CONFORMATIONAL DYNAMICS ON COMPLEX ENERGY LANDSCAPES*

8.1 Introduction

Complex transient structures are ubiquitous in chemical and biological reactions. Progress has been made in elucidating structures¹⁻³ (near) their equilibrium states, but to reach intermediate structures in the transition region between reactants and products the time resolution must be ≤ 1 ps.⁴ Pericyclic reactions—processes in which bonds are believed to be concertedly

^{*} Adapted from Goodson, B.M.; Ruan, C.-Y.; Lobastov, V.A.; Srinivasan, R.; Zewail, A.H., Chem. Phys. Lett. 2003, 374, 417.

forged and broken in a cyclic transition state—have such complex structures, and they occur on the ultrafast time-scale. These reactions, which are central in chemistry, can be described by the orbital symmetry correlations of Woodward and Hoffmann,⁵ with the resulting products and stereochemistry often depending on whether the reaction is activated by heat or light. An archetypical example is that of Cope rearrangement of 1,3,5-cyclooctatriene (COT3).⁶ The synthesis of COT3 gives a mixture of COT3 and bicyclo[4.2.0]octa-2,4-diene (BCO), and it has been shown that above 100 °C, both species rapidly interconvert *thermally* by an electrocyclic ring opening/closure process,⁷ as shown in Scheme 8–1.

In contrast, the *photochemistry* of COT3 (and BCO), which has been studied in solution⁸⁻¹¹ and in matrices¹²⁻¹⁵ for both the neutral and cationic species, has shown that COT3 undergoes electrocyclic ring opening. The product is 1,3,5,7-octatetraene (OT),¹⁰⁻¹⁴ and the reaction is shown in Scheme 8–2.

The nascent OT species is transient and cyclizes to (re-)form COT3 thermally on a time-scale of seconds;¹⁰ upon absorption of additional UV light, it isomerizes.^{10,15} (Similarly, BCO upon UV absorption gives predominantly OT, which ultimately gives COT3.¹²) For these complex reactions, it is essential to elucidate the structures involved, equilibrium and far-from-equilibrium (transients).

COT3 represents a particularly challenging system to study via UED for a variety of reasons, including the number of different structures potentially involved, the lack of symmetry in most of these structures, the large number of atoms in each species, and the complex landscapes of transient products. With the temporal and spatial resolutions achieved in UED-3, we performed the first ground-state electron diffraction study of this system and resolve the two structures (COT3 and BCO) involved in the thermally mediated interconversion. For the light-mediated reactions, following femtosecond UV excitation and imaging with ps electron pulses, we determined the transient structure involved in the ring opening (OT structures). Unlike ground-state reactions, the nascent structures of the ring

opening process are far-from-equilibrium, as shown below.

8.2 Methodology

Diffraction images were obtained with our third-generation UED apparatus. Briefly, ultraviolet femtosecond laser pulses (~200 μ J, ~267 nm, ~120 fs, 1 kHz repetition rate) were directed into the scattering chamber to initiate structural change, whereas the weaker beam (~5 μ J) was directed into a delay line and focused onto a back-illuminated silver photocathode to generate electron pulses via the photoelectric effect. The pulse width in these experiments was ~4 ps (~25 000 electrons). The pulses were accelerated into

the scattering chamber at 30 keV (de Broglie wavelength: 0.067 Å). Electron diffraction images were recorded with a low-noise image-intensified 2-D CCD camera assembly capable of single-electron detection. The camera length for these experiments (13.41 cm) was calibrated by comparing experimentally derived diffraction data obtained from high-purity CO₂ gas with literature values.¹⁶ The reaction zero-of-time, i.e., the overlap of the initiating femtosecond pulse and probing electron pulse, was determined by the ion-induced lensing technique.¹⁷ In a cross-beam geometry, the laser, electron, and molecular beam intersected in a region of ~400 µm wide. The molecular beam pressure was a few torr while the background pressure within the scattering chamber was ~2 × 10⁻⁴ Torr over the course of the experiment. Diffraction images were processed using computer-interface to the CCD camera.

