Substituent Effects on Dynamics at Conical Intersections: Cycloheptatrienes

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Supporting Information

ABSTRACT: Using selective methyl substitution, we study the effects of vibrational dynamics at conical intersections in unsaturated hydrocarbons. Here, we investigate the excited state nonadiabatic dynamics of cycloheptatriene (CHT) and its relation to dynamics in other polyenes by comparing CHT with 7-methyl CHT, 7-ethyl CHT, and perdeuterated CHT using time-resolved photoelectron spectroscopy and photoelectron anisotropy. Our results suggest that, upon $\pi\pi^*$ -excitation to the bright 2A" state, we observe an early intersection with the dark 2A' state close to the Franck–Condon



region with evidence of wavepacket bifurcation. This indicates that the wavepacket evolves on both states, likely along a planarization coordinate, with the majority of the flux undergoing nonadiabatic transition via conical intersections within 100 fs following light absorption. In CHT, large amplitude motion along the planarization coordinate improves the intra-ring π -overlap, yielding a delocalized electronic density. However, substitutions in 7 position, chosen to modify the inertia of the planarization motion, did not markedly alter the first step in the sequential kinetic scheme. This suggests that there is a crossing of potential energy surfaces before planarization is achieved and, thus, nonadiabatic transition likely takes place far away from a local minimum.

■ INTRODUCTION

Our understanding of the fundamental photophysical dynamics of small organic molecules is important because the photophysical behavior of biomolecules or other organic complexes can often be reduced to the dynamics of these small subunits. These dynamics are typically governed by conical intersections (CoIns) between potential energy surfaces. CoIns play a decisive role in the competition between ultrafast excited state processes and therefore influence product branching. CoIns can be classified based on their intersection topography $^{1-3}$ but simple rules governing their dynamics, needed to rationalize experimental findings, have yet to be developed. Alternatively, another classification could be by dynamical motifs, which are based on the behavior of characteristic subunits. We suggest that this is especially so in the unsaturated hydrocarbons where a few subtypes seem to recur. Two of these can be described as being of the ethylene subtype, i.e., dynamics that are localized on a single carbon-carbon double bond. The first of these includes a 90 degree twist about the C=C bond, combined with a pyramidalization of one of the two CH₂ groups; the second consists of a [1,2] hydrogen bridge, which can lead to a hydrogen shift, resulting in carbene formation and subsequent ground state chemistry.^{4–6} These two subtypes can be perceived in the dynamics of hydrocarbons such as butadiene, where initial rotation about the C–C single bond decouples the conjugated π -system,⁷ in stilbene^{8–10} and in unsaturated heteroatomic compounds such as acrolein.¹¹ In the case of cyclic, unsaturated hydrocarbons, the twisted-pyramidalized CoIn geometry is observed and may result in the breaking of a C–C bond via α -cleavage (next to the double bond) or by [1,3] hydrogen migration, as seen in cyclohexene.^{12–14} To draw attention to the idea of recurring dynamical motifs, the subunits where dynamics become localized were called dynamophores,¹⁴ by analogy with the chromophore, the subunit where light absorption appears localized. Here we seek another type of

Received: October 5, 2012 Revised: September 4, 2013 Published: September 9, 2013 dynamophore in the cycloheptatriene (CHT) moiety, involving a [1,7] sigmatropic H-migration.

The reaction paths of cycloheptatriene upon irradiation have been studied both experimentally^{15–23} and theoretically.^{24,25} It is believed that only three states participate in the dynamics: the ground state (1A') and two valence excited states (1A" and 2A'). The absorption spectrum of CHT is broad and structureless and its first maximum lies at $\lambda_{max} = 254$ nm (4.88 eV, see Figure 1), previously assigned exclusively to the



Figure 1. Absorption spectra of CHT and its alkylated derivatives, under saturated vapor pressure conditions at room temperature.

