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Modeling of Azobenzene-Based Compounds

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Abstract:
Azobenzene is by far the most studied photochromic molecule and its applications range from optical storage to bio-engineering. To exploit the great potential of azobenzene, one must achieve deep understanding of its photochemistry as single molecule in solution AS WELL AS in-chain moiety and pendent group in macromolecular structures. With the advent of computer-aided simulation scientists have been able to match experimental data with computational models. In this chapter, a review on the modeling of azobenzene-containing molecules in different conditions and environments IS provided with a special focus on advanced applications of photo-controllable materials, such as molecular machines and photoactivation of bio-molecules.

Keywords: Azobenzene, photochemistry, modeling, molecular machines, photo-switch
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1 Introduction

Azobenzene is an aromatic molecule where an azo linkage (–N=N–) joins two phenyl rings. In order to change geometry and electron donating/withdrawing character, different substituents can be bonded to the aromatic moieties, giving rise to a large class of azobenzene-derived compounds. Thanks to its rigid and anisotropic molecular core, azobenzene is an ideal liquid-crystal mesogen, either alone or in macromolecular compounds [1].

Among the numerous spectroscopic and photo-physical properties of azo-materials, their most important feature is their photochemistry. Independently from their substitutions, all azos are able to perform an efficient and reversible photoisomerization, which occurs upon absorption of a photon within the absorption band (Figure 1) [2].

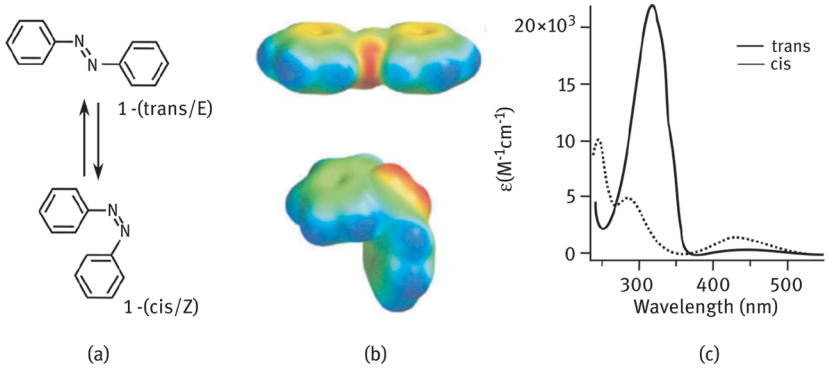

Figure 1: (a) Structures of trans and cis isomers of azobenzene. (b) Spacefilling models are colored by electrostatic potential (red—negative to blue—positive). (c) Electronic absorption spectra of the trans and cis isomers of azobenzene dissolved in ethanol [3].

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Even though the discovery of azo-compounds dates back to the mid-XIX century, the first evidence of the trans-cis isomerization was reported by Hartley in 1937, after observing a lack of reproducibility in absorbance measurements when azobenzene was exposed to light [4]. Since then, azobenzene has been vastly studied and its trans-cis photo-isomerization has become by far the most studied photochemical process of all times [5, 6].

In particular, the π-conjugated system gives rise to a strong electronic absorption in the UV-visible range of the spectrum, where the exact spectrum can be tailored via ring-substitution [7]. The spectra of trans- and cis-azobenzenes are distinct but overlapping (see Figure 1(c)). Trans-azobenzene shows a weak n–π* band near 440 nm and a strong π–π* transition near 320 nm. Cis-azobenzene has a stronger n–π* band also near 440 nm and shorter wavelength bands at 280 nm and 250 nm. The trans conformation of azobenzene is 10–12 kcal mol^{-1} more stable than the cis isomer so that, in the dark at equilibrium, trans is the dominant isomer (>99.99 %) [8]. The geometry of the trans conformation is almost planar and has a dipole moment near zero. The cis isomer, produced by irradiation with 340 nm light, adopts a bent conformation with its phenyl rings twisted ∼55° out of the plane from the azo group (Figure 1(b)) and has a dipole moment of 3 Debye. The trans isomer can be regenerated either by darkness − adapting the solution to re-establish the equilibrium or by irradiation at 450 nm. The photo-isomerization events occur with high quantum yields and minimal photo-bleaching. End-to-end distance for each isomer is also substantially different; the distance between the carbons at the para positions of the rings changes by ∼3.5 Å from trans to cis isomers. The applicability of azobenzene-based molecules as photo-switches and molecular machines has been possible thanks to the above mentioned geometrical difference and thanks to the fast timescale (few picoseconds) of the isomerization mechanism [9].