8.3 Structure Refinement

The modified molecular scattering intensity of each pair of atoms (i, j) in an isotropic sample can be written as:

$$sM(s) \propto \sum_{i,j} \frac{\sin(sr_{ij})}{r_{ij}} \cdot \exp(-\frac{1}{2}{l_{ij}}^2 s^2)$$
 (8–1)

where s is the momentum transfer parameter, r_{ij} is the internuclear separation between the two atoms, and l_{ij} is the corresponding mean amplitude of vibration. The corresponding radial distribution curves were obtained via Fourier (sine) transform of sM(s) curves:

$$f(r) = \int_{0}^{s_{\text{max}}} sM(s) \sin(sr) \exp(-ks^2) ds$$
(8-2)

where the damping constant k accounts for the finite s range of the detector. The procedures used for obtaining mean amplitudes of vibration and corresponding corrections for internuclear distances at high temperature were described elsewhere.¹⁸ The structure parameters are constructed using the internal coordinates of a geometrically consistent structural model for the molecule in terms of Z-matrix formalism. All data analysis and structural refinement were performed using software developed in this laboratory. Reported error bars represent one standard deviation of the least-squares fit. The quality of a given least-squares fit was evaluated in terms of the resulting statistical R value.¹⁶

8.4 DFT Calculations

All calculations utilized in this work were performed using the GAUSSIAN 98¹⁹ commercial quantum chemistry package on a Windowsbased PC. The B3LYP density functional theory (DFT) method (at the 6-311G** level) was employed to calculate the geometries, vibrational

8.5 Monte Carlo Global Structural Optimization

In order to ensure all possible structures are considered in the refinements, Monte Carlo sampling procedures are applied to search all possible good fits to the data (in terms of χ^2) in a configuration space set up by the Z-matrix coordinates. The distance between any two given structures is defined as the square root of the sum of the squared displacements between all corresponding nuclear coordinates of the two structures. Based on the distance between randomly sampled structures to a starting structure, the hyper configuration space is first partitioned and then searched for local minima. When the samplings within the partitioned subspace are found to converge to a local χ^2 minimum, the radius of convergence is determined along each adjustable coordinate in the Z-matrix to give the size of local minimum basin. Finally, lowest local minima structures are statistically analyzed to reveal the ensemble distribution of a global minimum structure.

8.6 Results and Discussion

A. Structures of Cope Rearrangement

The UED image obtained from the ground-state structures is shown in

Fig. 8–1(a); the corresponding 1-D radial average is shown in Fig. 8–1(b). The isomerization of 136COT to 135COT and the facile thermal equilibration between BCO and 135COT are some of the many interconversions of the C_8H_{10} isomers that have been observed. The latter, which is in fact a reversible Cope rearrangement involving a 1,2-diallylcyclobutane, has been shown by Cope *et al.*⁶ to be rapid at 100 °C. Such rearrangements are known to proceed via a six-center transition state. The interconversion of the three C_8H_{10} isomers – 136COT, 135COT, and BCO – is shown in Scheme 8–3.

Greathead and Orchard⁷ have measured the gas-phase equilibrium and rate constants for the isomerization of 136COT to 135COT between 390 and 490 K. The equilibrium constant for the 136COT \leftrightarrows 135COT reaction is given by the van't Hoff equation:

$$\ln K_1^0 = (0.24 \pm 0.04) + (13.78 \pm 0.15 kJ / mol) / RT$$
(8-3)

Similarly, the gas-phase equilibrium and rate constants for the isomerization of BCO to 135COT have been measured between 330 and 475 K. The corresponding equilibrium constant for the 135COT \leftrightarrows BCO reaction fits the van't Hoff equation:

$$\ln K_2^0 = (-1.20 \pm 0.02) - (0.40 \pm 0.07 kJ / mol) / RT$$
(8-4)

At the temperature of our experiment (433 K), 1,3,6-COT3 is in dynamic equilibrium with COT3 and BCO. From the above van't Hoff equations, the relative fractions of the three isomers at 160 °C are estimated to be ~1.3% 136COT, ~77.7% 135COT, and ~20.9% BCO. Due to the vanishingly small contribution (~1%) of the 136COT species, it was not considered further in our refinements.

