplet state can thus be calculated [32] as −0.48 and −0.06 eV, respectively. Thus ET to the viologen is much more strongly favoured from the excited singlet state of the porphyrin. The very small free energy change calculated in the case of the porphyrin triplet state likely accounts for the reason why residual triplet state absorption is observed in the transient spectra for **3** and does not appear to undergo oxidation.

The photophysical behaviour of **3** can be compared to previous studies of PET in the tetrad **1** [28]. The much larger fluorescence quenching rate of $2.3\times10^9\ s^{-1}$ obtained for **1** compared to the value of $5.0\times10^8\ s^{-1}$ for the flexibly linked dyad **3** suggests that the average electron donor–acceptor separation is greater in **3** and/or that significant chain rearrangements are required to bring the terminal chromophores into a suitable configuration for ET to occur. The remarkably long-lived charge separated state can be attributed to

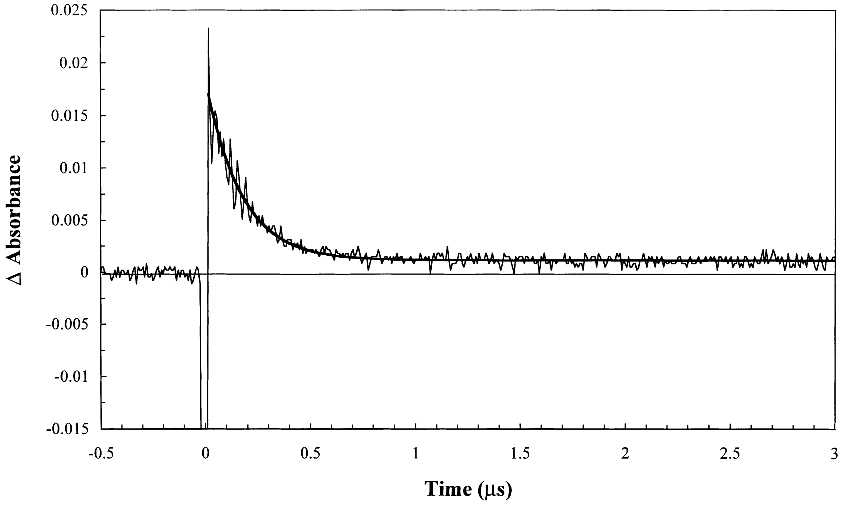


Fig. 6. Transient decay at 640 nm for **3** in acetonitrile following laser excitation at 572 nm. The solid line is a fit of the data to a decay lifetime of 170 ns attributed to MV^+ and a baseline component of 10% associated with the much longer-lived residual porphyrin triplet.

electrostatic repulsion between the positively charged terminal chromophores produced by ET increasing the average donor–acceptor separation and thus retarding the charge recombination process.

2.3. Calculations

Structural aspects of **3** were investigated using both ab initio HF/3-21G [33] and semi-empirical AM1 [34] theoretical models as implemented in the Q-Chem Version 1.1 [35] and GAMESS [36] programs, respectively. Of the many different possible conformations that may be adopted by the hexanoate chain, only two extreme ones, labeled ‘folded’ and ‘extended’, were investigated (Fig. 2).

Both AM1 and HF/3-21G methods gave similar gas phase optimized structures, the main difference being that the AM1 method indicates a greater amount of torsion about the 4,4′ bond in the viologen unit. This torsional angle is nearly zero for both folded and extended conformations at the HF/3-21G level, as shown in Fig. 2, but is about 45° at the AM1 level. In the folded conformation, the viologen prefers to adopt an approximately perpendicular disposition with respect to the porphyrin ring, rather than a parallel orientation, which is present in **1**, owing to structural constraints. The viologen group is quite close to the porphyrin ring in the folded conformation, the closest separation being about 4 Å at the HF/3-21G level. This proximity should allow for strong electronic coupling between the two chromophores in the folded conformation.

Both AM1 and HF/3-21G models predict substantial gas phase stabilization of the folded conformation, relative to the extended conformation, by 18.6 (AM1) and 23.9 (HF/3-21G) kcal/mol. The HF/3-21G stabilization energy is inflated by the basis set superposition error (BSSE), which is estimated to be about 8 kcal/mol, using the counterpoise method [29,37]. The BSSE corrected stabilization energy for the gas phase folded conformation of **3** is therefore about 16 kcal/mol.

