



Azobenzene-Substituted Triptycenes: Understanding the Exciton Coupling of Molecular Switches in Close Proximity

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Abstract: Herein, we report a series of azobenzene-substituted triptycenes. In their design, these switching units were placed in close proximity, but electronically separated by a sp^3 center. The azobenzene switches were prepared by Baeyer–Mills coupling as key step. The isomerization behavior was investigated by ^1H NMR spectroscopy, UV/Vis spectroscopy, and HPLC. It was shown that all azobenzene moieties are efficiently switchable. Despite the geometric decoupling of the chromophores, computational studies revealed exci-

tonic coupling effects between the individual azobenzene units depending on the connectivity pattern due to the different transition dipole moments of the $\pi \rightarrow \pi^*$ excitations. Transition probabilities for those excitations are slightly altered, which is also revealed in their absorption spectra. These insights provide new design parameters for combining multiple photoswitches in one molecule, which have high potential as energy or information storage systems, or, among others, in molecular machines and supramolecular chemistry.

Introduction

In recent years, azobenzenes (ABs) have turned out to be truly multitasking. They are no longer just used as dyes.^[1] Their ability to isomerize between the planar, energetically more stable (*E*)-AB to the twisted, metastable *Z* isomer makes them useful protagonists in energy and information storage,^[2] organocatalysis,^[3] photobiology and photopharmacology,^[4] host–guest chemistry,^[5] molecular mechanics,^[6] molecular machines^[7] and other areas of research.^[8] The reason for this multitude of application possibilities is the large change in geometry and length by the isomerization from (*E*)- to (*Z*)-AB.^[9] This *E*→*Z* isomerization can be triggered photochemically with light of around 300–360 nm. The AB can be conveniently switched back from *Z*→*E* with light of 450 nm or thermally.^[9] Moreover, it can also be isomerized by electrochemical stimulation as well as by mechanical stress.^[10] Despite this

versatility in properties and applications, the ideal connection of AB switches with other functional entities and their inter- and intramolecular interaction is still not fully understood; this can also be observed for other photoswitches.^[11] When combining the AB scaffold with (photo-)systems in general, these units can have an influence on the photochemical properties depending on the linkage.^[11a,d] By connecting, for example, two ABs in the *ortho*, *meta* or *para* position on the same phenyl ring, not only their absorption maximum is changed, but also their half-life and quantum yield differ drastically.^[11a]

To minimize the influence of joined photosystems on each other it is possible to spatially separate them by fixing them at a suitable distance.^[12] Moreover, connecting photosystems in the *meta* position (“*meta* rule”) often leads to less π -conjugation and, therefore, to practically independent behavior of the individual systems.^[11a,b,13] However, photochromic entities in close proximity, even if not directly conjugated, can influence each other. One option is the incorporation in cycles, in which upon isomerization a drastic conformational change is induced that alters the switching behavior of the other parts.^[14] One example of this behavior is the incorporation of two AB moieties in a ring system separated by a methylene linker. In this case, the expected stability order was overturned with the *Z,Z* isomer being most stable conformer because of ring strain.^[15] Less obvious and controllable are influences like for example energy transfer through space with distance being the crucial parameter.^[16]

To study the interaction of multiple, spatially close azobenzene units but electronically separated by a sp^3 center without influences like ring strain, one, two and three azobenzene moieties were attached to a triptycene scaffold in *meta* connection. Triptycene (1) as spacer unit is a bridgehead system with D_{3h} symmetry, which was first synthesized by Bartlett et al.^[17] Due to their high symmetry and rigidity,

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tritycene derivatives have been studied inter alia in the fields of molecular machines, supramolecular chemistry as well as material science.^[18] Besides the fundamental insights these switchable compounds offer application as molecular grippers as the all-*Z* form of a threefold substituted azobenzene triptycene exhibits a close cavity that can be reversibly opened with light (Figure 1).^[19]

Triptycene offers different connection patterns. Besides the number of azobenzenes connected, constitutional isomers also exist (*ortho* vs. *meta* and up vs. down, relatively). Herein, we present a systematic study comprising synthesis and photochemical characterization of all different *meta*-isomers. The study was supported by computations to reveal any interaction of the individual switches in detail.

