Optimization of Norbornadiene Compounds for Solar Thermal Storage by First-principles Calculations

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Molecular photoswitches capable of storing solar energy are interesting candidates for future renewable energy applications. Here, using quantum mechanical calculations we carry out a systematic screening of crucial optical (solar spectrum match) and thermal (storage energy density) properties of 64 such compounds based on the norbornadiene-quadricyclane system. While a substantial number of these molecules reach the theoretical maximal solar power conversion efficiency, this requires a strong red-shift of the absorption spectrum, which causes undesirable absorption by the photoisomer as well as reduced thermal stability. These compounds typically also have a large molecular mass, leading to low storage densities. By contrast, single-substituted systems achieve a good compromise between efficiency and storage density, while avoiding competing absorption by the photo-isomer. This establishes guiding principles for the future development of molecular solar thermal storage systems.

Introduction

The global energy demand is projected to increase twofold over the course of the next four decades necessitating widespread use of renewable energy sources.[1] Solar energy plays a key role in this context and can be harvested using e.g., photovoltaics or direct thermal heating.[2,3] Fluctuations in availability and demand, which typically follow opposite cycles, however, imply that energy storage technologies are needed for load leveling.[2,3] While battery technologies are in principle capable of providing this functionality, they face challenges with regard to cost and large-scale implementation.

Here, the direct conversion of solar to chemical energy provides an attractive alternative,[4] in particular in the form of so-called molecular solar thermal storage (MOST) systems based on the photo-induced isomerization of molecular compounds,[5,6] which circumvent storage of reactive gaseous species. In these materials photon absorption converts a low into a high-energy isomer, where the back-conversion is kinetically hindered but can be induced by a catalytic reaction or heating. Examples for these systems include stilbenes,[7,8] azobenzenes,[9–13] anthracenes,[14] ruthenium fulvalene compounds,[15] dihydroazulenevinylheptafulvene[16,17] as well as norbornadiene-quadricyclane systems.[18–21]

Material systems suitable for MOST applications need to fulfill a set of conditions that follow from the basic functional principle (Fig. 1):[22]

(1) *Solar spectrum match:* The absorption spectrum of the lower-energy isomer must overlap with the most intense region of the solar emission spectrum.

(2) *High quantum yield*: The photo-conversion that leads to the high-energy isomer must proceed with high efficiency.

(3) *Large storage energy density*: The isomerization energy density, i.e. the energy difference between the low and high-energy isomers relative to the molecular weight/volume, must be large.

(4) *Long time stability*: The barrier for the thermal back-conversion on the ground state energy landscape must be sufficiently large to enable long-term storage.

(5) *Low price*: The cost for raw materials, synthesis and integration must be competitive.
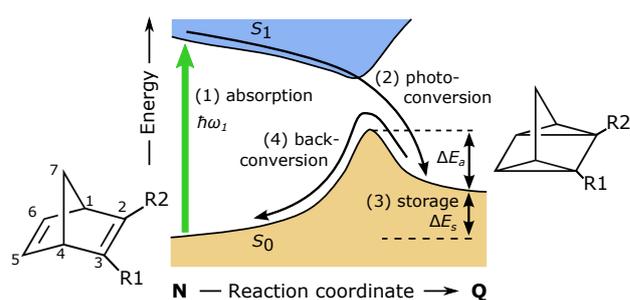
Figure 1. Schematic of ground state (S_0 surface, orange) and excited (S_1 surface, blue) energy landscapes connecting norbornadiene (**N**) to its higher-energy quadricyclane (**Q**) isomer. Molecular solar thermal storage involves the four stages indicated in the figure. The two isomers are depicted in the bottom part of the figure with R1 and R2 indicating the substitution sites considered in the present work.

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In the present work, we are concerned with systems based on norbornadiene (N) and its high-energy isomer quadricyclane (Q), which have attracted renewed interest due to advances pertaining to the synthesis of substituted variants.[18,19,23] Substitution provides a powerful means for manipulating both the ground and excited state landscapes, and thereby for tuning all five properties alluded to above. This versatility, however, also implies that the number of possible compounds is extremely large, which renders a purely experimental approach to exploring this parameter space impractical. Here, to fill this gap, we carry out a screening study of a matrix of 64 compounds using quantum mechanical calculations while carefully accounting for conformational effects. We focus on solar thermal match (1) and storage energy density (3), which as shown in prior work[20] can be predicted with good accuracy using single-reference methods based on density functional theory. The key findings are:

(i) It is possible to design molecules that reach the theoretical solar power conversion efficiency. This, however, requires a strong red-shift, which is associated with self-limiting absorption by the photo-isomer and a (much) reduced thermal stability, as well as two substituents, which increases the molecular mass and thus limits the storage density.

(ii) Single-substituted systems, on the other hand, yield reasonable solar power conversion efficiencies in conjunction with significantly higher storage densities possibly in excess of 600 kJ/kg, while avoiding competing absorption by the photo-isomer.

We identify several promising candidates and more importantly establish guiding principles for the future development of MOST systems in general and N-Q systems in particular.

We note that several substituted N-Q systems have been explored at the level of density functional theory (DFT) using a set of simple substituents, some of which appear to be difficult to realize experimentally.[24,25] The design of MOST systems with the help of theoretical methods has also recently been considered by e.g., Olsen *et al.*[17] as well as Liu and Grossman.[26]

The paper is structured as follows: The following section provides an overview of the computational details and codes used in this study. In the Results section, we then address solar spectrum match and solar power conversion efficiency, the self-limiting effect of absorption by Q on the conversion efficiency, and the storage density. The discussion of our findings can be found in the accordingly named section. Further details pertaining to the treatment of conformational effects and the computation of the solar power conversion efficiency in the presence of Q can be found in the Appendix.