The behavior of azobenzene trans-cis isomerization strongly varies on the environment in which the molecules are found; for single-molecule azos, the solvent or the presence of metals can influence the isomerization mechanism, while for macromolecular azo it is important to take into account the position of the azo group (in chain, side chain or cross-linker). To exploit azobenzene's full potential one must understand its environment-depending behavior and one way to accomplish deep insight is to match experimental data with modeling techniques. In this article, a review on the modeling of azobenzene-containing molecules in different conditions and environments will be provided.

2 Modeling the trans-cis isomerization of azobenzene and its functionalized derivatives

A great amount of research has been focused on the exact understanding of trans-cis isomerization of azobenzene in various conditions by means of various *ab initio* modeling techniques [10–13]. For example, Armstrong et al. [14] employed MOPAC (Molecular Orbital PACkage), a semiempirical quantum chemistry program based on Dewar and Thiel's NDDO approximation, to determine the normal modes and vibrational energies of azobenzene. One of their most outstanding results is the correct prediction of the increase in frequency in the azo stretch mode upon deuteration of the phenyl rings. The modes show vibrational coupling between the phenyl modes and the azo vibrations as previously hypothesized on the basis of experimental results. It is also interesting to note that Armstrong's calculation attempted to explain the reason why certain in-plane stretching frequencies give rise to relatively intense Raman and resonance Raman scattering. In Raman scattering, in fact, displacements along the N-N and C-N bonds give rise to the strongest scattering as well as the stretches along the azo bond provide the greatest intensity in the Raman scattering [15–17].

As mentioned above, the absorption spectrum of azobenzene shows two distinct bands: a strong π-π* absorption band peaking at ca. 290 nm (cis-form) and 320 nm (trans-form) and a much weaker n-π* band with a peak around 440 nm (cis- and trans-form). Spectroscopic measurements proved that the excitation of the trans-isomer in the n-π* or in the π-π* band leads to different quantum yields of ≈25% and 12%, respectively, suggesting two different mechanistic pathways for the isomerization. Upon reverse isomerization to cis-azobenzene, the trans-state is reached with a higher quantum yield of ≈50% [18]. Many studies on the photo-isomerization of azobenzene were performed after excitation of the lowest n-π* transition of the molecule; however for the π-π* higher energy transition several pathways have been proposed but a unite experimental-theoretical solution is still to be found. Studies on the π-π* transition of trans-azobenzene in the gas phase after UV excitation with 330 nm were performed by Schultz et al. [19]. Matching the femtosecond time-resolved photoelectron spectroscopy with *ab initio* molecular dynamics they identified two near-degenerate excited states, S_2 ($\pi_{NN}\pi_{NN}^*$) and $S_{3,4}$ ($2 \times \pi_{Ph}\pi_{NN}^*$), and proposed a new model for the isomerization mechanism invoking electron excitation from the aromatic rings. Following this work Satzger et al. [20] also addressed the photo-isomerization of azobenzene after excitation of the π-π* transition by femtosecond time-resolved absorption experiments for both trans-cis and cis-trans transitions and compared experimental data with the different models proposed elsewhere [11, 21]. The authors compared transient absorption data of trans-azobenzene and of cis-azobenzene

after π-π* excitation with n-π* excitation data. The experimental results indicate that in both cases (trans-cis) and (cis-trans) the isomerization reaction can be described by a two-step process, where after a short relaxation on the S_2 potential energy surface (decay time 0.13 ps) the main isomerization motion takes place on the S_1 potential energy surface. The difference as compared to n-π* excitation is that the isomerization reaction starts on a different point on the S_1 potential energy surface (outside the Franck-Condon region). This causes different relative intensities of the decay associated spectra. Nevertheless, the spectral shapes and decay times of the spectral components are similar to the ones obtained after n-π* excitation.

