Photoinduced processes in functionalized and organized dye systems
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Abstract

Here we report molecular orbital calculations of four quinoline-derived foldamers with increasing oligomeric length; dimer \textbf{O2P}, tetramer \textbf{O4P}, pentamer \textbf{O5P} and nonamer \textbf{O9P} functionalized with on one end an oligo(p-phenylene vinylene) (OPV) and on the other end a perylene bisimide (PDI) chromophore.

Photoinduced processes in the OPV-PDI electron donor-acceptor pair in chloroform and toluene have been previously reported.\textsuperscript{1} The helical properties of the bridge ensured that the chromophore separation distance through space is different from those through the bridge. The femtosecond photoinduced absorption measurements confirmed the fast formation of a charge separated state. Remarkably low attenuation factors ($\beta_{CS} \approx 10^{-2} \text{ Å}^{-1}$) were obtained from the experimental data, using either through space or through bridge separation distance.

Molecular orbital calculations rationalize the fast photoinduced charge separation, by revealing that the bridging foldamer mediates the charge transfer from donor to acceptor via the superexchange mechanism. The results show that when a helical bridge is separating the charge transfer couple, it is hampering a uniform description of the charge separation phenomena. Extra information is given for the nonamer, regarding AM1 structure, orbital energies and orbital shapes in the appendix.
6.1. Introduction

The rates of photoinduced charge transfer processes as a function of distance between donor and acceptor have received much attention during recent decades. In particular the processes occurring in the systems in which the donor and acceptor are bound to DNA can form extraordinary long-lived charge transfer states. Many efforts to understand and mimic these biological photophysical processes have focused on the design of artificial models in which the dependence of charge separation and charge recombination is monitored as a function of the distance between the donor and the acceptor. In these examples, the chromophores are either placed on top (co-facial) or next to each other (co-linear). For instance a co-facial positioning of the chromophores is achieved by using helical DNA, peptides, aromatic foldamers or a non-helical rigid linker as a scaffold to attach the chromophores. The examples of co-linear structures are of the systems in which the chromophores are connected by rigid bridges containing either conjugated or saturated moieties. As a consequence of the rigidity of these bridges, in all co-facial and co-linear positioning, the chromophore position is fixed and the distance between the chromophores through space is similar to the distance through the bridge.

Based on theoretical analyses and experimental observations, it has been proposed that the photoinduced charge transfer processes occur via either a super-exchange or charge hopping mechanism depending on the length and the electronic properties of the bridge as well as on how the chromophores are attached to the bridge. The distinction between the two mechanisms is the involvement of the bridge in the charge migration. In the super-exchange mechanism, the bridge solely plays the role of pure linker favoring the interaction between the donor and acceptor wave-functions whereas in the hopping mechanism the charge transfer processes can only occur with the attendance of the bridge unit resulting in a multi-step charge transport. It is proposed that the hopping mechanism, which is weakly dependent on the length of the linker, becomes more efficient than super-exchange at long distance.
The reflection of the exponential dependence of charge transfer process on distance is expressed in the attenuation factor $\beta^{4,15}$ in the equation:

$$k_{CS} = k_0 \exp(-\beta R_e)$$

In this equation, $k_0$ is the rate at close contact $R_0$ (the sum of Van der Waals radii of the donor and acceptor), $R_e$ is the edge-to-edge distance between donor and acceptor.

Typical attenuation factors found are $\beta = 0.6 - 1.2 \, \text{Å}^{-1}$ for hydrocarbon bridges, $\beta = 0.32 - 0.66 \, \text{Å}^{-1}$ for conjugated polyphenylenes, $\beta = 0.04 - 0.2 \, \text{Å}^{-1}$ for poly-enes and $\beta = 0.04 - 0.17 \, \text{Å}^{-1}$ for polyynes.\textsuperscript{17} A smaller attenuation factor indicates that the bridges can more effectively mediate the charge transfer.