Methodology

Construction of database

Following the lines of recent experimental work,[18] we consider substitutions on one of the double bonds of the norbornadiene molecule (Fig. 1). Seven donors and seven acceptors groups were selected based on known donor and acceptor motifs as well as an analysis of the feasibility of the corresponding synthesis facilitating future experimental realization of the compounds. The donors are all well know electron rich aromatic systems based on benzene (**D1**, **D2**, **D6**, **D7**) or thiophene (**D3**, **D4**, **D5**) substituted with electron donating groups such as methoxy (**D2**, **D4**, **D5**) or amino groups (**D6** and **D7**). The acceptors are based on benzene or thiophene, functionalized with electron withdrawing groups such as trifluoromethyl or cyano. Acceptors **A4**–**A7** are heteroatom containing electron deficient aromatic rings such as thienopyrrolodione (**A4**), diketopyrrolopyrrole (**A5**), benzothiazole (**A6**), thiadiazoloquinoxaline (**A7**), typically found in donor-acceptor polymers for solar energy applications[27–29] (Fig. 2). These substituents are also chemically and structurally similar to systems that have been previously synthesized.[18] In addition, we include hydrogen (**H**) in the set substituents, which leads to "single-substituted" systems.

In total one obtains a matrix of 64 compounds, which will be denoted by the concatenation of the donor and acceptor labels, e.g., **D1A5**. This set includes four of the six compounds studied previously[20] (**HH** = the unsubstituted molecule, **D2A1**, **D2A3**, **D6A1**).

Motivation of properties and methods

Substituted N-Q systems have been identified that feature high quantum yields and are based on available raw materials, thus to some extend fulfilling requirements (2) and (5) above.[30] Compared to the unsubstituted compound the modified materials exhibit a significant red-shift (1) and at least in some cases acceptable thermal stabilities (4). Improvements of solar thermal match (1) and storage energy densities (3) are therefore the most likely to have a significant impact. In prior work we have shown that single-reference methods based on time-dependent and independent DFT calculations provide acceptable to good accuracy with respect to the prediction of optical absorption and storage energies for a reference set of substituted compounds.[20] In particular calculations based on the B3LYP hybrid exchange-correlation functional[31,32] achieved a mean percentage error of less than 7% (< 0.3 eV) relative to experimental data for the first excitation (first maximum of the absorption spectrum) and a mean percentage error of 12% (11 kJ/mol) relative to complete active space (CAS) calculations for the storage energy. In the case of diaryl substituted compounds the DFT-B3LYP calculations actually underestimated the experimental absorption energies systematically by about 0.3 eV, which will be used below to apply a correction to the calculated excitation energies. Solvent effects as described at the level of the universal solvation model by
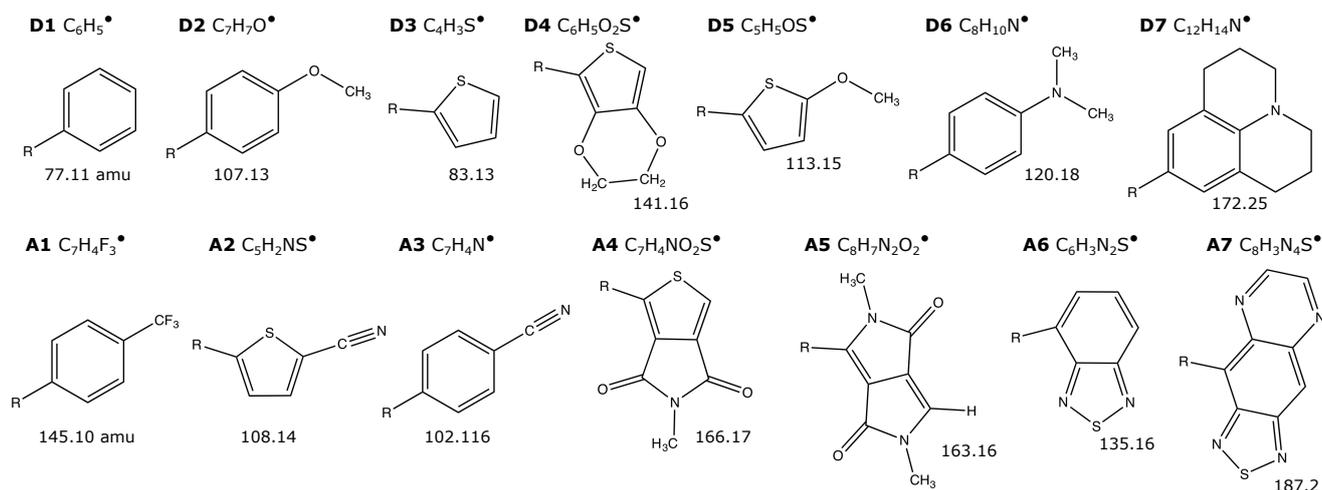
Figure 2. Overview of acceptor (**A**) and donor (**D**) substituents used to construct the database of compounds for property screening. These groups are inserted at positions R1 and R2 (see Fig. 1) of the norbornadiene/quadricyclane molecule. The molecular masses of each side group are given in atomic mass units (amu).

Marenich *et al.*[33] were found to cause a redshift of the excitation energies of 0.05 eV or less and a reduction in the storage energy by about 4 kJ/mol (also see Fig. 1 in the. Supplementary Information).

In the same context it was shown[20] that the barrier for the thermal Q→N back-conversion exhibits strong multi-reference character and is amenable to single-reference methods only in approximate fashion. Specifically, single-reference methods fail to capture the coupling between σ an π-orbital systems that gives rise to an avoided crossing and a finite curvature at the saddle point. As suitable methods such as CAS approaches are computationally too expensive for a screening approach, in the present study, only solar spectrum match and energy storage density were considered.

Computational details

Molecular geometries were generated by considering both isomers (norbornadiene and quadricyclane) with all possible combinations of donor and acceptor substituents and all of their possible conformers. Firstly, we note that the steric repulsion between the two substituents competes with the π-conjugation of the aromatic rings via the norbornadiene double bond (C2–C3). This results in two different kinds of conformers, where either the donor or the acceptor is more planar with respect to the C2–C3 bond (Fig. 1) while the other sidegroup is rotated out-of-plane due to steric hindrance. For substituents that do not possess C_2 symmetry with respect to the C2–R1/R2 bond, we consider 180 degree rotations about this bond. Furthermore, we include 180 degree dihedral rotations of the bridging oxygen atoms of **D2** and **D5**. This results in a total of 728 initial geometries including both single and double-substituted systems.

