Supplementary Material: A Comparative Ab-Initio Study of Substituted Norbornadiene-Quadricyclane Compounds for Solar Thermal Storage

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Molecular structure of the unsubstituted compound (1)

Detailed comparison unsubstituted norbornadiene and quadricyclane is presented in Tables 1 and 2.

Compilation of results from calculations of storage energy

The storage energies (electronic energy difference between N and Q) computed using CASPT2 as well as DFT are compiled in Table 3.

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Compilation of results from calculations of absorption behavior

The first excitation energies obtained from CASPT2 calculations are compiled in Table 4. Excitation energies and dipole strengths from TD-DFT calculations for the first five excitations of the molecules considered in this study are compiled in Tables 5 and 6. Figure 1 shows the molar attenuation coefficients in toluene obtained using different exchange-correlation functionals, which are based on the data presented in Table 6.

Convergence of MP2 and CCSD(T) calculations with basis set

As a further benchmark of our calculations, we performed an accurate comparison of computational and experimental results regarding the geometry and the gas-phase thermochemistry of the unsubstituted norbornadiene quadricyclane system (**1**). All geometries were fully relaxed

Table 1: Bond lengths r in Å and angles θ of norbornadiene compared to experimental values.

N	r(C2–C3)	r(C1–C2)	r(C1–C7)	θ(C1,C4,C7)
Experiment 1[1]	1.3362	1.5304	1.5567	
Experiment 2[a][2]	1.338	1.533	1.571	92.2°
PBE	1.343	1.544	1.562	92.2°
B3LYP	1.334	1.544	1.561	92.0°
B3LYP (aug-cc-vtzp)	1.329	1.540	1.558	92.0°
MP2 (aug-cc-vdzp)	1.358	1.542	1.564	92.4°
MP2 (aug-cc-vtzp)	1.342	1.532	1.553	92.3°
M06	1.329	1.532	1.546	92.2°

[a] Data from fit I; fit II yields and angle θ(C1,C4,C7) of 96°, which is not supported by the computational data.

Table 2: Bond lengths r in Å and angles θ of quadricyclane compared to experimental values.

Q	r(C–C(short))	r(C–C(long))	θ(C1,C7,C4)
Experiment[3]	1.518	1.562	98.50°
PBE	1.522	1.551	98.88°
B3LYP	1.517	1.550	98.85°
B3LYP (aug-cc-vtzp)	1.513	1.547	98.82°
MP2 (aug-cc-vdzp)	1.533	1.552	98.92°
MP2 (aug-cc-vtzp)	1.519	1.540	98.84°
M06	1.507	1.538	98.85°

Table 3: Storage energies in kJ/mol from CASPT2 as well as DFT calculations.

Compound	1	2	3	4	5	6
Vacuum						
CASPT2//CASSCF	91	100	101	99	99	99
CASPT2//PBE	94	96	97	98	97	102
PBE	71	91	87	86	86	90
B3LYP	99	115	113	112	112	115
CAM-B3LYP	87	100	98	96	96	99
M06-L	41	71	61	69	67	67
M06	53	62	68	68	67	74
M06-2x	65	75	76	73	75	74
Toluene						
PBE	64	86	83	82	83	87
B3LYP	93	111	109	108	108	112
CAM-B3LYP	80	96	94	93	93	96

Table 4: Excitation energies under vacuum conditions in eV from CASPT2 calculations.

Compound	1	2	3	4	5	6
CASPT2//CASSCF	5.32	4.47	4.40	4.29	4.22	3.96
CASPT2//PBE	5.32	4.15	4.04	3.94	3.82	3.66

Table 5: Excitation energies in eV and dipole strengths (given in brackets) in vacuum from TD-DFT calculations using different exchange-correlation functionals.