The use of bridges to spatially organize chromophores in an intermediate situation where the chromophores are positioned in both a co-facial and a co-linear arrangement has rarely been explored.\textsuperscript{4c} Examples include the investigation of chromophores with constrained molecular assemblies\textsuperscript{4c} or connected at ortho, meta or para positions by rigid aromatic molecular linkers.\textsuperscript{4c,9a-d,18} In both cases the chromophores are held at a relatively short distance from each other by non-helical bridges. These studies revealed that the effect of chromophore orientation on the charge transfer process, if any, depends highly on the system at hand. One hurdle in studying the effect of chromophore positioning in both a co-facial and co-linear arrangement lies in the difficulty to achieve large distances between the electron donor and acceptor and to simultaneously be able to control and tune their relative orientations. It has been proposed that helical foldamers possessing stable and predictable conformations are promising candidates, where the helicity of the bridge can be used as a scaffold to organize chromophores in space.\textsuperscript{1} Indeed, chemists have designed and synthesized a large variety of oligomeric and polymeric molecules that adopt predefined helical or extended conformations\textsuperscript{19} that are commonly used as peptide mimics the sizes of which sometimes approach those of small proteins.\textsuperscript{20}
The remarkably high structural robustness and predictability in different solvents and in the solid state\textsuperscript{21} of oligoquinoline amide foldamers are expected to enable the exact positioning of the chromophores in order to vary and control not only the distance between the donor and the acceptor, but also their relative orientation in space. As a result of the helicity of the foldamers the distance between the chromophores through space or through bridge is different. For this reason it is likely that the charge transfer pathways will depend on the foldamer that was studied.\textsuperscript{1}

Here, we report on calculations of a series of helical aromatic oligoquinoline amide based foldamers acting as a helical bridge between an electron donor, an oligo($p$-phenylene vinylene) (OPV) and an electron acceptor, a perylene bisimide (PDI) (Figure 6.1). This charge transfer couple was selected since the photophysics of the individual compounds and the charge-transfer pair have been thoroughly studied.\textsuperscript{22, 23} The calculations were performed on four different foldamer sequences ranging from dimer to nonamer that are all equipped with the same electron donor (OPV) and electron acceptor (PDI) rigidly connected to the quinoline foldamer. These molecules were designed to cover a well-defined array of distances and orientations between the chromophores.\textsuperscript{1} Remarkably low attenuation factors were obtained from spectroscopy, by either using the distance through space ($\beta_{CS} = 0.05$ Å$^{-1}$) or through the bridge ($\beta_{CS} = 0.02$ or 0.06 Å$^{-1}$). Molecular orbital calculations revealed electronic coupling through the bridging foldamer, where the degree of electronic interaction depends highly on the foldamer studied. These results show that the bridge is most likely mediating the charge separation between the chromophores. The current theoretical description\textsuperscript{4c, 24} that dictates an exponential relationship between the charge transfer rates and the distance between the donor and acceptor, either it being the distance through space or through bridge, seems to be insufficient to uniformly describe the charge separation phenomena when a helical bridge is separating the charge transfer couple.
6.2. Results and Discussion