The conformers for both N and Q were subsequently relaxed on the ground state energy surface according to DFT based on the B3LYP hybrid functional[31,32] as implemented in the NWChem code[34] using a 6-311++G** basis set (split-valence triple-zeta with diffuse *s* and *p* functions for all atoms as well as *d* polarization functions on non-hydrogen atoms and *p* polarization functions for hydrogen).[35,36] The storage energy was obtained from the difference between the electronic total energies of the fully-relaxed N and Q variants as described in the Appendix.[1]

The excitation spectra of both N and Q variants were calculated using time-dependent DFT. To improve the match with experimental spectra we included a constant scissors shift of 0.3 eV to compensate for the systematic underestimation of the optical gap by B3LYP that was pointed out in.[20] Solvent and vibrational contributions were not explicitly included for computational efficiency; rather we applied a universal broadening of 0.25 eV to the excitation spectra to approximate the experimental broadening. Note that this broadening is primarily due to vibrations and electronic lifetime effects. It is thus significantly larger than the solvent effect due to dielectric screening, which as pointed out above was previously found to be on the order of 0.05 eV for toluene.[20] Further details concerning the treatment of conformational effects can be found in the Appendix.

Results

Optical gap

For any solar energy harvesting system to be effective its absorption spectrum must overlap significantly with the so-

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[1] Note that while dispersive interactions were recently shown to have a significant impact on the energetics of azobenzenes,[12] their impact in the case of substituted N-Q systems was found to be small.[20] This result can be rationalized by observing that while in the case of the azobenzenes the relative proximity of the sidegroups changes significantly between the Z and E variants, there is no significant difference in this regard between the N and Q isomers considered in the present study.
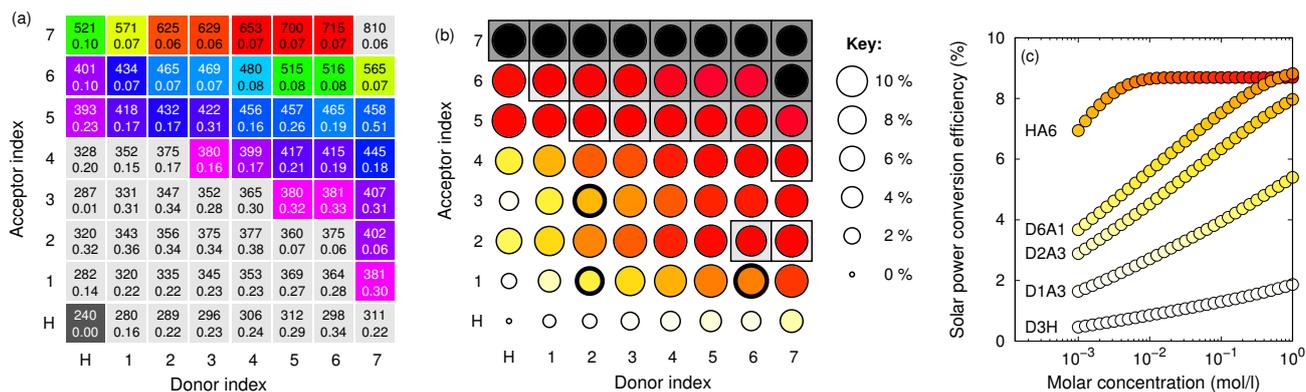
Figure 3. Solar spectrum match. (a) wavelength (top, in nm) and oscillator strength (bottom) of the optical first excitation of the respective most stable conformer for the matrix of molecular compounds considered in this work. The wavelength is also indicated by the color of the squares. Light gray squares indicate wavelengths outside the visible range that do overlap with the solar spectrum. Dark gray squares indicate excitations that do not overlap with the solar spectrum. (b) Solar power conversion efficiency according to η_{conv} to Eq. (1). Each circle corresponds to one compound, where the color represents the color of the light that is being transmitted. Compounds considered in previous experimental work[18] are highlighted by bold circles. Gray squares mark compounds for which the sum of storage energy ΔE_s, an activation energy of $\Delta E_a = 120\,kJ/mol$, as well as an additional energy gap δE exceeds the first excitation energy $\hbar\omega_1$, see Fig. 1. The shade of gray corresponds to the value of δE with the darkest (lightest) shade corresponding to $\delta E = 0\,eV$ (0.6 eV). (c) Solar power conversion efficiency as a function of the molar concentration. The color of the circles represents the color of the transmitted light. The compounds shown are marked in Fig. 7 and some are also included in Fig. 5.

lar spectrum. In fact, all substituted compounds cause a bathochromic (red) shift of the absorption relative to unsubstituted N and for the majority the first excitation occurs in the visible range [Fig. 3(a)]. The donors and acceptors in this study have been enumerated according to the average shift of the first excitation energy that they induce. This ordering correlates well with the extent of the conjugated π-system and as a result also the size (and mass) of the substituent (Fig. 2).

In general the acceptor substituent has a more pronounced effect on the optical spectrum than the donor. Going from **H** to **A7** causes an average shift by as much as 2.4 eV (286 nm to 636 nm), whereas the first excitation energy only changes by 0.9 eV between **H** and **D7** (333 nm to 433 nm). Also note that the oscillator strength associated with the first excitation is almost exclusively determined by the acceptor and exhibits a non-systematic variation with wavelength. The different magnitudes observed for acceptor and donor substitution, respectively, can be rationalized by observing that the acceptor group primarily shifts the lowest unoccupied molecular orbital (LUMO) energy and thus unoccupied states, whereas the donor group affects the highest occupied molecular orbital (HOMO). The apparently weaker impact of donor substitution on the excitation spectrum is thus related to the fact that occupied levels are more difficult to affect since they are coupled to the charge density and thus the potential.

While there is a strong correlation between acceptor (donor) and LUMO (HOMO) energy, for a given substituent the energy can still vary by as much as $\pm 0.5\,eV$. One can thus pre-select acceptor and donor combinations based on these trends but pronounced coupling effects have to be expected in the resulting compound.

Solar power conversion efficiency

The ability of different compounds to absorb solar energy can be assessed by comparing the solar power conversion efficiency,[6] which can be evaluated from the following expression

$$\eta_{conv} = \Delta E_s \int_{E_{cut}}^{\infty} d\omega \underbrace{\frac{P_{sol}(\omega)}{\hbar\omega}}_{\dot{N}(\omega)} \underbrace{\left[1 - 10^{-\varepsilon(\omega)Lc}\right]}_{ATT(\omega)} \bigg/ \int_{0}^{\infty} d\omega P_{sol}(\omega).$$

(1)

where a quantum efficiency of 100% has been assumed as motivated in Ref..[6] The integrations are carried out over a reference solar spectrum $P_{sol}(\omega)$ according to the AM1.5 Global standard.[2] The denominator represents the total power per area of the solar spectrum, which for the AM1.5 Global spectrum is normalized to 1000 W/m^2.

