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Theoretical Investigation on the Control of Macrocyclic Dihydroazulene/Azobenzene Photoswitches

Mostafa Abedi,[†] Mátyás Pápai,[†] Niels E. Henriksen,[†] Klaus B. Møller,[†] Mogens
Brøndsted Nielsen,[‡] and Kurt V. Mikkelsen^{*,‡}

[†]*Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby,
Denmark*

[‡]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100
Copenhagen Ø, Denmark*

E-mail: kmi@chem.ku.dk

Abstract

In this work, we focus on macrocyclic structures comprised of two dihydroazulene (DHA) units and one azobenzene (AZB) unit and the possibility for photoisomerizing one unit selectively by tuning the excitation energies of each individual unit. An unfortunate overlap between absorption bands of DHA and AZB as well as *trans*- and *cis*-AZB prevent us to have a full control on these macrocyclic structures and their absorption need to be separated. By means of time-dependent density-functional theory (TD-DFT) calculations, we investigate the effects of *ortho* substitutions of the AZB unit by fluorine and chlorine atoms on the absorption spectra of the DHA/AZB macrocycles. The calculations on the isolated AZB show that substitutions lead to distortion of the planar molecular structure, due to the repulsive interactions between halogen atoms, and to a systematic blue-shift of the $\pi\pi^*$ bands between 25 nm to 50 nm. Moreover, separations between 10 nm to 48 nm, depending on the substituent, are observed in the $n\pi^*$ bands. The results from the calculations on the substituted AZB-DHA-DHA macrocycles reveal significant separations of the DHA/*trans*-AZB and *trans*-/*cis*-AZB absorption bands by values of 46-73 nm and 15-52 nm, respectively, for different substitutions. We realize that *ortho* substitutions with mixed fluorine-chlorine atoms can provide the best separations in both $\pi\pi^*$ and $n\pi^*$ bands of AZB-DHA-DHA photoisomers. The results of this work offer a guideline for designing and synthesising new, efficient, and highly controllable materials applicable in devices for optical data storage and molecular electronics.

Introduction

Selective excitation of photoswitchable materials is of particular importance for controlling their photoexcitation properties. Macrocyclic structures built on the basis of several chromophores provide a convenient way to control the accessibility of particular building units. Azobenzenes (AZBs) present one important class of photoswitches that can reversibly be interconverted between *cis* and *trans* isomers under light irradiation.¹ 1,1-

Dicyanodihydroazulenes (DHAs) are another class of compounds that upon photoexcitation undergo an electrocyclic ring-opening reaction to form vinylheptafulvenes (VHFs)² that can exist in *s-cis* or *s-trans* conformers.³ The VHF isomer is not photoactive, but will in time thermally return to the more stable DHA one. Some of us have recently incorporated two DHA units and one AZB unit into a macrocyclic structure that can potentially exist as six isomers (in addition to various stereoisomers due to the stereocenter at C8a of DHA) as shown in Figure 1: *trans*-AZB-DHA-DHA (3 stereoisomers), *cis*-AZB-DHA-DHA (3 stereoisomers), *trans*-AZB-DHA-VHF (two stereoisomers), *cis*-AZB-DHA-VHF (two stereoisomers), *trans*-AZB-VHF-VHF, and *cis*-AZB-VHF-VHF.⁴ Photoisomerization of *trans*-AZB-DHA-DHA by irradiation at 365 nm leads to a simultaneous isomerization of *trans*-AZB to *cis*-AZB and of both DHAs into VHFs, ultimately forming *cis*-AZB-VHF-VHF. This isomer could be converted into *trans*-AZB-VHF-VHF by irradiation at 410 nm.⁴ These macrocycles can enable us to control accessibility to particular building units. An unfortunate overlap of DHA and *trans*-AZB as well as *trans*- and *cis*-AZB absorption bands leads to non-selective photoisomerization of *trans*-AZB-DHA-DHA. For a selective *trans*-to-*cis*-AZB and DHA-to-VHF photoisomerization, their absorption bands need to be separated. Such selective photoisomerizations could be of particular relevance for optical data storage devices, where individual units can be accessed in a controlled manner. For the case of AZBs, it has been shown that introducing halogen atoms such as fluorine and chlorine to *ortho* positions can effectively separate the $n \rightarrow \pi^*$ absorption bands in *cis* and *trans* isomers.^{5,6} For example, Bléger *et al.* using UV/Vis spectroscopy reported a 50 nm separation of the $n \rightarrow \pi^*$ band for tetra-*ortho*-fluoro-substituted AZB attached to -COOCH₂-CH₃ electron withdrawing groups in *para* positions. Herein, we present a theoretical investigation based on calculations of the absorption spectra of fluoro- and chloro-*ortho*-functionalized AZBs, introduced into macrocyclic structures with the aim of separating the DHA and AZB absorption bands. This can pave the way for the design of new and controllable molecules that exhibit sequential photoisomerizations.