1*A*" state.²⁶ However, there might be some oscillator strength to the 2*A*' state as well. Low energy electron impact spectroscopy evinced a second singlet state at 270 nm (4.60 eV),²⁷ whereas magnetic circular dichroism studies in hexane ($\lambda_{max} = 265$ nm) showed three extrema at 251, 284, and 302 nm.²⁸ These features were explained by a complex mixture of the low lying singlet states and, potentially, a nearby triplet state, which was found at 291 nm in the gas phase.²⁷

The ground state structure of CHT has a boat-like form with a CH_2 group and the intermediate double bond lying above the molecular plane spanned by the remaining four carbon atoms^{24,25} (see Figure 2). Upon photoexcitation to the 1A''



Figure 2. Ground state structure of cycloheptatriene.

state, the molecule experiences planarization forces. Along this coordinate, it was suggested that rapid passage through two CoIns results in quenching to the ground state within 100 fs.^{18,19} These authors propose that the first CoIn involves a nonadiabatic transition to the 2A' state, while the second CoIn is encountered during the [1,7] signatropic hydrogen shift. Since the vibrational frequency associated with the planarization coordinate is small and this vibrational period is longer than the initial dynamics (30–60 fs),^{16,18,19} an even earlier nonadiabatic crossing was suggested.¹⁸ Subsequent transient anisotropy experiments indicated that excitation at 263 nm may create a wavepacket which is a superposition of the 1A'' and 2A' states²¹ and evolves simultaneously on both states, likely along the planarization coordinate.

These proposed reaction mechanisms suggests that the photodynamics of CHT require a major rearrangement of the entire C7-skeleton. In the following, as in our previous studies, we aim to identify the dynamophore(s) at work in CHT. To

probe the role of the initial planarization motion, we used alkyl substitution at C7 in order to systematically vary the inertia of this critical mode (using 7-methyl-cycloheptatriene [Me-CHT] and 7-ethyl-cycloheptatriene [Et-CHT]). Moreover, we studied the perdeuterated species so as to obtain more specific information on the migrating hydrogen atom. We used time-resolved photoelectron spectroscopy (TRPES), which provides detailed information on both nuclear motion and electronic configurations²⁹ and allows for direct comparison with our previous studies of polyene dynamics at conical intersections.^{6,11,14} In order to increase our sensitivity to the evolution of electronic configurations, we performed polarization-dependent TRPES (i.e., photoelectron anisotropy^{30,31}). Time-resolved photoelectron anisotropy can be considered as a simplified but easily performed integrated measurement, as compared to more differential angular resolved techniques.^{32,33} This is briefly described in the experimental and results sections.

EXPERIMENTAL SETUP

Cycloheptatriene was obtained from Sigma-Aldrich with a nominal purity of 99%. 7-Methyl- and 7-ethyl-cycloheptatriene (Me-CHT and Et-CHT) were synthesized according to the procedure described in ref 34, and their purities were checked by ¹H and ¹³C NMR (Bruker, 250 MHz) and UV-absorption spectroscopy (Varian, Cary 5e). While Me-CHT contained traces of CHT, Et-CHT was essentially free of CHT residues. The purities of both samples were estimated to be better than 95%. Perdeuterated CHT (CHT- d_8) was synthesized by Dr. Eckert GmbH (Germany) according to the procedure described by Engdahl et al.³⁵ Its purity was checked by ¹H and ¹³C NMR in CDCl₃ (Bruker, 250 MHz), UV-vis spectroscopy (Varian, Cary 5e), and GC-MS. The major impurity was the $C_7D_6H_2$ species, and the total purity was found to be better than 90%. In our seeded molecular beam experiments, the samples were premixed with helium at concentrations between 1% (CHT) and 0.25% (Et-CHT).

Time-resolved photoelectron spectra were recorded using a magnetic bottle apparatus, as described in detail elsewhere.³⁶ Supersonic pulsed molecular beams of the premixed samples were expanded into vacuum using an Even-Lavie valve with a 200 μ m diameter conical nozzle at a backing pressure of 3 bar and a repetition rate of 1 kHz. A Ti:sapphire regenerative amplifier (Coherent, Legend) pumped by two 1 kHz Nd:YLF lasers (Positive Light, Evolution), seeded by a Ti:sapphire oscillator (Spectra Physics, Tsunami), itself pumped by a Nd:YLF diode pumped laser (Spectra Physics, Millennia), generated output pulses at a central wavelength of 800 nm and a pulse duration of 80 fs. Tunable excitation pulses were generated by sum frequency generation of the output pulse of a TOPAS (Light Conversion) with the laser fundamental, followed by doubling in a β -barium borate-crystal (BBO). The probe pulse at 400 nm was created by direct doubling of the fundamental beam. Energies of the pump and probe pulses were 1.2 and 12 μ J/pulse, respectively. The pulses were weakly focused into the interaction region by an f/100 spherical reflective optic, and the polarization of the laser pulses was controlled by a Berek compensator (New Focus) and set to magic angle with respect to each other. Polarization-dependent measurements were performed by rotating the polarization of the pump beam 45° with respect to the collection axis of the photoelectron spectrometer. Polarization of the probe beam was controlled by a rotatable $\lambda/2$ waveplate and set either parallel or perpendicular with respect to the pump beam. Care