Both COT3 and BCO ground-state structures were observed in our diffraction data. Our initial refinements examined the relative fraction of these structures in dynamic equilibrium, governed by the sample temperature and the energy difference between the molecules. A series of least-squares refinements were performed on the relative fractions of theoretical (DFT) COT3 and BCO structures, with systematic variation of the initial fractions. We obtained a global minimum with a 73.3:26.7 COT3:BCO ratio at 160 °C (with a statistical 1 σ uncertainty of ±2%), in good agreement with the value predicted by the results of previous chromatographic experiments (77.7:20.9).⁷ The resulting fit to the UED data using the unrefined DFT structures was excellent (*R*=0.105); the corresponding (black) residual curve is shown in Fig. 8–2.

To our knowledge, the structure of COT3 has not previously been studied in the gas phase; we, therefore, performed a partial refinement of its molecular structure with our electron diffraction data. To combat parametercorrelation problems, we reduced the number of adjustable parameters in our refinement by making the following simplifications:

- 1. The COT3 molecule was divided in half (along its pseudo- C_2 axis) and set each covalent CC distance on the "left" side of the molecule to be equal to the corresponding (refined) distance on the "right" side, plus a small difference predicted by our calculations (although all skeletal bond angles and torsional angles were still refined independently—see Table 7–1).
- Each covalent C-H distance was assigned one of two (refined) values, depending on its hybridization.
- 3. DFT-predicted values were used for all bond angles and torsional angles involving hydrogen atoms. Our refinement of the COT3 molecular structure was thus comprised of a total of 17 adjustable parameters (6 covalent distances, 6 skeletal bond angles, and 5 skeletal torsional angles). Subsequent fraction refinement left the COT3:BCO ratio essentially unchanged (72.5:27.5).

The results of the structural fit to our UED data are shown in Fig. 8–3, and the refined structural parameters are presented in Table 8–1 and compared with values predicted by DFT. Agreement between theory and experiment was further improved by the refinement, shown clearly by the reduced residual sM(s) curve (green) (see Fig. 8–2) and lower R value for the fit (0.068). The peaks in f(r) show contributions from both ground state structures, with covalent C–H and C–C distances at ~1.1 Å and ~1.4 Å, second nearest-neighbor C··H and C··C distances at ~2.2 Å and ~2.6 Å, and third and fourth nearest-neighbor C···H and C···C distances at ~2.7 Å to ~5 Å. The molecular structure obtained for COT3 from our UED data is shown alongside Table 7–1; the overall conformation of COT3 is "twist-boat" in nature (with C_1 symmetry), in agreement with previous solution-state NMR conformational studies,²⁰ as well as theoretical predictions reported here and in previous work.^{20, 21} Inspection of the corresponding structural parameters in Table 7–1 shows good agreement between the refined experimental values and those predicted by our DFT calculations. Some deviations from theory may be the result of parameter correlation (e.g., the apparent inversion of r_1 and r_3 , and of the two C–H distances); however, the observed differences are generally within the uncertainty of the refinement.

B. Ring Opening Reactions

To observe structures of the light-mediated reactions, we acquired UED images at three time delays (t) between the laser and electron pulses: – 100, –50, and +150 ps, all with a resolution of 4 ps. Unlike previous UED-3 experiments, only a single positive time slice was obtained in order to limit the amount of expensive sample used during the course of the experiment. The diffraction signal at –100 ps, which results only from parent structures,

was used as our reference in generating the diffraction difference images shown in Fig. 8–4. No diffraction signal was observed in the t = -50 ps image, differenced from the -100 ps image, as the electron pulse for both times only images the reactant structures. However, diffraction rings could be clearly seen in the +150 ps image, which are derived exclusively from structural changes induced by the femtosecond initiating pulses. The experimental $\Delta sM(s)$ and $\Delta f(r)$ curves at +150 ps are shown in Figs. 8–5 and 8–6.