Computational Methods

The geometry optimizations, vertical excitation energy and oscillator strength calculations were carried out using the GAUSSIAN 16 Rev A.03 suite of programs⁷ at the density-functional theory (DFT) and time-dependent DFT (TDDFT) levels utilizing the range-separated CAM-B3LYP functional⁸ in combination with the 6-31+G(d) basis set. The CAM-B3LYP functional has been successfully used for the DHA/VHF photoswitches and shown reliable performance.^{9–11} We perform frequency calculations at the same level to ensure that the optimized structures are at the minima on the PES and obtain Gibbs free energies at 298 K. The vertical excitation energies were computed by TDDFT based on the linear response (LR) formalism for ten lowest-energy singlet electronic states. Gaussian functions with full width at half maximum (FWHM) of 0.2 eV was used to account for the thermal broadening in the computed absorption spectra, guided by the experimental spectrum. It is well-known that excited-state phenomena such as absorption, radiative and non-radiative processes can be significantly affected by a solvent.^{12–18} It has always been a challenge to find an appropriate model to correctly and accurately characterize solvent effects by including the key parameters like hydrogen bonding and a polarizable environment. The accuracy of solvent models can be altered for various solvents and particularly, for affected solutes. In order to find a best-performing model for our study, we benchmark different solvation models. The details of calculations and results are discussed in S1 section of the Supporting Information. The results of the assessment indicate a good performance of the QM/IEFPCM model in prediction of the absorption spectra of the two *trans*-AZB-DHA-DHA and *cis*-AZB-VHF-VHF macrocyclic isomers, compared to the experimental data. The reliability of PCM in the description of solvent effects on the excited-state energetics has been previously shown for different compounds.^{12–14,16–20} For example, González and co-workers¹⁴ evaluated several explicit and implicit solvation models to describe the effects of hydrogen bonding and bulk solvent on the electronic excited states of pyridine, tropone and tropothione molecules. They showed a reliable performance of the PCM approach in the prediction of excitation energies

corresponding to $\pi\pi^*$ and $n\pi^*$ transitions, the latter transition dominated by strong hydrogen bonding effects.

Results and Discussion

The relative Gibbs free energies of all six macrocycles in their electronic ground state were computed in the QM/Gas and QM/IEFPCM models to compare their stability. According to Table 1, *trans*-AZB-DHA-DHA and *cis*-AZB-VHF-VHF are the most and least stable isomers, respectively. The order of stability of all the isomers is *trans*-AZB-DHA-DHA > *trans*-AZB-DHA-VHF > *trans*-AZB-VHF-VHF > *cis*-AZB-DHA-DHA $\approx$ *cis*-AZB-DHA-VHF > *cis*-AZB-VHF-VHF. It is also realized that the contribution of *cis* to *trans* AZB isomerization in energy stabilization of the macrocycles is larger than the VHF-DHA conversion. The solvation free energy (ΔG_{solv}) calculations in the QM/IEFPCM model show that the macrocycles are stabilized in solution by around 100 kJ/mol. From these calculations, the *cis*-AZB-VHF-VHF and *trans*-AZB-DHA-DHA isomers exhibit the two extremes, i.e., the largest and smallest sensitivity to the solvent, respectively, compared to the other isomers.