		PBE									
1	N	4.47	(0.00)	5.00	(0.01)	5.19	(0.01)	5.76	(0.00)	5.86	(0.00)
1	Q	5.00	(0.00)	5.44	(0.00)	5.51	(0.00)	5.62	(0.01)	6.06	(0.02)
2	N	3.21	(0.17)	3.71	(0.02)	3.80	(0.06)	4.01	(0.01)	4.03	(0.02)
2	Q	4.10	(0.00)	4.11	(0.00)	4.25	(0.00)	4.38	(0.00)	4.57	(0.01)
3	N	3.05	(0.18)	3.54	(0.04)	3.79	(0.00)	3.85	(0.01)	3.92	(0.04)
3	Q	3.73	(0.01)	3.85	(0.05)	3.98	(0.01)	4.22	(0.05)	4.44	(0.04)
4	N	2.86	(0.18)	3.46	(0.02)	3.62	(0.01)	3.84	(0.06)	3.85	(0.00)
4	Q	3.40	(0.04)	3.65	(0.01)	3.97	(0.03)	4.05	(0.04)	4.24	(0.01)
5	N	2.67	(0.21)	3.42	(0.01)	3.43	(0.02)	3.68	(0.14)	3.80	(0.01)
5	Q	3.06	(0.05)	3.60	(0.00)	3.70	(0.10)	4.00	(0.01)	4.18	(0.01)
6	N	2.54	(0.23)	3.16	(0.02)	3.41	(0.03)	3.58	(0.01)	3.68	(0.01)
6	Q	2.78	(0.02)	3.16	(0.01)	3.78	(0.12)	3.85	(0.02)	3.96	(0.01)
		B3LYP									
1	N	4.86	(0.00)	5.56	(0.01)	5.58	(0.01)	6.15	(0.00)	6.15	(0.02)
1	Q	5.47	(0.00)	5.84	(0.00)	5.95	(0.00)	6.08	(0.01)	6.53	(0.02)
2	N	3.70	(0.22)	4.32	(0.02)	4.53	(0.05)	4.63	(0.02)	4.70	(0.03)
2	Q	4.94	(0.00)	5.06	(0.00)	5.12	(0.00)	5.13	(0.00)	5.23	(0.00)
3	N	3.58	(0.22)	4.17	(0.04)	4.49	(0.01)	4.60	(0.07)	4.65	(0.02)
3	Q	4.54	(0.03)	4.67	(0.06)	4.83	(0.04)	5.01	(0.05)	5.11	(0.00)
4	N	3.40	(0.23)	4.11	(0.03)	4.45	(0.03)	4.49	(0.01)	4.54	(0.07)
4	Q	4.28	(0.08)	4.53	(0.01)	4.75	(0.02)	4.81	(0.07)	5.00	(0.02)
5	N	3.23	(0.26)	4.07	(0.01)	4.29	(0.03)	4.36	(0.14)	4.46	(0.01)
5	Q	3.99	(0.11)	4.47	(0.08)	4.51	(0.07)	4.74	(0.02)	4.90	(0.02)
6	N	3.11	(0.27)	3.88	(0.04)	4.16	(0.05)	4.26	(0.01)	4.35	(0.02)
6	Q	3.72	(0.03)	4.10	(0.02)	4.36	(0.03)	4.43	(0.06)	4.49	(0.11)
		CAM-B3LYP									
1	N	5.21	(0.00)	6.08	(0.02)	6.12	(0.03)	6.54	(0.03)	6.71	(0.00)
1	Q	5.97	(0.00)	6.30	(0.00)	6.48	(0.00)	6.62	(0.00)	7.15	(0.02)
2	N	4.17	(0.24)	4.90	(0.02)	5.15	(0.00)	5.29	(0.09)	5.43	(0.11)
2	Q	5.38	(0.00)	5.41	(0.00)	5.85	(0.09)	5.87	(0.03)	6.05	(0.05)
3	N	4.10	(0.25)	4.74	(0.05)	5.04	(0.01)	5.32	(0.12)	5.39	(0.16)
3	Q	5.00	(0.02)	5.25	(0.00)	5.38	(0.18)	5.68	(0.20)	5.73	(0.03)
4	N	3.97	(0.27)	4.74	(0.04)	5.01	(0.01)	5.26	(0.16)	5.38	(0.17)
4	Q	5.00	(0.02)	5.19	(0.10)	5.20	(0.11)	5.60	(0.26)	5.80	(0.02)
5	N	3.84	(0.32)	4.70	(0.03)	4.96	(0.02)	5.11	(0.28)	5.30	(0.01)
5	Q	4.88	(0.27)	5.03	(0.07)	5.07	(0.03)	5.53	(0.23)	5.62	(0.09)
6	N	3.76	(0.35)	4.46	(0.06)	4.85	(0.03)	4.89	(0.01)	5.05	(0.21)
6	Q	4.61	(0.03)	4.89	(0.23)	4.92	(0.01)	5.20	(0.02)	5.30	(0.34)