The diffraction curves at positive time, shown in Figs. 8–5 and 8–6, give the structures of the species along the primary reaction pathway. Energetically allowed reaction pathways, based on our DFT calculations, identify the ring opening to form OT as a definite pathway, but also identify another possible path for fragmentation (to form benzene and ethylene or 1,3-cyclohexadiene (CHD) and acetylene) or isomerization (to 1,3,6-COT3). Naturally we also consider all possible structures at the internal energy possible (up to 100 kcal/mol) of the parents (COT3 and BCO) and of transient OT (conformations of Fig. 8–7). The effect of the high internal energy is directly manifested in the structural parameters, as elevated vibrational amplitudes, inverted torsional distribution, and/or changes in averaged bond distances from those expected for the equilibrium structures.¹⁸ We found the best agreement, an R value of ~0.5 without refinements, when the reaction path is that of ring opening with the product being vibrationally hot. In

contrast, our fits with the hot 'parent' structures (1,3,5-COT3, 1,3,6-COT3, and BCO) were poor as judged by R values of ~0.9, ~1.0, and ~1.4, respectively. The depletion ratio of parents was fixed at 76:24 (COT3:BCO), adjusted for the slightly higher absorption cross-section of COT3 at 267 nm.⁶

The ring-opening pathway is also evident upon the inspection of the data $\Delta f(r)$ curves shown in Fig. 8–6. At the same positive time delay we observe peaks with *negative* and *positive* amplitudes: the negative peaks (red regions) correspond to the net *loss* of internuclear density (i.e., the loss of covalent and second, third, and fourth nearest-neighbor distances in the parent structures), whereas the positive peaks (blue regions) correspond to a net *gain* in internuclear density (e.g., the formation of new bond pairs at distances greater than 4 Å). Such a pattern is entirely consistent with ring-opening processes that form more extended structures in the transient species, and this is evident more quantitatively by the agreement between experiments (distances and amplitudes) and theory.

C. The Observation of Non-equilibrium Configurations in OT

The parent (COT3 and BCO) and product (OT) structures are nearly isoenergetic; thus, the OT structures formed by ring opening are left with high excess internal energy from the absorbed UV photons (>100 kcal/mol). Our previous UED studies of light-mediated pericyclic reactions showed that such energies can be directly manifested as changes in geometrical parameters and vibrational amplitudes from those expected with equilibrium structures.¹⁸ We therefore examined the UED signals for the signatures of such non-equilibrium product structures: namely, elevated vibrational amplitudes, non-equilibrium bond distances, and inverted torsional distributions.

The good fit of the UED data to the higher-energy *tcGct* structure provided the first indication of the non-equilibrium nature of OT; a thermally equilibrated conformer distribution (with an estimated Boltzmann temperature of ~1900 K) would be comprised mostly of lower-energy tcAct and tcAcc structures (~70%, based on thermochemical values obtained from our DFT calculations). Indeed, when we fit the UED signals with multiple conformers simultaneously, we found the best reproduction of our data using the canonical OT structures with a two-part mixture of highest-energy *ccGcc* structures (\sim 55%) and lowest-energy tcAct structures (\sim 55% / 45% ccGcc to tcAct; R=0.260). As before, theoretical mixtures with the ccAcc conformers gave lower-quality fits (or more often, led to insignificant or negative fractions of these conformers), indicating that the average OT structure in experiment is poorly represented by the *ccAcc*-type torsional our configurations. We also observed elevated vibrational amplitudes in all of our fits. To obtain the fitted results shown, the CC and CH vibrational amplitudes had to be respectively increased by an average of ~ 3.1 and ~ 2.3 times the ambient temperature values (at 433 K), corresponding to a $\sim 40\%$ increase over what would be expected for a thermally equilibrated distribution of the excess internal energy over the vibrational degrees of freedom.

