



# The Photodimerization of Anthracene-9-d<sub>1</sub>

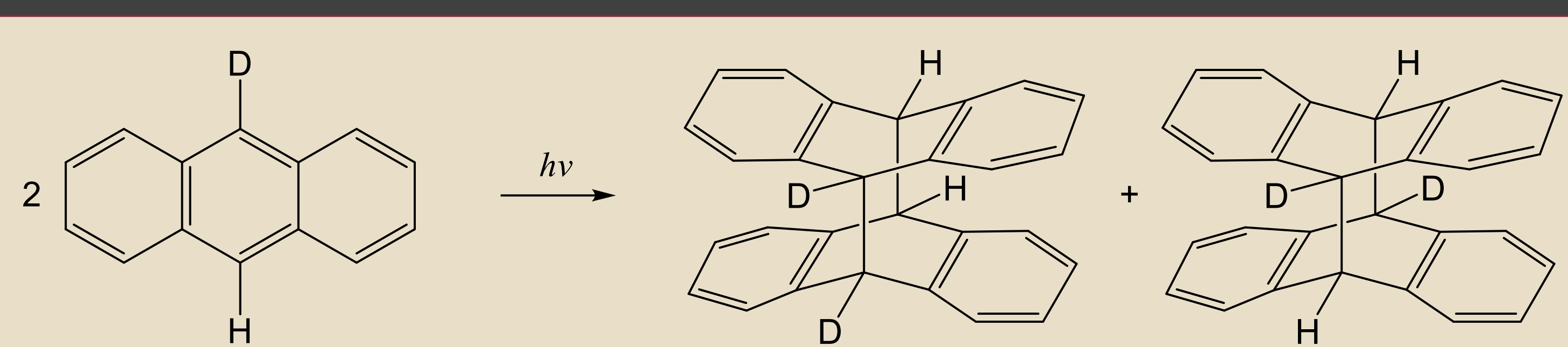
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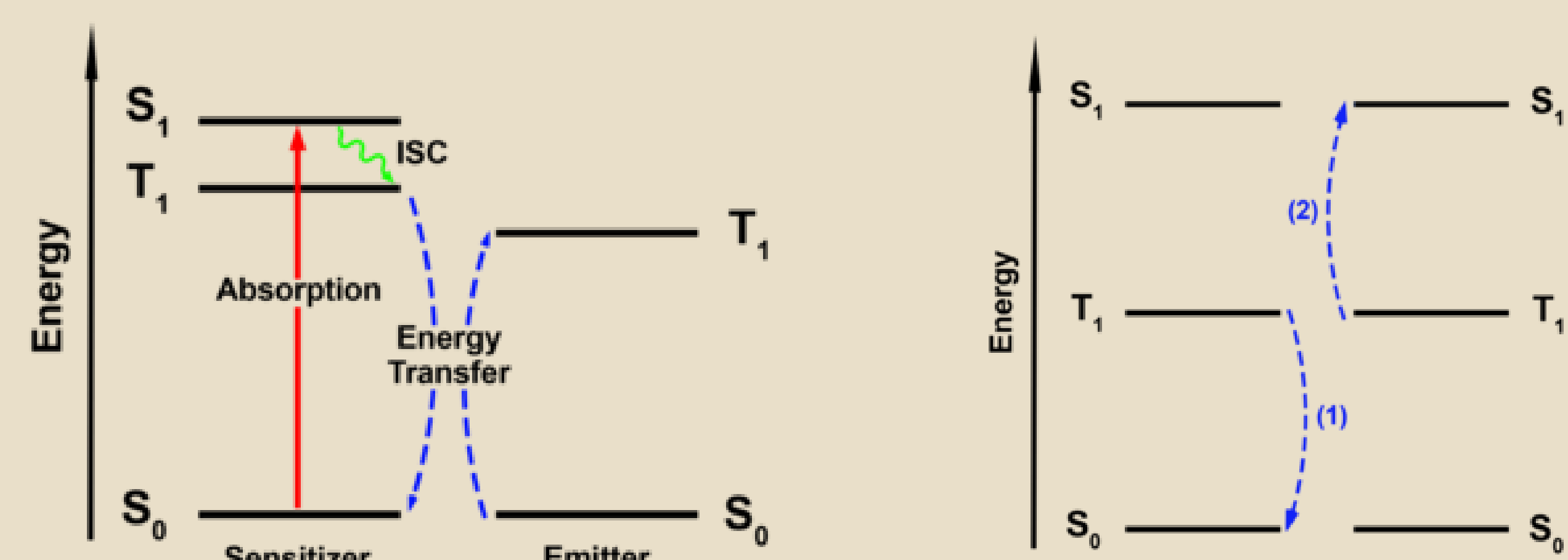