6.2.1. Molecular design

The calculation of the energy minimized structures of all oligomers from dimer to nonamer by molecular mechanics (MM2) enabled us to select a series of foldamers where both the orientation as well as the distance could be varied. To minimize the complexity of the calculations, the aliphatic tails of the chromophores were shortened. The analyses of the optimized structures revealed that the four foldamers listed in Figure 6.1 cover a wide variety of orientations and distances between the chromophores. In \textbf{O2P} the center-to-center donor-acceptor distance through space ($R_{DA}$) between the chromophores is calculated to be 15 Å and the dihedral angle between them is $\alpha_{DA} = 115^\circ$. The determination of $R_{DA}$ and $\alpha_{DA}$ is illustrated in the appendix (Figure A.6.6). The separation through the bridge ($R_{Bridge}$) is calculated as the shortest distance across the quinoline units, resulting in $R_{Bridge} = 18$ Å for \textbf{O2P}. The tetramer \textbf{O4P} ($R_{Bridge} = 33$ Å) and nonamer \textbf{O9P} ($R_{Bridge} = 69$ Å) both place the donor under a small angle with respect to the acceptor ($\alpha_{DA} = 28^\circ$ for \textbf{O4P} and $\alpha_{DA} = 15^\circ$ for \textbf{O9P}) separated by 6 Å and 14 Å, respectively, which can suggest that the charge separation pathways can be similar for these two compounds (Table 6.1). The structures of \textbf{O2P} and \textbf{O9P} show that the distance through space between the chromophores is similar in the two foldamers, while the distance through the bridge (18 \textit{versus} 69 Å) differs considerably. Therefore, a comparison between the results for these two foldamers should yield more insight in the effect of chromophore orientation and charge separation pathway. In the pentamer \textbf{O5P} a shorter through bridge separation distance than in \textbf{O9P} is achieved (40 \textit{versus} 69 Å), while the through space distance between the chromophores is increased to 22 Å since the chromophores are almost radially opposed ($\alpha_{DA} = 166^\circ$).
Figure 6.1. Molecular formula of the four foldamers (A) with appended chromophores described in this study, the PDI acceptor-reference chromophore (B), and top views the foldamer helix axis (C-left) and side views (C-right) of their energy minimized conformations. The helix backbones are shown in grey, the OPV units in blue and the PDI units in red. The alkyl chains of OPV and PDI units were replaced by methyl groups during energy minimization. The top views clearly show the similar orientations of the chromophores in O4P and O9P.
6.2.2. Electron transfer rate in the foldamers

Femtosecond transient absorption spectroscopy of the four compounds was performed with excitation at 525 nm (PDI chromophore) and detection in the near infra-red region. Then, the time constants of charge separation ($\tau_{CS}$) and recombination ($\tau_{CR}$) have been extracted by analyzing the traces at two different wavelengths. The results are summarized in Table 6.1.

Table 6.1. Characteristic rates for charge separation (CS) and charge recombination (CR) in chloroform for O2P, O4P, O5P and O9P as obtained from femtosecond transient absorption (fs-TA) measurements together with differently defined distances.1

<table>
<thead>
<tr>
<th>foldamer</th>
<th>$R_{DA}$ (Å)</th>
<th>$R_{edge}$ (Å)</th>
<th>$R_{Bridge}$ (Å)</th>
<th>$\tau_{CS}$ (ps)</th>
<th>$\tau_{CR}$ (ps)</th>
<th>$k_{CS}$ (s$^{-1}$)</th>
<th>$k_{CR}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2P</td>
<td>15</td>
<td>3.5</td>
<td>18</td>
<td>20</td>
<td>260</td>
<td>$5.0 \times 10^{10}$</td>
<td>$4.17 \times 10^{9}$</td>
</tr>
<tr>
<td>O4P</td>
<td>6</td>
<td>7.6</td>
<td>33</td>
<td>35</td>
<td>300</td>
<td>$2.8 \times 10^{10}$</td>
<td>$3.13 \times 10^{9}$</td>
</tr>
<tr>
<td>O5P</td>
<td>22</td>
<td>8.0</td>
<td>40</td>
<td>80</td>
<td>2200</td>
<td>$1.4 \times 10^{10}$</td>
<td>$0.47 \times 10^{9}$</td>
</tr>
<tr>
<td>O9P</td>
<td>14</td>
<td>13.8</td>
<td>69</td>
<td>50</td>
<td>720</td>
<td>$2.0 \times 10^{10}$</td>
<td>$1.35 \times 10^{9}$</td>
</tr>
</tbody>
</table>

The distances were determined from the optimized-MM2-calculated structures. $R_{DA}$ is the center-to-center distance calculated from the center of the PDI to the center of the OPV. $R_{edge}$ is the edge-to-edge distance; $R_{Bridge}$ is the distance through the foldamer bridge which was determined from the structures, while taking the shortest distance through the bridge.26

From Table 6.1 it is clear that charge separation is always faster than charge recombination. The short time constants for charge separation indicate that the formation of the charge separated state is much faster than the intrinsic decay of the PDI acceptor-reference chromophore (C13-PDI-P, Figure 1B).