That both ^{1}H NMR and photophysical studies suggest that the viologen and porphyrin groups in **3** are much further apart than is indicated by the gas phase optimized folded conformation imply that the solvent and possibly the counter-ion have a dramatic effect on the relative stabilities of the folded and extended conformations. This implication was investigated by carrying out continuum solvation calculations [38] at the AM1 level using the SM5.42 procedure [39] as implemented in GAMESOL V2.1 [40]. Geometry optimizations were carried out using two solvents having quite different dielectric constants, namely benzene (ε=2.27) and acetonitrile (ε=37.5). In these calculations, the optimization convergence criteria (the maximum gradient) was relaxed slightly to 0.0005 as opposed to the default value of 0.0001. The calculations predict that solvent has a strong influence on the relative energies of the two conformers. Whereas the folded conformation is more stable than the extended conformation by 18.6 kcal/mol in the gas phase, this preference is reversed in acetonitrile solvent; the extended conformation is now 16.2 kcal/mol more stable than the folded conformation. In benzene solvent, the two conformations are nearly isoenergetic, the extended conformation being slightly more preferred (by 0.9 kcal/mol). Interestingly, the optimized geometry of the folded conformation is not noticeably affected by solvent.

In summary, the AM1 solvent continuum calculations predict that the substantial gas phase stabilization of the folded conformation of **3**, relative to the extended conformer, is eliminated in solvents of low polarity and is even strongly reversed in high polarity solvents (such as acetonitrile). This prediction is qualitatively consistent with the ^{1}H NMR and photophysical studies on **3**, although it is likely that additional conformations of the hexanoate tether may be populated in solution. Some of these conformations will undoubtedly place the porphyrin and viologen groups in sufficient proximity to each other (<8 Å) to permit solvent-mediated PET to take place. Investigations of other viologen-containing multichromophoric systems also reveal either very weak or nonexistent complex formation. Thus, weak intramolecular complex formation in water was observed for aromatic-viologen systems linked by a polymethylene bridge [41], but no intermolecular complex formation was observed between a viologen group and a porphyrin unit, unless the latter was attached to additional complexing groups [42].

3. Conclusions

A flexibly linked porphyrin–viologen dyad **3** has been synthesized and PET between the terminal porphyrin donor and viologen acceptor chromophores investigated. In acetonitrile photophysical measurements indicate that approximately 80% of the dyad population are in suitable conformations to facilitate an ET process. The charge separation rate of $5\times10^8\,s^{-1}$ corresponds to a quantum efficiency of 36% for PET. These values are substantially smaller than the corresponding rate and quantum efficiency of $2.3\times10^9\,s^{-1}$ and 76%, respectively observed between the same terminal chromophores in the rigidly linked tetrad **1**. An explanation for these observations is that the average separation of the porphyrin and viologen moieties is greater in the flexibly linked dyad than in **1** and that chain rearrangements are required to bring the donor and acceptor into a suitable configuration to allow orbital overlap for the ET process to occur. The results of NMR studies and theoretical calculations support this interpretation and emphasise the important role of the solvent in determining conformations of the flexibly linked systems which favour ET. The relatively long-lived charge-separated state lifetime of 170 ns can be attributed to electrostatic repulsion between the positively charged radical ions retarding the back ET step. Such conformational control of charge separation and recombination processes should prove useful in the future design of structures for application in molecular photovoltaic devices.

4. Experimental details

4.1. Synthesis

4.1.1. General

Chemicals were purchased from Aldrich and used as received. Solvents were dried and reagents were purified where necessary using literature methods. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with Merck 5735 Kieselgel 60F. Column chromatography was carried out using Kieselgel 60 (0.040–0.063 mm mesh, Merck 9385). Melting points are not corrected. Low resolution mass spectra (MS) were obtained using either electron impact (EI) or electrospray (ES) mass spectrometry. NMR spectra were recorded at 300 MHz for proton frequency and 75 MHz for carbon frequency. Experimental methods used were based on those reported in the literature [43,44].