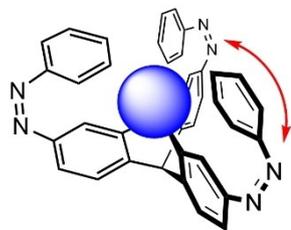
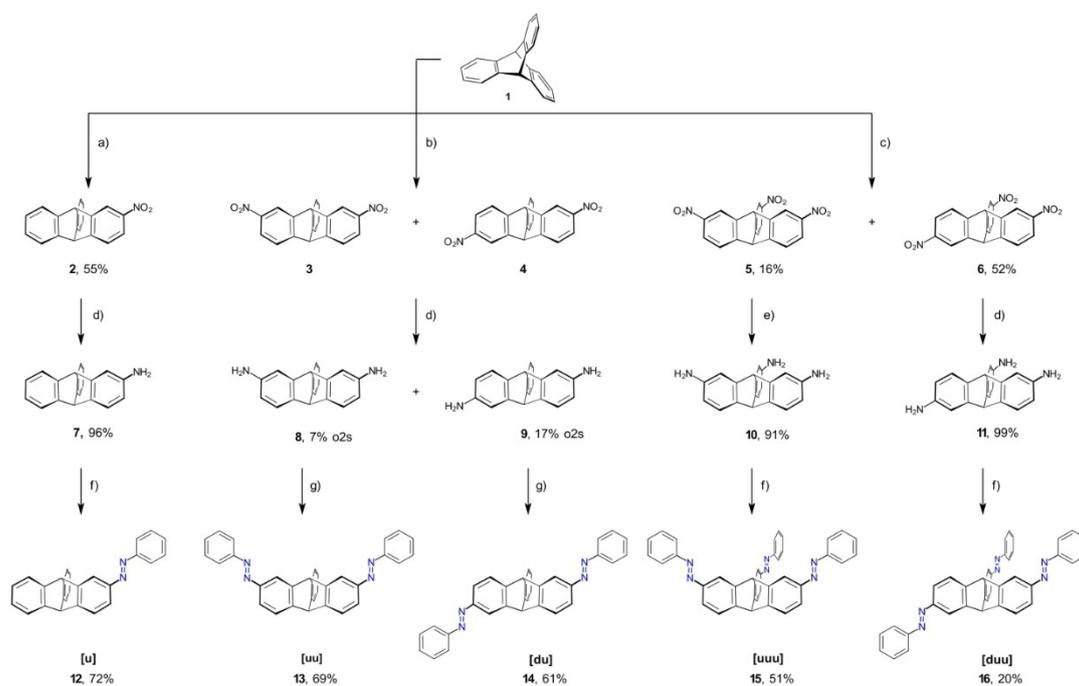


Figure 1. Azobenzene-triptycene as model for through-space interactions and potential molecular gripper.