There is no direct correlation between the through-bridge distance ($R_{Bridge}$) and charge separation rates, confirming that the bridge is indeed folded. As expected for these folded structure the rates do not follow the general trends normally observed for studies in which chromophores are oriented either in a co-facial or co-linear fashion.4-7 When plotting the logarithm of the rate constants ($k = 1/\tau$) for charge separation and
charge recombination against the distance through space between the chromophores (R_{DA}), the three points belonging to O4P, O5P and O9P are on a straight line while the shortest oligomer O2P deviates. The slope of this line yields the attenuation factor $\beta_{CS} = 0.05 \, \AA^{-1}$ for charge separation (Figure 6.2A) and $\beta_{CR} = 0.13 \, \AA^{-1}$ for charge recombination in chloroform (Figure 6.2B).

![Graphs showing charge separation and recombination rates](image)

**Figure 6.2** The dependence of the charge separation rate constant (A,C) and the charge recombination rate constant (B,D) with the separation distance through space (A,B) or through bridge (C,D) in chloroform. The black and gray values give the attenuation factors obtained directly from the linear fit (black or gray line).

From the molecular structure it is clear that the helical bridge is not $\pi$-conjugated, however, the attenuation factor ($\beta$) for charge separation is much smaller than normally observed for charge separation through a conductive $\pi$-conjugated bridge (0.32 - 0.66 Å⁻¹) and is in the range of $\beta$-values for polyynes (0.04 – 0.17 Å⁻¹).¹⁷ This
surprisingly fast charge transport in the system indicates the presence of strong electronic interactions between the donor, acceptor and bridge in the excited state and suggests a charge separation reaction that is mediated by the bridging foldamer.\textsuperscript{4, 6-7} For that reason, the logarithm of the charge separation or charge recombination rate constant against the distance through the bridge (Figure 6.2C, D) was also plotted. From these plots it is clear that either \textbf{O5P} or \textbf{O9P} deviates from the straight line that is formed by the remaining molecules. The obtained attenuation factor obtained again very low, \textit{e.g.} for the charge separation, $\beta_{CS} = 0.02$ Å\textsuperscript{-1} when discarding \textbf{O5P} and $\beta_{CS} = 0.06$ Å\textsuperscript{-1} when discarding \textbf{O9P} (Figure 6.2C), and remarkably similar when the through space chromophore separation is used. Although the attenuation factor seems to be independent on the distance that is used to calculate it, one should remember that for all three methods a different foldamer is discarded from the calculations (see figure A.6.1 in the appendix 6 for the edge-to-edge distance dependence of the rate constant). Therefore, a uniform theoretical description of the charge separation by using either the separation distance through space or through bridge is not possible when using helical bridges to separate the chromophores.

\subsection*{6.2.3. Molecular Orbitals}

To shed more light on the low attenuation factor and the deviation of one of the foldamers with respect to the three others when calculating $\beta$, we performed AM1 calculations using SPARTAN’04V1.0.3 (Wavefunction Inc.). From the energy minimized structures obtained from MM2, we achieved the optimized geometries with AM1, then the orbitals calculations were carried out based on these geometries. Within a frontier molecular orbital (FMO) description, excitation with \textit{e.g.} 530 nm corresponds to local PDI excitation and in the acceptor-reference compound \textbf{C13-PDI-P} this corresponds to the HOMO-LUMO transition. The \textbf{O2P}, \textbf{O4P}, \textbf{O5P}, and \textbf{O9P} systems show analogous electronic transitions. But, whereas the LUMO of these systems is very similar to the LUMO of the reference and entirely localized on the PDI, (more details in the figures A.6.2, and A.6.3 in the appendix 6) the highest
occupied molecular orbital that has a contribution on the PDI unit also has a significant, but varying, electron delocalization into the foldamer bridge (Figure 6.3).