4.1.2. 2-Acetoxy-5-nitroindane (4)

To a solution of 2-acetoxyindane (6.55 g, 37.2 mmol) in dichloromethane (200 ml) and acetic anhydride (200 ml) at 0°C was added powdered copper(II)nitrate trihydrate (18.0 g, 74.5 mmol). The mixture was slowly allowed to warm to room temperature and was then stirred overnight. The mixture was added carefully to concentrated ammonia solution with concomitant addition of ice such as to maintain the temperature of the solution below 40°C. The aqueous phase was separated from the organic and extracted with dichloromethane (200, 100 ml). The dichloromethane extracts were combined, washed with water (150 ml), dried (Na_2SO_4) and evaporated to dryness. The crude material was chromatographed on silica gel (eluent: dichloromethane) to afford 7.2 g (88%) of 2-acetoxy-5-nitroindane and 2-acetoxy-4-nitroindane in a ratio of 87:12 (^{1}H NMR). The desired isomer (**4**), 3.0 g (37%) was obtained after fractional recrystallization from absolute ethanol (60 ml) at room temperature; mp 86–88°C. ^{1}H NMR δ 2.02 (s, 3H); 3.09 (dd, J=17.3, 3.0 Hz, 1H); 3.10 (dd, J=17.3, 3.0 Hz, 1H); 3.37 (d, J=18.1 Hz, 1H); 3.39 (d, J=18.1 Hz, 1H); 5.58 (m, 1H); 7.37 (d, J=9.1 Hz, 1H); 8.09 (d, J=9.1 Hz, 1H); 8.09 (s, 1H). ^{13}C NMR δ 21.09, 39.36, 74.93, 119.83, 122.60, 125.11, 142.36, 147.58, 148.40, 170.71. MS (EI) *m/z* 222 (1), 162 (20), 161 (81), 144 (6), 115 (19), 43 (100), 42 (37).

4.1.3. 2-Acetoxy-5-acetaniloindane (5)

A mixture of **4** (2.91 g, 13.17 mmol), zinc (8.7 g, 133 mmol), acetic anhydride (5 ml) and acetic acid (35 ml) was prepared and heated at 120°C overnight. The mixture was cooled to room temperature, carefully neutralised with concentrated ammonia solution (45 ml) and extracted with dichloromethane (3×50 ml). The extracts were washed with water (2×50 ml), dried (Na_2SO_4) and evaporated to dryness. After column chromatography 2.87 g (93%) of **5** was obtained; mp 128–130°C. ^{1}H NMR δ 2.01 (s, 3H); 2.14 (s, 3H); 2.93 (dd, J=17.0, 3.0 Hz, 1H); 2.96 (dd, J=17.0, 3.0 Hz, 1H); 3.24 (dd, J=17.0, 4.5 Hz, 1H); 3.26 (dd, J=17.0, 4.5 Hz, 1H); 5.49 (tt, J=4.5, 3.0 Hz, 1H); 7.13 (d, J=8.3 Hz, 1H); 7.19 (d, J=8.3 Hz, 1H); 7.49 (s, 1H); 7.60 (bs, 1H). ^{13}C NMR δ 21.26, 24.27, 39.06, 39.63, 75.55, 116.86, 119.06, 124.70, 136.21, 137.08, 141.19, 169.00, 171.14. MS (EI) *m/z* 233 (1), 232 (1), 215 (1), 189 (3), 173 (87), 131 (69), 130 (33), 43 (100), 42 (26).