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was taken that the one color count rates of the probe pulse in the parallel and perpendicular geometry were identical. The in situ cross-correlation ($\tau_{cc} = 130$ fs), time zero, and the energy calibration transformation were measured using the known photoelectron spectrum of NO.^{38,39} The chirp and the crosscorrelation were controlled by a compressor containing a pair of VUV grade CaF₂ prisms. The time delay between the two pulses was controlled by a motorized linear translation stage. At each time delay, the (polarization dependent) pump–probe signal was corrected by dynamically subtracting background signals due to ionization by pump and probe pulses alone.

RESULTS

Steady-State Spectroscopy. The steady-state UV–vis spectra of CHT and its derivatives were studied under saturated vapor pressure conditions at room temperature (Cary Se, Varian) and are shown in Figure 1. As stated above, CHT shows an absorption maximum at 254 nm. This transition has $\pi\pi^*$ character²⁶ and is isolated from the next visible absorption band peaking below 200 nm (3*A*').⁴⁰ It has an almost Gaussian shape²³ ranging from 232 to 278 nm (full width at half-maximum). The methylated and ethylated species have spectra which are blue-shifted by 2 nm with respect to the maximum of CHT. CHT-*d*₈ shows a weak structure similar to the spectrum in liquid phase,²¹ with an absorption maximum at 252 nm.

Photoelectron Spectra. Time-resolved photoelectron spectra of all four samples were recorded at all three pump laser wavelengths of $\lambda_p = 250$, 263, and 278 nm, and a fixed probe wavelength of $\lambda_e = 400$ nm. The total energy of one 250 nm pump plus one probe photon is 8.05 eV, less than either the adiabatic ionization potential (IP_a, 8.29 eV^{40,41}) or the vertical ionization potential (IP_v, 8.57 eV⁴²) of CHT. Therefore, two probe photons are required for ionization and yield above threshold energies of 2.59(87), 2.34(62), and 2.09(37) eV for the three pump wavelengths, according to the IP_v (IP_a). The IPs of the substituted derivatives are essentially identical.⁴³

The full time-resolved photoelectron spectrum of CHT at λ_p = 250 nm is presented in the upper panel of Figure 3, while the remaining spectra are collected in the Supporting Information. The presented spectrum exhibits two intense maxima at 0.8 and 1.5 eV electron kinetic energy, which sit atop a weak, broad band originating at the energetic threshold for two-photon ionization. For convenience of discussion, we subdivided the spectrum into four different regions (1-4, where region 1)ranges from 0.3 to 0.7 eV, region 2 from 0.7 to 1.3 eV, region 3 from 1.3 to 1.7 eV, and region 4 from 1.7 eV to the ionization threshold for [1,2'] ionization. These same spectral regions were used for all molecules and all excitation wavelengths). A different representation of these data can be seen in the lower panel of Figure 3, where the energy slices of the spectrum were independently normalized. In this representation, the maximum of the signal can be seen to shift approximately 30 fs toward lower electron kinetic energies, which was interpreted in other polyenes such as cyclohexene and 1,4-cyclohexadiene¹⁴ as a signature of large amplitude motion.

Time constants and their decay associated spectra $A_i(E)$ were typically determined by a Levenberg–Marquardt global fitting routine wherein the 2D-data $S(E,\Delta t = t - t_0)$ are expressed as⁴⁴

$$S(E, \Delta t) = \sum_{i} A_{i}(E) \cdot P_{i}(\Delta t) \otimes g(\Delta t)$$
⁽¹⁾



Figure 3. In the upper panel, the photoelectron spectrum of cycloheptatriene, following excitation at $\lambda_p = 250$ nm and probing via two-photon 400 nm ionization, is shown. The vertical lines separate different dynamical regions, as discussed in the text. In the lower panel, slices are normalized to unit area (see text for details).

where $P_i(\Delta t)$ is the time-dependent population, $g(\Delta t)$ the experimentally determined Gaussian cross-correlation function, and t_0 the independently measured time zero of the experiment.