The enumerator corresponds to the power per area that is converted into the respective quadricyclane variant. It equals the product of the storage energy ΔE_s (Fig. 1) and the number of photons absorbed per unit time and area, where $\dot{N}$ is the photon flux at sea level and ATT is the attenuation. The latter depends on the sample thickness L, the molar concentration c, and the molar attenuation coefficient $\varepsilon(\omega)$. In the present work, we assume a thickness of 1 cm throughout; this value can be varied between approximately 0.1 and 10 cm with a very small impact on the results.

The molar attenuation coefficient $\varepsilon(\omega)$ can be computed from the excitation energies ω_k and dipole strengths f_k ob-

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tained from the TD-DFT calculations in appropriate units as follows,

$$\varepsilon(\omega) = \frac{N_A}{\ln 10} \frac{\pi e^2}{2\varepsilon_0 m_e c} \sum_k f_k g(\omega_k; \sigma). \tag{2}$$

Here, $g(\omega)$ denotes a normalized Gaussian function, which depends parametrically on the broadening factor σ. The latter was set to 0.25 eV to mimic the experimentally observed broadening.

Note that the integration is bound from below by a cut-off energy E_{cut}. From the basic energy diagram describing the N-Q conversion processes (Fig. 1), one can infer that a successful photo-isomerization requires the energy of the absorbed photon to be at least as large as the sum of the storage energy ΔE_s and the barrier for thermal back-conversion ΔE_a, i.e. $E_{cut} = \Delta E_s + \Delta E_a$. A sufficiently large back-conversion barrier is critical for long-term storage of the Q variant. At room temperature, ΔE_a values of 110 kJ/mol and 120 kJ/mol correspond to half-life times of 24 and 1,400 days, respectively, and approximately bracket the range that is useful for applications.[6] To evaluate Eq. (1), we therefore used $E_{cut} = \Delta E_s + 120$ kJ/mol, which ensures comparability with the analysis presented in Ref..[6] (As discussed above, an explicit calculation of the barriers is computationally too expensive in the context of the present screening study).
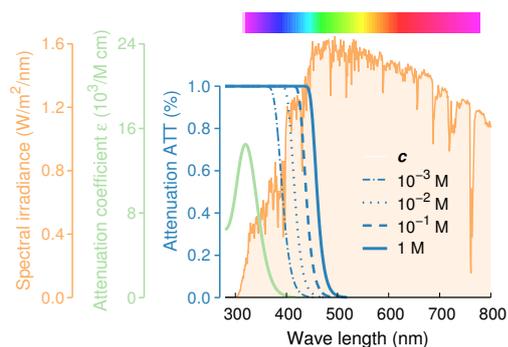
Figure 4. Molar attenuation coefficient according to Eq. (2) and absorption spectrum of **HA2** in comparison to the reference solar power spectrum AM1.5 Global. **HA2** yields a good compromise between solar spectrum match and storage density. The blue lines indicate increasing molar concentrations from left (dash-dotted line) to right (solid line).

Future solar thermal storage devices might include a fluid containing the MOST compound. Based on practical considerations involving the molecular storage capacity and the maximum obtainable temperature gradient,[6] one seeks to reach a concentration of 1 mol/L or more. We therefore first compare the performance of different compounds at $c = 1$ mol/L. Since in practice it might be difficult for some compounds to reach this range due to limited solubilities, we will consider the effect of smaller concentrations below. (Note that solubility and environmental impact of the solvent require detailed experimental and theoretical studies that need to be addressed in future work).

The calculated solar power conversion efficiencies η_{conv} fall between 1.7% and 9.5% [Fig. 3(b)] with 75% of the compounds reaching at least 7.5%. The previously synthesized compounds [marked by thick black circles in Fig. 3(b)] yield values of 6.5% (**D2A1**), 8.3% (**D2A3**), and 8.5% (**D6A1**). For comparison the theoretical maximum assuming $\Delta E_a = 120$ kJ/mol is 10.6%.[6]

Following Ref.,[6] hitherto we assumed an entirely flat S_1 energy landscape between the configuration coordinates corresponding to N and the saddle point. That is, however, an unlikely scenario. One should in fact require $\hbar\omega_1 \geq \Delta E_s + \Delta E_a + \delta E$, where $\hbar\omega_1$ is the energy difference between S_0 and S_1 at N and δE denotes the energy variation between the N and saddle point configurations on S_1 (Fig. 1). Based on calculations,[20,37] δE typically ranges between 0.5 eV and 1.0 eV, where the latter value applies to the unsubstituted compound (**HH**). This constraint immediately rules out all compounds based on **A7** and all double-substituted compounds based on **A6**. Compounds based on **A5** fall in the border region with 0.2 eV $< \hbar\omega_1 - \Delta E_s - \Delta E_s < 0.6$ eV [compare the shaded areas in Fig. 3(b)]. In this context, it should also be recalled that red-shifting using auxochromes is usually associated with a decrease in the thermal stability,[20,30,38] which provides a further reason for limiting the red-shift.

Concentration effects on absorption

It is instructive to consider the different contributions to η_{conv} individually. In the case of for example **HA2** [Fig. 4(a)], the first excitation line is located at 321 nm, which sets the center of the first peak of the molar attenuation coefficient $\varepsilon(\omega)$. From the expression for the attenuation ATT in Eq. (1) it is apparent that at $c = 1$ M and $L = 1$ cm already an attenuation coefficient $\varepsilon(\omega) \geq 0.01$/M cm is sufficient to reach saturation. As a result, although the first excitation lies in the violet part of the spectrum full absorption is already accomplished at approximately 480 nm, whence the transmitted light should appear yellow [Fig. 3(b)]. This implies that broadening due to vibrations, solvation, and a distribution of conformers[39] is actually crucial for harvesting a larger part of the solar spectrum.