4.1.4. 2-Acetoxy-5-acetanilo-6-nitroindane (6)

To a solution of **5** (0.50 g, 2.26 mmol) in acetic anhydride (7.5 ml) and acetic acid (7.5 ml) was added dropwise nitric acid (69%, 0.4 g). External cooling was applied as needed to maintain the temperature of the reaction below 45°C. After 30 min the solution was added to a mixture of ice (50 g) and concentrated ammonia solution (30 ml). The mixture was extracted with dichloromethane (3×30 ml). The dichloromethane extracts were washed with water (50 ml), dried over Na_2SO_4, and evaporated to afford 0.54 g (90%) of a mixture determined by ^{1}H NMR to consist of the 6-nitro-, 4-nitro-, and 7-nitro- derivatives of **5** in a 81:13:7 ratio. After flash chromatography on silica gel (eluent 10% ethyl acetate/dichloromethane) 0.27 g (48%) of the desired isomer **6** was isolated; mp 140–142°C. ^{1}H NMR δ 2.01 (s, 3H); 2.28 (s, 3H); 3.02 (dd, J=17.1, 2.4 Hz, 1H); 3.09 (dd, J=18.1, 2.6 Hz, 1H); 3.31 (dd, J=17.1, 6.0 Hz, 1H); 3.35 (dd, J=18.1, 6.4 Hz, 1H); 5.55 (m, 1H); 8.07 (s, 1H); 8.63 (s, 1H); 10.37 (bs, 1H). ^{13}C NMR δ 20.99, 25.43, 38.76, 40.38, 74.76, 117.85, 121.38, 134.05, 135.61, 136.04, 150.18, 168.96, 170.56. MS (EI) *m/z* 279 (1), 237 (1), 218 (39), 176 (100), 172 (15), 130 (18), 43 (81).

4.1.5. 5-Amino-6-nitroindan-2-ol (7)

A solution of **4** (146 mg, 0.53 mmol) in ethanol (1 ml) and concentrated hydrochloric acid (1 ml) was heated under reflux for 1 h. The ethanol was removed by evaporation under reduced pressure and the residue was diluted with water (5 ml) and made basic to pH 10 by the addition of solid potassium hydroxide. The mixture was saturated with sodium chloride, ether (15 ml) was added and then the entire mixture was passed through a pad of celite. The aqueous phase was extracted with further portions of ether (3×10 ml). The combined ether fractions were dried (Na_2SO_4) and evaporated to afford 94 mg (92%) of **7** sufficiently pure for further use; mp 145–147°C. ^{1}H NMR δ 1.65 (bs, 1H); 2.82 (dd, J=16.2, 3.0 Hz, 1H); 2.86 (dd, J=17.3, 3.0 Hz, 1H); 3.05–3.17 (m, 2H); 4.71 (m, 1H); 6.04 (bs, 2H); 6.68 (s, 1H); 7.97 (s, 1H). ^{13}C NMR δ 40.67, 42.08, 72.14, 114.25, 120.5, 130.50, 130.61, 145.85, 151.90. MS (EI) *m/z* 194 (100), 176 (29), 166 (36), 165 (46), 161 (91), 131 (25), 115 (51), 43 (81), 42 (35).

4.1.6. 5,6-Diaminoindan-2-ol (8)

Palladium on carbon (5%, 8 mg) was added to a solution of 7 (94 mg, 0.48 mmol) in ethanol (4.0 ml) and hydrazine hydrate (1.3 ml). The ensuing mixture was heated under reflux for 2 h after which time the solution had not turned colourless. A further portion of Pd/C (15 mg) was added and the mixture refluxed for another 2 h. The catalyst was removed by filtration and after evaporation of the solution to dryness 79 mg (99%) of **6** was obtained as a colourless solid. The product was used immediately as obtained as it decomposes on standing at room temperature precluding complete characterization. ^{1}H NMR (CD$_3$CN) δ 2.59 (dd, J=15.8, 4.1 Hz, 2H); 2.96 (dd, J=15.8, 6.0 Hz, 2H); 3.18 (bs, 5H); 4.48 (m, 1H); 6.48 (s, 2H).