As discussed in earlier studies, this 2D global fitting procedure gives satisfactory results only if the dynamics do not include rapid large amplitude motions.^{14,44} If, however, photoexcitation induces strong deformations of the carbon skeleton, the instantaneous vertical IP is likely to rise, as the cationic potential energy surfaces generally do not parallel those of the excited states. As a consequence, the Franck–Condon spectrum shifts toward lower photoelectron kinetic energies. In lieu of direct dynamics, we have found that one simple way to account for such dynamics (within global fitting) is by allowing time zero (t_0) of the fitting routine to be variable.¹⁴

Using eq 1, the time behavior of the photoelectron traces of CHT and its alkylated derivatives can be fit with two exponential functions with a globally fixed decay time and an individual t_0 for each energy slice (see Figures 1 and 2 in the Supporting Information). The first time constant (τ_1) is roughly 70 fs for all wavelengths and molecules (see values for each experiment in Table 1). A separate fit of the signal in region 4 only resulted in a time constant that was distinctively shorter by about 15 fs. Moreover, the TPRES lifetime in Et-CHT appeared to be slightly longer (~10 fs) than in CHT and Me-CHT in that region. The second time constant (τ_2) is

Table 1. Time Constants for the TRPES Measurements^a

$\begin{array}{c} \text{CHT} \\ \tau_1/\tau_2 \ \text{(fs)} \end{array}$	Me-CHT τ_1/τ_2 (fs)	Et-CHT τ_1/τ_2 (fs)	CHT- $d_8 \tau_1$ (fs)
80/310	75/350	80/310	100
80/310	55/220	70/290	90
60/310	60/350	65/380	80
	CHT τ_1/τ_2 (fs) 80/310 80/310 60/310	CHT τ_1/τ_2 (fs)Me-CHT τ_1/τ_2 (fs)80/31075/35080/31055/22060/31060/350	CHT τ_1/τ_2 (fs)Me-CHT τ_1/τ_2 (fs)Et-CHT τ_1/τ_2 (fs) $80/310$ 75/350 $80/310$ $80/310$ 55/220 $70/290$ $60/310$ $60/350$ $65/380$

^{*a*}Errors were typically ± 20 fs for the first time constant (τ_1) and ± 80 fs for the second time constant (τ_2).

about (250 ± 90) fs for all derivatives. Unfortunately, its amplitude is too small to reliably extract spectral differences between the molecules. In Figure 4, we show the ratios between



Figure 4. Global fitting of the time-resolved photoelectron spectra determines the fit time constants τ_i and their associated spectra $A_i(E)$. The ratios of the amplitudes $A_2(E)/A_1(E)$ are shown for cycloheptatriene at $\lambda_p = 250$, 263, and 278 nm.

the decay associated spectra $A_2(E)/A_1(E)$, which significantly increase toward lower electron kinetic energies. By contrast, the CHT- d_8 data can be fit with a single global time constant of (90 \pm 30) fs, with a reduced value of (70 \pm 15) fs in region 4 if treated separately. Here, the addition of a second time constant to the fit does not improve the reduced χ^2 significantly. Finally, the shift in time zero is shown in Figure 5 for pump wavelengths of $\lambda_p = 250$ and 278 nm.

The time-resolved photoelectron spectra recorded with $\lambda_p = 263$ nm and $\lambda_p = 278$ nm (see Supporting Information) are nearly identical for CHT and its alkylated derivatives, although the time shift in CHT seems to be 5–10 fs smaller than for the substituted systems (see Figure 5). The spectra of CHT, Me-CHT, and Et-CHT at $\lambda_p = 250$ nm, however, are different as the amplitudes in regions 3 and 4 have approximately half of the amplitude that they have at longer wavelengths (see Figure 5 in the Supporting Information).

A significant deviation from the alkyl substituted cycloheptatrienes can be seen in the time-resolved photoelectron spectrum of CHT- d_8 at 250 nm (see Supporting Information). Here, an additional peak at (0.88 ± 0.05) eV electron kinetic energy appears at $\Delta t = 0$. In addition, the time shift of the spectrum is nearly 15 fs longer in most energetic regions, as compared to the other molecules. This behavior is unique at $\lambda_p = 250$ nm and absent at longer pump wavelengths (compare also Figure 5).



Figure 5. Time zero shift of the time-resolved photoelectron spectrum for cycloheptatriene at (a) $\lambda_p = 250$ nm and (b) $\lambda_p = 278$ nm.