It is clear so far that the modeling of azobenzene photo-isomerization, its excited-state dynamics and nonadiabatic crossings between different electronic states has been a demanding subject of study for physicists and chemists even in the gas state [22–25]. Interestingly, one of the most challenging unexplored field is the understanding the molecular mechanism of the trans–cis conversion in a crowded environment, i.e. in a condensed or liquid phase. The incredible complexity and great importance of this topic were addressed by Tiberio et al. [26]. Even though almost all applications featuring an azo photo-isomerization take place in solution or solid-state (e.g. polymers), the clear majority of the theoretical information present in literature involves the isomerization in gas phase, where the conformational change is not hindered by the environment and where we can expect that the mechanism can be different. The authors underlined how the main challenge in the study involving solvent environment effects on the trans–cis isomerization can be attributed to the need for adequate modeling parameters to take into account both basic photochemistry with atomistic approach to the host–guest system. The approach adopted by Tiberio et al. consists in the study of n-π* [27] azobenzene transitions from the ground to the excited state and back during the time evolution in various low-molar-mass organic solvents (n-hexane, toluene, ethanol, anisole, ethylene glycol) by means of nonequilibrium molecular dynamics (MD) simulations. The simulations confirmed the results obtained by Ciminelli et al. [28] indicating that the dominant isomerization mechanism in solution is a mixed torsional–inversion mechanism, while in vacuum the isomerization follows predominantly a torsional one. Indeed, the pure inversion seems to occur only after the decay into the S_0 state, while in the excited state this pathway appears unlikely, as a high-energy barrier must be overcome. The analysis on azobenzene solvent-depending behavior showed how higher solvent viscosity seemed to increase the pure inversion contribution. Moreover, increasing viscosity clearly affects the rotational dynamics of AB, notably resulting in faster dynamics for the trans-isomer.

Azobenzene back isomerization, characterized by a relatively low activation energy (about 95 kJ/mol, i.e. less than 1 eV/molecule [29]), typically takes several hours or days can be accelerated by the presence of gold nanoparticles down to several minutes [30–33].

Titov et al. [34] attempted to clarify, via experimental and theoretical investigation, the mentioned catalytic effect of gold nanoparticles on thermal cis-trans isomerization of azobenzene molecules (Figure 2). One of the explanations for the catalytic activity of gold nanoparticles is related to electron transfer between the adsorbed molecule and the gold particle surface [35, 36]. Titov et al. performed density functional theory calculations of the activation energy barriers in order to investigate the effect on the isomerization rate of electron attachment and detachment from various azobenzene-containing molecules in aqueous solution. The results interestingly show that activation barriers are greatly lowered for azobenzene-containing molecules. Moreover, applying Eyring's transition state theory, they calculated absolute rates for thermal cis-trans isomerization to be about 1000 times larger for azobenzene-containing molecules upon electron attachment and withdrawal. Such large numbers are not in quantitative agreement with the obtained experimental values; however, that was also not expected because of differences of the experimental conditions and the idealized gas-phase type theoretical models adopted here.

