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

Anne Kunz,[a] Andreas H. Heindl,[a] Ambra Dreos,[b] Zhihang Wang,[b] Kasper Moth-Poulsen,[b] Jonathan Becker,[c] and Hermann A. Wegner*[a]

The performance of molecular solar thermal energy storage systems (MOST) depends amongst others 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 that is 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.[1,2] 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.[3,4] 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 by Weigert over 100 years ago.[5] In recent years, functional prototypes for MOST applications have been demonstrated.[6] While these ones are mostly based on the norbornadiene-quadricyclane system, other molecular entities have also been proposed.[3] Herein, the azobenzene represents a highly potent candidate as there is longstanding experience in studying this system as a dye as well as a molecular switch.[7,8] The storage energy of a given MOST system is based on the energy differrence between two states. In case of the azobenzene, this is the (*E*)-isomer as the lower energy state and the (*Z*)-isomer as the metastable high-energy state (Figure 1).

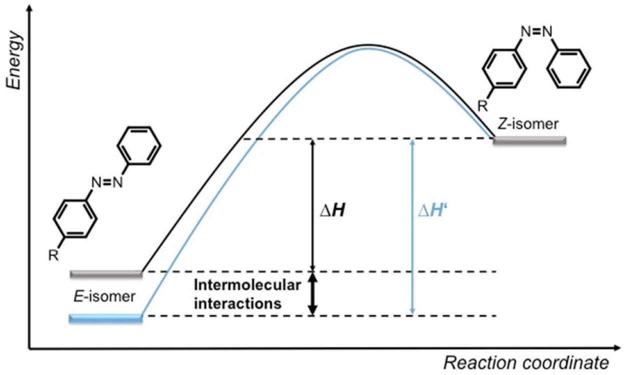

Figure 1. Increasing the storage energy in azobenzene molecular solar thermal storage (MOST) systems by intermolecular interactions.

Critical parameters for such MOST systems represent on one hand the actual storage energy: In case of the azobenzene the energy difference between the (*E*)- and the (*Z*)-isomer. Additionally, the barrier for the thermal back-conversion should be high enough to ensure long storage times. Besides these variables, the molecules should absorb as much light of the spectrum of the sun as possible in the lower energy form [(*E*)-azobenzene] and ideally not at all in the higher energy form [(*Z*)-azobenzene]. Finally, the quantum yield should be as high as possible for the conversion from (*E*)- to (*Z*)-azobenzene. The parent azobenzene has a storage energy of ~9–10 kcal/mol, which is in a medium range compared to other molecular entities discussed for MOST applications.[9] Another downside of

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[a] *A. Kunz, A. H. Heindl, Prof. Dr. H. A. Wegner*
Institute of Organic Chemistry
Justus Liebig University
Heinrich-Buff-Ring 17, 35392 (Giessen)
and
Germany and Center for Materials Research (LaMa), Justus Liebig University
Heinrich-Buff-Ring 16, 35392 Giessen (Germany)
E-mail: Hermann.a.wegner@org.chemie.uni-giessen.de
[b] *Dr. A. Dreos, Z. Wang, Prof. Dr. K. Moth-Poulsen*
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg (Sweden)
[c] *Dr. J. Becker*
Institute of Inorganic and Analytical Chemistry
Justus Liebig University
Heinrich-Buff-Ring 17, 35392 Giessen (Germany)

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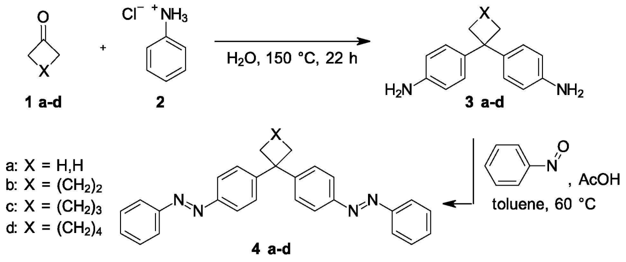
azobenzenes is, that the (*E*)-azobenzene absorbs UV-light, while the storage form absorbs in the visible range. Fortunately, the properties of azobenzene can readily be modified by changing the substitution pattern.[10] For example the introduction of fluorine atoms[11] as well as methoxy groups[12] shift the absorption to longer wavelength. There have been different strategies to increase the storage energy.[7,14–16] Stabilizing groups can influence the (*E*)-(*Z*)-energy difference even by subtle interactions such as London dispersion.[13] Feng[17–19] and also later Grossmann[20] used nanotemplating as a tool. Another approach is based on incorporating the azobenzene into macrocyclic structures to utilize strain energy in the (*Z*)-isomer.[21,22] Alternatively, azobenzenes can be connected to carbon nanotubes to improve the storage energy.[23]

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 (Figure 1).[24,25] 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.[13,26] 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.

As linkers between the azobenzene units, a methylene bridge was chosen. Such a methylene connector will keep the azobenzenes 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*)-azobenzenes with the surface of alkyl groups was targeted. Hence, besides dimethyl, cyclic alkanes such as cyclopentyl, cyclohexyl and cycloheptyl were selected.

The synthesis commences with the addition of aniline **2** to the corresponding ketone **1** (Scheme 1). 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 bisazobenzenes **4a–d** using the procedure optimized in our group for bisazobenzene compounds.[27,35]



Scheme 1. Synthesis of bis-azobenzenes **4** with different connectors.