Figure 6.3. Visualization of the highest doubly occupied molecular orbitals of the foldamers with a contribution on the PDI unit for \textbf{O2P} (A), \textbf{O4P} (B), \textbf{O5P} (C) and \textbf{O9P} (D). These orbitals contribute to the locally PDI excited state and give evidence of coupling with the bridge. Schematic representation of the energy levels and the charge transfer process between the OPV and PDI in the \textbf{O9P} after excitation of the HOMO-7, where \textit{H} stands for HOMO and \textit{L} denotes LUMO (E). Simplification of the charge transfer through the bridge (F).

Of course there are additional lower lying doubly occupied orbitals that have a more pronounced PDI contribution, but the delocalized orbitals depicted in Figure 6.3 will contribute to the “local PDI excitation” and enhance the electronic coupling in the excited state between PDI and OPV units. The HOMO-acceptor orbitals considered in Figure 6.3 serve to visualize how the \(\pi\) systems of the separate foldamer units mix into
the large aromatic PDI localized orbital resulting in electron delocalization of the PDI orbital over the foldameric part in an oscillating mode. Within an FMO description, excitation of the PDI is followed by charge separation which can be viewed as a HOMO acceptor-HOMO donor transition.

The relevant HOMO-acceptor orbital of **O9P** is shown in Figure 6.3D (this is the HOMO-7 of the whole **O9P** system), the corresponding HOMO-donor orbital is shown in Figure A.6.4. (in the appendix. This is the HOMO orbital of the whole **O9P** system). It can be seen that this OPV localized orbital also has substantial orbital coefficients on the foldamer bridge (just like the HOMO-7 of the system, but not as extensive) and the interaction of these the HOMO and HOMO-7 strongly suggests electronic coupling through the foldamer bridge and therefore it is likely that the helical bridge mediates the charge transfer process. These calculations further support that charge separation through the bridge is achieved via the superexchange mechanism. In a similar way, the charge recombination (Figure 6.2B, D) can be described by a LUMO-acceptor/HOMO-donor interaction. The fact that the LUMO of all four foldamers is very similar and localized on the PDI correlates with the much higher attenuation factor for charge recombination that is derived from the experiments (see reference 1).

The electronic coupling through the foldamer bridge as visualized by the MO calculations occur to a different extent for all foldamers and is expected to slightly modulate the molar absorption coefficients of the different systems (see UV/vis in the work of Schenning *et al.*¹). Because of the presence of only two bridge units in **O2P**, a significant amount of electronic coupling between the electron donor and acceptor exists which can account for the surprisingly fast charge separation reaction in this system (Figure 6.3A). This may explain the deviation of **O2P** from the other three oligomers when the distance through space is used to obtain the attenuation factor (Figure 6.2A). This enhanced electronic coupling also makes it difficult to compare **O2P** with **O9P** and with that to ascertain the effect of chromophore orientation on the charge transfer processes. From the MO calculations it becomes apparent that although the number of monomeric units is higher in the nonamer **O9P**, the electronic coupling
is more pronounced than in O5P, where it is almost absent (Figure 6.3C versus 6.3D). For this reason it seems more likely that in O9P the charge separation is mediated by the bridging foldamer and that O5P is the molecule that deviates when the distance through the bridge is used to ascertain the attenuation factor (Figure 6.2C).

6.3. Conclusion

We successfully performed calculations on electron donating (OPV) and electron accepting (PDI) chromophores on rigid helical scaffolds in which photoinduced charge transfer occurs. Molecular orbital calculations revealed significant electronic interactions through the bridging foldamer. With a variety of optical techniques we showed that excitation of the PDI leads to the formation of a charge separated state and that formation of triplet states can significantly contribute in the recombination pathway. All rates for charge separation were high and resulted in a surprisingly low attenuation factor, which is far below the value generally found for π-conjugated bridges. Attenuation factors were obtained by assuming charge separation through space or through the bridge, but each time one different foldamer needed to be discarded because it did not correlate with the behaviour of the three others. Therefore, a uniform description by the current theory does not hold when a helical foldameric bridge is used as a scaffold to organize the chromophores. Whereas in Förster energy transfer theory\textsuperscript{27} the angle between the transition dipole moments of the photoactive units is explicitly taken into account, a similar orientation factor is less straightforward in electron transfer theory.\textsuperscript{24} The attenuation factor currently describes only the influence on the electronic coupling of the intervening medium at varying distance but at constant orientation. Such insights are relevant for the investigation of charge transfer processes in both synthetic as well as biologic donor-bridge-acceptor systems.
6.4. References