Two important absorption bands for these isomeric macrocycles have been experimentally determined: band I at 460-490 nm and band II at 315-330 nm.⁴ These two bands are related to the maximum of absorption (λ_{max}) of each individual macrocycle building units: *trans*-AZB-R1 (R1 refers to -COOCH₂-Ph electron withdrawing groups in the *para* positions), *cis*-AZB-R1, DHA and *s-trans*-VHF. Table 2 reports the computed vertical excitation energies of these units at λ_{max} . The results show that the predicted λ_{max} values for the units agree very well with the experimental values in ACN. In Figure 2, we display the absorption spectra of each unit indicating the dominant contributions of the *s-trans*-VHF and *trans*-AZB-R1 units in bands I and II of the macrocycles, respectively. For further analysis, the nature of electronic transitions corresponding to bands I and II of the *trans*-AZB-DHA-DHA and

cis-AZB-VHF-VHF isomers were investigated by calculating the electron-hole pair natural transition orbitals (NTOs) for the dominant excited states. We realize the main contributions of $\pi \rightarrow \pi^*$ transition to the bands, as seen in Figures S3 and S4, are localized only on the *s-trans*-VHF unit in *cis*-AZB-VHF-VHF and on the *trans*-AZB-R1 and DHA units in *trans*-AZB-DHA-DHA.

In Figure 3, we collect the absorption spectra of all six macrocycle isomers. As we noted, band I is dominated by *s-trans*-VHF unit and thus an identical spectra should be seen for the macrocycle isomers that only undergo *cis* to *trans*-AZB-R1 isomerization. According to Figure 3, similar absorption spectra can be seen for *trans*- and *cis*-AZB-VHF-VHF, *trans*- and *cis*-AZB-DHA-VHF, and *trans*- and *cis*-AZB-DHA-DHA isomers indicating a good agreement between our calculated results and the experimental observations⁴. The calculated absorption spectra can be used to identify the pathways of isomerization. It can be found, for example, from direct relation between the absorption intensity of band I and the formation of the VHF unit. Starting from *trans*- or *cis*-AZB-DHA-DHA with no DHA-VHF conversion and the minimum intensity through the intermediate *trans*- or *cis*-AZB-DHA-VHF one, we reach to *trans*- or *cis*-AZB-VHF-VHF with the full conversion of the DHAs to VHF and maximum intensity.

As seen in Figure 2, the overlap between the absorption bands ($\pi\pi^*$) of *trans*-AZB-R1 and DHA hampers us to selectively excite these two units in the macrocycles. Similarly, the strong overlap between *cis*- and *trans*-AZB-R1 isomers in band I ($n\pi^*$) also needs to be separated for the selective excitation of these two isomers. We investigate the influence of *ortho* substitutions of the AZB-R1 units by halogen atoms, fluorine and chlorine, on the absorption spectra of the macrocycles. For this purpose, we first systematically substitute the hydrogen atoms in *ortho* positions of the isolated AZB-R1 isomers by fluorine and chlorine atoms, reoptimize the structures, and compute the absorption spectra. Figure 4 presents the computed spectra of different substitutions of *cis*- and *trans*-AZB-R1 isomers. The results show a systematic blue-shift (from 25 nm to 50 nm) of $\lambda_{\max}$ in the $\pi\pi^*$ bands of *trans*-AZB-R1

by going from the unsubstituted isomer to the one substituted by four chlorine atoms, while such shift cannot be seen in the case of the *cis*-AZB-R1 isomer. This leads to a notable band separation of DHA from *trans*-AZB-R1. The observed separation is interpreted as follows. The *ortho* substitutions of *trans*-AZB-R1 by fluorine and chlorine atoms remove the planarity of the AZB structure by rotation of the phenyl rings around the C-N bond and minimizing the sterical hindrance. This is due to the repulsive interactions between halogen atoms, in which the tetra-fluoro and tetra-chloro isomers exhibit the smallest and largest distortions, respectively, due to the size of atomic radius. By analysis of the NTOs, shown in Figure 5, we realize that the *ortho*-halogen substitutions stabilize π molecular orbital energies induced by $\sigma - \pi$ mixing leading to increase of the $\pi\pi^*$ energy gap from 6.3 eV to 7.1 eV and 7.6 eV for the unsubstituted, tetra-fluoro and tetra-chloro isomers, respectively, and thus the blue-shift of absorption bands. We calculated the absorption spectrum and NTOs of the planar isomer substituted by four chlorine atoms (without geometry optimization). The results show the same spectrum and molecular orbitals as the planar unsubstituted one, confirming that the observed blue-shift is indeed due to the distortion of the molecular structure.

