Supporting Information for:

Bridging the Gap between the Gas and Solution Phase:Solvent Specific Photochemistry in 4-tert-Butylcatechol

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A. Static UV/Vis of 4-TBC

**Fig. S1**: UV-Vis of 4-TBC in the vapour (black line), cyclohexane (blue line) and acetonitrile (red line).
B. Additional experimental methods: preparation of 4-TBC- $d_2$

1 g of 4-tert-butylcatechol (4-TBC) was added to an oven-dried 50 ml round bottom flask, which was then evacuated under vacuum and back filled with dry N$_2$ three times before adding 20 ml of D$_2$O. The solution was stirred under dry N$_2$ for 18 hrs. D$_2$O was then removed by lipholysation (freeze dry). This process was repeated twice and the yield was assumed to be quantitative. The hydroxyl proton peak in the NMR spectrum of 4-TBC (5.44-5.79 ppm, 2H) (Fig. S2) was reduced by 95% as shown Fig. S3.

Cyclohexane and acetonitrile used for the deuterated sample scans were freshly distilled over CaH$_2$ under dry N$_2$, collecting only the middle 80% of the distillate to ensure minimum atmospheric water contamination. Distillations were all carried out immediately prior to sample preparation.

An appropriate amount of the 4-TBC-$d_2$ was weighed and placed in an oven-dried ampule, which was evacuated and backfilled with dry N$_2$. 5 ml of deuterated methanol (MeOD) was then added to the ampule and stirred overnight. MeOD was then removed under high vacuum at room temperature immediately prior to scans. The anhydrous solvents were then cannula transferred into the ampule under dry N$_2$. The prepared samples were once again cannula transferred into the airtight flow set up that had been pre-evacuated and backfilled with dry N$_2$. A positive pressure was applied to the sample from the dry N$_2$ line for the duration of the TEAS scans to prevent H$_2$O in the atmosphere from leaking into the flow cell line. NMR was performed on recovered samples after scans, indicating only 20% of the sample was protonated by the end of TAS scans, see Figure S4.

![NMR spectrum of 4-TBC, the green label denotes the alcohol hydrogen peak.](image-url)
Fig. S3: NMR spectrum of 4-TBC-$d_2$, the alcohol hydrogen peak is absent due to deuteration.

C. Kinetic analysis of (gas-phase) 4-TBC$^+$ and H$^+$ transients

Fig. S4: NMR spectrum of 4-TBC-$d_3$ after TAS scans. The alcohol hydrogen peak labelled green is now present, indicating some protonation of the deuterated sample.
All transients obtained from TR-IY and TR-VMI were modelled using exponential decay functions, which are convoluted (+) with a Gaussian instrument response function, \( g(\Delta t) \). All 4-TBC+ and 4-TBC-d2+ were fitted using a bi-exponential decay function \( P(\Delta t) \):

\[
P(\Delta t) = \left[ g(\Delta t) \ast \left( 1 - A \exp\left( \frac{-\Delta t}{\tau_1} \right) \right) \right] + \left[ g(\Delta t) \ast \left( 1 - B \exp\left( \frac{-\Delta t}{\tau_2} \right) \right) \right]
\]

(1)

and H+ and D+ transients were fitted using a bi-exponential rise function \( H(\Delta t) \):

\[
H(\Delta t) = \left[ g(\Delta t) \ast \left( A \exp\left( \frac{-\Delta t}{\tau_1} \right) \right) \right] + \left[ g(\Delta t) \ast \left( B \exp\left( \frac{-\Delta t}{\tau_2} \right) \right) \right]
\]

(2)

We note that we use \( \tau_1 \) and \( \tau_2 \) here for the rise/decay time constants for simplicity. In the main text, these are specifically labelled according to each individual dynamical process being probed.

D. Kinetic analysis of (solution-phase) cyclohexane, 4-TBC in cyclohexane and 4-TBC in acetonitrile

All transients obtained from the TAS were modelled using a combination of \( n \)-exponential decay functions, which are convoluted with a Gaussian instrument response function, \( g(\Delta t) \) and takes the general form:

\[
C(\Delta t) = \sum_{i=1}^{n} \left[ g(\Delta t) \ast A_i \exp\left( \frac{-\Delta t}{\tau_i} \right) \right]
\]

(3)

The cyclohexane solvent response is obtained using the same method as cyclohexane/4-TBC transient shown in figure 3, and were fitted with \( n = 3 \) exponential decay functions revealing three solvent lifetimes: \( \tau_1 = 23 \) fs, \( \tau_2 = 408 \) fs and \( \tau_3 = 447 \) ps. Both the 4-TBC and 4-TBC-d2 in cyclohexane transients were fitted using \( n = 4 \) (tetra-)exponential decay functions where the first three exponentials are locked to the extracted solvent response exponentials as given above. 4-TBC and 4-TBC-d2 in acetonitrile transients were fitted using two exponential decay functions where negligible solvent response is observed. Further details and an illustrative example may be found in the Supporting Information of the following: Greenough, S. E. et al. Solvent Induced Conformer Specific Photochemistry of Guaiacol. Phys. Chem. Chem. Phys. 2014, 16, 16187-16195

We once again note that we use \( \tau_i \) as the decay time constants for simplicity. In the main text, these are specifically labelled according to each individual dynamical process being probed.
E. Transient absorption spectra of 4-TBC and solvent transients

Fig. S5: a) Selection of TAS of 35 mM 4-TBC-d$_2$ in cyclohexane with an excitation wavelength of 267 nm. b) Cyclohexane transient retrieved by integrating a 5 nm slice from the TAS of cyclohexane at various pump-probe time delays ($\Delta t$). The kinetic fit is shown as a red line.

Fig. S6: a) Selection of TAS of 35 mM 4-TBC-d$_2$ in acetonitrile with an excitation wavelength of 267 nm. b) Acetonitrile transient retrieved by integrating a 5 nm slice from the TAS of acetonitrile at various values of $\Delta t$. The transient shows a convolution of two instrument response functions, one caused by the front CaF$_2$ window of the Harrick cell and the other caused by acetonitrile. After the instrument response, no other dynamics are observed and therefore no solvent contribution is present in the dynamics of 4-TBC in acetonitrile after the instrument response.
F. Calculation methods, ground state and excited state geometries.

**Fig. S7:** Calculated minimum geometries in the ground state ($S_0$) and first excited state ($S_1$) of 4-TBC in its intramolecular hydrogen bonded (closed) and non-intramolecular hydrogen bonded (open) calculated in Gaussian09 conformers using M052X and CAM-B3LYP functionals with a 6-311G** basis set.