

Electronic Supplementary Information for Multifactor theoretical modeling of solar thermal fuels built on azobenzene and norbornadiene scaffolds

Reuben Szabo,[†] Khoa N. Le,^{†,‡} and Tim Kowalczyk^{*,†}

[†]*Department of Chemistry, Advanced Materials Science and Engineering Center, and
Institute for Energy Studies, Western Washington University, Bellingham, WA, USA*

[‡]*Department of Chemistry, University of Oregon, Eugene, OR 97403*

Contents

1	Supplementary figures: Basis set sensitivity of DFT reference calculations	2
2	Supplementary figures: Transition states and photoisomerization quantum yields of substituted norbornadienes	4
3	Supplementary figures: Transition states and photoisomerization quantum yields of substituted azobenzenes	6
4	Additional computational details	7
5	Optimized geometries of STF compounds in the benchmark sets	7
	References	7

1 Supplementary figures: Basis set sensitivity of DFT reference calculations

Figure S1: Basis set sensitivity of the ground-state energy with the ω B97X-D functional, calculated with four different triple- ζ basis sets and plotted relative to the 6-31G* basis set used in the manuscript.

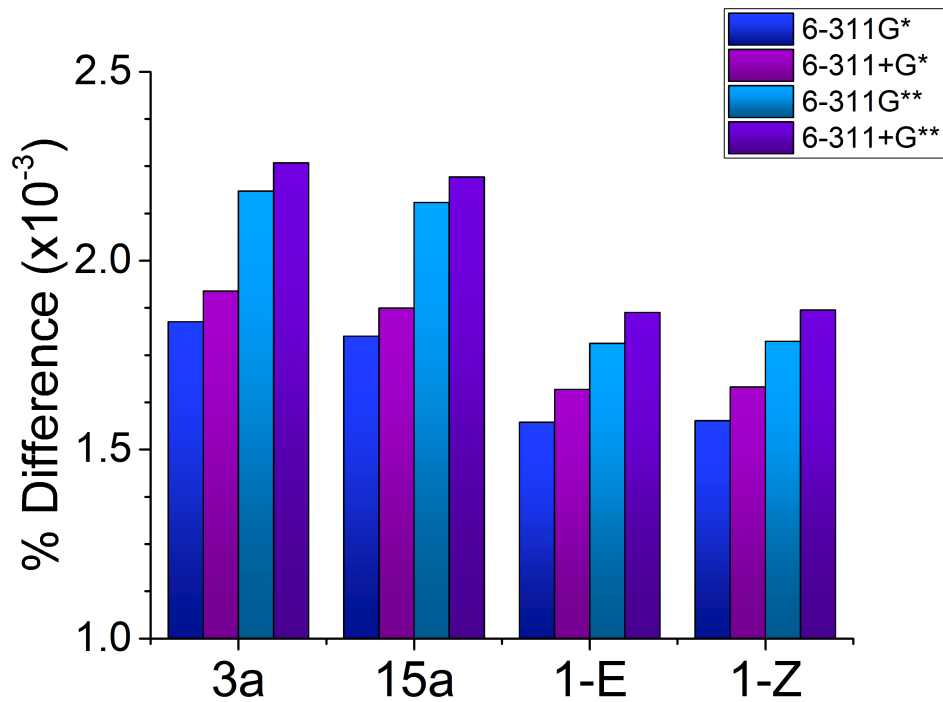
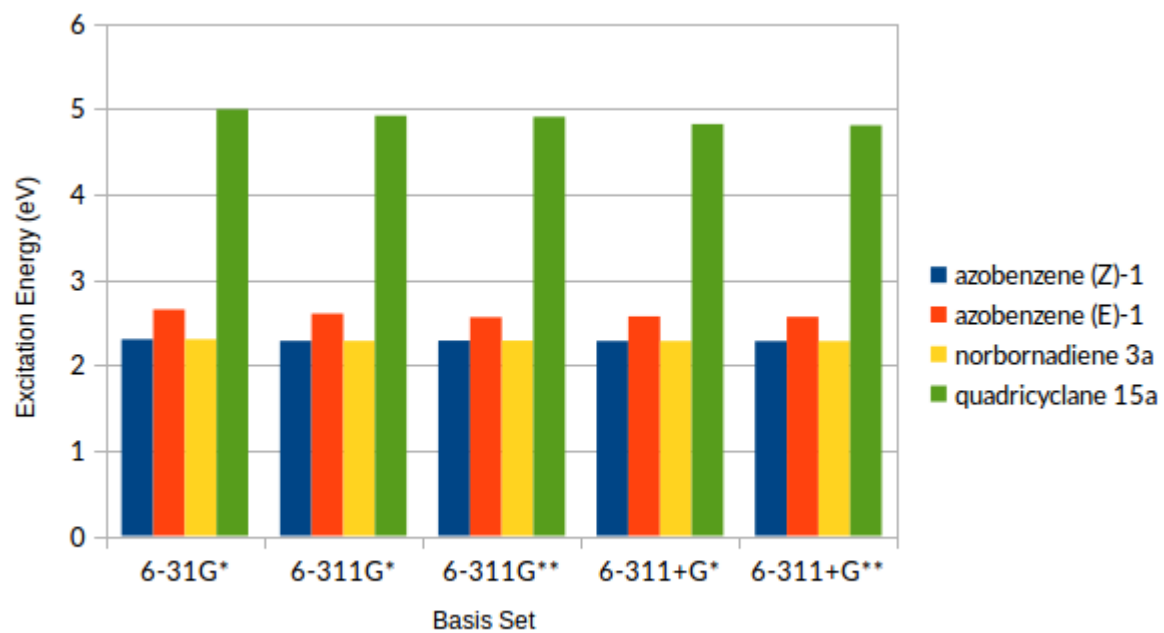


