ABSTRACT: In the current study, we present nonadiabatic (NAMD) and adiabatic molecular dynamics simulations of the transition-state dynamics of photoexcited cyclooctatetraene (COT). The equilibrium-state structure and absorption spectra are analyzed using the semiempirical Austin Model 1 potential. The NAMD simulations are obtained by a surface-hopping algorithm. We analyzed in detail an active excited to ground state relaxation pathway accompanied by an S1/S0(Dah) → S0(Dah) → S0(Dah) double-bond shifting mechanism. The simulated excitation lifetime is in good agreement with experiment. The first excited singlet state S1 plays a crucial role in the photochemistry. The obtained critical molecular conformations, energy barrier, and transition-state lifetime results will provide a basis for further investigations of the bond-order inversion and photoswitching process of COT.
excited-state dynamics and determine the relaxation pathways of photoexcited COT.

The excited-state molecular dynamics of COT is calculated using Tully’s fewest switches surface hopping (FSSH) approach combined with empirical decoherence corrections and trivial crossing tracking algorithms as implemented into the Nonadiabatic Excited-state Molecular Dynamics (NEXMD) package. By applying the collective electron oscillator method with the semiempirical Austin Model 1 (AM1) Hamiltonian at the configuration interaction singles (CIS) level, the NEXMD can routinely handle the NAMD simulation up to 20 picoseconds (ps). This package has been successfully applied to the modeling of photoinduced processes in many other molecular systems.

Our simulations find that COT has nonaromatic equilibrium boat-shaped structures in the ground state and higher excited states and planar antiaromatic metastable structures in the ground state. The equilibrium structure in $S_0$ is aromatic (Figure 1a). The transition between the three aromaticities may be induced either thermally or photochemically. A geometric optimization was performed by starting with a boat-shaped or planar structure in all $S_n$ to $S_1$ states. We were unable to optimize the structure of COT ($S_n$) due to the small band gap with $S_1$ pointing to the lack of a well-defined potential-energy minimum (as detailed in the Supporting Information). As shown in Figure 1a, both of the $D_{2d}$ symmetric boat-shaped minimum nonaromatic structures and the planar $D_{4h}$ symmetric transition antiaromatic structures can be obtained by a geometric optimization in $S_0$ with a slightly higher potential energy ($\Delta E = 0.5$ eV) for the planar $D_{4h}$ structure. The significant variances between the single- and double-bond lengths (listed in the Figure 1 caption and refs 28 and 29) identified their aromaticity. For comparison, the native minimum $S_1$ structure has an aromaticity with $D_{4h}$ symmetry due to its planar geometry and a vanishing C–C bond length difference (0.005 Å). The band gaps are then analyzed based on the true boat-shaped $S_0$ optimal structure. Table 1 compares the vertical excitation energies calculated by different methods. As with other systems, the semiempirical AM1/CIS results in red-shifted energies compared to time-dependent density functional theory (TD-DFT) and ab initio CASSCF/CASPT2 methods. Importantly, the relaxation rates during the excited-state dynamics are closely related to the energy gaps between states but not to the absolute values of the transition energies from the ground state. Therefore, the AM1/CIS approach is appropriate to conduct the COT NAMD simulation due to the good agreement of band gaps with other higher-level methods (e.g., TD-DFT and CASPT2).

Figure 1b shows the state transition density (TD) plotted for the first three singlet excited states of COT evaluated at the boat-shape $S_0$ optimal geometry. The TD of $S_1$ state is evenly distributed at each C atom, while these quantities for $S_2$ and $S_3$ are disorderedly distributed around the nonplanar ring. Figure 1c shows the same excited-state TDs, based on the $S_0$ transition geometry. In the antiaromatic planar geometry, all three lowest electronic states exhibited an even TD distribution based on its symmetry around the ring. The antisymmetric structure of $S_0$ and $S_1$ TDs with respect to the horizontal and vertical planes, respectively, is pronounced. For comparison, the TDs of the $S_1$ aromatic planar structure are also shown in Figure 1c. The $D_{4h}$ COT has a pair of half-filled and degenerate nonbonding $\pi$-orbitals (i.e., delocalized $\pi$-bond), in which the electrons freely move around the ring, as reflected by a broader $S_2$ and $S_3$ TD distribution in $D_{4h}$ than in $D_{4v}$.

**Figure 1.** (a) Ground-state minimum geometry $D_{2d}$ with bond lengths 1.344 Å (C=C) and 1.479 Å (C–C). Ground-state transition (meta-stable) geometry $D_{4h}$ with bond lengths 1.336 Å (C=C) and 1.442 Å (C–C). Native optimal $S_1$ geometry $D_{4h}$ with equal C–C bond lengths of ~1.387–1.382 Å. (b) Orbital plots of the TD for the lowest three electronic states at the ground-state optimized geometry. (c) The same but for the ground-state transition geometry. (d) The same but for the optimal $S_1$ geometry. (e) Calculated absorption spectrum of COT at 300 K showing individual contributions of the eight lowest excited electronic states. (inset) The total absorption profile combining $S_1$ to $S_0$ contributions.