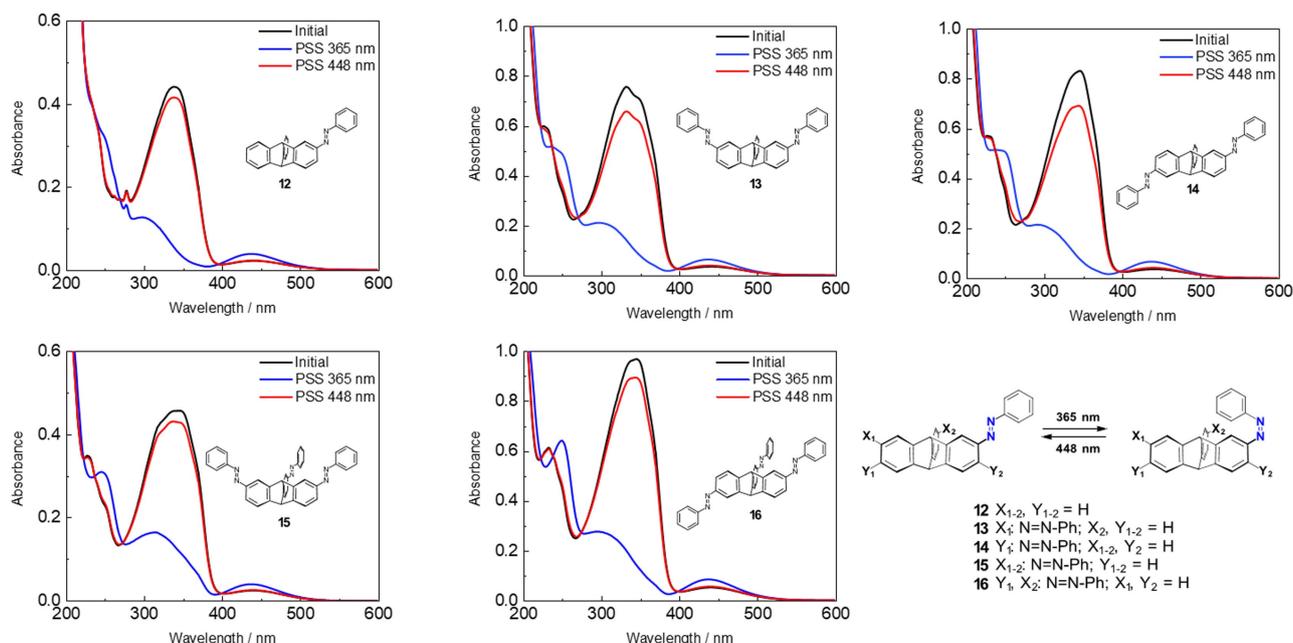
Results and Discussion

Synthesis

A synthetic route starting from commercially available unsubstituted triptycene (**1**) was developed to access the desired *meta*-azobenzene-substituted triptycenes (*meta*-TrpABs) **12–16**. The Baeyer–Mills coupling reaction as key step was the method of choice to install the azobenzene moiety from the aminotriptycenes **7–11** with nitrosobenzene. This reaction has been proven to be reliable in various azobenzene syntheses by others as well as by us.^[11f,14b,20] The aminotriptycenes **7–11** required should be prepared by hydrogenation of nitrotriptycenes **2–6**, which can be synthesized by nitration of unsubstituted triptycene (**1**). As the first step, triptycene **1** was nitrated under various conditions (Scheme 1). Optimization was required to provide satisfactory yields for the desired substitution patterns. For the triple *meta*-nitration nitrotriptycene **6** is always preferably formed in relation to nitrotriptycene **5**. In this process excess of fuming nitric acid in acetic acid was applied to yield the nitrotriptycene **6** in 52% and nitrotriptycene **5** in yields of 16%, respectively.^[21] For double nitration best yields were achieved with KNO_3 and trifluoroacetic anhydride (TFAA), providing mostly **3** and **4** as mixture of isomers.^[22] This mixture of **3** and **4** was used without further purification in the following hydrogenation reaction, after which the two isomers could be separated by column chromatography as aminotriptycenes **8** and **9**.^[23] For single *meta* nitration, concentrated nitric acid was used.^[24] After hydrogenation, the obtained aminotriptycenes **7–11** were condensed in a Baeyer–Mills coupling reaction with nitrosobenzene to obtain the target



Scheme 1. Synthesis route towards *meta*-TrpABs **12–16**. a) conc. HNO_3 , 75°C , 24 h; b) KNO_3 , TFAA, ACN, RT, 24 h; c) fuming HNO_3 , AcOH, 0°C , 1 h; d) H_2 , Pd/C, MeOH, overnight; e) H_2 , Pd/C, MeOH, 2 h; f) nitrosobenzene, AcOH, toluene, 60°C , 24 h; g) nitrosobenzene, AcOH, toluene, 60°C , 48 h. o2: over two steps.