In our studies of the light-induced ring opening of CHD to form highenergy (ground state) HT, we observed a stretched CC single-bond distance in addition to an inverted torsional configuration and elevated vibrational amplitudes—that persisted in the average product structure for at least 400 ps. In order to obtain an improved representation of the ensemble-average OT structure (and with our previous UED observations of far-fromequilibrium structures in mind) we performed a Monte-Carlo / least-squares refinement of the three CC single bonds and the corresponding dihedral angles using the experimental $\Delta s M(s)$ curve.

Because of the high sensitivity achieved here, the different conformations of transient OT structures (Fig. 8–7) were further examined in the UED analysis and reduced to the gauche structures. The higher energy gauche structure, so-called tcGct, was found to be the best of the R values. Being a dominant structure at high energies elucidates its non-equilibrium state of dynamics. If equilibrium structures are the only one present at the Boltzmann temperature of ~1900 K (determined by the internal energy), the lower-energy *anti* structures (*tcAct* and *tcAcc*) would be the dominant one(s) (~70%), contrary to the findings. The CC and CH vibrational amplitudes for the refined gauche structure are increased by an average of ~3.1 and ~2.3 times the ambient temperature values (at 433 K), corresponding to a ~40% increase over what would be expected for a thermally equilibrated distribution of the excess internal energy over the vibrational degrees of freedom.

In order to determine the nature of the landscape of molecular conformations and to obtain a final representation of the ensemble-average OT structure, we performed a Monte Carlo/least-squares refinement of the three CC single bonds and the corresponding dihedral angles. Our search of the configuration space began at the all folded OT (*ccGcc*) structure, freeing the parameters to change ± 0.25 Å for the C–C bonds and $\pm 180^{\circ}$ for the dihedral angles. After 375,000 sampling steps, 22 local minima that gave nearly identical fits to the UED data were obtained (with R = 0:33-0:36 for the difference curves). Further least square refinements were applied to the local minimum structures, but their scopes of adjustments were limited within the radius of convergence associated with each minimum. The results of these fits are generally superb (with R = 0:32-0:35 for the difference curves) as shown in Figs. 8–6 and 8–8.

The success in reaching this determination of the complex structures with multiple conformations was finally confirmed from the transient-only diffraction curves. Figs. 8-8(a,b) show the comparison of the experimental and theoretical sM(s) and f(r) of these transient-only curves, obtained using the structural parameters of the first minimum of the Monte Carlo/leastsquares refinements. Fig. 8–8(c) shows the structures of five selected minima superimposed for comparison, as well as a table summarizing the values of the refined parameters. The structures of all minima clearly show considerable gauche tcGct/ccGct character and not the anti equilibrium OT structures (Fig. 8-7), indicating an inverted (non-Boltzmann) torsional distribution. This non-Boltzmann behavior is also revealed in the disparities of the torsional motions and in the corresponding CC single bond distances. We found that the two terminal torsions (ϕ_1, ϕ_3) in the side groups of OT have broad distributions ($\pm 40^{\circ}$); in contrast, the torsion at the central C–C bond (ϕ_2) , which establishes the gauche character of OT, is rather confined ($\pm 6^\circ$). Correspondingly, the central C–C bond distance (r_2) was found to be slightly lengthened while all the rest of the C-C bonds remain at (near) equilibrium distances. These far-from-equilibrium structures reflect large amplitude torsional motions comprised of ϕ_1 , ϕ_3 , and r_2 , which are involved in the ring opening of COT3. The motions persist for long times and are resolved in our experiments. Moreover, they are not in thermal equilibrium with the rest of molecular motions as shown here and for even less complex structures. The results are surprising in that the persistence of torsional motions across large complex energy landscape and for long times indicate a bottleneck in energy redistribution between these very low frequency modes and the surrounding thermal bath modes.