Figure S2: Basis set dependence of the restricted open-shell PBE0 vertical excitation energy for each isomer of two representative compounds: (*Z*)-**1**, (*E*)-**1**, norbornadiene **3a**, and quadricyclane **15a**.



2 Supplementary figures: Transition states and photoisomerization quantum yields of substituted norbornadienes

Figure S3: Carbon-carbon distance b_1 (from PBE0 TS calculation) versus experimental quantum yield. $R^2 = 0.641$.

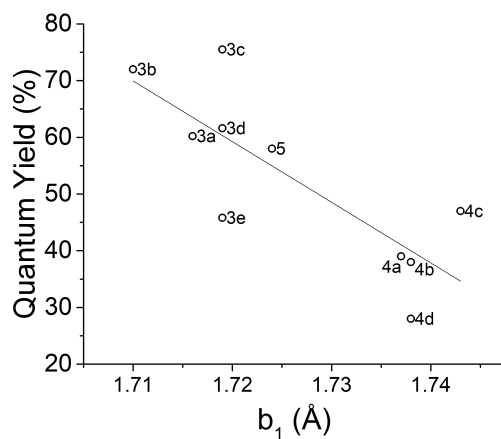


Figure S4: Carbon-carbon distance b_2 (from PBE0 TS calculation) versus experimental quantum yield. $R^2 = 0.397$.

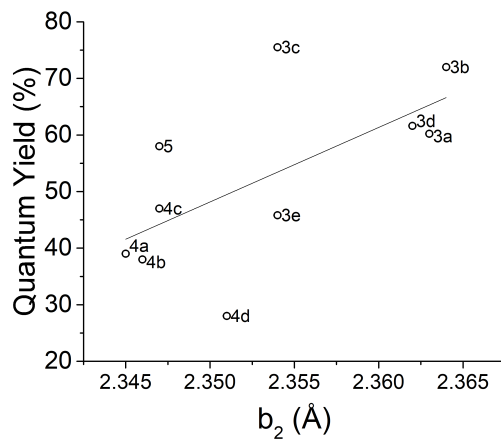


Figure S5: Carbon-carbon distance b_1 (from PBE0 TS calculation) versus storage energy calculated with DFT and the PBE0 functional. $R^2 = 0.826$.

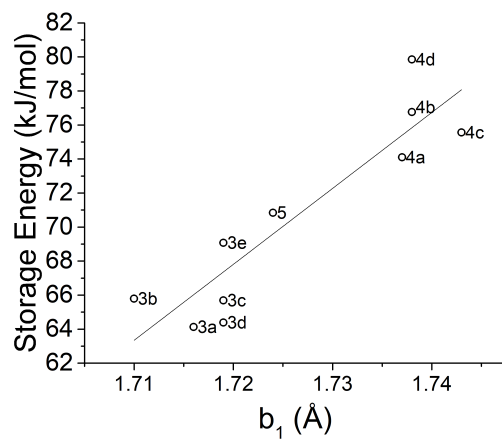
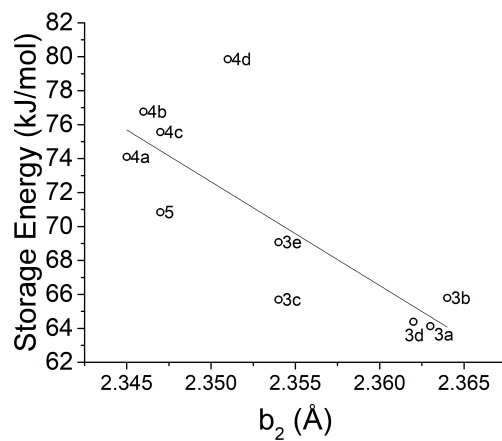


Figure S6: Carbon-carbon distance b_2 (from PBE0 TS calculation) versus storage energy calculated with DFT and the PBE0 functional. $R^2 = 0.633$.