Scheme 2. UV-Vis spectroscopy of (*meta*)-TrpABs **12–16** in acetonitrile/H₂O (90:10) at a concentration of $2 \times 10^{-5} \text{ mol L}^{-1}$. The solutions were irradiated with light of 365 nm (purple) and subsequently with light of 448 nm (blue) until the PSS was reached.

TrpABs **12–16** in yields up to 72%. TrpAB **14** is chiral and was accordingly obtained as a mixture of enantiomers. The enantiomeric ratio was not examined, but is subject of future research.

Isomerization studies

After successful synthesis the photochemical properties of all synthesized *meta*-TrpABs **12–16** were studied by UV/Vis spectroscopy in acetonitrile (see the Supporting Information for acetonitrile and Scheme 2 for acetonitrile/water 90:10). The proportion of water had no noticeable influence on the switching properties (see the Supporting Information). In comparison to the parent AB, the TrpABs exhibited slightly redshifted $\pi \rightarrow \pi^*$ transitions at around 340 nm. For all *meta*-TrpABs **12–16** the decrease in the absorption maxima of the $\pi \rightarrow \pi^*$ transition after irradiation of 365 nm indicating $E \rightarrow Z$ photoisomerization.

Although the initial absorbance of the all-*E* spectra (black spectra, Scheme 2) could not be reached, irradiation at 448 nm initiated $Z \rightarrow E$ back photoisomerization (purple spectra, Scheme 2). Additionally, the isomerization of the *meta*-TrpABs **12–16** was followed by ¹H NMR spectroscopy in [D₃]acetonitrile, which confirmed the results of the UV-Vis experiments. Furthermore, all possible isomers (for **12** *E* and *Z*, for **13** and **14** *EE*, *EZ*, *ZZ* and for **15** and **16**, *EEE*, *EEZ*, *EZZ*, *ZZZ*) could be detected after irradiation with different wavelength in the ¹H NMR spectra (see the Supporting Information). The exact compositions of isomers present in the PSSs were also determined by HPLC. The spectroscopic and photoisomerization results are summarized in Table 1. For all compounds an overall percentage of azobenzene moieties in the *Z* state after

Table 1. Irradiation wavelengths of the *E* isomers and photostationary state (PSS) compositions for AB moieties in *E* or *Z* in (*meta*)-TrpABs **12–16** determined by HPLC at the corresponding isobestic points of the spectra.

TrpAB	$E \rightarrow Z$ 365 nm PSS composition [%]		$Z \rightarrow E$ PSS composition [%]	
	$E^{[c]}$	$Z^{[c]}$	$E^{[c]}$	$Z^{[c]}$
12 ^[a]	6	94	80	20
13 ^[b]	8	92	78	22
14 ^[b]	6	94	78	22
15 ^[a]	31	69	80	20
16 ^[a]	16	84	79	21

[a] For $Z \rightarrow E$ isomerization, samples were irradiated at 448 nm. [b] For $Z \rightarrow E$ isomerization, samples were irradiated at 425–430 nm. [c] Percentage of AB units in *E* or *Z*. Ratios of the individual isomers can be found in the Supporting Information.

irradiation with light of 365 nm was over 80%, except for *meta*-TrpAB **15**. In this case, the increased steric demand could be a reason for the lower overall (*Z*)-AB concentration. Back isomerization to ~80% (*E*)-AB moieties was possible for all *meta*-TrpAB **12–16** by irradiation of light into the $n \rightarrow \pi^*$ transition bands, located at around 430 nm (Scheme 2) and to ~100% (*E*)-AB by heating to 70 °C.

Computation

The molecular geometry of TrpAB **12** has *C*_s point group symmetry. The first excited electronic *S*₁ state possesses the well-known $n\pi^*$ character of azobenzenes and has an excitation energy of 2.86 eV (calculated with linear-response time-dependent density functional theory, TDDFT;^[25] for details see the Supporting Information). The $\pi \rightarrow \pi^*$ excitation corresponds to

the S_2 state and is slightly red-shifted with an excitation energy of 4.17 eV compared to standard AB, whose S_2 state is at 4.37 eV at the same level of theory. The transition dipole moment of the π - π^* absorption is oriented along the longitudinal axis (Figure 2) of the AB moiety.