Molecular Orbital Calculations of Helical Foldamer


Chapter 6


Appendix 6

Chapter 6, and the manuscript it is based on, contains a rather small selection of computational results obtained for the various foldamer systems. In order to make this selection more clear as well as to give an impression of the total quantity of computational work and results, this appendix is added. Furthermore, results on the PDI reference compound and the OPV donor are included. Figure A.6.1 shows the edge-to-edge distance dependence of the rate constant, as discussed in the main text.

Figure 6.3 of the main chapter visualizes the highest doubly occupied molecular orbitals of the foldamers with a contribution on the PDI unit. Why were these particular orbitals chosen? How do the other orbitals look like? The answers to these questions are clarified in this appendix.

Figure A.6.2 presents frontier orbitals of the reference compounds PDI and OPV. Figure A.6.3 shows the frontier MOs of the four foldamers systems. The resemblance of the LUMO of the PDI acceptor of the foldamers to the PDI reference LUMO is clear. The HOMO of the PDI reference, which is slightly asymmetric, can now easily be recognized in the HOMO-X for the various foldamer systems. It is this acceptor-orbital that mixes with the foldamer bridge to a different extent for the various systems.

Figure A.6.4 presents a larger number of orbitals for O9P and the energies of the various orbitals of this system are given in Figure A.6.5, together with those of the reference compounds. Figure A.6.4 and A.6.5 give a more accurate vision of the complexity of the computational outcome. Table A.6.1 and A.6.2 give some details of the computational procedures and results. Figure A.6.6 gives the definition of the parameters listed in table A.6.2.

The last section of this appendix discusses the appropriateness of the method applied. For further studies it is advised to use DFT methods or to calculate orbitals for the
MM2 minimized structures and to incorporate all side-groups present in the actual molecules. Figure A.6.7 compares AM1 and MM2 structures.

**Figure A.6.1.** The edge-to-edge distance for each foldamer ($R_{\text{edge}}$) (left) and the fit to obtain the attenuation factor while O5P was discarded from the fit (right) in CHCl$_3$

<table>
<thead>
<tr>
<th></th>
<th>LUMO</th>
<th>HOMO</th>
<th>HOMO-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI</td>
<td>-2.48846</td>
<td>-8.71447</td>
<td>-8.86168</td>
</tr>
<tr>
<td>OPV</td>
<td>-0.99035</td>
<td>-8.22140</td>
<td>-8.74880</td>
</tr>
</tbody>
</table>

**Figure A.6.2.** Visualization of the frontier molecular orbital calculations for PDI (above) and OPV (below) together with energies (eV)
Figure A.6.3. Visualization of frontier molecular orbital calculations for O2P, O4P, O5P, and O9P showing the HOMO, LUMO and the highest filled orbital HOMO-x that has a contribution on the PDI moiety.
Figure A.6.4. Visualization of the molecular orbital calculations (from LUMO +4 to HOMO -13) and their energies of the nonamer (O9P).
Figure A.6.5. The orbital energy level scheme of nonamer (O9P) relative to those of OPV and PDI (see also figure A.6.2 to A.6.4)

Table A.6.1. Some detailed information on the AM1 calculations of O2P, O4P, O5P and O9P

<table>
<thead>
<tr>
<th></th>
<th>O2P</th>
<th>O4P</th>
<th>O5P</th>
<th>O9P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of atoms</td>
<td>199</td>
<td>263</td>
<td>295</td>
<td>423</td>
</tr>
<tr>
<td>Number of electrons</td>
<td>586</td>
<td>770</td>
<td>862</td>
<td>1230</td>
</tr>
<tr>
<td>CPU calculation time for equilibrium geometry(^{(a)})</td>
<td>2 hours</td>
<td>4 hours</td>
<td>11 hours</td>
<td>52 hours</td>
</tr>
<tr>
<td>Heat of formation (kcal/mol)</td>
<td>-236.9</td>
<td>-290.4</td>
<td>-311.7</td>
<td>-413.6</td>
</tr>
</tbody>
</table>