As pointed out above, large concentration in excess of 1 M are desirable and targeted for applications. Yet, solubility limits in standard solvents used in the laboratory and for current demonstration devices can be significantly lower.[18] It is therefore instructive to consider the effect of concentration on the absorption spectrum. This aspect is also interesting with respect to fundamental experimental studies, as attenuation coefficients are usually measured using very dilute solutions.

Obviously decreasing the concentration shifts the onset of absorption to shorter wavelengths [Fig. 4(a)]. The structure of the solar spectrum in the ultraviolet and blue regions, however, causes a non-linear variation of the solar power conversion efficiency η_{conv} with concentration [Fig. 3(c)].
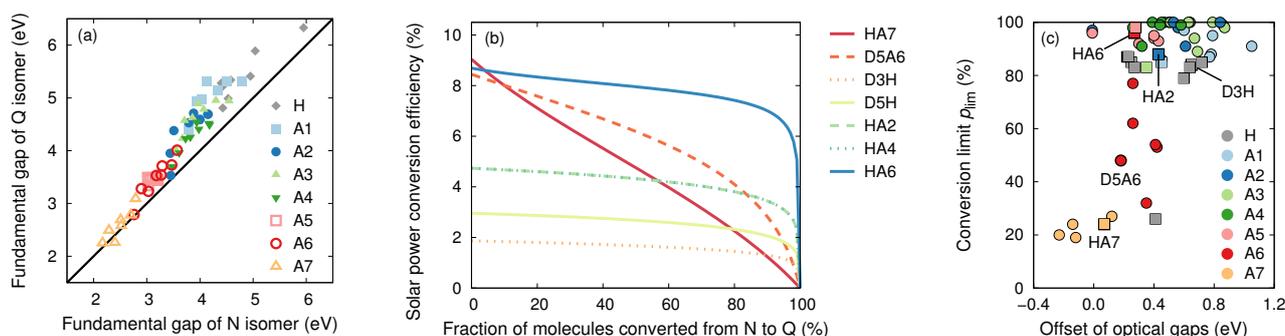
Figure 5. Competing absorption by quadricyclane (also see Fig. 2 of the Supplementary Information). (a) Correlation between the fundamental gaps of quadricyclane and norbornadiene. If the gap of Q approaches the gap of N, absorption by quadricyclane becomes notable. (b) Solar power conversion efficiency according to Eq. (4) as a function of the fraction of molecules converted from N to Q. (c) Fraction of molecules converted to Q, at which the solar power conversion efficiency has dropped to 75% of its initial value as a function of the difference between the optical gaps of N and Q.

This applies in particular to strongly red-shifted systems such as **HA6** and **D6A1**.

Competing absorption by quadricyclane

As N is converted to Q, the latter can in principle absorb sunlight as well and thus compete for photons with N. While for the unsubstituted system the first excitation energy of Q is more than 1 eV higher than for N, this value can be expected to be notably lower for substituted systems due to the effect of substituents on the coupling of HOMO and LUMO in N and Q.[20]

Here, we first consider the difference between the fundamental gaps, which can be expected to closely follow the behavior of the optical gaps. This analysis reveals that as the fundamental gap of the N isomer shrinks the absolute offset between the gaps of N and Q decreases [Fig. 5(a)]. As a result, for compounds with stronger bathochromic shifts the absorption range of the Q variant is likely to approach that of its N counterpart. This implies that part of the solar power is now absorbed by Q and thus does not contribute to power conversion. For fundamental gaps below approximately 3 eV (410 nm) and in particular for **A7**-substituted systems, the difference can be less than 0.2 eV suggesting that absorption by the Q isomer can have a very significant effect on η_{conv}.

To model this effect quantitatively, one can generalize Eq. (1) as shown in the Appendix, which leads to Eq. (4). To evaluate this expression, we used the absorption spectra of Q conformers calculated within TD-DFT. For many of the strongly red-shifted compounds such as **HA7** (offset between optical gaps of N and Q: $\Delta E_g = 0.07$ eV) or **D5A6** ($\Delta E_g = 0.18$ eV), the absorption due to Q gives rise to a rapid decrease in the solar power conversion efficiency η_{conv} [Fig. 5(b)], dramatically limiting the usefulness of such a compound for solar energy conversion.

The effect is notable for all compounds albeit at very different levels. As a suitable measure, we consider the fraction of Q conversion p_{lim}, at which the initial solar power conversion efficiency has been reduced to 75% of its initial value, $\eta_{conv}(p_{lim}) = 0.75\eta_{conv}(0)$ [Fig. 5(c)]. In practice, p_{lim} ought to be as large as possible.

Generally, p_{lim} is small if the difference in the optical gaps of N and Q is $\lesssim 0.2$ eV. The effect also appears to be coupled to specific acceptor groups as it is most pronounced for compounds that contain **A7** and **A6**. For the majority of compounds $80\% < p_{lim} < 90\%$ and again several of the single-substituted systems are among the top performers.

The previous analysis clearly demonstrates the importance of absorption by the photo-isomer, which thus must be included as a relevant parameter not only in designing N-Q compounds but for MOST systems in general as equivalent effects should also occur e.g., in stilbene, azobenzene, or ruthenium fulvalene compounds.

Storage density
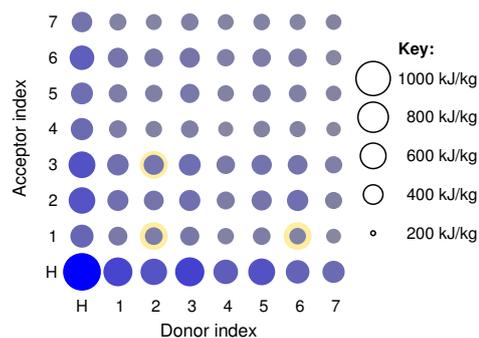
Figure 6. Storage mass density. Each circle corresponds to one compound, where the size represents the storage density. Compounds considered in previous experimental work[18] are marked by yellow circles. The compound in the lower left corner (**HH**) is unsubstituted norbornadiene.

A viable MOST material must not only capture solar power but also achieve a high storage density. The latter is determined by the energy difference between N and Q as well as the mass and/or volume of the molecule. Since the

effective volume is sensitive to solvation conditions and difficult to determine from electronic structure calculations, following earlier work[26] we only consider the storage density per mass.