It is interesting to compare the present results of ring opening in the COT3/BCO system with our previous UED studies of light-mediated pericyclic reactions in CHT and CHD. The observation of an inverted torsional configuration and highly elevated vibrational amplitudes indicate the non-equilibrium nature of the OT structures following ring opening and are similar to the highly elevated vibrational amplitudes we observed in CHT (following a [1,7]-sigmatropic hydrogen-shift), as well as the inverted torsional configuration we observed in HT (following electrocyclic ring opening of CHD). However, it is interesting to note that no stretched C-C distances are observed in OT (at least not one that lasts 150 ps), a clear difference from our previous UED observations of a significantly stretched C-C distance (to ~1.7 Å) in HT that lasted for at least 400 ps. In this previous report, we hypothesized that the resulting far-from-equilibrium structures observed by UED may reflect memory of the structural features of the excited molecule at the point of decent to the ground-state surface. While the electrocyclic ring-opening reactions of COT3 and CHD both resulted in the

observation of inverted torsional configurations in the hot product structures, the absence of non-equilibrium (stretched) covalent distances in OT may indicate that the reaction surface of COT3 may have more in common with that of CHT than with that of CHD. Such potential similarities are reminiscent of those observed for COT3 and CHT in the solution-phase resonance Raman experiments of Mathies and co-workers:¹¹ their results suggested that the while the initial wave packet motion for CHD is indeed along the expected conrotory ring-opening coordinate, the initial motion of COT3 (like CHT) was toward ring-planarization (and not ring opening). The connection between the structural features observed in these systems by UED and the landscapes of the corresponding energy surfaces awaits further

experimental and theoretical investigation.

The photochemical changes uncovered by UED, in conjunction with previous studies in the literature, provide a detailed description of the initial dynamics that lead to the disrotatory ring opening of COT3. The nuclear evolution launched by the absorption of a photon is immediately directed towards bringing the eight members of the ring into the same plane. Since complete planarization is impossible without severe bond angle strain, this movement amounts to the distribution throughout the ring of the torsion originally present primarily in the saturated portion of the ring. The absence of movement along the CH₂-twisting coordinate reveals that this step of the reaction does not occur until further along the reaction coordinate. Thus, the ring opening of COT3 is a sequential reaction: the planarization step precedes any significant evolution along the more intuitive reactive modes, including the actual opening of the ring (lengthening of the CH_2 – CH_2 bond), and rehybridization (methylene C–H bond shortening) and movement of the CH_2 groups into the plane (CH_2 –twisting). However, it is important to note that the preliminary planarization step does not preclude the reactive changes from occurring in a concerted fashion, as predicted by pericyclic reaction theory. The planarization step establishes the proper orientation required for the changes in bonding orbital overlap to occur.

Although the photochemical reaction of COT3 is more closely allied chemically to the ring-opening reaction of cyclohexadiene, its excited-state dynamics more closely parallel those of cycloheptatriene, which involve significant evolution along a low-frequency "boat-to-boat" mode and which exhibit no evolution along the reactive C–H stretching coordinate. Both triene's rings are boat structures that exhibit large movements towards planarity when excited and delay motion along their respective "reactive modes" until after the planarization is well under way. While both cycloheptatriene and COT3 exhibit similar excited-state dynamics, their unique ground-state structures require different movements to achieve the orbital overlap that will facilitate the subsequent stages of the reactions. Both of these trienes can be contrasted to the excited-state dynamics of cyclohexadiene, which is only slightly nonplanar. Cyclohexadiene exhibits nuclear evolution along the "reactive modes" indicative of a conrotatory ringopening reaction immediately after excitation: the CH_2 - CH_2 bond lengthens as the CH_2 groups twist towards the molecular plane in a conrotatory fashion. The similarities and differences between the initial excited-state dynamics of these three systems suggest that a planar or near-plane structure is required before a pericyclic reaction can proceed.

