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DOI

[10.1351/pac200375081055](https://doi.org/10.1351/pac200375081055)

Publication date

2003

Document Version

Final published version

Published in

Pure and Applied Chemistry

[Link to publication](#)

Citation for published version (APA):

Brouwer, A. M., Fazio, S. M., Frochot, C., Gatti, F. G., Leigh, D. A., Wong, J. K. Y., & Wurpel, G. W. H. (2003). Photoinduced dynamics in hydrogen-bonded rotaxanes. *Pure and Applied Chemistry*, 75(8), 1055-1060. <https://doi.org/10.1351/pac200375081055>

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Photoinduced dynamics in hydrogen-bonded rotaxanes*

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Abstract: Two classes of rotaxanes are described in which photoinduced processes modulate a large-amplitude motion. In the first type, *E*–*Z*-isomerization of a fumaric diamide unit to a maleic diamide leads to a substantial weakening of the hydrogen bonds between the diamide and the macrocyclic ring that surrounds it. As a result, the rate of the pirouetting motion is increased approximately by six orders of magnitude. In the second type, intermolecular photoinduced electron transfer is used to induce a reversible shuttling motion on a time scale of microseconds. Medium effects on the rate of shuttling are presented.

INTRODUCTION

Mechanical motion at molecular levels is known to play a vital role in living organisms. The functions of such motion are highly variable, ranging from intracellular processes such as DNA replication to movement of much bigger parts of an organism via muscle action. The molecular details of the mechanisms involved in motor protein action are in many cases unknown, but in general a crucial role is played by large-amplitude conformational changes that are controlled by binding and release of auxiliaries. Energy is mostly consumed to modulate the binding process, not directly to induce motion. In this respect, the working principle of motor proteins is drastically different from that of engines in our macroscopic world [1,2].

When control of large-amplitude motion is achieved in synthetic molecules and assemblies, the concept of molecular machinery can be developed. Indeed, several research groups have demonstrated controlled rotational and translational motion of submolecular components, driven by a variety of fuels [3–14].

In the present contribution, we will discuss two case studies in which we use photons as a stimulus to influence large amplitude motions in [2]rotaxanes. These interlocked molecules consist of a macrocyclic ring **1**, which surrounds a “thread” molecule (e.g., **2** or **3**) having “stopper” groups at the ends that are so large that the macrocycle cannot slip over them. Scheme 1 shows the building blocks of the rotaxanes **5** (**5** = **2** ⊂ **1**) and **6** (**6** = **3** ⊂ **1**) discussed in the first case study.

The strongest interactions between ring and thread are the hydrogen bonds between the four amide groups in the ring and the two amide bonds of the thread. These are, in fact, the interactions that play a key role in the template-based synthesis of this class of molecules [15,16]. Rotaxanes are partic-

*Lecture presented at the XIXth IUPAC Symposium on Photochemistry, Budapest, Hungary, 14–19 July 2002. Other presentations are published in this issue, pp. 999–1090.

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Scheme 1 Macrocyclic ring **1** and fumaramides **2** and maleamides **3**; building blocks of rotaxanes **5** and **6**, respectively (see Fig. 1).

ularly interesting for studies of intermolecular interactions because the interlocking prevents dissociation of the building blocks into two molecules, even when the interaction energy is not very large.

PHOTOISOMERIZATION AS A TRIGGER OF MOLECULAR MOTION

The fumaric unit in **2E** is a very efficient template for the synthesis of rotaxane **5E**. Its isomer **2Z**, on the other hand, is not a useful template at all. Molecular (stochastic) dynamics simulations indicate that the interaction enthalpy between the macrocycle **1** and thread **2E** in rotaxane **5E** is 5 kcal/mol more negative than the interaction enthalpy in rotaxane **5Z** [17–19]. The reason is that on average two fewer hydrogen bonds are present in **5Z** than in **5E**. Figure 1 shows the energy-minimized structures. Recently determined X-ray structures are in good agreement with these [14].

Fig. 1 Structures of **5E** (left) and **5Z** (right), obtained via energy minimization with the MMFF94 force field using the GBSA solvent model for chloroform [18,19].