\(^{(a)}\) see computational details
From the AM1 geometry-minimized structures, we have taken the twist angle ($\phi_T$) as the angle between the planes defined by the PDI unit and the first phenyl group of the OPV donor (closest to the bridge). The dihedral angle ($\alpha_{DA}$) is the angle between the centroids of the two chromophores. The edge-to-edge distance ($R_{edge}$) is the closest distance between the PDI unit and the OPV unit (Figure A.6.6). The results were presented in table A6.2. The distance through the bridge $R_{Bridge}$ has been determined from the structures, while taking the shortest distance across the quinoline units.

Figure A6.6. Determination of $R_{edge}$ (distance between the points 1 and 2), $\alpha_{DA}$ (angle between the two vectors), and $\phi_T$ (twist angle between the two planes containing the first phenyl group of the donor OPV and the PDI acceptor).

Table A6.2. Structural parameters obtained from the MM2 and AM1 minimized structures of O2P, O4P, O5P and O9P.

<table>
<thead>
<tr>
<th>Foldamer</th>
<th>$R_{edge}$</th>
<th>$R_{DA}$</th>
<th>$R_{Bridge}$</th>
<th>$R_{edge}(\AA)$</th>
<th>$\phi_T$</th>
<th>$\alpha_{DA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2P</td>
<td>3.5</td>
<td>15</td>
<td>18</td>
<td>5.3</td>
<td>69</td>
<td>108</td>
</tr>
<tr>
<td>O4P</td>
<td>7.6</td>
<td>6</td>
<td>33</td>
<td>4.2</td>
<td>61</td>
<td>7</td>
</tr>
<tr>
<td>O5P</td>
<td>8.0</td>
<td>22</td>
<td>40</td>
<td>11.9</td>
<td>87</td>
<td>144</td>
</tr>
<tr>
<td>O9P</td>
<td>13.8</td>
<td>14</td>
<td>69</td>
<td>21.3</td>
<td>51</td>
<td>40</td>
</tr>
</tbody>
</table>
The accuracy of theoretical model associates with the computational requirements. Ducasse et al.\textsuperscript{1} reported that the optimizing the helix geometry with DFT provided good results. However, it costs much time, e.g. the foldamer bridge containing 112 atoms required 17 days for geometry optimizations on a personal computer IBM P690. The AM1-optimized structure of the bridge was more extended than the MM2 and maybe also than the X-ray structure (Figure A6.7). H. Jiang et al.\textsuperscript{2} indicated that the structure of the foldamer bridge obtained from a simple energy minimization using the MM3 force field in Macromodel was in good agreement with the X-ray diffraction. Therefore, to get a better description of these foldamers, it is advised to use DFT methods or to calculate orbitals for the MM2 minimized structures and to incorporate all-sided groups present in the actual molecules.

\textbf{Figure A.6.7.} Structures obtained from MM2 (left) and AM1 (right) methods.
Computational details

The molecular structures were first obtained by a simple energy minimization using MM2.\textsuperscript{2,3} Then, the obtained conformer of the four molecules \textit{O2P, O4P, O5P} and \textit{O9P} was optimized using the semi-empirical AM1 method to get the equilibrium structure. The molecular orbitals were calculated at fixed iso-values of 0.001 electrons/au\textsuperscript{3}. Note that this is a more diffuse representation than the standard one. Total time of calculation for e.g. the nonamer system (\textit{O9P}) was 52 hours on a standard computer (PC/x86; 1.8 GHz). The chiral substituents of the OPV-units and the long alkyl substituents on the imide nitrogen were removed in order to reduce the number of atoms.

Reference for Appendix 6

