



Digest Paper

Designing photoswitches for molecular solar thermal energy storage



Anders Lennartson, Anna Roffey, Kasper Moth-Poulsen*

Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden

ARTICLE INFO

Article history:

Received 17 October 2014

Revised 9 January 2015

Accepted 27 January 2015

Available online 11 February 2015

Keywords:

Molecular switches

Molecular design

Solar energy

Molecular solar thermal

Isomers

Photochemistry

ABSTRACT

Solar energy conversion and solar energy storage are key challenges for a future society with limited access to fossil fuels. Certain compounds that undergo light-induced isomerisation to a metastable isomer can be used for storage of solar energy, so-called molecular solar thermal systems. Exposing the compound to sun light will generate a high energy photoisomer that can be stored. When energy is needed, the photoisomer can be catalytically converted back to the parent compound, releasing the excess energy as heat. This Letter gives examples of selected molecular solar thermal systems found in the literature. The focus of the Letter is on examples where molecular design has been used to improve the performance of the molecules, and as such it may serve as an inspiration for future design. The selected examples cover five widely studied systems, notably: anthracenes, stilbenes, azobenzenes, tetracarbonyl-fulvalene-diruthenium compounds and norbornadienes.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

Introduction	1457
The anthracene system	1457
The stilbene system	1458
The azobenzene system	1458
The fulvalene diruthenium system	1459
The norbornadiene system	1460
Outlook	1463
Acknowledgments	1464
References and notes	1464

Introduction

Photoinduced isomerisation of organic molecules and organometallic compounds has been proposed as a possible way to store solar energy in the form of latent chemical bonds.^{1–3} In these so-called molecular solar thermal systems (MOST), a parent photoisomer is irradiated by light and transformed into a high energy metastable photoisomer. The photoisomer can subsequently be converted back to the original parent compound by exposure to a catalyst or by heating. During the back conversion the photoisomer releases the stored energy in the form of heat. Several factors need to be optimised when designing a MOST system, including energy storage density, solar spectrum match (the ability of the molecule to absorb a large fraction of the solar spectrum), quantum yield of pho-

toconversion, the half-life of the high energy isomer and thereby the height of the barrier for back conversion. To optimise all these factors at the same time in a single molecular system is a challenging task, yet an intriguing challenge. With this digest article we present examples of different attempts to optimise molecular systems towards MOST applications. Our examples include engineering of anthracenes (see section ‘The anthracene system’), stilbenes (see section ‘The stilbene system’), azobenzenes (see section ‘The azobenzene system’), fulvalene-diruthenium compounds (see section ‘The fulvalene diruthenium system’) and norbornadienes (see section ‘The norbornadiene system’). Our selection of examples is chosen to highlight how one can proceed in optimising the systems by chemical design.

The anthracene system

The photodimerisation of anthracene was suggested as a method to convert light into chemical energy as early as 1909.^{4,5}

* Corresponding author. Tel.: +46 (0)761996855.

E-mail address: kasper.moth-poulsen@chalmers.se (K. Moth-Poulsen).

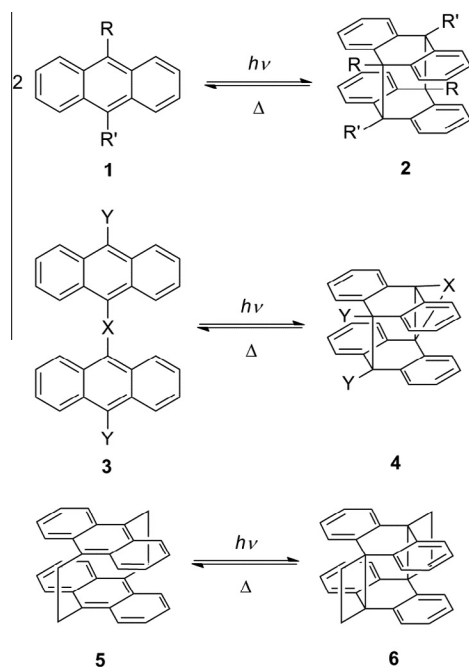


Figure 1. Photo-induced dimerisation of anthracene and cyclisation of linked anthracene dimers.

Anthracene is a rigid aromatic hydrocarbon, which dimerises via a [4+4] cycloaddition upon absorption of light at ca. 400 nm.^{3,6} It then re-emits the stored energy as heat by thermal treatment or by irradiation with UV light (below 300 nm), thus conforming to established criteria for a MOST material.⁷ The quantum efficiency (σ) for the forward reaction is concentration dependant, approaching 0.3 at high concentration, with a storage enthalpy ($\Delta H_{\text{storage}}$) of 65.2 kJ/mol.⁶ By functionalising the anthracene monomer (**1**, Fig. 1) with donor and acceptor groups the enthalpy could be increased to 83.6 kJ/mol ($R=H$, $R'=CN$), though the quantum efficiency remained concentration dependant.^{8,9}

In order to increase the quantum efficiency and disassociate it from concentration, Jones et al. synthesised a range of linked anthracene dimers **3–6**.⁶ Quantum efficiencies of up to 0.29 were achieved with the singly bridged system (**3**; $X=CHOH$, $Y=H$), and $\Delta H_{\text{storage}}$ was as high as 72.3 kJ/mol (for $X=CH_2$, $Y=H$). The highest quantum yield, however, was seen for the doubly bridged system at 0.36, though the storage enthalpy was reduced to 35.5 kJ/mol. In the case of the singly linked dimer, the four-membered ring produced when $X=CH_2CH_2$ leads to a greater $\Delta H_{\text{storage}}$ than the three-membered ring produced when $X=CH_2$ (72.3 and 61.0 kJ/mol, respectively).