The conversion of **5E** into **5Z** and the same isomerization process in a series of related rotaxanes have been accomplished by irradiation of rotaxane solutions at 254 nm [14]. Although at this wavelength the aromatic groups in the macrocyclic ring **1** absorb much more strongly than the fumaric unit smooth photoconversion was achieved. Quantitative studies of this reaction are in progress.

The effect of photoisomerization on molecular dynamics is dramatic. The macrocyclic ring undergoes a large-amplitude motion in which it rotates around an axis coinciding with the double bond in fumaric rotaxanes such as **5E**, which is coupled to a ring inversion from one chair conformation (see Fig. 1) into another. In the process, the intercomponent hydrogen bonds are effectively broken and reformed. Dynamic ¹H NMR studies have shown that the barrier for this process is 13.4 kcal/mol in the *E*-isomer of a rotaxane closely related to **6**. In the *Z*-isomer, it is only 6.8 kcal/mol: the rate of rotation

is increased by more than six orders of magnitude [14]. The ability to modify the strength of interaction between “binding station” and macrocycle can also be used to induce translational motion in systems in which the thread is longer and contains more stations. Work along these lines is in progress [20].

Direct irradiation into the UV-absorption band of the rotaxanes **5** and **6** leads to preparatively useful photoisomerization, but a complete conversion of *E* to *Z* isomers is impossible because both isomers are excited at 254 nm. We therefore considered triplet sensitization as a means toward selective isomerization. It has been known for a long time that when the triplet excitation energy of two alkene geometrical isomers is sufficiently different, a sensitizer can be used which transfers energy only to the lower-energy isomer, thus removing this from the reaction mixture. In this way, for example, *E*-stilbene and diethylfumarate can be converted cleanly into their *Z*-isomers [21].

For thread **3E** this scheme works very well. With sensitizers with an energy in the range 62–70 kcal/mol, selective energy transfer occurs to **3E**, while the triplet energy of **3Z** is so high that its triplet state cannot be populated. In this way, practically complete conversion to the *Z*-isomer proved possible (Fig. 2). Somewhat surprisingly, for the corresponding rotaxane **6**, the method works less well. A higher sensitizer energy is necessary before conversion becomes effective, and the highest percentage of *Z*-isomer obtained is 70 %. Several factors may be important in causing this difference. The apparent difference in triplet energy may be due to different conformations being adopted by the “free chromophore” **3E** and the hydrogen-bonded chromophore in **6E**, but it could also be a direct electronic effect of the hydrogen bonds on the energy of the ground and excited states. Normally, relaxation of olefin triplets to the ground-state surface occurs at or near a twisted configuration, where the energy gap with the ground state is small. Formation of either isomer can occur from this twisted state. The hydrogen bonds in the *E*-isomer of the rotaxane **6** are likely to resist the twisting of the double bond. Thus, other decay pathways may become important, in which the double bond is left in the *E*-configuration. Yet another possibility is that energy transfer to the sterically shielded chromophore in **6E** is impeded. Experiments to test all these possibilities are in progress.

Fig. 2 Percentage of *Z*-isomer formed after prolonged irradiation of a sensitizer with a triplet energy given at the horizontal axis in the case of **3** (triangles) and **6** (squares). For sensitizer triplet energies > 62 kcal/mol (**3**) or > 65 kcal/mol (**6**), this corresponds to the photostationary state.

PHOTOINDUCED ELECTRON TRANSFER AS A TRIGGER OF MOLECULAR MOTION

Because hydrogen bonds are to a large extent electrostatic in nature, changing the electron density on one or more of the atoms involved can be expected to have significant effects on the strength of interaction. Scheme 2 shows the molecular structure changes that take place upon reduction and oxidation of the naphthalimide unit in rotaxane **7** [7].

Scheme 2 When the naphthalimide unit in rotaxane **7** is reduced, electrochemically or by means of intermolecular photoinduced electron transfer, the preferred conformation changes: in the neutral ground state, the macrocycle **1** binds to the succinamide station (right-hand side of the structures) (**7**-succ). In the reduced form, it moves over to the naphthalimide (**7**-succ $\rightarrow$ **7**-ni). Upon charge recombination, the reverse co-conformational change occurs (**7**-ni $\rightarrow$ **7**-succ).

