Forward and Backward Pericyclic Photochemical Reactions Have Intermediates in Common, Yet Cyclobutenes Break the Rules

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Photochemical pericyclic reactions are believed to proceed via a so-called pericyclic minimum on the lowest excited potential surface (S_1), which is common to both the forward and backward reactions. Such a common intermediate has never been directly detected. The photointerconversion of 1,3-butadiene and cyclobutene is the prevailing prototype for such reactions, yet only diene ring closure proceeds with the stereospecificity that the Woodward–Hoffmann rules predict. This contrast seems to exclude a common intermediate. Using ultrafast spectroscopy, we show that the excited states of two cyclobutene/diene isomeric pairs are linked by not one, but by two common minima, p* and ct*.

Starting from the diene side (cyclohepta-1,3-diene and cycloocta-1,3-diene), electrocyclic ring closure passes via the pericyclic minimum p*, whereas ct* is mainly responsible for cis–trans isomerization. Starting from the corresponding cyclobutenes (bicyclo-[3.2.0]heptene-6 and bicyclo[4.2.0]octene-7), the forbidden isomer is formed from ct*. The path branches at the first (S_2/S_1) conical intersection towards p* and ct*. The fact that the energetically unfavorable ct* path can compete is ascribed to a dynamic effect: the momentum in C=C twist direction, acquired—such as in other olefins—in the Franck–Condon region of the cyclobutenes.

Introduction

Pericyclic reactions are governed by the Woodward–Hoffmann (WH) rules,[1] which are nowadays derived from state correlations (see for example, refs. [2] and [3]). In photochemically allowed (thermally forbidden) reactions, the reactant ground state (S_0) correlates with a two-electron excited state of the product and vice versa. The crossing of the two pairs of correlated states is avoided and creates 1) a barrier in S_0 that prevents the reaction from occurring in the ground state, and 2) a "pericyclic minimum" (p*) on the lowest excited surface S_1 that is common to both the forward and backward reactions; this collects population from any initially excited state and funnels it through a conical intersection (CI) to the S_0 minima of product and reactant. An early version of this scheme was developed by van der Lugt and Oosterhoff;[4] modern quantum chemistry and ultrafast spectroscopy have added the CI as the funnel outlet from p* and introduced considerations of dynamics instead of equilibration (see refs. [2], [3], [5] and [6], for example).

The most widely used prototype of this scheme is the photochemical ring closure of 1,3-butadiene and the corresponding opening of cyclobutene. The WH rules predict that photochemical ring opening of a *cis*-disubstituted cyclobutene (CB) leads to the isomeric *cis,cis*-diene (ccD) or *trans,trans*-diene (ttD) on a so-called disrotatory path that conserves mirror symmetry (Scheme 1 a). The (C_2-symmetric) conrotatory path, leading to the *cis,trans*-diene (ctD), is photochemically forbidden. Nevertheless, the forbidden isomer is usually observed in sub-

stantial yields, sometimes even dominating.[7–9] This is one of the few known exceptions to the WH rules and is in contrast to the perfect disrotatory stereospecificity exhibited by diene ring closure. A hot ground-state mechanism for formation of the conrotatory diene isomer has been considered in detail, but has been excluded by experimental evidence.[10]

The behavior is in conflict with Scheme 2 a, which shows a common funnel (CI_p) for ring opening and closing and a separate *cis–trans* isomerization path (via CI_{ct}) for the diene.[11] A solution to this dilemma is suggested by the high-level calculations of Olivucci and co-workers, which indicate molecular geometries near CI_p that are so highly twisted that ctD is also accessible from there.[12–15] This is illustrated in Scheme 2 b where branching to all the observed products occurs in one common region, denoted by "IS" (intersection space), which contains several close-lying energy minima (CIs).[16] The crucial feature,

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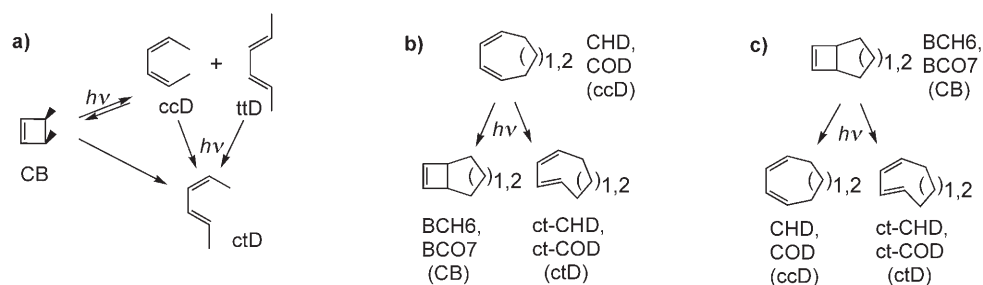
Scheme 1. Photochemical ring opening of cyclobutenes along with ring closing and *cis–trans* isomerization of dienes.
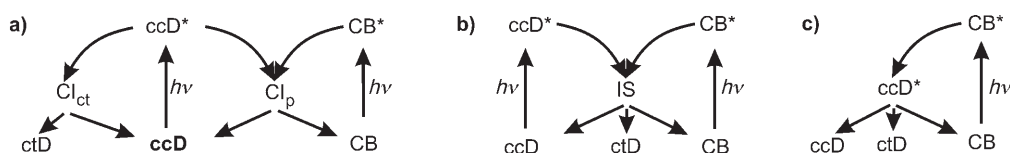
Scheme 2. Possible photochemical paths (with intermediate states) from dienes (ccD) and cyclobutenes (CB).