**Table 1.** Comparison of the Vertical Excitation Energies (in eV) for the First Three Singlet Excited States of COT for Different Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM1/CIS</td>
<td>3.06</td>
<td>4.95</td>
<td>4.97</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>3.61</td>
<td>5.34</td>
<td>5.35</td>
</tr>
<tr>
<td>CASSCF</td>
<td>6.26</td>
<td>7.01</td>
<td>6.54</td>
</tr>
<tr>
<td>CASPT2</td>
<td>4.00</td>
<td>5.75</td>
<td>6.00</td>
</tr>
</tbody>
</table>

*TD-DFT simulations were performed with PBE0 functional and 6-31G* basis set.*
To perform the NAMD simulations, we first conducted a sampling of the initial conformational structures by running a 520 ps ground-state adiabatic molecular dynamics (AMD) trajectory of COT in a vacuum using a Langevin thermostat at 300 K with a time step of 0.1 fs. Following a 20 ps equilibration period, 1000 snapshots of geometries and velocities were sampled every 0.5 ps as the initial conditions. The absorption spectrum analysis was performed on those initial samples with a Gaussian line shape and full width at half-maximum (fwhm) of 0.36 eV. The spectrum, shown in Figure 1e, includes the contributions of the eight lowest-energy excited states. The weakly absorbing $S_1$ feature (a tiny peak at 3.1 eV) reflects a forbidden $S_0$ to $S_1$ excitation (dark state). The higher-energy states $S_2$–$S_8$ are optically bright transitions forming a strong absorption band between 5.0 and 5.8 eV. These results are in a good agreement with early COT measurements in a dye laser solution, which indicated an extremely weak absorption near 4.43 eV and an intense spectrum at 5.5–6.9 eV.\(^{30,51}\)

The initial excited states were populated according to a Franck–Condon window $g_i(r, R) = f_1 \exp[-T^2(E_{i,\text{las}} - E_i)^2]$, where $f_1$ and $E_i$ are the oscillator strength and energy of excited state $i$, and $E_{i,\text{las}}$ is the energy of a Gaussian laser pulse $f(t) = \exp(-t^2/2T^2)$, centered at 5.0 eV, that corresponds to the maximum of the absorption for the $S_4$ state (see Figure 1e), with a $T = 0.36$ eV fwhm. The excited-state dynamics were then investigated using surface-hopping NAMD in vacuum at 300 K with a nuclear time step of 0.025 fs and an electron time step of 0.005 fs (see our previous NEXMD applications for more detail\(^{17–19}\)). Eight excited states were included in the simulations to allow for possible transitions to higher energy. The instantaneous decoherence correction and trivial un avoided crossings tracking were activated.

During NAMD, the overall nonradiative relaxation across a trajectory ensemble can be monitored by tracking the evolution of the averaged adiabatic state populations, TD profile, and COT geometry features. Figure 2a shows the quantum-state populations\(^{19}\) in an NAMD simulation. According to the Franck–Condon window with a 5.0 eV light impulse, the initially excited electronic states were concentrated around the $S_1$–$S_6$ band of states. Approximately 50% of the trajectories relaxed back to $S_1$ in 100 fs. After 400 fs, 90% of the trajectories have arrived in $S_1$. To monitor the spatial energy transfer, the averaged time-dependent localization of the electronic TD among different fractions\(^{10}\) of the COT molecule was tracked across the 1000 trajectories in total as depicted in Figure 2b. The transition density is evenly separated into two fractions (see the inset of Figure 2b) on the ring, in which fragment F2 collected the TD contributions from C atoms 1, 2, 3, 4, and their bonding H atoms (refer to the inset in Figure 2e), and fragment F1 is the sum of the TD from the rest of the carbon atoms. Finally, Figure 2c–e plots the relevant geometric features (bond length, dihedral angle, and bond length alternation) monitoring the geometry evolution of COT in the NAMD process. The selection of these parameters is detailed in the Supporting Information.

