



Theoretical insight into azobis-(benzo-18-crown-6) ether combined with the alkaline earth metal cations



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ABSTRACT

It is desirable to research the photoswitchable supramolecular catalysts by theoretical methods. The azobis-(benzo-18-crown-6) ether (butterfly-AZO for short) combined with the alkaline earth metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) investigated by using both density functional theory (DFT) and reactive molecular dynamics (reactive MD) simulations in this article. DFT calculations demonstrated that butterfly-AZO... Ba^{2+} is a suitable photocontrol catalytic candidate and its isomerization is mainly controlled by the N=N rotational mechanism. Furthermore, 100 independent reactive MD simulations demonstrated that 100% *trans* isomers of butterfly-AZO... Ba^{2+} translated to the *cis* forms, in good agreement with the experimental data of ~95%.

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1. Introduction

Metal cation coordination chemistry has been the main stream in supramolecular science. Besides, the well known metal cation complexing agents are molecular receptors based on macrocyclic ligands, such as crown ethers [1], TOC sheets [2], porphyrin blocks [3] and so on. These cyclic molecules which composed of oxygen donor atoms can bind cations in their cavities, especially alkali metal ions [4–6] and alkaline earth metal ions [7,8]. Azobenzene, one of the most famous photosensitive chromophore unit, can undergo *trans*–*cis* isomerization in response to light irradiation [9–12], thermal induction [13,14] and electric fields stimuli [15–18]. Majority studies have carried out to exploit the photo-switching properties of azobenzene to yield new classes of smart materials such as molecular switches [19–21], motors [22,23], and so on. For instance, by introducing the azobenzene moiety into the crown ethers, the function of crown ethers can be controlled by an on-off light switch [24–26].

A bis(crown ether) bridging two crown ether rings by an azobenzene moiety, the azobis-(benzo-18-crown-6) ether for example, is also photoresponsive. Because the molecule of azobis-(benzo-18-crown-6) ether is shaped like a butterfly, named butterfly-AZO in this article. It can be able to accommodate alkaline earth metal cations with its two adjacent crown ether rings, and the complexes are expected to selectively catalyze the basic

ethanolysis of esters and anilides. One of the metal cations serves as a binding unit for the carboxylate anchoring group, and the other delivers an activated ethoxide ion to the substrate carbonyl [27]. The catalytic activities can be reversibly controlled by light-driven changes in geometric structure of the molecule between *trans* (anti-parallel) and *cis* (parallel) forms. When the “butterfly wings” fold (*trans* form → *cis* form), the geometry is more favorable for the chemical reaction of reactants, and this state is “ON”; conversely, is “OFF” (shown in Scheme 1).

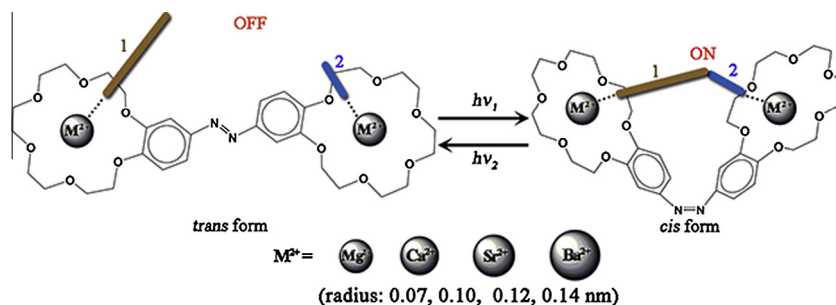
The studies of artificial photo-controlled catalysis systems are instructive. Computational and theoretical methods are powerful tools to calculate the properties of complexes, such as geometric structures, binding energies, absorbance spectra, mechanism of isomerization and quantum yield. In this work, the complexes of butterfly-AZO with the alkaline earth metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} or Ba^{2+}) were studied theoretically. Our results can provide some theoretical basis for the development of supramolecular catalysts.

2. Computational details

DFT calculations were performed on the complexes of butterfly-AZO and metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) at the B3LYP/6-31G(d, p) level. The LANL2DZ effective core potentials for the alkaline earth metal cations were employed in DFT calculations. Since the real systems are electrically neutral, two chloride ions were added on both sides of the metal cations. The interaction

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Scheme 1. Photoisomerization of the butterfly-AZO complexing with the alkaline earth metal ion (Mg^{2+} , Ca^{2+} , Sr^{2+} or Ba^{2+}). The catalytic activities can be reversibly controlled by light-driven changes in geometric structure of the molecule between *trans* and *cis* forms. When the “butterfly wings” fold, the geometry is more favorable for the chemical reaction of reactants, and this state is “ON”; conversely, is “OFF”.

energy between an ether ring and a metal cation, E_{int} , was calculated as:

$$E_{\text{int}} = \frac{E_{\text{total}} - (E_{\text{butterfly-AZO}} + E_{\text{MCl}_2})}{2} \quad (1)$$

The basis set superposition error (BSSE) [28] was corrected by counterpoise method [29] in the binding energies calculations. The absorption spectra were predicted by using time-dependent density functional theory (TDDFT). All the QM calculations were carried out with Gaussian 09 program [30].