## Background

- Anthracene photodimerization, a  $[4\pi+4\pi]$  cycloaddition reaction, occurs via a singlet excimer ( $^1AA^*$ ) in two ways
- In the first,  $^1AA^*$  forms when singlet excited anthracene,  $^1A^*$ , encounters ground state anthracene,  $^1A$
- In the second, two triplet excited states,  $^3A^*$ , encounter and undergo triplet-triplet annihilation (TTA) to form nine encounter pairs (a quintet, a triplet and a singlet); the singlet is assumed to be ( $^1AA^*$ )
- Deuterium substitution at the 9 position of A can influence dimerization due to (1) a secondary kinetic isotope effect (KIE) and (2) an electron-nuclear hyperfine effect (hfi)
- The KIE is the difference in the rate of CC bond formation with and without the D
- The hfi effect is the interaction of the magnetic moments of the spins of electrons and nuclei; this effect may cause a difference in the efficiency of interconversion of TTA spin states when D is substituted for H



## Excitation to triplet state via sensitizer (S) and TTA (R)



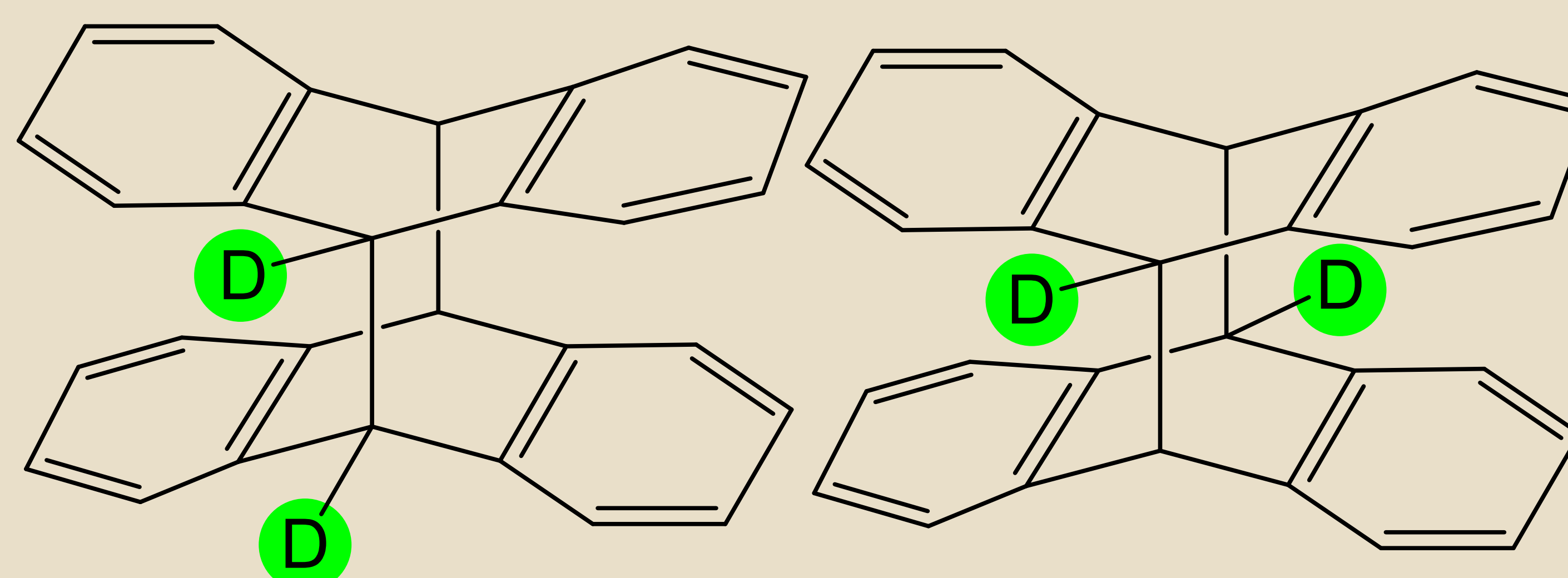
## References

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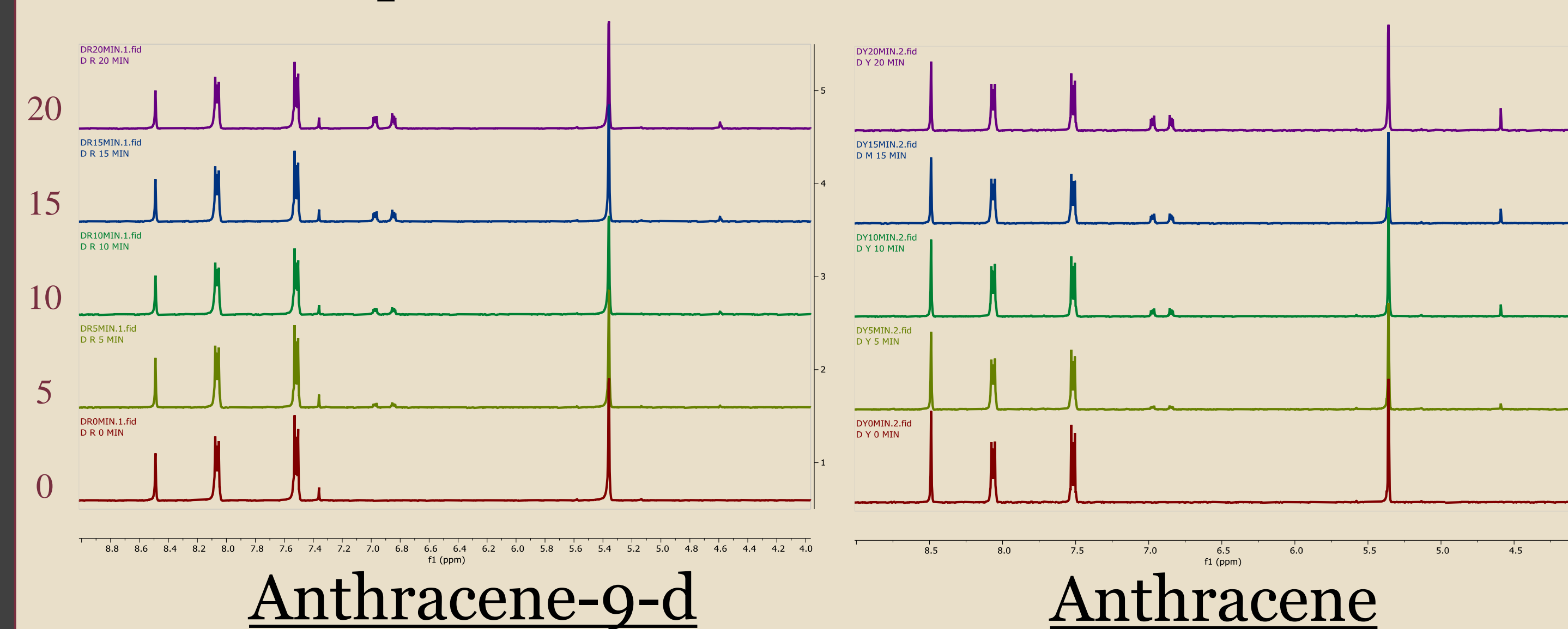
## Methods