Photoelectron Anisotropy. Photoelectron anisotropy can be defined in analogy to liquid phase transient anisotropy^{45–47}

$$r(E, \Delta t) = \frac{S_{\parallel}(E, \Delta t) - S_{\perp}(E, \Delta t)}{S_{\parallel}(E, \Delta t) + 2S_{\perp}(E, \Delta t)}$$
(2)

Here, $S_{\parallel}(E,\Delta t)$ and $S_{\perp}(E,\Delta t)$ are the total photoelectron yields for pump and probe polarizations being parallel (||) or perpendicular (\perp) with respect to each other.

The photoelectron anisotropy can be considered as a simple version of the full photoelectron angular distribution (PADs, see refs 29, 32, 33, and 48 for an overview). The time evolution of $r(E,\Delta t)$ can be due to molecular rotation³⁰ or an evolving electronic character, either due to adiabatic evolution on a given potential energy surface or due to nonadiabatic processes (internal conversion) between electronic states. In this sense, nontrivial changes in r(E,t) are a signature of the evolution of electronic character during the dynamics. Although, as an integrated measurement, photoelectron anisotropy experiments yield less detailed information about the ionization dynamics, it is a simple extension of the standard TRPES technique which provides additional information on the electronic character. The anisotropy signal can give information similar to that obtained from velocity map imaging. For a more detailed comparison of photoelectron anisotropy with PADs, see ref 30.

Examples of photoelectron anisotropy measurements for CHT at $\lambda_p = 250$ and 278 nm and CHT- d_8 at $\lambda_p = 250$ nm are shown in Figure 6. Additional spectra of Me-CHT and Et-CHT at $\lambda_p = 278$ nm can be found in the Supporting Information. The four traces in each figure represent the energy regions 1–4. As can be seen in these traces, the time-zero anisotropies are highest in regions 1 and 4 (0.25, averaged over the traces of CHT, Me-CHT, and Et-CHT at 278 nm) but smaller in regions 2 (0.18) and 3 (0.12). Given the signal-to-noise ratio of these anisotropy experiments, it is difficult to extract accurate time constants for the decay; nevertheless, certain trends can be



Figure 6. CHT at $\lambda_p = 250$ nm (upper left panel) and $\lambda_p = 278$ nm (upper right panel) and for CHT- d_8 at $\lambda_p = 250$ nm (lower panel) as defined by eq 2. The photoelectron counts of I_{\parallel} and I_{\perp} were summed over regions 1 to 4, as indicated in Figure 3

identified. Region 3 shows wavelength independent and exponential decay constants of (120 ± 30) fs, while the signal in region 4 seems to decay on a longer time scale. In CHT- d_8 , all regions behave similarly to CHT, aside from a slightly increased value around time zero. At 250 nm, the anisotropies of CHT are slightly lower and the decay is faster than at 278 nm, especially in regions 1 and 2. However, the anisotropy values in these regions are significantly higher in the deuterated species (see Figure 6) where they can reach as high as 0.3.

Assignment of the Spectra. The time-resolved photoelectron spectrum of CHT at $\lambda_p = 250$ nm (see Figure 3) is dominated by two sharp bands, at 1.5 and 0.8 eV, with a short vibrational progression. These structures sit atop a weak continuum which spans the whole spectrum and shifts toward lower electron kinetic energies at longer time delays. We first discuss the broad continuous band. The onset, expected at an electron kinetic energy of 2.87 eV, is weak and has its first maximum at 2.16 eV, seen best in the upper right panel of Figure 3 and in Figure 5 of the Supporting Information. This maximum most likely originates from ionization of the initially excited bright $\pi\pi^*$ state (1A"), rationalized by the Koopmans' scheme⁴⁹ depicted in Figure 7. Photoexcitation leads to excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Koopmans'-type photoionization removes the



Figure 7. Pump-probe Koopmans' correlation scheme for CHT. The pump pulse excites the bright A'' state via HOMO \rightarrow LUMO transition from where it can be ionized to the ground state of the ion (D_0) by removing the electron from the LUMO. The 1A'' state couples with the 2A' state, which has multireference character. Ionization from the 2A' state can correlate to both the ground and the first excited ionic states $(D_0 \text{ and } D_1)$.

electron from the LUMO, leaving the molecule in its ionic ground state (D_0). The 2A' state has multireference character

and moderate electronic overlap with both the ionic ground D_0 and the first excited state D_1 . Despite strong Koopmans' correlations between the 1A'' and D_0 state, the Franck– Condon overlap is likely to be poor since the minimum of D_0 is planar,⁵⁰ whereas the ground state of CHT has a boat-like structure.²⁴ This is the origin of the large difference between adiabatic and vertical IPs and explains the relatively small signal observed in region 4. Upon excitation, the system planarizes since the minimum energy geometries of both the 2A' state and the 1A'' state are planar.^{24,25,51} This motion improves the Franck–Condon overlap with D_0 , explaining the delayed rise of the ionization efficiency into D_0 . As the initial electronic energy is converted into vibrational energy in the neutral excited states, the photoelectron spectrum shifts to lower kinetic energies, consistent with the temporal evolution seen in the experiment.