The $n\pi^*$ bands (HOMO $\rightarrow$ LUMO transitions) of the *trans*-AZB-R1 isomer are also affected by the *ortho* substitutions, as shown in the inset of Figure 4. The most apparent effect of replacing hydrogen atoms with fluorine or chlorine ones can be seen in the growth of this band. This is a consequence of distortion of the planar molecular structure by the substitutions and reduction of point group symmetry of the molecule from C_2 to C_1 , which leads to an increase in transition dipole moment and thus in transition probability (oscillator strength). We note that for the parent AZB molecule (without any *ortho* and *para* substitutions), with C_{2h} symmetry, the oscillator strength of the $n\pi^*$ band is exactly zero. This is because the related $A_g \rightarrow B_g$ transition is forbidden by the Laporte selection rules. Most importantly, we observe separations of the $n\pi^*$ bands between 10 nm to 48 nm, providing a possibility to excite selectively either *cis* or *trans* AZB-R1 isomer. To understand the $n\pi^*$ separation, we analyze the corresponding molecular orbital energies. We

find that *ortho*-halogen substitutions of the *trans*-AZB-R1 isomer do not change considerably the orbital energy of n and π^* leading to only a small difference in $\lambda_{\max}$ (between 465 nm and 474 nm; see the solid lines in the inset of Figure 4). For the tetra-chloro *trans*- and *cis*-AZB-R1 isomers, the orbital energy of both n and π^* are similar causing only 10 nm separation, while in the tetra-fluoro *trans*-AZB-R1 case, we observe a stabilization of the π^* -orbital by 0.3 eV with respect to the *cis* isomer resulting in 48 nm separation. The larger separation in tetra-fluoro AZB may be ascribed to more reduction of the electron density on the rings by fluorine atoms than chlorine, due to the larger electronegativity, resulting in stabilization of the π^* -orbital. It should be noted that, the calculated value of 48 nm for the *cis/trans* separation of functionalized AZB-R1 with four fluorine atoms is in excellent agreement with the experimental value of 50 nm reported by Bléger *et al.*⁵ in ACN. Moreover, we study the influence of -COOCH₂-Ph electron withdrawing groups in the *para* positions of the tetra-*ortho*-fluoro substituted *trans*-AZB-R1 isomer. We find that the *para* substitutions lead to 10 nm and 17 nm red shift of $\pi\pi^*$ and $n\pi^*$ bands, respectively, consistent with the experimental values with -COOCH₂-CH₃ groups (~ 8 nm for both bands)⁵. The observed red shifts are attributed to the reduction of the electron density on the rings and N=N bond by -COOCH₂-Ph electron withdrawing groups leading to lowering the π^* -orbital energies and thus decreasing $\pi\pi^*$ and $n\pi^*$ energy gaps.

The calculations on the isolated AZB-R1 isomer have shown a significant blue-shift in the $\pi\pi^*$ band of the *trans*-AZB-R1 isomer by *ortho*-halogen substitutions suggesting a possibility for a separation between the DHA and *trans*-AZB-R1 bands in the macrocycle. We study the impacts of *ortho* substitutions of the AZB-R1 units on the absorption spectrum of the macrocycles. *trans*-AZB-DHA-DHA is the most stable isomer and the photoinduced excitation initiates from this isomer. Therefore, the substitution effects are mostly important for this case. Figure 6 illustrates the absorption spectra of unsubstituted and fluoro- and chloro-substituted of these two macrocycle isomers. Interestingly, substitutions by fluorine and, particularly, chlorine or mixed fluorine-chlorine atoms lead to the full separation

of band II ($\pi\pi^*$), for individual DHA and *trans*-AZB-R1 bands. According to Table 3, the DHA/*trans*-AZB-R1 band separation varies between 46 nm to 73 nm. Furthermore, we observe a considerable separation between 15 nm to 52 nm for band I ($n\pi^*$) related to *cis*- and *trans*-AZB-R1 isomers (see Table 3). Our results show that among the substituted AZB-DHA-DHA isomers, those with mixed fluorine-chlorine atoms, AZB(Cl2-F2)-DHA-DHA and AZB(ClF-ClF)-DHA-DHA, exhibit noticeable separations in both $\pi\pi^*$ and $n\pi^*$ bands, which allow the selective excitation of each units of the macrocycles. Finally, we survey the effects of *ortho*-halogen substitutions on the relative Gibbs free energies for all six macrocycles. The results show that the substitutions do not alter the order of energy stability compared to the unsubstituted isomers.