The storage density is an important parameter to optimize since it together with the heat capacity is directly related to the maximal temperature gradient that can be obtained upon heat release.[6] A minimal storage density for a MOST system has thus been proposed to be $300\,\mathrm{kJ/kg}$, which exceeds the storage density of water ($\Delta T = 50°\mathrm{C}$, $\Delta H_s = 209\,\mathrm{kJ/kg}$), sand ($\Delta H_s = 42\,\mathrm{kJ/kg}$), and salt hydrates ($\Delta H_s = 250\,\mathrm{kJ/kg}$),[22] leading to a temperature rise under adiabatic conditions of approximately $150°\mathrm{C}$.

The *storage energy* ΔE_s of the compounds considered in this work is restricted to a rather small range from 100 to $130\,\mathrm{kJ/mol}$. It is more sensitive to donor than to acceptor substitution, which can be rationalized in the converse way as in the case of the optical gap: Donor groups primarily affect occupied states, whence they have a more pronounced on the total energy.

Norbornadiene is a relatively small molecule, the mass of which (92 amu) is comparable to the masses of the substituents (83 to 187 amu, Fig. 2). In conjunction with the small variation in ΔE_s, this implies that the variation of the *storage densities* from 271 for **D7A4** and $638\,\mathrm{kJ/kg}$ for **D3H** can be primarily attributed to mass differences between the substituents [Fig. 6]. It is therefore not surprising that the highest storage densities in excess of $600\,\mathrm{kJ/kg}$ are obtained for single-substituted systems (e.g., **D3H**: $638\,\mathrm{kJ/kg}$; **D1H**: $631\,\mathrm{kJ/kg}$; **D2H**: $547\,\mathrm{kJ/kg}$) while the best double-substituted compounds reach only about $400\,\mathrm{kJ/kg}$ (e.g., **D3A3**: $415\,\mathrm{kJ/kg}$; **D2A3**: $408\,\mathrm{kJ/kg}$).

The predicted storage densities can be compared to the values of azobenzene ($225\,\mathrm{kJ/kg}$, Ref.[40]) and a Li-ion battery ($> 600\,\mathrm{kJ/kg}$, Ref.[41]). In practice MOST systems including both N-Q and azobenzene derivatives are usually solvated e.g., in toluene, which reduces the effective storage density.

Discussion

A high-performance material ought to combine a high storage density with good solar spectrum match along with the other properties identified above. The present results demonstrate that for many compounds these two properties are anti-correlated [Fig. 7]. This observation can be rationalized by recalling that among the compounds considered here

(i) the bathochromic shift of the absorption spectrum is induced by an extension of the conjugated π-system, which is correlated with larger side groups and thus larger mass, while

(ii) the storage density is only relatively weakly affected by substitution and thus primarily determined by the mass of the side groups.

For the majority of double-substituted systems the shift of the absorption spectrum is strong enough to obtain a solar power conversion efficiency of more than 8%. This approaches the theoretical limit of 10.6% which is imposed by basic considerations concerning the energy balance in the system as discussed above. Yet, the storage density of these compounds is rather low [data points in the upper left corner of Fig. 7].

By contrast, the single-substituted systems achieve much higher storage densities at the expense of lower solar power conversion efficiencies. Among the latter group of compounds there are, however, several candidates that provide a good balance between storage density and conversion efficiency. In particular, **HA2**, **D3H**, and **D5H** appear as strong candidates for further exploration.
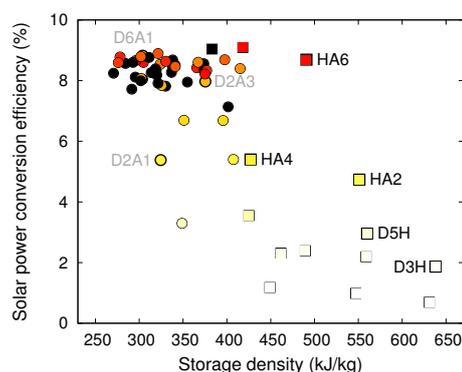
Figure 7. Solar power conversion efficiency vs storage density. Squares and circles mark single and double substituted compounds, respectively. Compounds considered in previous experimental[18] and theoretical work[20] are indicated by gray symbols and text. Several compounds that represent extreme behavior or a good balance of properties are marked by bold symbols and identified by labels. Compounds that violate the condition $\Delta E_s + \Delta E_a + \delta E < \hbar\omega_1$ for $\Delta E_a = 120\,\mathrm{kJ/mol}$ are shown by fully black symbols. For all other compounds the color is representative for the color of the transmission spectrum.

It is remarkable that the first excitation maxima for these materials fall inside the ultra-violet region of the spectrum. Yet, at sufficiently high concentrations broadening due to thermal vibrations, solvent effects as well as multiple conformers can be expected to push the absorption at least for **HA2** and **D5H** into the visible range providing enough overlap with the solar spectrum to yield reasonable solar power conversion efficiencies. Unlike for some of the compounds with very large bathochromic shifts, these compounds also are much less affected by competing absorption of solar power by the quadricyclane variant [Fig. 5]. Finally, for the same reason the barrier for thermal back-conversion is likely to be higher suggesting also a superior capacity for long-term storage.[20,30,38]

In this context, it is instructive to consider the eventual importance of the solar power conversion efficiency. The ultimate cost of any energy technology is determined by a number of factors such as e.g., cost of fuel, material, and infrastructure, in conjunction with physical parameters such as e.g., conversion efficiency and storage density. In the case

of solar harvesting technologies there is no cost associated with the fuel whence the cost for energy production is usually dominated by material and infrastructure. From the perspective of cost effectiveness, lower solar power conversion efficiencies are therefore tolerable.

The above considerations suggest that the optimization of the storage density is more critical than the maximization of the efficiency. Lower efficiencies are furthermore favorable since they require smaller red-shifts, limiting detrimental effects on the thermal stability of Q as well as competing absorption between N and Q. In this regard, systems such as **HA2**, **HA4**, and **D3H** could be interesting candidates.

Conclusions

In the present work we employed electronic structure calculations to determine strategies and identify substituents that can enhance the performance of norbornadiene-based MOST systems. Focusing on solar spectrum match and storage density, we scanned the properties of 64 compounds generated by combining seven different donors and acceptor groups, respectively.