Introducing a second AB moiety at the triptycene unit parallel to the existing one results in TrpAB 13 (Figure 2), which also has C_s point group symmetry. The n - π^* excitations (now S_1 and S_2) are localized at each AB branch, are basically unaffected by each other and possess excitation energies of 2.84 and 2.85 eV, respectively. In contrast, the π - π^* excitations of the individual AB branches change significantly due to excitonic coupling effects between them.

As a consequence, the two corresponding states S_3 and S_4 are red and blue shifted by approximately 0.15 to 4.01 and 4.32 eV, respectively. The excitonic coupling can be understood in terms of vector sums or phase combinations of the two transition dipole moment vectors of the individual π - π^* excitations (Figure 2). The out-of-phase combination leads to stabilizing interaction introducing a red shift whereas the in-phase combination gives a destabilizing interaction causing a blue shift of the excitation. As neither interaction is parallel or in-line, both excited states retain reasonable oscillator strengths. This manifests as peak broadening within the theoretical spectrum (Figure S14) and can also be seen in the experimental spectrum comparing TrpABs 12 and 13 (Scheme 2).

When the second azobenzene moiety is introduced at the “down” position of the triptycene unit leading to TrpAB 14, the excitonic coupling is reduced. This can be rationalized as the two interacting transition dipole moments are further apart, because they are positioned on opposite sides of the triptycene core. This leads to smaller shifts of the excitation energies of the $\pi\pi^*$ states now being found at 4.07 and 4.28 eV. Due to the more linear orientation of the transition dipole moments, the difference in oscillator strength between the $\pi\pi^*$ states, however, becomes larger than in TrpAB 13, as the out-of-phase

and in-phase combinations of the transition dipole moments become more constructive and more destructive, respectively. Therefore, the blue shifted in-phase transition retains very low oscillator strength and does not manifest as peak broadening in the calculated spectrum (Figure S15).

Introducing a third AB unit to the remaining phenyl ring of the triptycene unit such that the whole molecule exhibits C_{3v} point group symmetry yields TrpAB 15. The n - π^* excitations (S_{1-3}) still remain largely unaffected and stay localized at the individual azobenzene branches with excitation energies of 2.84, 2.85 and 2.85 eV. In this highly symmetric molecule TrpAB 15, the pattern of the excitonic coupling between the three individual π - π^* excitations reflects the molecular point group symmetry and exhibits two degenerate stabilized states S_4 and S_5 at 4.02 eV and one destabilized state S_6 at 4.50 eV. The out-of-phase degenerate combinations herein correspond to the E irreducible representation, whereas the in-phase combination has A_2 symmetry (Figure 3). Due to the diagonal orientation of the transition dipole moments all states retain significant oscillator strength.

When the third AB group is introduced in the “down” position of the remaining phenyl ring of the central triptycene unit, the resulting system TrpAB 16 exhibits C_s symmetry leading to non-degenerate out-of-phase combinations of the A'' and A' symmetry of the $\pi\pi^*$ states (Figure 4). The corresponding excitation energies are now 4.03, 4.07 and 4.40 eV for S_4 , S_5 , and S_6 , respectively. The now more linear orientation of the transition dipole moments leads again also to different oscillator strengths with the in-phase combination having a significantly reduced transition probability. This then substantiates with the absence of the blue shifted shoulder in the calculated spectrum of TrpAB 16 compared to that of TrpAB 15. This is in agreement with the experimental spectra, since the π - π^* band of TrpAB 15 is clearly broader than the π - π^* band of TrpAB 16 (see the Supporting Information for superimposed absorption spectra of 15 and 16).