- Solutions for direct irradiation were prepared by dissolving A and A-9-d each in dichloromethane
- Solutions were transferred to special NMR tubes and degassed using 4 freeze-pump-thaw cycles to  $2.1 \times 10^{-4}$  Torr
- Direct irradiation was done in a merry-go-round apparatus with a Hanovia 200-W Hg Lamp, filtering out light wavelengths below 313 nm
- $^1H$  NMR spectra were recorded before irradiation, every 5 min of irradiation up to 20 min. and after a full hour of irradiation
- Rates of A loss were based on relative peak areas in the  $^1H$  NMR spectra

## Head-to-head (HH) and Head-to-tail (HT) Isomers



## $^1H$ NMR spectra in the course of direct irradiation



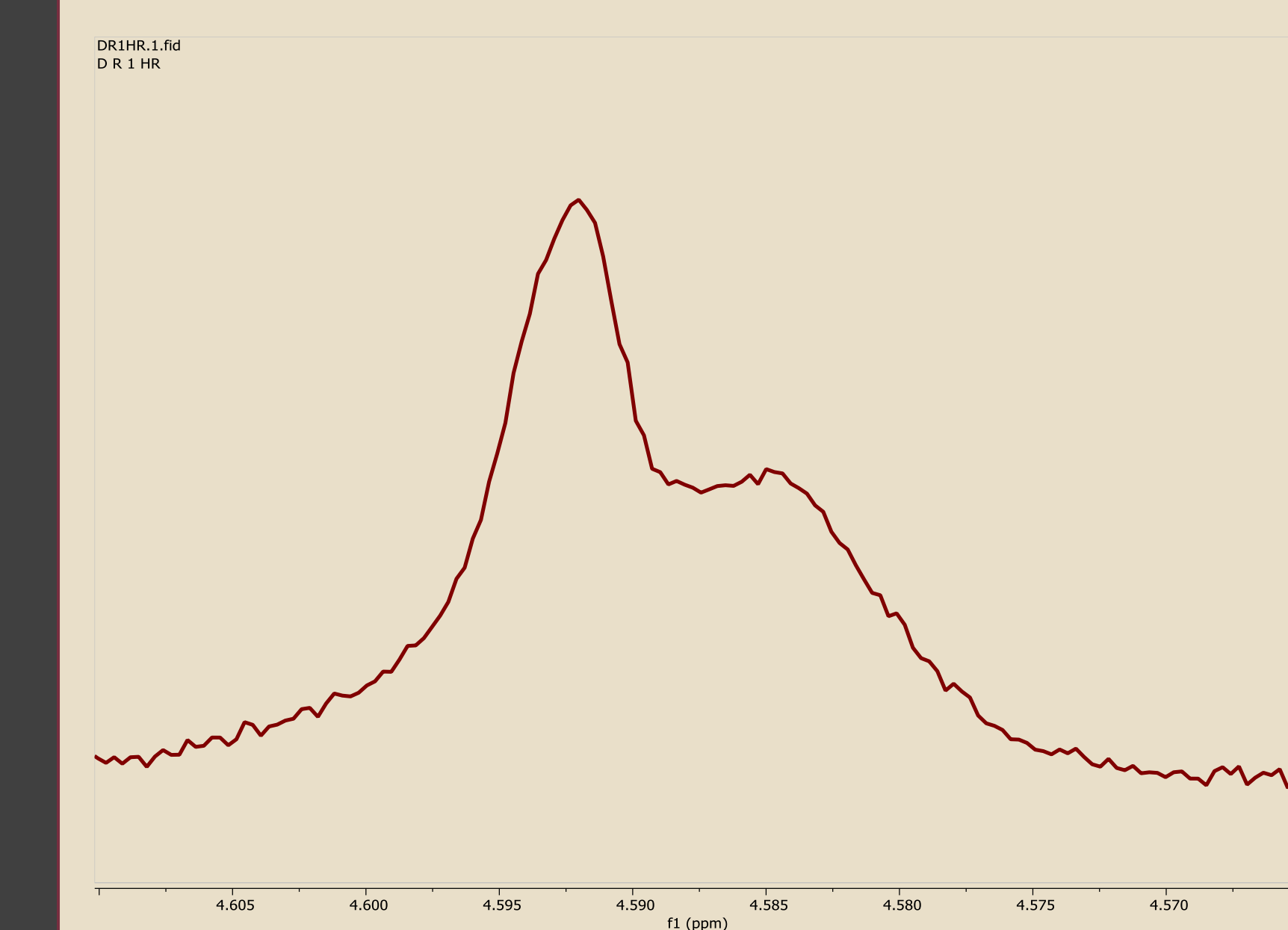
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## Conclusions