Spectrum match. The absorption spectra of all substituted compounds exhibit a considerable red-shift, which for the substituents considered here can be attributed to the expansion of the conjugated π-system. As a result, there is rough correlation between the size (and mass) of the substituents and the magnitude of the shift that is induced. Furthermore, acceptor substituents appear to be generally more efficient for inducing a spectral shift than donors.

Competing absorption by quadricyclane. The calculations show that for compounds with significant bathochromic shifts, the fundamental gap of Q approaches the gap of N, which is usually significantly smaller. This causes notable absorption by the Q variant effectively competing for photons with the N→Q photoisomerization process. As a result, the efficiency of the N→Q conversion can quickly drop as a function of Q concentration strongly limiting the efficiency of the overall process.

Storage density. The calculated storage densities range from approximately 270 to 640 kJ/kg. Since the storage *energy* is only relatively weakly affected by substitution, the major factor determining the storage energy *density* is the molecular mass. As a result there is a trade-off between storage density and solar spectrum match for the studied compounds.

Finally, we have discussed different factors that affect MOST performance. It was argued that for N-Q based systems it is not likely not to be beneficial to maximize the solar power conversion efficiency as it is usually associated with a deterioration of thermal stability of Q and absorption competition between N and Q. Rather a balance ought to be struck with storage density. Based on the present analysis, we suggest that further experimental and theoretical studies should focus on single-substituted systems or double-substituted systems with one of the substituent being very small.

In terms of further theoretical and modeling work, a number of additional properties ought to be considered that currently cannot be covered in a screening study of the present size. Based on this work, it will, however, be possible to carry out these investigations on a much smaller set of compounds. Specific properties of interest in the context of MOST systems include for example the barrier for back-conversion. As alluded to above, this requires computationally much more demanding techniques that can account for the multi-reference character of the transition state. Of special interest in this context are strategies that can be employed to overcome at least partially the correlation between the onset of absorption and the barrier for thermal backconversion.[20]

Another area of interest concerns vibrational and solvent related effects. Primarily as the result of different dielectric properties, solvents can impact not only the ground state potential energy surface (storage energy and thermal stability) but also the excited landscape (absorption spectrum). From a practical and environmental stand point it is also pivotal to identify solvents and compound-solvent combinations that simultaneously enable large solubilities and are environmentally friendly. With regard to vibrational effects, in particular the low energy rotations of the side groups with respect to the bond to the parent group deserve further study.

Acknowledgments

Appendix

Treatment of conformational effects

In the present work, we included conformers corresponding to rotations of the substituents relative their bond to the parent compound as well as rotations of oxygen bridge bonds such as in **D2** and **D5**. The resulting configurations relaxed at the DFT-B3LYP level fall within a relatively narrow energy range on the order of $k_B T$ at room temperature (26 meV = 2.49 kJ/mol). The statistical probability to observe conformation i with energy E_i and degeneracy n_i at temperature T is given by the Boltzmann factor

$$\rho_i(T,E) = \mathscr{Z}^{-1} n_i \exp\left(-E_i/k_B T\right) \qquad (3)$$

with

$$\mathscr{Z} = \sum_i n_i \exp\left(-E_i/k_B T\right)$$

where $\mathscr{Z}$ is the conformational partition function (or state sum).

The storage energy for any compound was obtained by taken the difference of the thermodynamically averaged energies of N and Q at 300 K according to

$$\Delta E_s = \langle E_Q \rangle_{300\,\text{K}} - \langle E_N \rangle_{300\,\text{K}}$$
$$= \sum_i E_{\text{tot,Q}}^{(i)} \rho\left(300\,\text{K}, E_{\text{tot,Q}}^{(i)}\right) - \sum_i E_{\text{tot,N}}^{(i)} \rho\left(300\,\text{K}, E_{\text{tot,N}}^{(i)}\right),$$

Similarly, the molar attenuation coefficients were computed for the N and Q isomers separately as

$$\varepsilon_{\text{N/Q}}(\omega) = \sum_i \varepsilon_{\text{N/Q}}^{(i)}(\omega) \rho\left(300\,\text{K}, E_{\text{N/Q}}^{(i)}\right).$$

Solar power conversion efficiency in the presence of quadricyclane

To model the limiting effect of Q absorption on the N→Q conversion quantitatively, we generalize Eq. (1) to the case of solution. To get the total amount of absorbed photons, we use the additivity of absorption coefficients and get

$$\dot{N}_{\text{N+Q}}^{\text{abs}}(\omega) = \left\{ 1 - 10^{-\left[\varepsilon_{\text{N}}(\omega)c_{\text{N}} + \varepsilon_{\text{Q}}(\omega)c_{\text{Q}}\right]L} \right\} \frac{P_{\text{sol}}(\omega)}{\hbar\omega}.$$

The absorption will give rise to a photon count profile $\dot{N}(z)$ inside the sample. Over any given slice $[l, l+dl]$, the probability of absorption of norbornadiene or quadricyclane is directly proportional to their respective absorption coefficients, $d\dot{N} = d\dot{N}_{\text{N}} + d\dot{N}_{\text{Q}}$, where $d\dot{N}_{\text{N}} = -\varepsilon_{\text{N}}(\omega)c_{\text{N}}dz/\ln(10)$ and $d\dot{N}_{\text{Q}} = -\varepsilon_{\text{Q}}(\omega)c_{\text{Q}}dz/\ln(10)$. This implies that the fraction of photons absorbed by norbornadiene per the total number of photons absorbed is given by an expression

$$S_{\text{N}}(\omega) = \frac{c_{\text{N}}\varepsilon_{\text{N}}(\omega)}{c_{\text{N}}\varepsilon_{\text{N}}(\omega) + c_{\text{Q}}\varepsilon_{\text{Q}}(\omega)}.$$

To get the efficiency for norbornadiene/quadricyclane mixture, one then obtains the relation

$$\eta_{\text{conv}}(p) = \Delta E_s \int_{E_{\text{cut}}}^{\infty} d\omega S_{\text{N}}(\omega) N_{\text{N+Q}}^{\text{abs}}(\omega) \bigg/ \int_0^{\infty} d\omega P_{\text{sol}}(\omega), \tag{4}$$

where $c_{\text{N}} = (1-p)c$ and $c_{\text{Q}} = pc$. This expression reduces to Eq. (1) in the case of a pure norbornadiene, $p = 0$.