Conclusion and Outlook

In this work, we present a computational investigation on the newly synthesized macrocyclic DHA/AZB photoisomers. Upon light radiation by 365 nm, the most stable *trans*-AZB-DHA-DHA isomer converts to *cis*-AZB-VHF-VHF.⁴ The overlap between the absorption bands of the DHA and *trans*-AZB-R1 units as well as of *trans*- and *cis*-AZB-R1 isomers prevent us to control the photoexcitation behaviour of these macrocycles by a selective excitation of each building units. By means of TD-DFT calculations, we study the effects of *ortho*-fluoro and -chloro substitutions of the isolated AZB-R1 isomers on the absorption spectra. The results show a systematic blue-shifting in the $\pi\pi^*$ bands from unsubstituted towards tetra-*ortho*-fluoro and tetra-*ortho*-chloro isomers. We find a direct relationship between the distortion of the AZB structure and the magnitude of absorption blue-shifting. The analysis of NTOs reveals that the molecular structural distortions, caused by the *ortho*-halogen substitutions, stabilize the π molecular orbitals induced by $\sigma - \pi$ mixing and therefore increasing the $\pi\pi^*$ energy gap. Furthermore, we observe a considerable separation between 10 nm to 48 nm in the $n\pi^*$ bands by the substitutions. The effects of *ortho* functionalizations of the

AZB-R1 unit within the macrocycle was then investigated. Our calculations indicate that *ortho* substitutions by mixed fluorine and chlorine atoms make the absorption bands of the DHA/*trans*-AZB-R1 and *trans*-/*cis*-AZB-R1 units well-separated and allows fully selective excitation of each unit. The results of this study provide valuable information for designing and synthesising new, efficient, and highly controllable materials, applicable in devices for optical data storage.

In future works, the computational results of this work could be verified experimentally by synthesis and characterization of the halogen substituted structures. Furthermore, it would be worthwhile to study the effects of *ortho*-halogen substitutions of the AZB unit on the photochemical properties of the macrocycles. It has been shown that internal coordinates involving nitrogen atoms and the neighboring carbon atoms in AZB play a dominant role in the *cis*↔*trans* photoisomerization.^{1,21} Therefore, it can be speculated that the substitutions of the AZB unit can affect the mechanism of photorelaxation processes of the DHA/AZB macrocycles occurring upon light absorption. This certainly deserves a comprehensive study from both experimental and theoretical perspectives.

Associated Content

Supporting Information

Details of calculations and results for the assessment of solvation models and electron-hole pair natural transition orbitals (NTOs) of the dominant excited states involved in bands I and II of the *cis*-AZB-VHF-VHF and *trans*-AZB-DHA-DHA isomers calculated using the QM/IEFPCM model at the TD-CAM-B3LYP/6-31+G(d) level of theory.

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Figure 1: Schematic illustration of molecular structures of *trans*-AZB-DHA-DHA (*RS*; *meso*) and *cis*-AZB-VHF-VHF isomers.

Table 1: Relative Gibbs free energies (in kJ/mol) with respect to *trans*-AZB-DHA-DHA and solvation free energies (ΔG_{solv}) (in kJ/mol) of the six macrocycles calculated within QM/Gas and QM/IEFPCM models at the CAM-B3LYP/6-31+G(d) level of theory.

	QM/Gas	QM/IEFPCM	ΔG_{solv}
<i>trans</i> -AZB-DHA-DHA	0.0	0.0	-93.6
<i>cis</i> -AZB-DHA-DHA	55.0	48.9	-99.8
<i>trans</i> -AZB-DHA-VHF	19.6	10.4	-102.8
<i>cis</i> -AZB-DHA-VHF	61.5	46.8	-108.3
<i>trans</i> -AZB-VHF-VHF	34.9	21.7	-106.8
<i>cis</i> -AZB-VHF-VHF	78.6	56.1	-116.1

Table 2: Vertical excitation energies (in nm) of DHA, *s-trans*-VHF, *trans*-AZB-R1 and *cis*-AZB-R1 units as well as *trans*-AZB-DHA-DHA and *cis*-AZB-VHF-VHF at $\lambda_{\max}$ using QM/IEFPCM model computed at the TD-CAM-B3LYP/6-31+G(d) level of theory. The values in parentheses are computed oscillator strengths. The values in square brackets are experimental molar absorptivity ϵ in $\text{M}^{-1} \text{cm}^{-1}$ taken from Ref. 4.