8.7 Conclusions

We have exploited the unmatched spatio-temporal resolution of ultrafast electron diffraction to probe the molecular structures resulting from thermal- and light-mediated electrocyclic reactions in COT3—one of the most challenging systems studied by UED to date. For the thermal processes, we were able to observe COT3 and BCO structures in dynamic equilibrium and performed a partial refinement of the COT3 molecular structure. For the light-mediated processes, we determined that OT—the primary product of the photochemical reaction pathway—has a non-equilibrium structure manifested by an inverted torsional configuration and highly elevated vibrational amplitudes (but no stretched C–C bond distances). This nonequilibrium structure is a direct result of the high excess internal energy deposited by the absorbed UV radiation.

These discoveries have ramifications in the studies of macromolecular dynamics since torsional modes of this type have been identified as important in the first steps of protein folding.²² Because the dynamics are comprised of elementary steps made by torsions, directing large amplitude motions in restricted nuclear subspace makes possible the effective movements of residues (proteins) and bases (DNA). Unlike the time scale of a single bond (femtoseconds), the longer times involved in these torsions (10–100s of picoseconds) and their localization and isolation may be a key for biological function of macromolecules.

In the future, observing the *structural dynamics* of ring opening in COT3 and other conjugated polyenes may shed new light onto the structural ramifications of energy redistribution and the choice of reaction pathway, permitting not only a more complete comparison with the pericyclic reactions studied previously by UED, but also yielding new insight into a wide class of photophysical and photochemical processes found throughout chemistry and biology.



Scheme 8-1. Thermal Cope rearrangement of 1,3,5-cyclooctatriene (COT3) to bicyclo[4.2.0]octa-2,4-diene (BCO).



Scheme 8-2. Light-mediated electrocyclic ring opening of 1,3,5-cyclooctatriene (COT3) to 1,3,5,7-octatetraene (OT).

Scheme 8-3. Ground-state species in thermal equilibrium: 1, 3, 6-cyclooctatriene (1, 3, 6-COT3), 1, 3, 5-cyclooctatriene (1, 3, 5-COT3), and bicyclo[4.2.0]octa-2,4-diene (BCO). At the temperature of the experiment (160 °C), the respective equilibrium fractions are $\sim 1\%$, $\sim 78\%$, and $\sim 21\%$.

Figure 8-1. Diffraction of ground-state COT3 and BCO structures in thermal equilibrium. (a) 2-D UED image obtained following division by the atomic (Xe) reference signal. (b) Corresponding 1-D diffraction data (blue curve) obtained via radial summation of the 2-D data. The smooth baseline curve is shown in red.

Figure 8-2. Ground-state molecular scattering curves. Comparison of theoretical (red) and experimental (blue) sM(s) curves following refinement of the relative fractions of the COT3 and BCO structures, and partial refinement of the COT3 structural parameters; see text. The magnified (×2) residual curves were obtained from two different fits: the top residual (black) was obtained from a fraction-fit of the DFT ground-state structures without refinement, whereas the improved residual (green) was obtained from the partial refinement of the COT3 structural parameters combined with a fraction fit.

Figure 8-3. Ground-state radial distribution functions. Comparison of corresponding theoretical (red) and experimental (blue) f(r) curves obtained following sine transformation of the sM(s) curves in Fig. 7-2. The fraction fit results in ~73% COT3 and ~27% BCO; see text.