As indicated by Garavelli et al.\(^3\), the photoinduced double-bond shifting mechanism included a transfer of localized $\pi$-bonds to form a delocalized aromatic $\pi$-system (Figure 2a) during the $D_{2d}$ to $D_{2h}$ structure transformation. A similar process is observed in our SH-NAMD simulations. As shown in Figure 2b,c, the $D_{2d}$ structure has an uneven TD distribution in the $S_{1,2,3}$ states and a uniform TD distribution in $S_1$. Therefore, the strong TD fluctuation between the F1 and F2 segments in the initial 150 fs of dynamics in Figure 2b reflects an energy redistribution due to the fundamental $\pi$-bond transformation underpinning the double-bond shift. Meanwhile, the significant bond-length oscillation shown in Figure 2e was observed in the first 100 fs. Such oscillations in photoexcited molecular dynamics frequently signify the appearance of coherent electronic-vibrational dynamics persisting across an ensemble of trajectories.\(^{32}\) Finally, when the molecule relaxes to a $D_{2h}$ aromatic structure ($S_1$), the localized $\pi$-bonds overlap to form a delocalized aromatic $\pi$-system across all C atoms of the ring. This explains the uniform TD
distribution across fragments and diminishing bond length alternation when most of the trajectories were transferred to $S_1$ after 150 fs.

Internal conversion in molecular systems across a manifold of excited electronic states occurs on ultrafast time scales, typically below $\sim 1$ ps. In contrast, because of a large energy gap, nonradiative transitions back to the ground state usually happen on much longer (tens of picoseconds to nanosecond) time scales. Here, barrierless ultrafast photoisomerizations such as rhodopsin dynamics are notable exceptions. Descriptions of non-Born–Oppenheimer transitions to the ground state have an inherent multireference character and cannot be properly described with a single-reference method such as Hartree–Fock or density functional theory (DFT). For example, as mentioned in other published works, conical intersections between the ground and excited states in the latter methods have an incorrect dimensionality owing to the Brillouin theorem. This calls for the use of alternative approaches. In a previous study, we introduce a simple “Open-GS” method to treat such transitions to the ground state: when the system is in the lowest-energy excited state and the energy gap between the ground and excited states ($\Delta E_{S_{0}-S_{1}}$) is smaller than a certain threshold (normal 0.5 eV), the nonadiabatic transition is enforced, and the dynamics continues on the ground-state potential energy surface (PES). Indeed, the $\Delta E_{S_{0}-S_{1}}$ energy gap is becoming small in the COT molecule (see the Supporting Information) once the trajectory approaches the $S_1$/$S_0$ conical intersection seam. We set a threshold $\Delta E_{S_{0}-S_{1}} = 0.1$ eV to enforce the transition from the $S_1$ to the $S_0$ state with an excess of electronic energy redistributed into nuclear kinetic energy. Accordingly, to model the final phase of COT photoinduced dynamics (i.e., $S_1$/$S_0$ transition), we selected 300 configurations from NAMD, which have stabilized in the $S_1$ state for 10 fs without hopping upward to $S_2$ as the initial conditions for the AMD simulation in the $S_1$ state at 300 K. As this dynamics progressed, 291 terminated trajectories (out of 300 total) reached the $S_1$/$S_0$ conical intersection seam within 20 ps of the $S_1$ AMD. These trajectories were then reinitiated at the $S_0$ state.

Figure 3a–d plots the geometric features and energy profile for a typical trajectory in an $S_1$ AMD simulation. The trajectory sampling on the $S_1$ PES in Figure 3c indicates that it traverses an energy barrier ($\sim 0.3$ eV) before reaching the $S_1$/$S_0$ conical intersection. When the barrier at 3.2 ps is crossed, a slight folding of the $D_8$ planar structure is detected, which is reflected as the valleys in the dihedral angle and average bond length plot (Figure 3a,b). By combining the geometric features with the $\Delta E_{S_{0}-S_{1}}$ energy gaps shown in Figure 3d, we conclude that the folding deformation of the planar structure is accompanied by an increase of the $\Delta E_{S_{0}-S_{1}}$ observed near the...
The results clearly show that, after crossing the energy barrier, the folded $S_1$ structure needs to convert back to a less-folded conformation to be able to reach the $S_1/S_0$ conical intersection. Compared to ref 8, the “planar-like” CI structure observed in our AMD simulations is somewhere between previously suggested folded (quasitetraedral, CI$_h$) and (triangular -(CH)$_3$- kink as CI$_{L}$). We believe that such intermediate structures appear due to thermal effects in AMD, where trajectories reach the extended $S_1/S_0$ crossing seam at different conical intersection conformations, eventually producing crossing points with intermediate structures with respect to the two extreme points located by the minimized energy paths presented in ref 8. Finally, the $S_1$ AMD simulation is terminated once the $\Delta E_{S_0, S_1}$ gets below 0.1 eV (Figure 3d).

Similar energy crossing features were observed in all $S_1$ AMD simulations; however, the $S_1$ AMD trajectory lengths varied significantly. Compared to the $S_{0 \rightarrow 1}$ to $S_1$ relaxation occurring within ~400 fs, the $S_1$ to $S_0$ transition appears between 1 and 12 ps. In some extreme cases (>10%), the trajectory can stay on $S_1$ for over 20 ps. Figure 4a shows the total excitation lifetime distribution of $S_1$. The peaks at ~1.6 ps of the histogram plot indicated the possible excitation lifetime of COT before reaching the $S_1/S_0$ crossing.