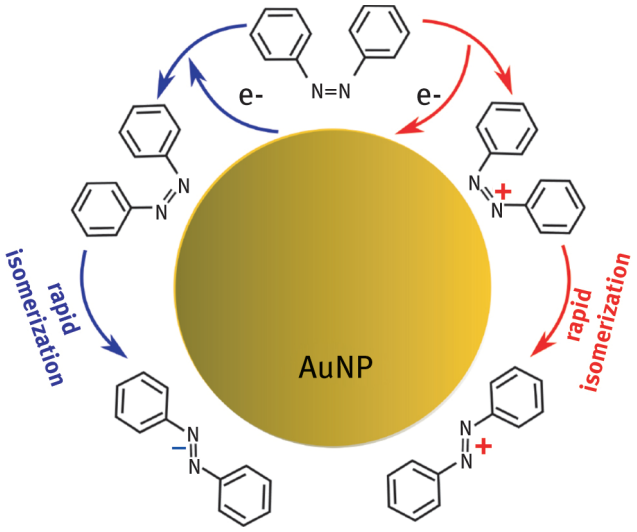

Figure 2: Gold nanoparticle catalysis of thermal cis-trans isomerization in azobenzene-containing molecules upon electron attachment and withdrawn.

As vastly reported in the literature photochemical and thermal isomerizations of azobenzene are strongly affected not only by intermolecular interactions but also by intramolecular ones. For example, bulky substituents at the ortho-positions alter the photochemical isomerization [37, 38]. The effect of ring strain in macrocyclic azobenzene dimers has been studied previously in literature [39, 40]. Interestingly, Norikane et al. [41] were able to give a fresh insight on previously unraveled relationship between structure and photochemical/thermal isomerization of azobenzene moieties in azobenzene macrocyclic dimers with comparison to noncyclic azobenzene dimers. In both cases, upon irradiation with UV light, each (trans/trans) isomer exhibited a stepwise photo-isomerization to give the corresponding (trans/cis) isomer, followed by isomerization to yield the (cis/cis) isomer. Considering the quantum yields for the isomerization, it is clear that the photochemical isomerization of macrocyclic azo was altered by its cyclic structure. Ring strain, in fact, could cause shifts in the absorption spectra of the azobenzene chromophore and perturbations in molecular motion in the excited state. Ab initio calculations, performed using Gaussian 98 program package with HF/6-31G** basis, were employed to estimate the ring strain of each isomer in their ground electronic states. In accordance with experimental data, it was found that the ring strain in the macrocyclic azobenzene dimer increases the activation energy and activation entropy for the thermal cis-trans isomerization of the azobenzene moiety. This knowledge of the correlation between structure and reactivity of azobenzene gives significant information for controlling the isomerization to establish photo-responsive functional materials that utilize the isomerization of azobenzene.

One of the most extensive theoretical study on azo-derivatives cis-trans thermal isomerization and the effect of substituents and solvents has been reported by Dokic et al. [42]. About 90 azobenzene-derived molecules have been studied in that work. For all of them, cis and trans isomers have been calculated and transition states have been investigated. Balancing computational cost and accuracy, B3LYP/6-31G* model was chosen, together with Eyring transition state theory and a polarizable dielectric continuum model to treat solvents. In most cases the isomerization reaction proceeds through a linear transition state indicative of an inversion mechanism.

Following the schematics reported in Figure 3, the authors found that the transition state is not reached by pure inversion along the angle α but rather by simultaneous rotation around the C-N=N-C dihedral angle ω. The linear transition state can be stabilized very efficiently with acceptors in ortho and para positions. In the case of double and triple substitution, substituents on one ring have an additive effect on activation energies and kinetics, while for substitution on both rings no simple additivity rule is found. For push−pull azobenzenes the reaction mechanism depends on the solvent, changing from inversion to rotation in polar environments. On a semiquantitative level, the environment increases the rates according to a Kirkwood scenario in which the molecules are treated as dipoles in a polarizable continuum. Bulky azobenzenes, which were also investigated experimentally by Dokic [42], are obtained by adding tert-butyl groups. It is found that generally these bulky compounds behave similar to conventional azobenzenes. In this case the kinetics obtained by theory are in good agreement with experimental data, at least as far as activation energies are concerned. Also trends observed by systematic variation of substituents and the polarity of the solvent are nicely reproduced and can be rationalized.