Superimposed on this broad shifting band, the sharp maxima at 0.8 and 1.5 eV are both independent of the excitation wavelength. This behavior could be a signature of photoionization from a lower lying state, as excess electronic energy due the pump process is converted into internal energy. Similar behavior was found in TRPES studies of substituted cyclopentadienes.⁴⁴ The two peaks are separated by approximately 0.75 eV, close to the difference between D_0 and D_1 . This suggests the tentative assignment of these peaks as originating from the 2A' state, whereas especially region 4 can be assigned to originate from the 1A'' state alone. Further evidence for this assignment is provided by the photoelectron anisotropy results. In regions 2 and 3, the anisotropy is significantly lower compared to regions 1 and 4. For symmetry reasons, the transition dipole moments from the ground state to the 1A''and 2A' state are perpendicular with respect to each other, leading to an angular spreading of the lab-frame ionization dipole moment direction upon internal conversion. This results in a lower observed anisotropy in accordance with the wellknown equation47

$$r(\Delta t) = \frac{x}{2} (3\langle \cos^2 \beta(\Delta t) \rangle - 1),$$

$$x = \begin{cases} 2/5 \text{ for } m + n = 2 \\ 4/7 \text{ for } m + n = 3 \end{cases}$$
(3)

where β is the angle between the transition dipole moments for pump and probe processes and *m* and *n* are the number of pump and probe photons, respectively. Time-resolved photoelectron spectra recorded at $\lambda_p = 278$ and 263 nm appear similar and exhibit similar time constants, indicating that the dynamics are roughly independent of pump energy, suggestive of a barrier-free reaction path.

Another view of the dynamics can be obtained by comparing the time-resolved photoelectron spectra with respect to the photoelectron kinetic energy dependent delays in the rise of the signal (Figure 5). At the onset of the band at 1.5 eV, assigned to ionization into D_0 , the spectrum appears delayed by about 15 fs with respect to that of the origin of the 1A'' state in region 4. This can be understood as the time required for the wavepacket to reach the 1A''-2A' CoIn. This value seems reasonable given the proximity of the two states in the Franck–Condon region. However, it is likely not long enough to achieve complete planarization (we calculated the relevant frequency to be about 211 cm⁻¹ at the B3LYP/cc-pVDZ level). Furthermore, if complete planarization were required before internal conversion, alkylation in 7 position would be expected to inertially delay the rise of the band in region 3, as the planarization frequency decreases to 140 cm⁻¹ in Me-CHT. This behavior, however, cannot be seen in our alkylation studies, leading to the conclusion that the wavepacket largely accesses the 2A' manifold in a nonplanar geometry, agreeing with the analysis of Trushin et al.¹⁸

We can extract further information about the excited state dynamics via analysis of the time evolution of the anisotropy. In the simplest case, anisotropy decay is due to rotational dephasing.³⁰ Under our molecular beam expansion conditions, the rotational temperature of the molecules is estimated to be 50–100 K,⁵² resulting in a dephasing time $\tau_{i,\text{deph}} = (I_i/2k_\text{B}T)^{1/2}$ of about 1 ps for the smallest moment of inertia I_{i} , and around 800 fs when including all three moments. Apart from rotation, the only process that causes anisotropy to decay is an electronic evolution of the wavepacket and, hence, a time-dependent population of the excited states. Since the rotational reorientation is slower than the observed anisotropy decay, especially in regions 2 and 3, the anisotropy signal originates from a time-dependent population of the 1A'' and 2A' states (vide supra). The population evolves with a time constant of (120 ± 30) fs and therefore does not trivially follow the time constants of the TRPES experiments. This is in accordance with the idea that the wavepacket bifurcates along the planarization coordinate in the 1A" and the 2A' states, leading to a time evolution that is more complex than a simple kinetic reaction scheme.

