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Title: Intermolecular London Dispersion Interactions of Azobenzene Switches for Tuning Molecular Solar Thermal Energy Storage Systems

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Abstract: The performance of molecular solar thermal energy storage systems (MOST) depends i.a. on the amount of energy stored. Azobenzenes have been investigated as high-potential materials for MOST applications. In the present study it could be shown that intermolecular attractive London dispersion interactions stabilize the (E)-isomer in bisazobenzene linked by different alkyl bridges. Differential scanning calorimetry (DSC) measurements revealed, that this interaction leads to an increased storage energy per azo-unit of more than 3 kcal/mol compared to the parent azobenzene. The origin of this effect has been supported by computation as well as X-ray analysis. In the solid state structure attractive London dispersion interactions between the C=H of the alkyl bridge and the π-system of the azobenzene could be clearly assigned. This concept will be highly useful in designing more effective MOST systems in the future.

The development of energy storage solutions is one of the most urgent tasks for modern societies. While there is tremendous effort in storing electrical energy, the ability of harvesting the energy of the sun and release it at a given point of time as heat is also of importance since heating and cooling constitutes nearly half of the final energy use in the EU. In this respect molecular solar thermal energy storage (MOST) systems, sometimes also referred as solar fuels, represent an attractive solution for both short (hours) and long term (seasonal) solar energy storage. The general principle is based on converting a molecule from one state into another metastable state with higher energy. The concept has been proposed already in the 1970s. In contrast to altering the azobenzene moiety itself the interaction of the individual molecules with each other can also contribute to increase the overall storage energy. Stabilizing groups can in some cases shift the absorption to longer wavelength. There have been different strategies to increase the storage energy. Stabilizing groups can influence the (E)-(Z)-energy difference even by subtle interactions such as London dispersion. Feng and also later Grossmann used nanotemplating as a tool. Another approach is based on incorporating the azobenzene into macrocyclic structures to utilize strain energy in the (Z)-isomer. Alternatively, azobenzenes can be connected to carbon nanotubes to improve the storage energy.

In contrast to altering the azobenzene moiety itself the interaction of the individual molecules with each other can also contribute to increase the overall storage energy. The connection between the molecules should be loose enough, that they can be easily broken upon isomerization and rebuild during the back reaction. Therefore, weak interactions, such as London dispersion as part of the van-der-Waals interaction might be a good choice adding beneficial stabilizing effects to the system. Herein, we envisioned probing these interactions by connecting two azobenzenes with different sized linkers. Although the stored energy/weight is a key parameter to quantify the performance of a MOST system, the fundamental insights might promote the design of more efficient MOST systems.
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As linkers between the azobenzene units, a methylene bridge was chosen. Such a methylene connector will keep the azobenzene sufficiently apart due to the low flexibility, but also allows for the introduction of substituents to induce intermolecular interactions. To harvest the London dispersion energies, alkyl substituents with different sizes were introduced. Specifically, the interaction of the (E)-azobenzene with the surface of alkyl groups was targeted. Hence, besides dimethyl, cyclic alkanes such as cyclopentyl, cyclohexyl and cycloheptyl were selected. Such a methylene connector will keep the azo group sufficiently apart due to the low flexibility, but also allows for the physical stability of the photostationary state of all-(Z), (E,Z), all-(E) of ~65%, 25%, 10% was observed. Compounds 4a and 4d showed higher all-(Z) ratios of up to 75%. As the thermal all-(Z) to all-(E) isomerization is crucial for the possible storage time, the process has been studied exemplarily for compound 4a by 1H NMR spectroscopy revealing a t1/2 for the all-(Z) of 2.5 h (SI, Table S7).

To study the thermodynamic properties, differential scanning calorimetry (DSC) has been performed on all compounds. (Table 1 & SI). The storage enthalpies of molecules 4a-d as well as for unsubstituted azobenzene were measured by DSC on neat samples that have been irradiated at 365 nm in solution (10 mg / 3 mL in dichloromethane-d2, SI, Figure S8, S10, S12, S14, S16). The solvent was removed under continuous irradiation at 365 nm and exclusion of ambient light by blowing a N2-stream over the sample. Then, 1H NMR spectroscopy was conducted to determine the degree of conversion (SI, Figure S7, S9, S11, S13, S15). The molar storage enthalpy of a single (Z)-azo group in the mixture of the (E,E), (E,Z) and (Z,Z)-isomers was calculated based on the measured storage energy density and the degree of conversion. Although the electronic and steric properties of all investigated individual azobenzene units are the same, there is a significant deviation in the energy difference between the (E)- and the (Z)-isomer of the studied compounds. The highest storage enthalpy was determined for the cyclohexane substituted derivative 4c, followed by compound 4b with the cyclopentyl bridge. The smallest enthalpies were determined for the dimethyl 4a and the cycloheptane 4d azobenzene. After the DSC measurements again, 1H NMR spectroscopy was utilized to ensure the integrity of the compounds. All compounds 4a-d showed larger storage energies per azouinit compared to the parent azobenzene, which has been measured by the same method (Table 1, entry 5). The value compares well with the literature.\[28\]