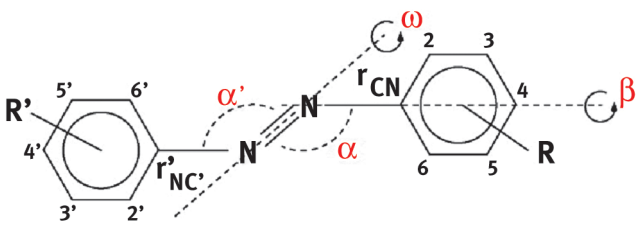

Figure 3: Schematics for the labeling procedure of the atoms in azobenzene derivatives.

3 Modeling molecules with the azobenzene unit in their constitutive structure

As discussed above, azobenzene molecules are almost never found on their own, but most applications revolve around azobenzene-based molecules or polymers [1, 43–46]. Understanding the behavior of the azo moieties in complex structures is of the key importance for obtaining high-quality performance of the final application. This section reports some of the main studies on molecular modeling and theoretical studies of azobenzene-based materials, including polymers, inorganic materials and non-covalent interactions.

Photo-irradiation of polymers containing azobenzene either in the backbone or as a pendant group can cause reversible changes in physical properties such as surface wettability, viscosity and solubility [47, 48]. These types of specialty polymers containing photochromic groups which induce reversible property changes are termed photo-responsive polymers [49].

Siewierski et al. [50] reported on the preparation of azobenzene-based monolayers on silicon. Exposure to 354 nm light slightly decreased the water contact angles of the azobenzene monolayers. In contrast to modeling studies which predicted ≈3 Å changes in the position of terminal groups upon trans-to-cis isomerization and a consequent decrease in film thickness [51], an unexplained experimental observation is the increase in film thickness (as measured by X-ray reflectivity) upon photoirradiation. Zhang et al. [52] described a new series of hydrogen-bonding species in a novel hydrazide-modified p-metoxyazobenzene derivatives, called D3, D6 and D10, synthesized according to a procedure reported elsewhere [53]. The hydrazide moiety can be viewed as a hybrid structure, composed of a primary amide function and a terminal amino group, which has mutual electronic and steric influence on the hydrogen-bonding formation between hydrazide groups. The exhibited thermal behavior of these compounds may also relate to the π–π stacking of p-methoxy azobenzene or phenyl groups. The intermolecular hydrogen bonding and molecular alignment patterns were evidenced from experimental data obtained via both temperature-dependent infrared (IR) spectroscopy and *ab initio* computational models [54]. Temperature-dependent IR spectra effectively illustrate the reversible re-organization of the molecules, and 2D correlation IR spectral analysis for the amide and amino groups reveals two different hydrogen-bonding patterns: parallel arrangement with ordered alignment in D10 and D6, and less-ordered anti-parallel alignment in D3. Length and odd/even number of the alkyl spacer in azo-containing macromolecules play an important role in the molecular alignments and the hydrogen-bonding formations, as well as in the liquid crystal properties of Dn.

Molecular dynamics (MD) simulation has been employed by Heinz et al. [55] to examine the molecular-level orientation and reorganization of model azobenzene derivatives in the interlayer space of layered silicates upon laser excitation. The modeling method was compared to experimental data, such as X-ray diffraction and UV/vis absorption measurements. The synthesis and characterization of hybrid structures of this kind have long been reported in literature, always featuring the great limit posed by the evaluation and control on the location and the orientation of the intercalated azo dyes [56, 57] as shown in Figure 4.

MD results show uniform reversible changes in basal plane spacing of montmorillonite up to 2.8 Å (14 %) upon trans-cis isomerization of attached azo-containing ionic surfactants. Experimentally, Okada et al. have shown nonuniform reversible optical switching of the gallery height for semiflexible surfactants up to 10 Å (41 %) in the presence of phenol and uniform reversible optical switching of 0.9 Å (4 %) without co-intercalates [56]. The absence of changes in gallery spacing for azobenzene derivatives with attached flexible hydrocarbon chains at low packing density without co-intercalates are well explained by simulation.