Table 6: Excitation energies in eV and dipole strengths (given in brackets) in toluene from TD-DFT calculations using different exchange-correlation functionals.

|		PBE									
1	N	4.48	(0.00)	5.01	(0.01)	5.33	(0.01)	5.93	(0.00)	5.99	(0.00)
1	Q	5.11	(0.00)	5.49	(0.00)	5.63	(0.00)	5.70	(0.01)	6.17	(0.02)
2	N	3.22	(0.17)	3.70	(0.02)	3.80	(0.07)	4.00	(0.01)	4.04	(0.02)
2	Q	4.00	(0.00)	4.00	(0.01)	4.14	(0.00)	4.27	(0.00)	4.54	(0.01)
3	N	3.05	(0.18)	3.54	(0.04)	3.79	(0.00)	3.85	(0.01)	3.91	(0.05)
3	Q	3.67	(0.01)	3.79	(0.06)	3.92	(0.00)	4.18	(0.05)	4.39	(0.03)
4	N	2.83	(0.19)	3.44	(0.02)	3.57	(0.01)	3.83	(0.09)	3.84	(0.00)
4	Q	3.29	(0.05)	3.57	(0.01)	3.90	(0.04)	3.97	(0.04)	4.19	(0.01)
5	N	2.61	(0.20)	3.36	(0.01)	3.41	(0.00)	3.66	(0.17)	3.78	(0.01)
5	Q	2.94	(0.06)	3.53	(0.02)	3.57	(0.08)	3.95	(0.01)	4.13	(0.01)
6	N	2.46	(0.24)	3.08	(0.02)	3.35	(0.03)	3.53	(0.02)	3.65	(0.01)
6	Q	2.67	(0.02)	3.07	(0.00)	3.66	(0.13)	3.78	(0.02)	3.87	(0.01)
		B3LYP									
1	N	4.88	(0.00)	5.57	(0.01)	5.70	(0.02)	6.28	(0.02)	6.31	(0.00)
1	Q	5.56	(0.00)	5.88	(0.00)	6.07	(0.00)	6.14	(0.00)	6.63	(0.02)
2	N	3.69	(0.22)	4.32	(0.02)	4.51	(0.05)	4.63	(0.01)	4.70	(0.04)
2	Q	4.84	(0.00)	4.96	(0.00)	5.03	(0.00)	5.11	(0.00)	5.22	(0.00)
3	N	3.56	(0.23)	4.16	(0.04)	4.47	(0.01)	4.58	(0.07)	4.65	(0.01)
3	Q	4.55	(0.03)	4.66	(0.04)	4.80	(0.05)	4.97	(0.02)	5.07	(0.04)
4	N	3.37	(0.23)	4.10	(0.02)	4.41	(0.03)	4.48	(0.01)	4.52	(0.08)