3 Supplementary figures: Transition states and photoisomerization quantum yields of substituted azobenzenes

Figure S7: Reverse isomerization energy barrier of azobenzenes and corresponding C-N=N-C dihedral angles reported as difference from 90 °.

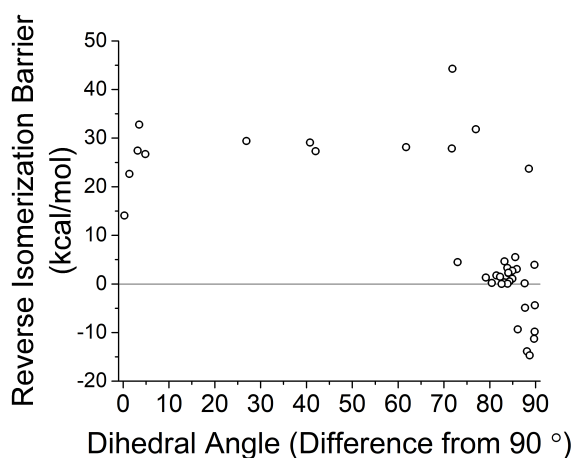
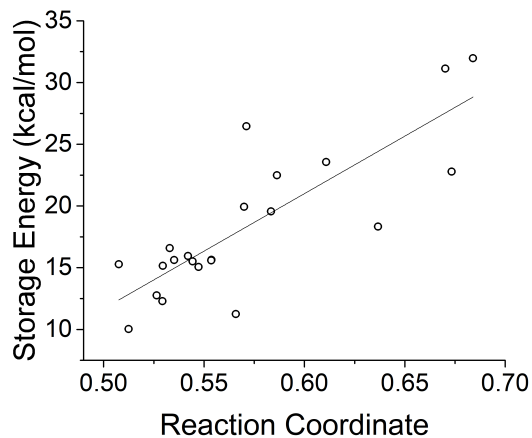


Figure S8: DFT calculated storage energies for azobenzenes (with the PBE0 functional) compared to the position of the (PBE0) transition state along the reaction coordinate. The *trans* configuration is located at 0 on the reaction coordinate, and the *cis* configuration is located at 1. $R^2 = 0.678$.



4 Additional computational details

As described in the main text, we employed the SCC-DFTB method with colinear spin polarization^{1,2} to allow for unpaired electron density. For fluorinated compounds 3c and 3e, lacking atomic spin constants for fluorine, we substituted those tabulated for oxygen as the closest set available.³ We generally observe that the energy is highly insensitive to the spin polarization term in these compounds. The excited state energies were found using our modified version of the DFTB+ code which includes an implementation of Δ DFTB.

5 Optimized geometries of STF compounds in the benchmark sets

Optimized geometries are provided for the stable and metastable isomer for each STF candidate in the benchmark set in the .zip archive SzaboLeKowalczyk.structures.zip. All geometries provided in the archive were optimized at the ω B97X-D/6-31G* level of theory in Q-Chem. For consistency, the numerical labels for the compounds are derived from the labels introduced in Refs. 4 and 5 for the azobenzenes and norbornadienes, respectively.

References

- (1) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifer, G. Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. *Phys. Rev. B* **1998**, *58*, 7260.
- (2) Köhler, C.; Seifert, G.; Elstner, M.; Overhof, H.; Frauenheim, T. Approximate density-functional calculations of spin densities in large molecular systems and complex solids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5109–5114.

- (3) Köhler, C. Berücksichtigung von Spinpolarisationseffekten in einem dichtefunktional-basierten Ansatz. Ph.D. thesis, Universität Paderborn, 2004.
- (4) Liu, Y.; Grossman, J. C. Accelerating the Design of Solar Thermal Fuel Materials through High Throughput Simulations. *Nano Lett.* **2014**, *14*, 7046–7050.
- (5) Quant, M.; Lennartson, A.; Dreos, A.; Kuisma, M.; Erhart, P.; Börjesson, K.; Moth-Poulsen, K. Low Molecular Weight Norbornadiene Derivatives for Molecular Solar-Thermal Energy Storage. *Chem. Eur. J.* **2016**, *22*, 13265–13274.