Barrett et al. [58] presented their study on azo-based block copolymers. In their work, a pump/relax procedure was applied to analyze the thermal cis-trans isomerization behavior of the azo groups. All samples show a fast isomerization process due to strained cis isomers, trapped below the glass transition temperature of the film, followed by a slower isomerization process. More recently, Toshchevikov et al. [59] have proposed a microscopic theory of light-induced deformation in amorphous side-chain azobenzene polymers taking the internal structure of azobenzene macromolecules explicitly into account. When the system is irradiated with

polarized laser light, a mechanical stress, caused by reorientation of macromolecules due to interactions of chromophores in side chains with the light, is applied to the system. All experimental results were in optimal agreement with quantum chemical calculations obtained using density functional theory [60]. Depending on the architectures of oligomers, a sample can be either stretched or uniaxially compressed along the polarization direction of the laser light. The light-induced stress can be larger than the yield stress at characteristic light intensities used in experiments. This result explains the possibility of irreversible sample deformation under homogeneous illumination and, hence, the possibility of the inscription of surface relief gratings. The authors showed that the irreversible elongation of a sample decreases with increasing temperature, with critical temperature (corresponding to the point when the irreversible elongation disappears) independent of the glass-transition temperature, T_g. These results demonstrate the great potential of the proposed microscopic orientation approach for describing the photoelastic properties of different azobenzene polymers [61].

Polyimides containing azobenzene side groups have been synthesized by polycondensation reaction by Sava et al. [62]. The authors present photochromic studies proving that the azobenzene groups are able to isomerize even when incorporated in a rigid chain system. However, the cis-isomer maximum conversion degree reported in this work is lower than the flexible chain polymers. For example, in solutions the maximum cis-isomer content can reach 70%, in solid state only maximum values of 39% can be obtained. Taking into consideration the ratio between the trans–cis isomerization and the cis–trans relaxation processes, this class of materials is recommended both for nano-manipulation and surface relief grating applications also because the polymers present a good thermostability and the degradation process starting for all the products above 300°C and have a glass transition temperature in the range of 185–230°C.

Azobenzene can also be found in a bridged form or used as cross-linker, and relative computer models can be found in literature. For example, Jiang et al. [63] reported their study on density-functional-based molecular dynamics simulations applied to isomerization of azobenzene and bridged azobenzene induced by n-π* excitation. The quantum yield was found to be about 25% for azobenzene, in agreement with experiment [64], and about 45% for bridged azobenzene (B-Azo), which is again consistent with experiment [65]. In those simulations that did produce isomerization, the range of calculated S_1 lifetimes was 330−480 fs for azobenzene and 22−32 fs for bridged azobenzene. In the simulation shown in detail, the lifetime of the S_1 excited state in trans-azobenzene was found to be about 400 fs, with the whole trans−cis isomerization process completed in approximately 500 fs. The S_1 lifetime in trans-B-Azo was found to be only about 30 fs, an order of magnitude shorter, just as in the earlier work by Böckmann et al. [66]. However, the full trans−cis isomerization for B-Azo requires about 430 fs, which is comparable to the timescale for azobenzene. The reason for this is that the twisting of the phenyl rings in B-Azo around the CN bonds is hindered by the presence of the bridge structure.

4 Achieving photo-controllable materials

This section is dedicated to the application of molecular simulation in azobenzene-based materials and technology, from biomolecules control, to molecular machines and other applications.

4.1 Biomolecules

A great amount of interest has been dedicated to the study of optical control of peptide/protein conformation which could be a powerful biochemical tool for tuning protein properties in diverse systems [67, 68]. Powerful chromophores, such as azobenzene, can theoretically be used for reversible conformational control of proteins [69, 70].

Kumita et al. [71] reported on the reversible means of controlling helix stability that involved the incorporation of a photo-isomerizable azobenzene cross-linking reagent into an engineered peptide system obtaining a promising result in need of improvement. The same group published an upgraded version of cross-linked peptides, designed applying a molecular modeling strategy, that significantly extend the versatility of this approach to the photocontrol of protein structure [72].