Reactive molecular dynamics (reactive MD) simulations [31] were employed to simulate the dynamics of *trans*-*cis* isomerization of butterfly-AZO and butterfly-AZO... Ba^{2+} in vacuo, respectively. The polymer consistent force field (PCFF) [32] was adopted. Since the parameters of alkaline earth metal cations are absent in PCFF, sodium was selected and the system was fitted by the charge from quantum mechanics calculations of butterfly-AZO... Ba^{2+} . All MD simulations were carried out using the discover module in Materials Studio package [33]. The canonical NVT ensemble at 298 K was using a Nose thermostat [34]. The velocity Verlet algorithm [35] was applied using a time step of 1 fs.

3. Results and discussion

3.1. Optimized structures and binding properties

Model compounds were all optimized into their local minima of the potential energy surfaces by B3LYP/6-31G(d,p)//LANL2DZ calculations. The DFT results for the equilibrium geometries are given in Table 1.

The bond length of $\text{N}=\text{N}$ ($r_{\text{N}=\text{N}}$) and $\text{C}-\text{N}$ ($r_{\text{C}-\text{N}}$) of the butterfly-AZOs are about 1.25 Å, 1.43 Å for *cis* forms and 1.26 Å, 1.41 Å for *trans* forms, respectively. The elongation of the azo bond concomitantly with the shortening of the $\text{N}-\text{C}$ indicates a more

delocalized π system overlap *trans* than *cis* derivatives. Besides, the optimized *trans* structures are almost planar, which is reflected by the dihedral angles of $\text{C}=\text{N}=\text{N}-\text{C}$ (ω_1) and $\text{N}=\text{N}-\text{C}-\text{C}$ (ω_2). Furthermore, a gradually reduce of ω_1 and ω_2 of *cis*-butterfly-AZO... Mg^{2+} to *cis*-butterfly-AZO... Ba^{2+} is observed, and this change indicates that the benzene rings of AZOs tending to form parallel structures.

In order to characterize the conformations of ether rings in butterfly-AZOs, $r_{\text{O} \cdots \text{O}}$ (Å), deviation (%) and α (°) are defined as shown in Scheme 2. Among them, the former two represent the size and shape of the ether rings, and the last one characterizes roughly the relative position of the ether rings to the *trans*-AZO plane. It can be found that the ether rings in *trans* structures become more large and round when they complexing with Ba^{2+} cations ($r_{\text{O} \cdots \text{O}} = 5.61$ Å, deviation = $-1.9 \sim 1.1\%$ for *trans* form), this is presumably related to the large cations radius of Ba^{2+} . However, the ether rings become elliptic under the influence of the distribution of lone pair electrons of $\text{N}=\text{N}$ altering from both sides in *trans* form to one side in *cis* form. In addition to the change of the ether rings' shape, the relative position of ether rings is also changed when *trans*-butterfly-AZO complexing with the different alkaline earth metal cations. The value of α is 133.1° (with Mg^{2+}), 146.1° (with Ca^{2+}), 158.7° (with Sr^{2+}) and 176.6° (with Ba^{2+}) respectively, which indicates a more planar molecular structure of *trans*-butterfly-AZO... Ba^{2+} . For better understanding, the optimized structures of butterfly-AZO complexing with the different alkaline earth metal cations are shown in Fig. 1. On the left are the *trans* isomers. Intuitively, “butterfly wings” gradually flat from top to bottom. The distance between two Ba^{2+} cations is the largest among *trans*-butterfly-AZOs. On the right are the *cis* isomers. “Butterfly wings” become face-to-face when complexing with Ba^{2+} , and the distance between two Ba^{2+} cations is the shortest among *cis*-butterfly-AZOs. From the discussion of geometric structures, butterfly-AZO... Ba^{2+} is the most suitable catalytic candidate obviously.

Table 1

The selected structural parameters and the interaction energies of the *trans*- and *cis*-butterfly-AZO combined with the alkaline earth metal ion (Mg^{2+} , Ca^{2+} , Sr^{2+} or Ba^{2+}), respectively.

Butterfly-AZO	ion	$r_{\text{N}=\text{N}}$ (Å)	$r_{\text{C}-\text{N}}$ (Å)	$\omega_{\text{C}-\text{N}=\text{N}-\text{C}}$ (°)	$\omega_{\text{N}=\text{N}-\text{C}-\text{C}}$ (°)	$r_{\text{O} \cdots \text{O}}$ (Å)	Deviation (%)	α (°)	Interaction energy (kcal/mol)
trans-	–	1.26	1.41	179.8	178.5	5.54	$-7.4 \sim 4.6$	152.0	–
	Mg^{2+}	1.26	1.42	179.3	175.4	5.44	$-7.5 \sim 8.7$	133.1	–57.337
	Ca^{2+}	1.26	1.41	178.7	179.8	5.30	$-0.9 \sim 0.3$	146.1	–75.648
	Sr^{2+}	1.26	1.41	179.1	178.3	5.45	$-1.3 \sim 1.7$	158.7	–73.653
	Ba^{2+}	1.26	1.41	179.8	177.1	5.61	$-1.9 \sim 1.1$	176.6	–64.735
cis-	–	1.25	1.43	11.2	146.5	5.49	$-27.3 \sim 25.1$	–	–
	Mg^{2+}	1.25	1.42	9.6	159.3	5.54	$-16.3 \sim 21.9$	–	–59.848
	Ca^{2+}	1.25	1.43	8.9	160.2	5.53	$-9.3 \sim 22.6$	–	–72.274
	Sr^{2+}	1.25	1.43	6.2	134.7	5.63	$-6.8 \sim 21.4$	–	–68.798
	Ba^{2+}	1.25	1.44	6.7	133.9	5.74	$-7.0 \sim 19.6$	–	–53.451

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