		QM/IEFPCM	Experimental
DHA	$\pi\pi^*$	353 (0.5278)	354 [16500]
<i>s-trans</i> -VHF	$\pi\pi^*$	443 (0.9678)	472 [32000]
<i>trans</i> -AZB-R1	$\pi\pi^*$	328 (1.4109)	326 [29100]
	$n\pi^*$	465 (0.0007)	462 [610]
<i>cis</i> -AZB-R1	$n\pi^*$	441 (0.0427)	434 [1100]
<i>trans</i> -AZB-DHA-DHA	band I	471 (0.0213) $\{\pi\pi^* \text{ on AZB \& DHA}\}$	462 [620]
	band II	332 (1.2333) $\{\pi\pi^* \text{ on AZB \& DHA}\}$	330 [46100]
<i>cis</i> -AZB-VHF-VHF	band I	460 (0.9256) $\{\pi\pi^* \text{ on VHF}\}$	492 [32300]
	band II	303 (0.1488) $\{\pi\pi^* \text{ on VHF}\}$	316 [27800]

Figure 2: The absorption spectra of the DHA, *trans*-AZB-R1, *s-trans*-VHF and *cis*-AZB-R1 units computed using the QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory. The spectra are broadened by Gaussian functions with FWHM=0.2 eV.

Figure 3: The absorption spectra of the six macrocycles computed within QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory. The spectra are broadened by Gaussian functions with FWHM=0.2 eV.

Figure 4: The absorption spectra of the unsubstituted and fluorine- and chlorine-substituted AZB-R1 isomers computed by the QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory. The solid and dashed lines represent the spectra for *trans*-AZB-R1 and *cis*-AZB-R1 isomers, respectively. The spectra are broadened by Gaussian functions with FWHM=0.2 eV.

Figure 5: Electron-hole pair natural transition orbitals (NTOs) of the dominant excited states involved in band II ($\pi\pi^*$) of the (a) *trans*-AZB(H4), (b) *trans*-AZB(F4), (c) *trans*-AZB(Cl2-F2), (d) *trans*-AZB(ClF-ClF) and (e) *trans*-AZB(Cl4) calculated by the QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory. The ϵ values are the corresponding orbital energies in eV. The λ values quantify the fraction of pair contribution to the excitation.

Figure 6: The absorption spectra of the unsubstituted and *ortho* fluorine- and chlorine-substituted AZB-DHA-DHA macrocyclic isomers computed by the QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory. The solid and dashed lines represent the spectra for *trans* and *cis* isomers, respectively. Color codes: AZB-DHA-DHA–black; AZB(F4)-DHA-DHA–blue; AZB(Cl2-F2)-DHA-DHA–green; AZB(ClF-ClF)-DHA-DHA–cyan; AZB(Cl4)-DHA-DHA–red. The spectra are broadened by Gaussian functions with FWHM=0.2 eV.

Table 3: Vertical excitation energies (in nm) of the DHA, *trans*-AZB-R1 and *cis*-AZB-R1 units at $\lambda_{\max}$ as well as the DHA/*trans*-AZB-R1 and *cis*/*trans*-AZB-R1 separations (in nm) of band II ($\pi\pi^*$) of *trans*-AZB-DHA-DHA and band I ($n\pi^*$) of *cis*-AZB-DHA-DHA isomers substituted by fluorine and chlorine atoms in the *ortho* positions calculated using QM/IEFPCM solvation model at the TD-CAM-B3LYP/6-31+G(d) level of theory.

	band II ($\pi\pi^*$)			band I ($n\pi^*$)		
	DHA	<i>trans</i> -AZB-R1	Separation	<i>trans</i> -AZB-R1	<i>cis</i> -AZB-R1	Separation
<i>trans</i> -AZB(F4)-DHA-DHA	354	308	46	492	-	52
<i>cis</i> -AZB(F4)-DHA-DHA	343	275	68	-	440	
<i>trans</i> -AZB(Cl4)-DHA-DHA	354	283	71	482	-	15
<i>cis</i> -AZB(Cl4)-DHA-DHA	344	275	69	-	467	
<i>trans</i> -AZB(Cl2-F2)-DHA-DHA	355	283	72	471	-	26
<i>cis</i> -AZB(Cl2-F2)-DHA-DHA	343	274	69	-	445	
<i>trans</i> -AZB(ClF-ClF)-DHA-DHA	355	282	73	481	-	34
<i>cis</i> -AZB(ClF-ClF)-DHA-DHA	343	278	65	-	447	

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