Figure 8-4. Diffraction-difference images of transient structures in light-mediated reaction of COT3. **(Top)** 2-D difference images obtained at 50 and +150 ps. **(Bottom)** Corresponding 1-D diffraction difference signals obtained via radial summation of the 2-D images. The raw diffraction data are shown in black, whereas the Fourier-filtered curves are shown in blue; the smooth base-line curve used for the fit of the +150 ps data is shown in red.

net depletion-bond breaking-of internuclear pairs, whereas the red regions correspond to net gain-bond formation-of internuclear pairs. The green curve was obtained by sine transform of the theoretical sM(s) curve **Figure 8-6.** COT3 difference curves. Experimental $\Delta f(r)$ curve (blue); the blue highlighted regions represent in Fig. 8-5.

the OT torsional degrees of freedom as follows: positions 1, 3, and 5 in a given name correspond to torsion around single bonds, whereas positions 2 and 4 correspond to torsion around double bonds (and hence are always 'c' for 'cis' in the conformers of cis, cis-OT). Positions 1 ground state), symmetries, and values for single-bond torsional angles. The nomenclature convention used in the figure corresponds to Figure 8-7. Equilibrium (cis, cis) OT conformer structures obtained via DFT (6-311G** level) including energies (relative to the COT3 and 5 may be denoted 't' (for trans) or 'c' (or 'c'); however, the use of 'A' (Anti) and 'G' (Gauche) was deemed more appropriate for position 3.

transient-only *sM*(*s*) curves for the diffraction signal at +150 ps; the theoretical curve was obtained using the structural parameters of Figure 8-8. Transient-only structures obtained from UED curves. (a) Comparison of theoretical (red) and experimental (blue) the first minimum of the Monte Carlo/least-squares refinements. (b) Corresponding experimental and theoretical transient-only f(r)curves. (c) Overlaid skeletal structures for the five selected minima obtained from the Monte Carlo/least-squares refinement.

	Bond distance/Angle	Value	Theory
	r1(C1-C2) r2(C2=C3) r3(C3-C4) r4(C4=C5) r5(C5-C6) r6(C6=C7) r7(C7-C8) r8(C8-C1) r(C-H) 'sp3' r(C-H) 'sp2'	1.464 ± 0.040 1.321 ± 0.025 1.483 ± 0.077 1.367 ± 0.055 $r_5 = r_3 + 0.0087^{\circ}$ $r_6 = r_2 + 0.0048^{\circ}$ $r_7 = r_1 + 0.0005^{\circ}$ 1.518° 1.072 ± 0.033 1.113 ± 0.018	1.502 1.339 1.458 1.348 1.467 1.344 1.503 1.537 1.096 1.088
	$\begin{array}{c} \alpha_1(1-2-3) \\ \alpha_2(2-3-4) \\ \alpha_3(3-4-5) \\ \alpha_4(4-5-6) \\ \alpha_5(5-6-7) \\ \alpha_6(6-7-8) \\ \alpha_7(7-8-1) \\ \alpha_8(8-1-2) \end{array}$	129.2 ± 5.3 122.8 ± 2.1 128.2 ± 7.5 133.5 ± 9.8 132 ± 10 134.1 ± 6.8 117.6^{b} 119.1^{b}	125.2 125.6 128.3 131.7 134.8 132.6 116.5 113.5
	$ \phi_1(1-2-3-4) \\ \phi_2(2-3-4-5) \\ \phi_3(3-4-5-6) \\ \phi_4(4-5-6-7) \\ \phi_5(5-6-7-8) \\ \phi_6(6-7-8-1) \\ \phi_7(7-8-1-2) \\ \phi_8(8-1-2-3) $	20 ± 22 37 ± 39 3 ± 41 -36 ± 15 -17 ± 48 27 ^b 48 ^b -94 ^b	2.3 39.8 6.9 -39.3 -4.9 1.6 70.5 -90.9

^aParameter not fit; obtained using the deviation values predicted by DFT at the 6-311 G** level ^bDependent parameter (not fit)

Table 8-1. Structural coordinates obtained for COT3 from the least-squares partial refinement of UED data, compared with values obtained from theoretical DFT calculations. Some uncertainties of the fit are somewhat larger than the instrumental limits (~0.01 Å for ground state structures) due to the correlation effects among fitting parameters in the twist-boat structure.

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