4.1.7. 7,12,17,22-Tetraphenylcyclopenta[1,2-g]quinoxalino [2,3-b]porphyrin-2-ol (9a)

To a solution of the diamine **8** (40 mg, 0.24 mmol) in dichloromethane (14 ml) was added a solution of tetraphenylporphyrindione (120 mg, 0.19 mmol) in dichloromethane (20 ml). The ensuing solution was stirred at room temperature for 1 h and then evaporated to dryness. The residue was dissolved in a minimum of chloroform and chromatographed on silica gel (eluent 5% ethyl acetate/dichloromethane) to afford 133 mg (92%) of **9a** as a dark purple solid; mp>250°C. ^{1}H NMR δ −2.54 (s, 2H); 1.69 (d, J=5.7 Hz, 1H); 3.19 (dd, J=17.0, 3.4 Hz, 2H); 3.44 (dd, J=17.0, 5.0 Hz, 2H); 4.85 (m, 1H); 7.69–7.94 (m, 14H); 8.11–8.28 (m, 8H); 8.72 (s, 2H); 8.92 (d, J=4.9 Hz, 2H); 8.96 (d, J=4.9 Hz, 2H). ^{13}C NMR δ 42.50, 73.66, 117.00, 121.63, 125.53, 126.81, 126.84, 127.87, 127.96, 128.03, 133.96, 134.06, 134.50, 137.88, 139.67, 140.65, 141.97, 142.00, 144.37, 146.10, 152.11, 154.84.

4.1.8. 7,12,17,22-Tetraphenylcyclopenta[1,2-g]quinoxalino [2,3-b]porphyrin 5-bromopentane-1-carboxylate (10)

To a solution of 6-bromohexanoyl chloride (41 mg, 0.19 mmol) and pyridine (20 mg, 0.25 mmol) in dichloromethane (2 ml) was added dropwise a solution of **9a** (132 mg, 0.17 mmol) in dichloromethane (10 ml). After 4 h additional portions of pyridine (50 mg, 0.63 mmol) and 6-bromohexanoyl chloride (80 mg, 0.37 mmol) were added and the mixture left to stir for 3 days. The solution was washed with 10% ammonia (10 ml), dried over Na$_2$SO$_4$ and evaporated to dryness. The residue was chromatographed on silica gel (eluent 60–75% dichloromethane/light petroleum) to afford 132 mg (81%) of the ester **10** as a dark purple solid. mp>250°C. ^{1}H NMR δ −2.53 (s, 2H); 1.38–1.52 (m, 2H); 1.57–1.69 (m, 2H); 1.78–1.89 (m, 2H); 2.27 (t, J=7.5 Hz, 2H); 3.29 (dd, J=17.3, 1.9 Hz, 2H); 3.38 (t, J=6.8 Hz, 2H); 3.53 (dd, J=17.3, 5.7 Hz, 2H); 5.68 (m, 1H); 7.69–7.96 (m, 14H); 8.12–8.29 (m, 8H); 8.73 (s, 2H); 8.94 (d, J=4.9 Hz, 2H); 8.97 (d, 4.9 Hz, 2H). ^{13}C NMR δ 23.98, 27.51, 32.27, 33.41, 34.12, 39.44, 75.74, 116.91, 121.19, 126.74, 126.79, 127.54, 127.82, 127.92, 127.99, 133.84, 134.02, 134.42, 137.81, 139.57, 140.51, 141.85, 141.90, 143.83, 145.90, 152.13, 154.78, 173.24.

4.1.9. 7,12,17,22-Tetraphenylcyclopenta[1,2-g]quinoxalino [2,3-b]porphyrin 5-(4,4'-bipyridino)pentane-1-carboxylate (11)

A mixture of the bromide **10** (60 mg, 0.063 mmol), 4,4′-dipyridyl (190 mg, 1.44 mmol) and sodium iodide (27 mg, 0.18 mmol) in dimethyl formamide (3 ml) was heated at 70°C for 3 days and then evaporated to dryness under high vacuum. The crude product was washed with several portions of ether to remove the unreacted 4,4′-dipyridyl and then chromatographed on silica gel (eluent 10% methanol/dichloromethane) to afford 58 mg (79%) of the pyridinium adduct 10. mp>250°C. ^{1}H NMR δ −2.62 (s, 2H); 1.34 (m, 2H); 1.60 (m, 2H), 1.90 (m, 2H); 2.24 (t, J=7.1 Hz, 2H); 3.28 (d, J=16.2 Hz, 2H); 3.38 (dd, J=16.2, 4.9 Hz, 2H); 4.64 (t, J=7.5 Hz, 2H); 5.62 (m, 1H); 6.97 (d, J=6.0 Hz, 2H); 7.68–7.93 (m, 16H); 8.02–8.30 (m, 10H); 8.72 (s, 2H); 8.90–8.95 (m, 4H); 9.01 (d, J=6.4 Hz, 2H). ^{13}C NMR δ 23.95, 25.25, 31.04, 33.79, 39.50, 61.27, 76.02, 116.94, 121.06, 121.83, 125.23, 125.60, 126.91, 127.69, 127.94, 128.12, 133.8, 134.2, 134.47, 137.93, 139.57, 140.27, 140.46, 141.76, 144.05, 145.05, 145.66, 151.02, 152.05, 153.34, 154.96, 173.05. MS (ES) *m/z* 1026, 513, 299, 285, 157, 105.