As shown in Figure 5, the cis form of the cross-linker is predicted to be compatible with an α-helical conformation of the peptide, whereas the trans form of the cross-linker is too extended for such a spacing and its related to the unfold peptide in solution. The importance of this work relies on the fact that the activities of proteins with key helical domains involved in function, such as leucine zippers [73] and helix-loop-helix transcription factors [74], and certain proteins involved in signal transduction [75], might be reversibly photo-controlled using azo-based reagents. Such photo-controlled proteins could be useful for probing the importance of timing in biochemical networks.

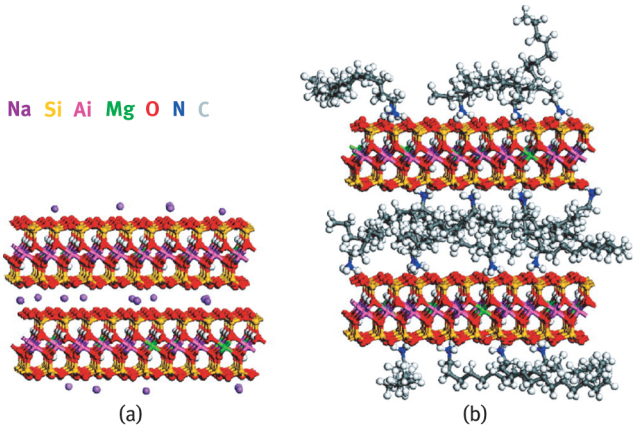

Figure 4: Molecular structure of (a) sodium montmorillonite and (b) n-dodecylammonium montmorillonite. The gallery spacing of the layered structure depends on the grafting density and on the molecular volume of the cationic surfactant.

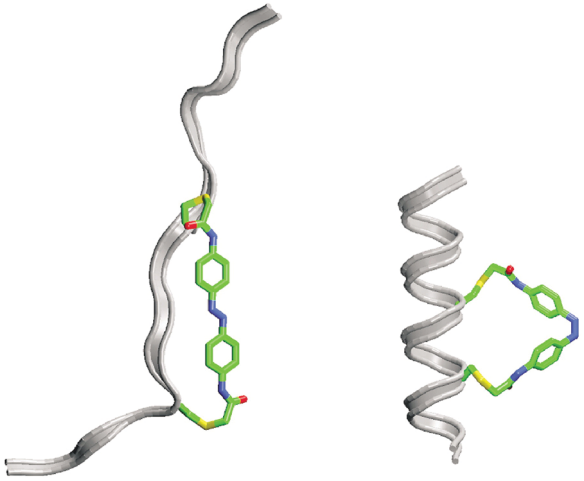

Figure 5: Energy-optimized molecular models of peptides attached to the azobenzene cross-linker in its trans (left) and cis (right) form as reported by Flint et al. (2002).

Mitus et al. [76] formulated the concept of dye semi-intercalation employing Monte Carlo simulation and backing up experimental data by Sou et al. [77]. Featuring a complementary mechanism between full intercalation [78] and guest–host behavior [79], the semi-intercalation theory describes the scenario where the dye molecule is partially immobilized by the surfactant chains imposing steric hindrance to its photo-isomerization, as depicted in Figure 6 for DNA–cetyltrimethylammonium (CTMA) complexes.

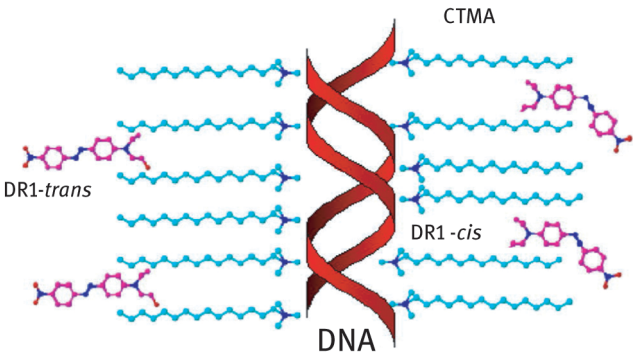

Figure 6: Illustration of the semi-intercalation of DR1 in a DNA–CTMA biopolymer showing the origin of memory effect upon light excitation.