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Entry for the Table of Contents

Getting the most out of MOST

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Optimization of Norbornadiene Compounds for Solar Thermal Storage by First-principles Calculations

Using first-principles calculations we explore a large number of substituted norbornadiene-quadricyclane systems for molecular solar thermal storage (MOST). The champion compounds are molecules with a single acceptor substitution. They can achieve storage densities in excess of 550 kJ/kg and very good solar thermal match with the prospect of mid to long term thermal stability.
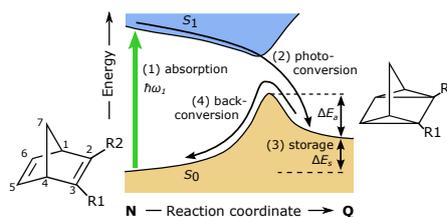
Supplementary Information:
Optimization of Norbornadiene Compounds for
Solar Thermal Storage by First-principles Calculations

Mikael Kuisma,[a] Angelica Lundin,[b] Kasper Moth-Poulsen,[b] Per Hyldgaard,[c] and Paul Erhart[a]*
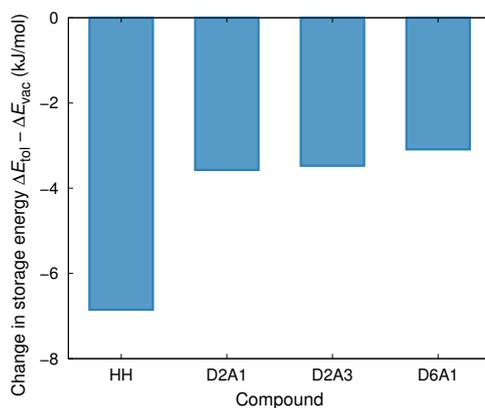
Figure 1. Energy difference between the storage energy in vacuum ΔE_{vac} and toluene ΔE_{tol} for selected compounds. For the substituted compounds the difference $\Delta E_{\text{tol}} - \Delta E_{\text{vac}}$ is on the order of $-4\,\text{kJ/mol}$ or less.

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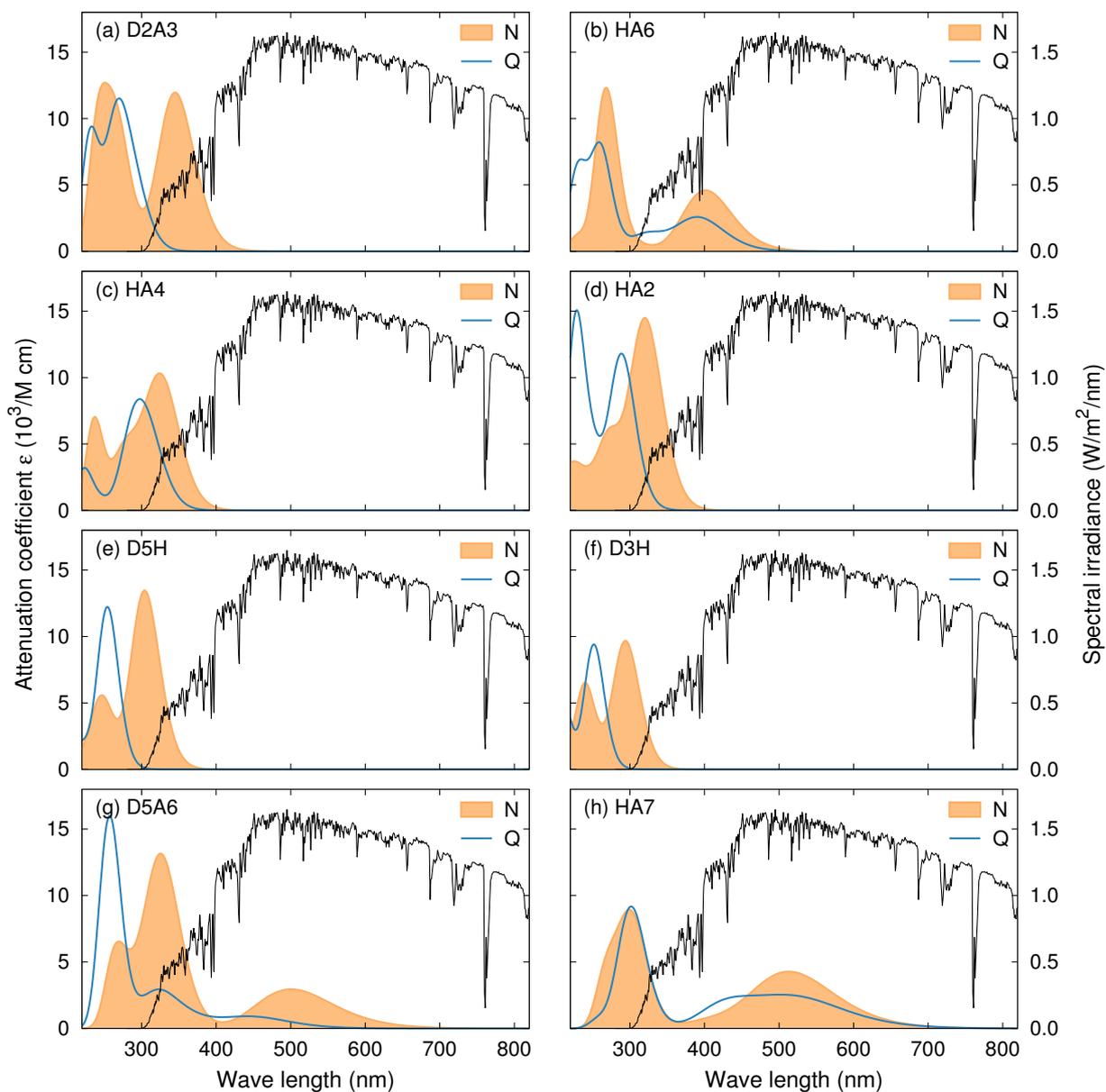
Figure 2. Attenuation coefficients of both the norbornadiene (N) and quadricyclane (Q) isomers for selected compounds. The attenuation coefficients were obtained by averaging over different conformations as described in the paper. The black solid line represents the AM1.5 solar spectrum.