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 Supporting Information Figure S2-S5). There is only marginal optical difference between the four derivatives **4a–d**. The photostationary state was determined in solution by ^{1}H NMR analysis (dichloromethane-d_2). 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 exemplary for compound **4a** by ^{1}H NMR spectroscopy revealing a $t_{1/2}$ for the all-(*Z*) of 2.5 h at 50 °C (Supporting Information, Table S7).

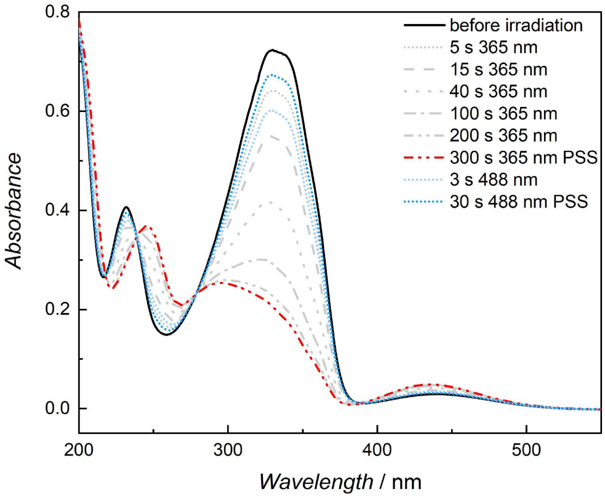


Figure 2. Switching process of **4c** analyzed by UV-Vis spectroscopy ($2*10^{-5}$ mol/L in acetonitrile).

To study the thermodynamic properties, differential scanning calorimetry (DSC) has been performed on all compounds. (Table 1 & Supporting Information). 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

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_{comp} [kcal/mol]	ΔH_{DSC} [kcal/mol]
1	H, H	12.4	10.6
2	$(CH_2)_2$	12.4	11.7
3	$(CH_2)_3$	12.2	13.1
4	$(CH_2)_4$	12.2	10.8
5	Azobenzene	12.4	9.3

365 nm in solution (10 mg/3 mL in dichloromethane-d_2, Supporting Information, Figure S8, S10, S12, S14, S16). The solvent was removed under continuous irradiation at 365 nm and exclusion of ambient light by blowing a N_2-stream over the sample. Then, ^{1}H NMR spectroscopy was conducted to determine the degree of conversion (Supporting Information, 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** azobenzenes. After the DSC measurements again, ^{1}H NMR spectroscopy was utilized to ensure the integrity of the compounds. All compounds **4a**–**d** showed larger storage energies per azounit 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]

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[29] with D3(BJ) dispersion correction[30] using the def2-TZVP basis set[31] (Figure 3 and Supporting Information). 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.

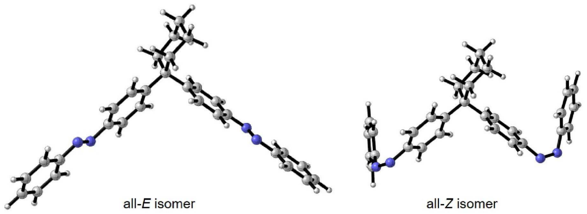

all-*E* isomer
all-*Z* isomer

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

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.[32] Also, the interactions of cycloalkanes have been addressed. Thereby, it could be shown that σ/σ and π/π dispersion are equally important.[33] Furthermore, the interactions of cycloalkanes with benzene was investigated by measuring the enthalpies and volumes of mixing.[34] 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** as well as for **4a** (Figure 4). 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 photoisomers in molecular switches. In the presented study different alkyl-substituted bis-azobenzenes have been prepared,

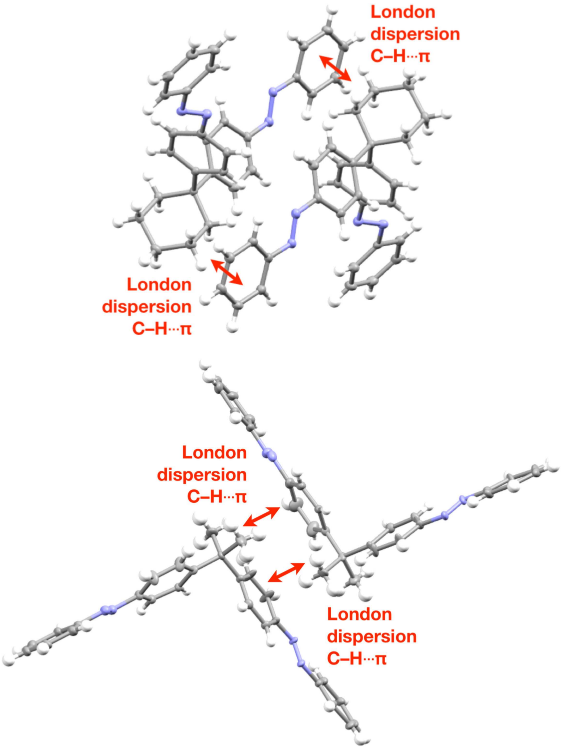


Figure 4. Part of the solid-state structure showing two molecules of **4c** with proposed C–H–π and London dispersion interactions (top) and of **4a** (bottom). CCDC 1916020 (**4c**) and 1916021 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of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

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.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: azobenzene · London dispersions · thermal energy storage · molecular switches · noncovalent interactions

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