Time-resolved spectroscopy has been used to monitor the shuttling process. After excitation by a nanosecond laser pulse (355 nm), the naphthalimide chromophore undergoes rapid intersystem crossing. In the T_1 state it reacts with an electron donor present in solution (1,4-diazabicyclooctane = DABCO). Because the ion pair formed is in the triplet spin state, charge recombination is relatively slow, and free ions are formed with high yield. The radical anion of the naphthalimide unit has a strong and sharp absorption peak near 420 nm. When the macrocycle moves over from the succinamide station to form hydrogen bonds to the radical anion, the absorption peak shifts ca. 5 nm to shorter wavelength. Although this shift is not large, it is readily monitored using transient absorption spectroscopy. Importantly, the thread-only (compound **4**, structure not shown) does not show such a peak shift. Also upon electrochemical reduction of **7** and **4**, a blue-shifted naphthalimide anion absorption is observed for **7**.

The rate at which the peak shifts as measured in the transient absorption experiments allows a convenient and rather accurate determination of the rate of shuttling. It turns out that in acetonitrile at room temperature it is $1.35 \times 10^6 \text{ s}^{-1}$, while it is slightly lower in less polar nitrile solvents: $0.45 \times 10^6 \text{ s}^{-1}$ in propionitrile and $0.21 \times 10^6 \text{ s}^{-1}$ in butyronitrile. By measuring the shuttling rate as a function of temperature, the Arrhenius activation energy could be determined. Remarkably, the activation energies are the same within experimental error in acetonitrile and butyronitrile, 8.7 ± 0.7 and $8.3 \pm 0.4 \text{ kcal/mol}$, respectively. The difference in the rates is entirely due to the different preexponential factors, $2 \times 10^{12} \text{ s}^{-1}$ and $2 \times 10^{11} \text{ s}^{-1}$, respectively.

It is rather difficult to interpret these results, because the shuttling process may involve a number of steps. The height of the activation barrier indicates that the breaking of hydrogen bonds is an important rate-determining factor. The solvent effect on this rate can be attributed to the effect of polarity: in more polar solvents the hydrogen bonds are weaker. It is, however, not obvious to which extent such an effect shows up in the activation enthalpy or the activation entropy. After the hydrogen bonds to the succinamide station are broken, the macrocycle moves over the thread, and forms hydrogen bonds with the naphthalimide anion. There is a chance that this move is unsuccessful, and the macrocycle falls back in

the original reactant well. Because the thread used in **7** is flexible, it is conceivable that the naphthalimide anion assists the shuttling.

Finally, preliminary experiments have been performed to test the dependence of the shuttling on viscosity. Ideally, for this purpose, a series of polar solvents with different viscosities but similar polarities would be used, but, unfortunately, such solvents are not available. Instead, we used solutions of poly(methacrylonitrile) (average mw 20 000) in acetonitrile. A solution containing 33 % of this polymer at room temperature is highly viscous: in a test tube, it flows only on a time scale of minutes, and it cannot be stirred by conventional means. In such a medium, we were no longer able to detect shuttling on a time scale of ca. 100 μ s. More quantitative determinations of shuttling rates, macroscopic rheological properties, and microscopic mobilities and effective polarity of such solutions are in progress.

CONCLUDING REMARKS

Two types of photoresponsive rotaxanes have been discussed in which rotational and translational motion can be induced by a photochemical stimulus. The first type can be characterized as a molecular switch, in which different stable states corresponding to *E* and *Z* isomers are accessible. The second type is a molecular shuttle, in which photoinduced electron transfer leads to motion in one direction, and after subsequent back-electron transfer, the motion is reversed. In both cases, photons are the energy source for switching states, but the motion of the macrocyclic ring is a spontaneous motion for which thermal energy from the environment is used. In this respect, a strong analogy exists with the dynamics of motor proteins, but not with the mode of operation of macroscopic engines.

ACKNOWLEDGMENTS

This work was supported by the TMR initiative of the European Union through contract FMRX-CT97-0097 (DRUM), the Netherlands Organization for Scientific Research (Nederlandse Organisatie voor Wetenschappelijk Onderzoek, NWO), the Dutch *National Research School Combination: Catalysis*, and the EPSRC.

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