The stilbene system

Stilbenes (Fig. 2) are a class of organic compounds which undergo a *E–Z* photoisomerisation when exposed to light in the range 300–700 nm, making them interesting compounds with regard to solar energy storage since some derivatives absorb light well into the visible part of the solar spectrum. A major drawback, however, is the low storage enthalpy associated with this isomerisation, only 5 kJ/mol for unsubstituted stilbene, **7**.^{10,11} Mancini and co-workers investigated the stilbene-like compounds 9-styrylacridines (**8–12**), and discovered that the storage enthalpy (also 5 kJ/mol for unsubstituted 9-styrylacridine) could be greatly increased by introducing different functional groups.^{10,11} When one phenyl unit was functionalised with an electron donating amine group (**8**) the stored enthalpy increased four-fold, through increased electron delo-

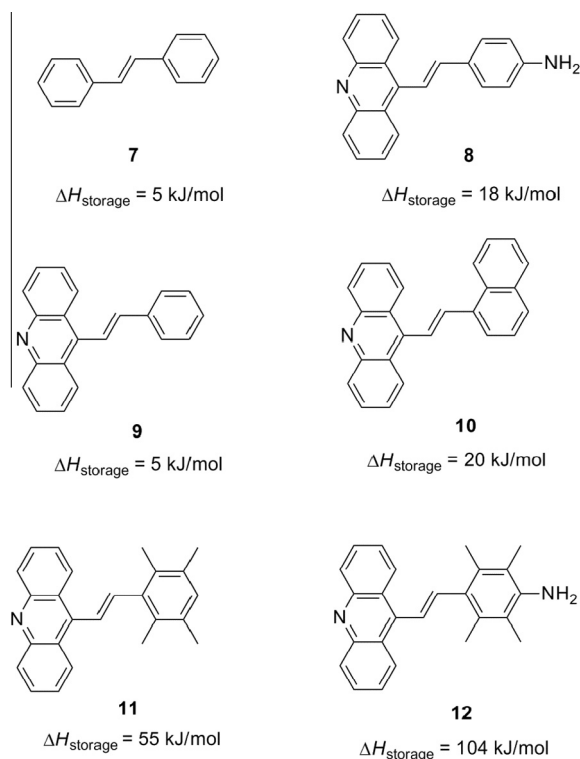


Figure 2. Structure and storage enthalpy of *E–Z* isomerisation of stilbene (**7**) and related compounds.

calisation in the structure.¹¹ A similar effect was observed when the phenyl ring was replaced by a 1-naphthyl group (**10**), also furthering the conjugated system and thereby stabilising the *E* isomer, while the *Z* isomer is believed to be less affected due to its strained angular geometry and thereby limited π -conjugation.¹¹

A further improvement on the storage enthalpy was achieved when the steric bulk about the phenyl moiety was increased through the addition of four methyl groups (2,3,5,6-tetramethylstyrylacridine, **11**).^{10,11} The ortho methyl groups are believed to destabilise the *Z* isomer, thereby increasing the storage enthalpy to 55 kJ/mol. The highest enthalpy, however, was observed when the two above effects were combined in the tetramethyl-aminostyrylacridine, **12**. The increased delocalisation and steric hindrance have concomitant but opposing effects, lowering the energy of the *E* isomer while destabilising the *Z* isomer respectively, leading to a storage enthalpy of 104 kJ/mol (close to that of a chemical bond).¹¹

The azobenzene system

Azobenzenes (Fig. 3), are among the most widely studied molecular photoswitches and have attracted recent attention in the field of molecular solar thermal storage. Azobenzenes absorb light in the visible range (absorption onset ca. 400 nm) and release heat upon re-isomerisation from *Z–E*.² Though these compounds drew attention in the 1980s as potential MOST systems, their low storage enthalpy (41.5 kJ/mol¹² for azobenzene; **13**) and low activation barrier to re-isomerisation ($t_{1/2}$ = ca. 4 days for **13**) lead to them being largely discounted.^{12,13} Recent computational work, however, has prompted renewed interest in these systems.^{14,15} Grossman and Kolpak performed a DFT study on azobenzene covalently bound to carbon nanotubes (CNTs). The CNTs acted as templates conferring a close-packed, ordered arrangement of molecules. The storage energy per azobenzene molecule increased by up to 30% compared to the free state, due to favourable interactions between close-packed molecules stabilising the *E* isomers relative

Download English Version:

<https://daneshyari.com/en/article/5262329>

Download Persian Version:

<https://daneshyari.com/article/5262329>

[Daneshyari.com](https://daneshyari.com)