The use of azobenzene polymers in the photo-control of biological systems is a vast and very significant topic, properly reviewed by Goulet-Hanssens et al. [80].

4.2 Molecular machines

Molecular machines are nanometer-sized factories and self-repairing structures where complex and responsive processes operate under exquisite control and translational and rotational movement is directed with precision and fueled by chemical and light energy [81]. Molecular modeling on precision applications can be a breakthrough method to obtain fine tuning of the final properties [82].

One of the most interesting applications of computer-aided modeling to molecular machines has been provided by Kohlmeyer et al. [83]. The authors described a new class of molecular machines that has a hingelike motion, so-called light-driven molecular hinges. The characteristic structure of a hinge is two planes that are connected at their edges through an axis; the motion of the hinge allows a transformation between open and closed states. When two hinges connect the two rigid planes, efficient motion of the hinges must occur in a cooperative manner; i.e., a configuration in which one hinge is open and another is closed either will not exist or will be very unstable. The molecular motion in above described system is induced by photochemical trans-cis isomerization of azobenzene units; cooperative effects and ring strain restrict the molecular motion [84]. The motion (close and open) (see Figure 7) can be operated by alternate irradiation with UV and visible light. The trans/trans and cis/cis isomers are thermally stable at 40°C, and the photochemical closure reaction (from trans/trans to cis/cis i\somer) is dependent on the intensity of the light used because of the short-lived intermediate (trans/cis isomer).

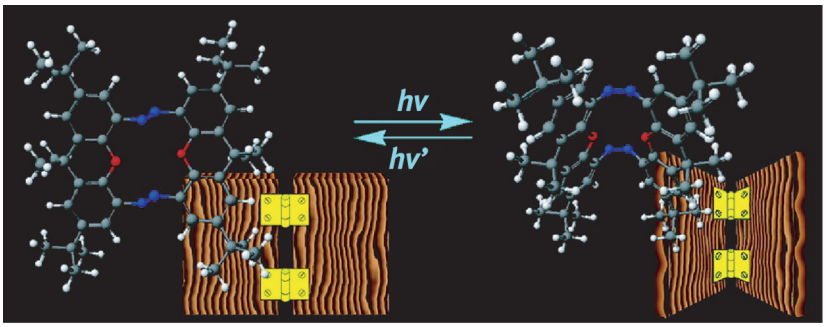

Figure 7: Molecular structures of trans-trans (left) and cis-cis (right) isomers of a light-driven azobenzene-based molecular hinge, optimized by AM1 calculations (top), and graphical representations of these two isomers (bottom).

The change in molecular shape is large, and therefore such systems might be of use in various fields, e.g., as storage devices or other switching devices. The highly-regulated motion of the hinge has a potential to display drastic switching behavior, especially for anisotropic media such as liquid crystals.

5 Conclusions

This article provides an insight on the modeling techniques applied to azobenzene molecules in gas or condensed state and to azobenzene moieties in larger molecules.

The mechanism for cis-trans isomerization is a complex subject that still garners debate in the literature. The most recent accounts using dynamic (time dependent) simulations favor a mixture of the twisting and rotation reaction coordinates, two pathways which were previously assumed to be independent. The interconversion process is also influenced by the solvent medium and steric effects which might preclude one particular switching mode.

Despite the development of numerous model chemistries to simulate the mechanism associated with light-induced isomerization, it is of key importance to find innovative approaches able to precisely explain and support all the experimental observations. Understanding the urgency for new statistical approaches that correctly reproduce light-driven phenomena in azobenzene-containing molecules could represent a breakthrough step for the improvement of all new azobenzene-based commodity and specialty applications.

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