Photoisomerization of *cis,trans*-1,4-diphenyl-1,3-butadiene

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Introduction

Photoisomerization of ***cis,trans*-1,4-diphenyl-1,3-butadiene** (*ct*-DPB) occurs via UV-induced rotation around C=C bonds through the S_1 ($\pi\rightarrow\pi^*$) excited state, converting it to *trans,trans* (*tt*-DPB) and *cis,cis* (*cc*-DPB) isomers. Femtosecond transient absorption studies in ethanol revealed evidence of **two-photon excitation** of DPB isomers[5]. This study tests whether two-photon excitation can also be induced using conventional medium-pressure Hanovia Hg lamps (200 W and 450 W) at 313 nm. Quantum yields (Φ) for *ct*-DPB → *tt*-DPB photoisomerization are measured by **^{1}H NMR spectroscopy** in $CDCl_3$ with *trans*-stilbene as the actinometer.

Background Information

DPB isomers were irradiated and the twisted intermediates were trapped by ethanol[2]. Based on this, a mechanism for DPB photoisomerization and photoaddition was proposed: *cc*-DPB forms phenyl cation/benzyl anion intermediates before yielding ethers, while *ct*-DPB and *tt*-DPB forms a trans-zwitterionic intermediate before yielding ethers. An experiment by the Saltiel group[5] observed a small positive *ct*-DPB absorption band at ~365 nm, which is attributed to a trans-zwitterionic intermediate. This study uses the transient absorption data reported to align the data obtained from Hanovia Hg lamp irradiation with the proposed mechanism for DPB isomerization.

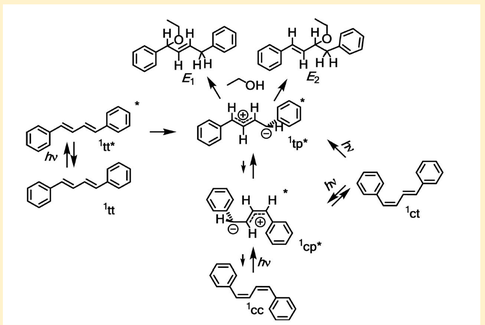


Figure 1. Proposed mechanism for DPB photoisomerization and photoaddition. E1 and E2 are ether products from the photoaddition of ethanol to DPB.[2]

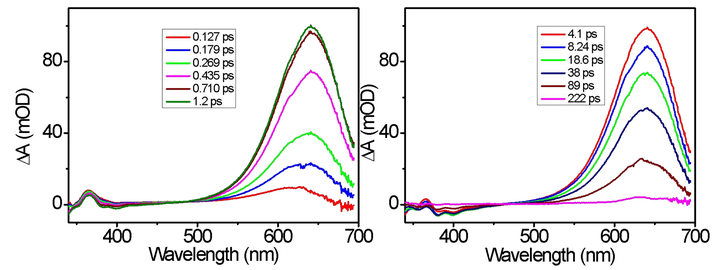


Figure 2. *ct*-DPB isomerization in ethanol with 575 μW laser power at a) earlier and b) later time scale.

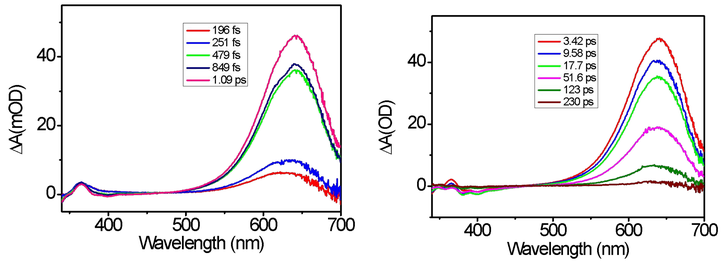
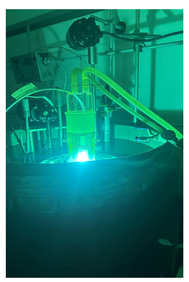
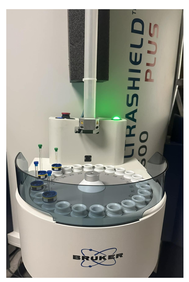


Figure 3. *ct*-DPB isomerization in ethanol with 300 μW laser power at a) earlier and b) later time scale.

Experimental Methods

I. Synthesis of *cis,trans*-DPB

II. Irradiation of *cis,trans*-DPB with **200 W** and **450 W**

Degassing	Irradiation	Evaporation	^{1}H NMR
			
Remove dissolved oxygen	*π → π* transition to the S_1 excited state*	*Evaporate solvent & crystallize solute*	*Quantify different types of ^{1}H atom present*

Results

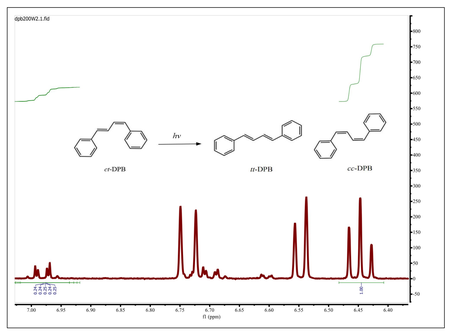


Figure 4. ^{1}H NMR of *ct*-DPB at 200 W for 120 minutes in ethanol
%conversion = 10.4%
$\Phi_{ct\text{-DPB}} = 0.1646 \pm 0.007961$

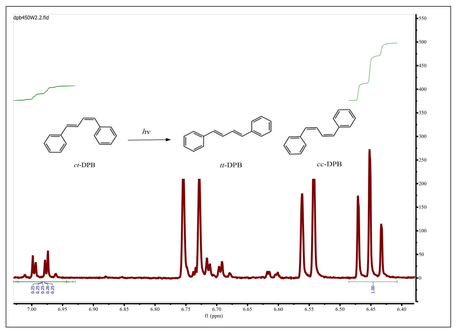


Figure 5. ^{1}H NMR of *ct*-DPB at 450 W for 45 minutes in ethanol
%conversion = 9.28%
$\Phi_{ct\text{-DPB}} = 0.1551 \pm 0.02893$

Discussion

$\Phi_{ct\text{-DPB}}$ is consistent with that of 0.15 ± 0.02 reported by Saltiel and Redwood (2016). The 200 W and 450 W quantum yields show **no statistically significant dependence on light intensity** within experimental error. They are near-identical which is consistent with single-photon excitation. This is because Hanovia Hg lamps cannot generate the high intensities required for two-photon excitation. Future studies should employ transient spectroscopy because laser sources can allow more photon absorption, allowing the induction of two-photon excitation.

References

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