4	Q	4.25	(0.10)	4.52	(0.01)	4.70	(0.07)	4.73	(0.02)	4.96	(0.02)
5	N	3.16	(0.27)	4.06	(0.01)	4.22	(0.03)	4.33	(0.15)	4.44	(0.01)
5	Q	3.91	(0.13)	4.32	(0.12)	4.47	(0.01)	4.73	(0.02)	4.87	(0.02)
6	N	3.04	(0.28)	3.82	(0.04)	4.11	(0.05)	4.21	(0.01)	4.33	(0.05)
6	Q	3.62	(0.03)	4.04	(0.01)	4.30	(0.03)	4.38	(0.14)	4.53	(0.06)
		CAM-B3LYP									
1	N	5.23	(0.00)	6.11	(0.03)	6.20	(0.02)	6.65	(0.03)	6.86	(0.00)
1	Q	6.06	(0.00)	6.33	(0.00)	6.60	(0.00)	6.67	(0.00)	7.24	(0.02)
2	N	4.17	(0.24)	4.90	(0.02)	5.15	(0.00)	5.28	(0.09)	5.43	(0.11)
2	Q	5.39	(0.00)	5.41	(0.00)	5.78	(0.02)	5.83	(0.09)	6.00	(0.02)
3	N	4.08	(0.26)	4.73	(0.05)	5.03	(0.01)	5.31	(0.12)	5.39	(0.17)
3	Q	5.02	(0.02)	5.23	(0.00)	5.38	(0.17)	5.66	(0.23)	5.82	(0.01)
4	N	3.95	(0.27)	4.73	(0.04)	5.00	(0.01)	5.24	(0.16)	5.38	(0.18)
4	Q	5.01	(0.03)	5.14	(0.22)	5.17	(0.00)	5.60	(0.24)	5.83	(0.02)
5	N	3.79	(0.33)	4.69	(0.03)	4.95	(0.03)	5.08	(0.27)	5.27	(0.00)
5	Q	4.80	(0.36)	5.03	(0.03)	5.06	(0.03)	5.49	(0.12)	5.62	(0.14)
6	N	3.72	(0.36)	4.44	(0.05)	4.84	(0.02)	4.93	(0.08)	5.05	(0.14)
6	Q	4.57	(0.03)	4.84	(0.20)	4.95	(0.07)	5.18	(0.02)	5.26	(0.27)
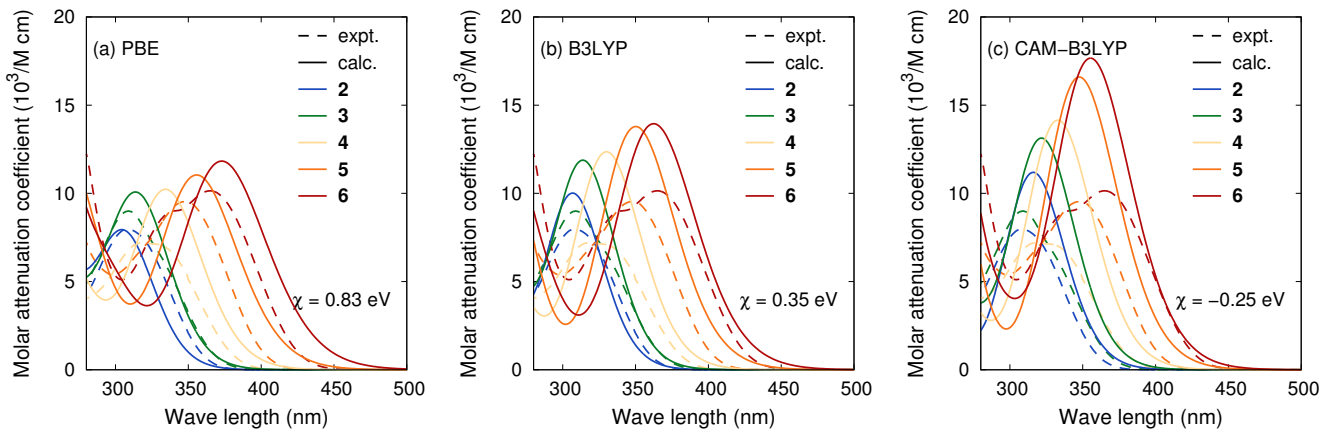
Figure 1: Comparison of the molar attenuation coefficients of **2**–**6** from experiment[4] and (a) PBE, (b) B3LYP, and (c) CAM-B3LYP calculations. A smearing using a width of $0.25\,\mathrm{eV}$ was applied to the latter to mimic the broadening due to vibrations. The calculated spectra are unshifted.