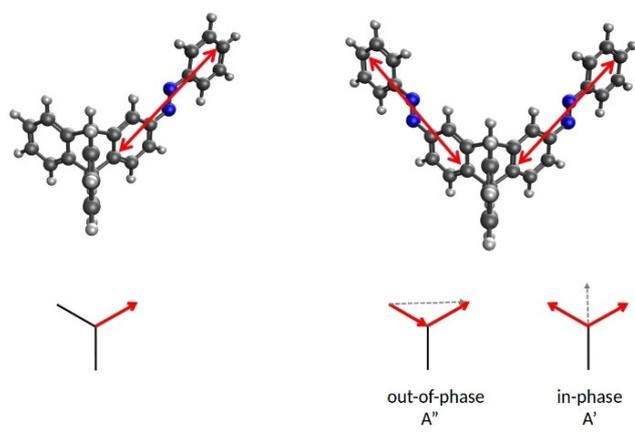


Figure 2. Vector representation of the transition dipole moments of the π - π^* excitations in TrpAB 12 (right) and TrpAB 13 (left) and the respective out-of-phase and in-phase combinations in 13, which represent the excitonically coupled states S_3 and S_4 in 13.

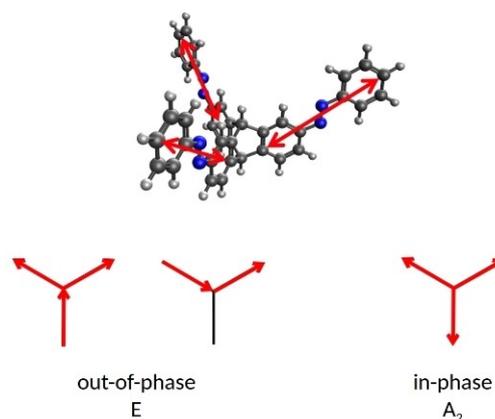


Figure 3. Vector representation of the transition dipole moments of the π - π^* excitations in TrpAB 15 and the respective out-of-phase and in-phase combinations representing S_4 to S_6 .

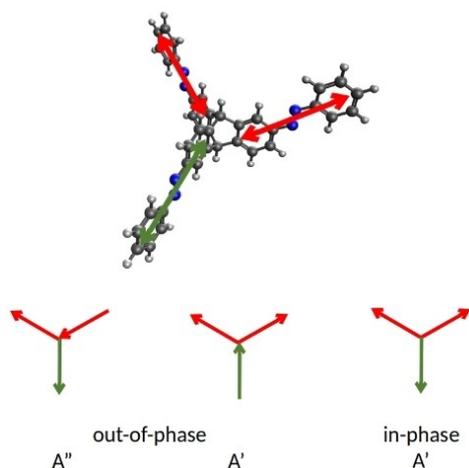


Figure 4. Vector representation of the transition dipole moments of the π - π^* excitations in [duu] TrpAB **16** and the respective out-of-phase and in-phase combinations representing S_4 to S_6 . The reduced symmetry leads to three non-degenerate excitonically coupled excited states.

Conclusion

In summary, five different combinations of TrpABs in the *meta* position **12–16** were successfully synthesized with a Baeyer–Mills coupling reaction as the key step. UV/Vis and ^1H NMR spectroscopy confirmed that **12–16** are able to photoisomerize. Their exact compositions of isomers in the photostationary states at different excitation wavelength were determined by HPLC at their specific isosbestic points. All compounds were able to isomerize to a *Z* composition of 69–94%. Photochemical back-isomerization to an *E* composition of $\sim 80\%$ was achieved in all cases; this makes the substances not only interesting as switchable hosts, but also as possible information and energy storage systems. Moreover, calculations revealed the n - π^* excitations to be practically unaffected by the neighboring AB units. In contrast, the π - π^* excitations of the individual AB units in the TrpAB derivatives change significantly due to excitonic coupling effects obeying, like textbook examples, the molecular point group symmetry.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: azo compounds · computational chemistry · excitonic coupling · isomerization · photochemistry

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