Time (min)	%A left	[A] ( $\times 10^{-3}$ M)	$\Delta[A]$ ( $\times 10^{-3}$ M)	% <sup>9d</sup> A left	[ <sup>9d</sup> A] ( $\times 10^{-3}$ M)	$\Delta[9dA]$ ( $\times 10^{-3}$ M)	$\Delta[A] / \Delta[9dA]$
0	100%	5.04	0	100%	5.44	0	-
5	95.8%	4.83	0.21	96.0%	5.22	0.22	0.95
10	91.2%	4.62	0.42	92.1%	5.01	0.43	0.98
15	87.1%	4.39	0.65	88.6%	4.82	0.62	1.05
20	82.9%	4.18	0.86	84.2%	4.58	0.86	1.00

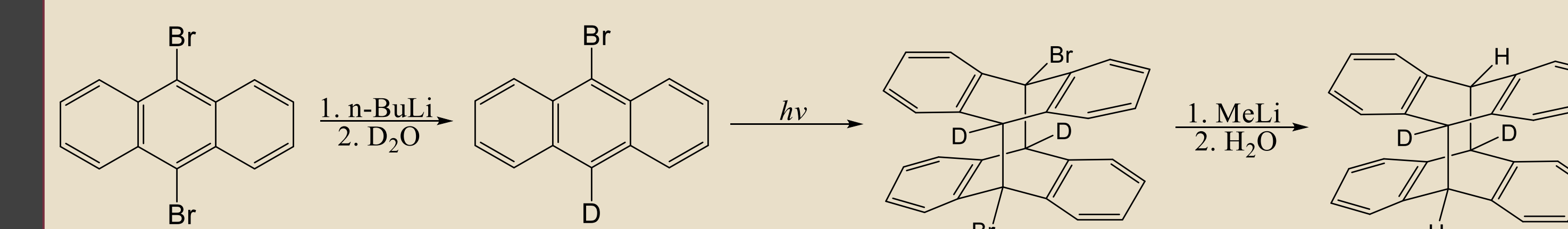
No secondary D KIE present under direct irradiation.

## Bridgehead NMR Peaks: Each peak corresponds to either the HH or HT isomer



- Looking at the bridgehead NMR peak one can tell that either the HH or HT isomer forms more than the other; the ratio was determined to be about 1:2.75, which is highly unexpected.
- The cause of the disparity is unknown, but we suspect it is due to polar interactions created by the increased electron density around C in CD bonds relative to CH bonds.

- Our future plans are to find the location of the HT dimer peak through the 9-bromo-10-deuteroanthracene dimer (below).



- Additionally, we plan to compare the sensitized dimerization between A and A-9-d to determine if secondary D KIE or hfi are present in the triplet pathway.