with the exception of CASPT2 and CCSD(T), for which single-point calculations were carried out based on CASSCF and MP2 geometries, respectively. All calculations are performed with NWChem 6.5[5] except for CASSCF and CASPT2, which were performed with MolCas 8.0.[6–8] The MP2 results were extrapolated to the complete basis set (CBS) limit as suggested by Halkier *et al.*[9,10] while the CCSD(T) data were extrapolated to the CBS limit following Jurecka et al.[11]. The results of our calculations for ΔE are compiled in Table 7.

The experimental reference value for ΔH is $92 \pm 1\,\mathrm{kJ/mol}$. To obtain ΔE we substract the $\Delta H - \Delta E$ difference obtained at the DFT level, i.e.

$$\Delta E_{\mathrm{expt}} = \Delta H_{\mathrm{expt}} - (\Delta H_{\mathrm{DFT}} - \Delta E_{\mathrm{DFT}}). \quad (1)$$

Using B3LYP data (see main text), we then obtain $\Delta E_{\mathrm{expt}} = 94 \pm 1\,\mathrm{kJ/mol}$.[12] The extrapolated CCSD(T) value of $\Delta E = 95.5\,\mathrm{kJ/mol}$, which represents the highest level of calculation among our calculated data, is in fact in very good agreement with the experimental value. Both ΔE_{expt} and $\Delta E_{\mathrm{CCSD(T)}}$ are shown as reference values in Fig. 4(b) of the main article.
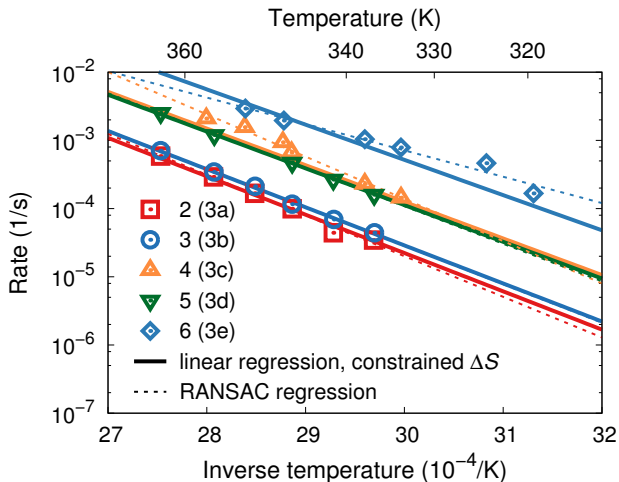

Figure 2: Comparison of different approaches for fitting the experimental data for thermal Q→ back-conversion. While the assessment indicates a certain level of uncertainty regarding the thus obtained barriers, it highlights the systematic variation of the conversion rates across the compounds, which are ordered by onset of absorption. For conveniences, the numbers in the legend given in brackets refer to the compound enumeration used in Gray et al.[4].

Table 7: Storage energies (electronic contribution only) for the unsubstituted norbornadiene-quadricylane system at different levels of calculation.

Method	Basis set	ΔE (kJ/mol)
M06	6-311+G*	54.73
PBE	6-311+G*	71.06
B3LYP	6-311+G*	99.71
B3LYP	aug-cc-pvdz	91.62
B3LYP	aug-cc-pvtz	96.80
MP2	aug-cc-pvdz	93.76
MP2	aug-cc-pvtz	86.03
MP2	aug-cc-pvqz	83.89
MP2	(extrapolated[a])	82.59
CASPT2//CASSCF	ANO-S DZP	97.91
CASPT2//CASSCF	aug-cc-pvdz	95.22
CCSD(T)//MP2	aug-cc-pvdz	106.02
CCSD(T)//MP2	aug-cc-pvtz	98.92
CCSD(T)	(extrapolated[b])	95.48

[a] Extrapolation of MP2 data to basis set limit[9,10]
[b] Extrapolation of CCSD(T) data to MP2 basis set limit.[11]

Experimental back-conversion barriers

The thermal stability of the substituted compounds considered in the present study has been previously investigated experimentally.[4] To this end, the absorbance increase associated with the N variant was measured as a function of time at different temperatures. The resulting data was fitted to the Eyring equation to extract the enthalpy barriers for back-conversion along with the associated entropies. The thus obtained data exhibits notable error bars and a pronounced correlation between entropy and enthalpy. Furthermore, the half-life times, which compound enthalpies and entropies, exhibit a very noticeable correlation with the onset of absorption; this is very much unlike the barriers for which no clear trend can be observed. These observations alongside the arguments put forth in the "Transition state" section of the paper prompted us to reinspect these data.

In this context, we refitted the experimental data for the time dependence of the absorbance using both the random sample consensus (RANSAC) method as implemented in scikit-learn[13] and constrained linear regression. The RANSAC algorithm is designed to account for data with outliers, albeit typically more suitable for larger data sets. In the case of the constrained linear regression, we fitted the data sets for all five compounds simultaneously using different enthalpies for each compound but only one value for the entropy. Both approaches yield good representations of the data of equal or better quality than the original fit (Fig. 2 and Table II of the main paper). While this illustrates the difficulty of obtaining reliable values for the barriers, more importantly it demonstrates that the conversion enthalpies and the onset of absorption (or alternatively the absorption maximum) are indeed correlated with each other (Fig. 7 of the main paper).

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