4.1.10. Zinc (II) 7,12,17,22-Tetraphenylcyclopenta[1,2-g]quinoxalino-[2,3-b]porphyrin 5-(4′-methyl-4,4′-bipyridino)pentane-1-carboxylate bishexafluorophosphate (3)

To a solution of the pyridylpyridinium salt **11** (220 mg, 0.19 mmol) in chloroform (13.5 ml) was added a solution of zinc acetate monohydrate (105 mg, 0.48 mmol) in methanol (13.5 ml). After stirring at room temperature for 3 h the solution was evaporated to dryness. The residue was dissolved in chloroform and washed with water (2×50 ml). The chloroform solution was filtered through celite and the celite was thoroughly washed with additional portions of chloroform. The combined chloroform solutions were evaporated to afford 134 mg of **12**. To this were added dimethyl formamide (3.0 ml) and methyl iodide (1.5 ml). The ensuing mixture was heated at 50°C overnight and then evaporated to dryness under high vacuum. The crude product was dissolved in a solution prepared by the addition of a solution of ammonium hexafluorophosphate (1.8 g, 11.0 mmol) in water (10 ml) to acetone (80 ml). The acetone was evaporated from the solution and the precipitate collected and dried under high vacuum. ^{1}H NMR indicated partial demetallation had occurred. Therefore the product was dissolved in acetone (2 ml) and methanol (10 ml) and a solution of zinc acetate monohydrate (45 mg, 0.21 mmol) in methanol (1.0 ml) was added. After being stirred for 2 h at room temperature the mixture was evaporated to dryness and the product reprecipitated from a mixture of ammonium hexafluorophosphate (0.5 g, 3.0 mmol), water (10 ml) and acetone (80 ml) as previously described. After washing the precipitate with water and drying it at 70°C under high vacuum over phosphorous oxide 103 mg (39%) of **3** was obtained. mp>250°C. ^{1}H NMR (d_6-acetone) δ 1.40–1.54 (m, 2H), 1.56–1.71 (m, 2H), ca. 2.00–2.14 (m, 2H, obscured by d_5-acetone signal), 2.30 (t, J=7.2 Hz, 2H), 3.31 (d, J=16.6 Hz, 2H), 3.62 (dd, J=17.3, 5.3 Hz, 2H), 4.34 (s, 3H), 4.75 (t, J=7.9 Hz, 2H), 5.69 (m, 1H), 7.69–7.93 (m, 14H), 8.03–8.29 (m, 8H), 8.34 (d, J=6.8 Hz, 2H), 8.60 (d, J=6.4 Hz, 2H), 8.74–8.89 (m, 8H), 2.28 (d, J=6.8 Hz, 2H). ^{13}C NMR (d_6-acetone) δ 23.74, 25.21, 30.78, 33.47, 39.28, 48.15, 48.52, 61.79, 75.79, 117.05, 123.01, 124.81, 126.17, 126.47, 126.57, 126.85, 127.07, 127.60, 130.98, 131.84, 133.45, 133.78, 134.06, 134.15, 140.35, 140.86, 143.03, 143.14, 144.81, 146.29, 148.88, 149.53, 150.27, 152.31, 172.38. MS (EI) 1249 (M-PF6), 1103, 552, 206.