The synthesis commences with the addition of aniline 1 to the corresponding ketone 2 (Scheme 2). While the bisanilines 3a and 3c could be obtained in good yields, the results for the other ketones were rather low. This discrepancy can be related to difficulties in the purification for the five and the seven-membered rings. While the dimethyl as well as the cyclohexyl compound can be conveniently purified by crystallization, the other two derivatives had to be isolated by column chromatography, which was hampered by polarity and solubility issues. The bisanilines 3 were then condensed by a Baeyer-Mills reaction to the target bisazo compounds 4a-d using the procedure optimized in our group for bisazobenzene compounds.\[27\]

All compounds 4 can be isomerized by irradiation in solution at 365 nm and back with 450 nm. The switching process can be conveniently followed by UV-Vis spectroscopy (Figure 2, and SI Figure S2-S5). There is only marginal optical difference between the four derivatives 4a-d. The photostationary state was determined in solution by 1H NMR analysis (dichloromethane-d2). For compounds 4b and 4c, a photostationary state of all-(Z), (E,Z), all-(E) of ~65%, 25%, 10% was observed. Compounds 4a and 4d showed higher all-(Z) ratios of up to 75%. As the thermal all-(Z) to all-(E) isomerization is crucial for the possible storage time, the process has been studied exemplarily for compound 4a by 1H NMR spectroscopy revealing a t1/2 for the all-(Z) of 2.5 h (SI, Table S7).

Figure 1. Increasing the storage energy in azobenzene molecular solar thermal storage (MOST) systems by intermolecular interactions.

Scheme 2. Synthesis of bis-azo compounds 4 with different connectors.
In order to investigate the effects further, a computational modeling study of the storage energy was performed. All structures were optimized at the PBE0 density functional theory level with D3(BJ) dispersion correction using the def2-TZVP basis set (Figure 3 and SI). There are negligible deviations in the overall structure of all compounds for the (all-E) as well as for the (all-Z)-isomer. Furthermore, there was no interaction of the bridging unit with the azobenzene parts detectable.

In general, an increased storage enthalpy can be rationalized by a destabilization of the (Z)-isomer or a stabilizing effect on the (E)-isomer. While the bridging units are more or less shielded in the (all-Z)-isomer, the star-shaped arrangement in the all-(E)-isomers allows close intermolecular interaction between the alkyl-bridge and the aromatic parts of the azo-units. There have been intensive studies on aromatic-aromatic interaction showing that the T-shaped arrangement in the benzene dimer is most favorable. Also, the interactions of cycloalkanes have been addressed. Thereby, it could be shown that σ/σ and π/π dispersion are equally important. Furthermore, the interactions of cycloalkanes with benzene was investigated by measuring the enthalpies and volumes of mixing. In these results the strongest interaction has been determined for cyclohexane and to a less extend for cycloheptane and cyclopentane mirroring our results on the (E)-(Z)-energy difference in compounds 4. Combining the experimental and computational data we propose, that in the all-(E) isomer there is an intermolecular interaction composed of the contact of the π-face of the azobenzene with the cycloalkane bridge by London dispersion.

Thankfully, a single crystal could be obtained of compound 4c (Figure 4) as well as for 4a. The proposed interaction between the cyclohexyl part in 4c with the aryl ring of a second molecules can be seen. The C–H–π distance is below 3.5 Å, which are typical for this kind of interactions. In compound 4a also C–H–π contacts between two molecules can be observed. However, the increased dispersion donor strength of cyclohexane compared to a methyl group can be attributed to the stronger interaction. Although crystal-packing effects cannot be excluded to influence the arrangement of the molecules, this stabilizing effect on the (E)-isomer could be assigned to the increased energy gap between the (E)- and the (Z)-isomer determined in the DSC measurements.

In conclusion, it has been demonstrated that even subtle intermolecular interactions, such as C–H–π London-dispersion interactions can have a considerable effect on the stabilization of photosomers in molecular switches. In the presented study different alkyl-substituted bis-azobenzenes have been prepared, their photochemical properties investigated as well as their thermodynamic parameters. It could be revealed, that although all azobenzenes are electronically equal, that increasing London dispersion strength lead to an increased energy difference between (E)- and (Z)-state. Such interactions can be used to design efficient compounds for MOST systems in the future.

**Table 1.** Storage enthalpies per azobenzene unit of compounds 4a-d by computations (PBE0-D3(BJ)/def2-TZVP) and by DSC measurements (including parent azobenzene as comparison).

| Entry | X      | ΔH_{all-E} / kcal/mol | ΔH_{all-Z} / kcal/mol |
|-------|--------|-----------------------|-----------------------|
| 1     | H H    | 12.4                  | 10.6                  |
| 2     | (CH₃)₂ | 12.4                  | 11.7                  |
| 3     | (CH₃)₃ | 12.2                  | 13.1                  |
| 4     | (CH₃)₄ | 12.2                  | 10.8                  |
| 5     | Azobenzene | 12.4                  | 9.3                   |

**Figure 3.** Optimized geometry of the all-(E) and the all-(Z)-isomer of compound 4c (PBE0-D3(BJ)/def2-TZVP).

**Figure 4.** Part of the solid-state structure showing two molecules of 4c with proposed C–H–π and London dispersion interactions (top) and of 4a (bottom). CCDC 1916020 (4c) and 1916021 (4a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
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Keywords: azobenzene • London dispersions • molecular solar thermal energy storage • molecular switches • noncovalent interactions

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