Finally, we collected the $S_1/S_0$ crossing configurations sampled from $S_1$ AMD simulations, when the gap $\Delta E_{S_0, S_1}$ becomes smaller than 0.1 eV. These AMD trajectories were continued on the ground-state $S_0$ potential energy surface at 300 K (i.e., transitions to the ground state were enforced) with the excess of energy ($\Delta E_{S_0, S_1}$) being dispersed in a nuclear kinetic energy. In this way, the photoproduct of COT is connected with the thermal reaction paths that include the $S_0$ potential energy surface. As a comparison, pure thermal reaction channel simulations were also initiated on $S_0$ from a ground-state optimized $D_{2d}$ boat shape and planar $D_{4h}$ COT structures, respectively. Figure 4b shows the time-dependent energy profiles of both $D_{2d}$ and $D_{4h}$ thermal reaction dynamics on $S_0$; it takes ~0.2 ps for the system to reach the target temperature (300 K), then the plots demonstrate that the planar $D_{4h}$ COT ultimately equilibrates to a $D_{2d}$ boat-shaped structure by crossing an energy barrier. As shown in Figure 4c, the $S_0$ AMD starting from the $S_1/S_0$ conical intersection structure exhibits a coinciding equilibration progress as the thermal reaction path of the planar $D_{4h}$ structure, and the structure at the observed barrier from the thermal reaction MD is similar to the $S_1/S_0$ crossing points where the excited-state branches of the MD are terminated. This establishes the connection between the $S_1/S_0$ crossing structure and the continuous $S_0$ simulations for a thermal reaction channel and, further, clarifies the final phase of COT in the ground-state dynamics toward an equilibrium boat-shaped geometry.

In summary, our dynamical simulations provide a comprehensive map of excited-state relaxation pathways in the photoexcited cyclooctatetraene. We used our NEXMD software to perform the nonadiabatic molecular dynamics simulation ($S_{0 \rightarrow 1}$ to $S_1$ states) and adiabatic molecular dynamics simulation (at $S_1$ and $S_0$ states) of COT at ambient conditions. An active excited to ground-state relaxation pathway accompanied by a complete double-bond shifting progress of COT was determined as follows: boat-shaped $D_{2d}$ structure ($S_{0 \rightarrow 1}$) $\rightarrow$ planar $D_{4h}$ structure ($S_1$) $\rightarrow$ slightly folded $S_1$ metastable structure $\rightarrow$ planar $D_{4h}$ at $S_1/S_0$ conical intersection $\rightarrow$ boat-shaped $D_{2d}$ ground-state equilibrium structure. Observed structural changes agree well with those determined from the high-level ab initio simulations. Moreover, the excitation lifetime obtained from our molecular dynamics simulation shows an excellent agreement with the experimental measurements. Our detailed dynamical results can thus provide a fundamental basis for further investigating the bond-order inversion and photoswitching process in the COT molecular systems.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01397.

Potential energy analysis and geometric features analysis (PDF)

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J. Phys. Chem. Lett. 2021, 12, 5716−5722
ACKNOWLEDGMENTS

H.S., S.T., and S.M. acknowledge support from the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under Contract Nos. KC0301030 and KC030103172684 and Award No. DE-SC0019484. H.S. and S.T. acknowledge support of the Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos 87545, New Mexico, United States; orcid.org/0000-0001-5547-3647; Email: serg@lanl.gov

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Notes

The authors declare no competing financial interest.

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Non-adiabatic Molecular Dynamic Study of the Relaxation Pathways for Photoexcited Cyclooctatetraenes: Supporting Information

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S1. Potential Energy Analysis

Fig S1. Ground to $S_2$ potential energy profile of $D_{8h}$ symmetric planar structure running in $S_1$ AMD simulation.
According to the potential energy plots shown in Fig S1 and S2. The potential of $S_2$ will be overlapped with $S_3$ when the COT structured in a boat-shaped. On the other hand, the potential of $S_2$ will be close to $S_1$ when COT in a planar structure. It shows that there is no local minimum on $S_2$ except the $S_2/S_1$ conical intersection. Indeed, we unable to optimize the structure of COT in $S_2$. 

Fig S2. Ground to $S_3$ potential energy profile of $D_{2d}$ symmetric planar structure running in $S_2$ AMD simulation.
S2. Geometric Features Analysis

Fig S3. Geometric features analysis: (a.) Average Bond-Length, (b.) Dihedral Angles, and (c.) Bond Length Alternation (BLA). These 3 geometric features show significantly distinguishing between the planar and boat-shaped structure. Therefore, they are used to monitor the geometry evolution of COT during NAMD process.