4.2. Photophysical studies

Photophysical measurements were carried out as reported previously [28]. Solvents were spectroscopic grade and solutions were degassed by multiple freeze-pump-thaw cycles before measurements. Corrected fluorescence spectra were recorded on a SPEX Fluorolog II fluorimeter using an excitation wavelength of 572 nm. Fluorescence decay profiles were obtained by the time-correlated single-photon counting technique using a mode-locked and cavity-dumped dye laser (Spectra-Physics 3500) as the excitation source. The total instrument response function is approximately 80 ps and fluorescence decays were analyzed using reconvolution routines based on the Marquadt algorithm [45]. Goodness of fit to single and double exponential functions was assessed by inspection of weighted residuals and the magnitude of the reduced chi-square and Durban–Watson fitting parameters. Transient absorption measurements utilized a flash photolysis apparatus incorporating a Nd:Yag laser pumped optical parametric oscillator (Continuum NY61/Casix OPO BBO-3B) providing 7 ns pulses at 572 nm for excitation of the samples and a xenon lamp analysing source. Excitation energies were kept below 5 mJ to minimize second order effects. Transient spectra were obtained using a spectrograph (Acton Research Corporation SpectraPro-300i) and intensified CCD camera (Princeton Instruments ICCD-MAX). Transient decays were recorded using a photomultiplier tube/digital oscilloscope (Hamamatsu R928/Tektronix TDS-520) and analyzed as outlined elsewhere [28,46].

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References

[1] M.N. Paddon-Row, Acc. Chem. Res. 27 (1994) 18.

[2] J.R. Miller, G.L. Closs, Science 240 (1988) 440.

[3] P.F. Barbara, T.J. Meyer, M.A. Ratner, J. Phys. Chem. 100 (1996) 13148.

[4] N.S. Hush, M.N. Paddon-Row, E. Cotsaris, H. Oevering, J.W. Verhoeven, M. Heppener, Chem. Phys. Lett. 117 (1985) 8.

[5] H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, E.J.W. Verhoeven, N.S. Hush, J. Am. Chem. Soc. 109 (1987) 3258.

[6] A.M. Oliver, M.N. Paddon-Row, J. Kroon, J.W. Verhoeven, Chem. Phys. Lett. 191 (1992) 371.

[7] M.R. Roest, J.W. Verhoeven, W. Schuddeboom, J.M. Warman, J.M. Lawson, M.N. Paddon-Row, J. Am. Chem. Soc. 118 (1996) 1762.

[8] M.R. Wasielewski, Chem. Rev. 92 (1992) 435.

[9] Y. Zeng, M.B. Zimmt, J. Am. Chem. Soc. 113 (1991) 5107.

[10] H. Han, M.B. Zimmt, J. Am. Chem. Soc. 120 (1998) 8001.

[11] J.R. Winkler, H.B. Gray, Chem. Rev. 92 (1992) 369.

[12] J.R. Telford, P. Wittung-Stafshede, H.B. Gray, J.R. Winkler, Acc. Chem. Res. 31 (1998) 755.

[13] S.O. Kelley, R.E. Holmlin, E.D. Stemp, J.K. Barton, J. Am. Chem. Soc. 119 (1997) 9861.

[14] R.E. Holmlin, P.J. Dandliker, J.K. Barton, Angew. Chem. Int. Ed. Engl. 36 (1997) 2715.

[15] D. Gust, T.A. Moore, A.L. Moore, . Acc. Chem. Res. 26 (1993) 198.

[16] H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada, Y. Sakata, Angew. Chem. Int. Ed. Engl. 36 (1997) 2626.

[17] D. Gust, T.A. Moore, L.R. Makings, P.A. Liddell, G.A. Nemeth, A.L. Moore, J. Am. Chem. Soc. 108 (1986) 8028.

[18] Y. Sakata, H. Tatemitsu, E. Bienvenue, P. Seta, Chem. Lett. (1988) 1625.

[19] J.P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L.i De Cola, L. Flamigni, V. Balzani, Inorg. Chem. 30 (1991) 4230.

[20] A. Osuka, T. Najata, K. Maruyama, N. Mataga, T. Asahi, L. Yamazaki, Y. Nishimura, Chem. Phys. Lett. 185 (1991) 88.