At longer delay times ($\Delta t \ge 300$ fs), the photoelectron signal is dominated by contributions from the slower process (associated with τ_2). To analyze these slower dynamics, we will begin with the experiments at $\lambda_p = 250$ nm. In this case, the anisotropy of CHT exhibits a faster decay than at $\lambda_p = 278$ nm (see Figure 6). This can be interpreted as being due to a more efficient crossing from the 1A" to the 2A' state in the Franck-Condon region, based on the notion that the excess energy provided by the pump pulse may increase the nonadiabatic transition probability.¹¹ This also agrees with the TRPES data. In regions 3 and 4, the signal is reduced as compared to regions 1 and 2, and the amplitude ratio A_2/A_1 in region 1 is only 5%, as compared to roughly 20% at longer wavelengths (see Figure 4). This behavior could in principle indicate the presence of an energetically low lying state. However, since no other states are known to cross in this region, we speculate that another possible explanation is a mixing of the 1A'' and 2A' characters further along the reaction coordinate, as visualized in the proposed reaction path in Figure 8. The bifurcation ratio would be dependent on the excess energy (see next section for the consequences). From the S_1 state, the wavepacket has direct access to the CoIns with the ground state. Nevertheless, the wavepacket presumably continues to evolve in the excited states for at least $\tau_2 = 250$ fs and recrosses to ground state at a later time

Substitution Effects. Surprisingly, alkylation of CHT at the 7-position results in only minor changes to the dynamics. At λ_p = 278 and 263 nm, a shift in time-zero is visible but small, not exceeding 5–10 fs when comparing CHT with Me-CHT and Et-CHT (see Figure 5). These findings not only rule out the requirement of complete planarization for internal conversions from 1*A*" to 2*A*' (and subsequently 2*A*' to the ground state), they show more generally that the modes actively involved in the dynamics do not depend significantly on the 7-substituent. It is conceivable that the bond alternation coordinate might be more important for driving rapid access to the 1*A*"–2*A*' conical intersections. Trushin et al. suggested that the position of the



Figure 8. Proposed scheme for photoinduced dynamics in CHT following excitation by a UV-photon to the 1A'' state. At the first intersection between the 1A'' and the dark 2A' state, close to the Franck–Condon region, the wavepacket can access both potential energy surfaces. At a later point, the character of the excited states mix. Return to the ground state proceeds either via a conical intersection to the ground state or via a [1,7] sigmatropic hydrogen shift.

alkyl group is statistically distributed between the equatorial and the axial position leading to variable dynamics due to the modified accessibility of the hydrogen migration channel.¹⁸ However, other evidence suggests that the alkyl groups are mainly located in equatorial position³⁴ and, therefore, such variability of the hydrogen migration channel is unlikely.

Interestingly, CHT- d_8 behaves differently from CHT: the CHT- d_8 data can be fitted to a monoexponential decay with a significantly longer time constant. At $\lambda_p = 250$ nm, the timeresolved photoelectron spectrum exhibits an additional peak at 0.9 eV, the shift in time zero is more prominent, and the anisotropy does not rise at long time delays. These findings provide additional insight into the overall dynamics of CHT. The increase in time constant upon deuteration was observed in previous studies and was explained by the isotope effect on D-atom migration.^{18,21,23} In a simple picture of ballistic motion, the mass effect of deuteration would lead to a prolongation of the dynamics²¹ by a factor of $(m_{\rm D}/m_{\rm H})^{1/2} = \sqrt{2}$, and this seemed to match some experimental findings.^{18,21,22} We suggest, however, this simple picture fails to explain our results since it cannot explain the absence of a longer time constant in the deuterated sample. We speculate that this behavior could be due to an overall mass effect leading to a deceleration of the wavepacket, as compared to undeuterated CHT. As nonadiabatic processes depend on derivative couplings, velocities of passage through CoIns will be important. Such effects could lead to velocity-dependent branching at CoIns, as was discussed for the case for the $S_1 - S_0$ internal conversion in acrolein.¹¹ We note that the absence of a second time constant is also seen in the anisotropy data. Comparing the anisotropies of CHT and CHT- d_8 at $\lambda_p = 250$ nm, we find that the anisotropy of CHT- d_8 does not rise at longer delay times and therefore is inconsistent with our proposed mechanism outlined in the previous section. We note, however, that the anisotropies of Me-CHT and Et-CHT also do not show an anisotropy rise (see Figures 3 and 4 in the Supporting Information). The most likely explanation of this finding is a smaller mixing ratio for this molecule. Finally, the time-resolved photoelectron spectrum of $CHT-d_8$ at $\lambda_{\rm p} = 250$ nm is different from the other wavelengths/molecules since it shows a replica of the 1A'' dynamics at time zero

around 0.9 eV electron kinetic energy (see Figure 5 and the full time-resolved photoelectron spectrum in the Supporting Information). The presence of this peak is also reflected by the anisotropy, which is distinctly higher in region 2 than that of any other sample. The origin of this peak must be due to an energetic shift in the electronic bands, possibly in the intermediate Rydberg manifold. Such a shift of an electronic state upon deuteration would be surprising. Further investigation will be required in order to discern the character of this band.