[21] S.L. Mecklenburg, B.M. Peek, B.W. Erickson, T.J. Meyer, J. Am. Chem. Soc. 113 (1991) 8540.

[22] L.F. Cooley, S.L. Larson, C.M. Elliott, D.F. Kelley, J. Phys. Chem. 95 (1991) 10694.

[23] S.L. Larson, L.F. Cooley, C.M. Elliott, D.F. Kelley, J. Am. Chem. Soc. 114 (1992) 9504.

[24] J.M. Lawson, D.C. Craig, A.M. Oliver, M.N. Paddon-Row, Tetrahedron 51 (1995) 3841.

[25] K.A. Jolliffe, S.J. Langford, M.G. Ranasinghe, M.J. Shephard, M.N. Paddon-Row, J. Org. Chem. 64 (1999) 1238.

[26] J.M. Lawson, M.N. Paddon-Row, W. Schuddeboom, J.M. Warman, A.H.A. Clayton, K.P. Ghiggino, J. Phys. Chem. 97 (1993) 13099.

[27] M.R. Roest, J.W. Verhoeven, W. Schuddeboom, J.M. Warman, J.M. Lawson, M.N. Paddon-Row, J. Am. Chem. Soc. 118 (1996) 1762.

[28] K.A. Jolliffe, T.D.M. Bell, K.P. Ghiggino, S.J. Langford, M.N. Paddon-Row, Angew. Chem. Int. Ed. Engl. 37 (1998) 916.

[29] K.A. Jolliffe, S.J. Langford, A.M. Oliver, M.J. Shephard, M.N. Paddon-Row, Chem. Eur. J. 5 (1999) 2518.

[30] M.N. Paddon-Row, E. Cotsaris, H.K. Patney, Tetrahedron 42 (1986) 1779.

[31] M.J. Shephard, M.N. Paddon-Row, J. Phys. Chem. A 103 (1999) 3347.

[32] D. Kuciauskos, S. Lin, G.R. Seely, A.L. Moore, T.A. Moore, D. Gust, T. Drovetskaya, C.A. Reed, P.D.W. Boyd, J. Phys. Chem. 100 (1996) 15926.

[33] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[34] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, . J. Am. Chem. Soc. 107 (1985) 3902.

[35] B.G. Johnson, P.M.W. Gill, M. Head-Gordon, C.A. White, J. Baker, D.R. Maurice, T.R. Adams, J. Kong, M. Challacombe, E. Schwegler, M. Oumi, C. Ochsenfeld, N. Ishikawa, J. Florian, R.D. Adamson, J.P. Dombroski, R.L. Graham, A. Warshel, Q-Chem V. 1.1, Q-Chem Inc, Export, PA, 1997.

[36] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Computs. Chem. 14 (1993) 1347.

[37] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[38] C.J. Cramer, D.G. Truhlar, Rev. Comput. Chem. 6 (1995) 1.

[39] T.H. Zhu, J.B. Li, D.A. Liotard, C.J. Cramer, D.G. Truhlar, J. Chem. Phys. 110 (1999) 5503.

[40] J. Li, T. Zhu, G.D. Hawkins, D.A. Liotard, C.J. Cramer, D.G. Truhlar, Gamesol V. 2.1, University of Minnesota, Minneapolis, 1997.

[41] J.W. Park, B.A. Lee, S.Y. Lee, J. Phys. Chem. B 102 (1998) 8209.

[42] M.J. Gunter, T.P. Jeynes, M.R. Johnston, P. Turner, Z. Chen, J. Chem. Soc., Perkin Trans. 1 (1998) 1945.

[43] M. Antolovich, A.M. Oliver, M.N. Paddon-Row, J. Chem. Soc., Perkin Trans. 2 (1989) 783.

[44] L.R. Milgrom, J. Chem. Soc., Perkin Trans. 1 (1983) 2535.

[45] K.P. Ghiggino, T.A. Smith, Prog. React. Kin. 18 (1993) 375.

[46] T.D.M. Bell, T.A. Smith, K.P. Ghiggino, M.G. Ranasinghe, M.J. Shephard, M.N. Paddon-Row, Chem. Phys. Lett. 268 (1997) 223.