DISCUSSION

We summarize our view of the salient features in the dynamics of CHT as follows: (1) the excitation is to a bright state (1A''), which is nearby to a weakly absorbing state (2A'); (2) the ring alternation coordinate may be important for internal conversion and would render the dynamophore a delocalized moiety; (3) complete planarization does not seem to be of central importance in accessing the 1A''-2A' conical intersections; (4) there is evidence for bifurcation of the wavepacket in the excited states; and (5) the kinetic model suggests the involvement of two sequential internal conversions. These features indicate both similarities (recurring motifs) to and differences from the dynamics of other polyenes such as ethylene⁴⁻⁶ or cyclohexa-1,3-diene.⁵²⁻⁵⁶

It is instructive to compare 1,3-butadiene (BTD)^{7,57} with CHT. In both cases, the two lowest excited singlet states are energetically close, with one being spectroscopically dark. In both cases, large amplitude motion can be seen in the photoelectron spectra, indicating a strong deformation of the carbon skeleton.^{29,14} In addition, the bright and the dark excited states of both molecules follow analogous deformation coordinates; planarization in the case of CHT and C-C twist in the case of BTD. This deformation is symmetry conserving (C_s) for CHT and are Franck–Condon active modes, as confirmed by resonance Raman spectroscopy.¹⁷ The intersection, however, is accessed only through an additional symmetry breaking mode,⁵⁵ contradicting the van der Lugt– Oosterhoff model.²⁷ It seems to be the case that, in CHT, the first internal conversion between the bright and the dark excited state is delocalized along the Franck-Condon active motion. This is supported by the observation of similar time scales for the dynamics of the 1A" state in CHT and the 7substituted CHTs. Despite these similarities between CHT and BTD, their excited state reaction dynamics are clearly different: in BTD, there is a competition between a localized (ethylenelike) and a delocalized pathway.' Large amplitude twisting motion about the central C-C single bond decouples the two ethylenic units, leading to localized dynamics. In contrast, large amplitude motion in CHT seems to reinforce delocalized dynamics. Rather than decoupling its π -system, CHT planarization results in the overlap between its π -orbitals increasing with respect to the ground state, thereby retaining delocalization and, likely, leading to a prolonged excited state lifetime.

CONCLUSIONS

We used TRPES and photoelectron anisotropy to study the excited state dynamics of CHT upon photoexcitation to the bright $\pi\pi^*$ state (1*A*"). Through selective alkyl substitutions, we investigated the role of the planarization coordinate in the excited state dynamics. Our results suggest that the initial

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nonadiabatic transition is delocalized and occurs before complete planarization of the ring. We suggest further that the reaction path does not follow the simple scheme characteristic of many polyenes, namely, an excitation to a bright valence state and return to the ground state after passing through an intermediate dark state. In contrast, CHT shows an early crossing between the 1A" and 2A' excited states with planarization likely occurring on both of these surfaces. Because of the insensitivity of the observed time constant to 7-alkyl substitution, we suggest that the nonadiabatic transition is delocalized. In CHT, there seems to be evidence for bifurcation due to the wavepacket being in the excited state for a prolonged time. This does not seem to happen in the deuterated species suggesting that the inertia in specific modes may be important for the diabatic vs adiabatic branching. We are currently undertaking an ab initio multiple spawning trajectory study which will address the excited state nonadiabatic dynamics of CHT. Finally, we emphasize the utility of simple photoelectron anisotropy experiments. Many of the state assignments were aided by the use of this simple technique. The small incremental effort required to execute these experiments offers a simple alternative to full time-resolved photoelectron angular distribution measurements.

ASSOCIATED CONTENT

S Supporting Information

Comparison of monoexponential and biexponential fitting schemes, anisotropy data of Me-CHT and Et-CHT excited at 278 nm, excerpts from the decay associated spectra of CHT, table of time constants, and time-resolved photoelectron spectra of all molecules under discussion at pump wavelengths of $\lambda_p = 250, 263$, and 278 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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