as proposed in ref. [17], is that the formation of ctD is also accessible from the CB side, because branching between the *cis–trans* isomerization and ring-opening and ring-closing channels is late (i.e. within the IS). Scheme 2c shows a third interpretation—"adiabatic" ring opening—in which excited CB produces excited ccD, which then partly isomerizes to ctD;[9, 15, 18] this mechanism provides a way for CB to open non-stereospecifically without formally breaking the WH rules. The goal of this work was to check these ideas by monitoring the forward and backward paths in a time-resolved experiment. We show that none of the three mechanisms of Scheme 2 tells the full story.

Comparing the forward and backward reactions is generally difficult, because in thermal equilibrium the diene normally exists as a mixture of single-bond conformers (*s-cis* and *s-trans*), whose photochemistry differs.[19] We have therefore chosen for study cyclohepta-1,3-diene (CHD) and cycloocta-1,3-diene (COD), which are fixed in *s-cis* conformations, and their isomers bicyclo[3.2.0]hept-6-ene (BCH6) and bicyclo-[4.2.0]oct-7-ene (BCO7, Scheme 1b-c). In recent studies of CHD and COD by femtosecond time-resolved spectroscopy in the gas phase, we found evidence for an additional earlier branching to two decay channels, and assigned the minor one to ring closure and the dominant one to *cis–trans* isomerization (Figure 1).[17] Vertical excitation via an allowed transition initially leads to the lowest $\pi\pi^*$ (one-electron excited) state, the so-called spectroscopic state denoted by its symmetry designation (1B) in Figure 1. From there, the population flows to the "dark" two-electron excited 2A surface via the 1B/2A surface crossing, where it branches toward two minima, ct* and p* (favoring *cis–trans* isomerization and ring closure, respectively). Departure from them takes place via two CIs (or two locations in the IS) within τ_3(ccD) (=48 and 53 fs for CHD and COD, respectively) and τ_4(ccD) (286 and 118 fs for CHD and COD), respectively, towards the ground-state minima of products and reactant.[17] The experiment affords time constants and estimates of the energies of the excited states accessed by the molecule following UV excitation and discerns whether the corresponding decay processes are consecutive or parallel,[20] but gives no information on the direction of motion. That is, the investigation of the dienes alone[17] cannot decide between the schemes of Figure 1a and 1b. Figure 1a would correspond to Scheme 2a. In Figure 1b the two paths are drawn so that they remain adjacent to each other, both to the right-hand side of the first branching. We have preferred this version in ref. [17] because theory supports this idea. It predicts similar geometries for the 2A minima as well as for the ensuing CIs.[13–15] If this surface topology is correct, both minima must also be accessible from the side of the excited cyclobutene. We have now experimentally checked this expectation, investigating the ring-opening dynamics of the isomeric cyclobutenes BCH6 and BCO7.

Results and Discussion

Time Constants and Their Assignment

As with the dienes,[17] the cyclobutenes were excited in the gas phase (10^{-7}–10^{-4} mbar) by a UV pump pulse (150 fs, 196 nm, populating predominantly the $\pi\pi^*$ state; a superimposed Rydberg absorption has a 6–10 times smaller cross section[9]) and their decay was probed by nonresonant ionization, measuring the yields of the parent and two fragment ions as a function of the pump–probe delay time. The signals were fitted by a sum of exponentials (with time constants τ_i and ionization probabilities as parameters) and, where necessary, convolution with the pump and probe pulses. The shorter wavelength (196 nm) required for excitation of the cyclobutenes unfortunately implies, besides the longer pulse length, a poorer signal-to-noise ratio, in particular in the weak tail of the pump pulse, than in the case of the dienes. Therefore, we could only extract time constants $\tau_i \geq 30$ fs and evaluate signals that were larger than 0.5% of the maximum (see the Supporting Information for details). Nevertheless, the results allow a conclusive comparison with those of the dienes.
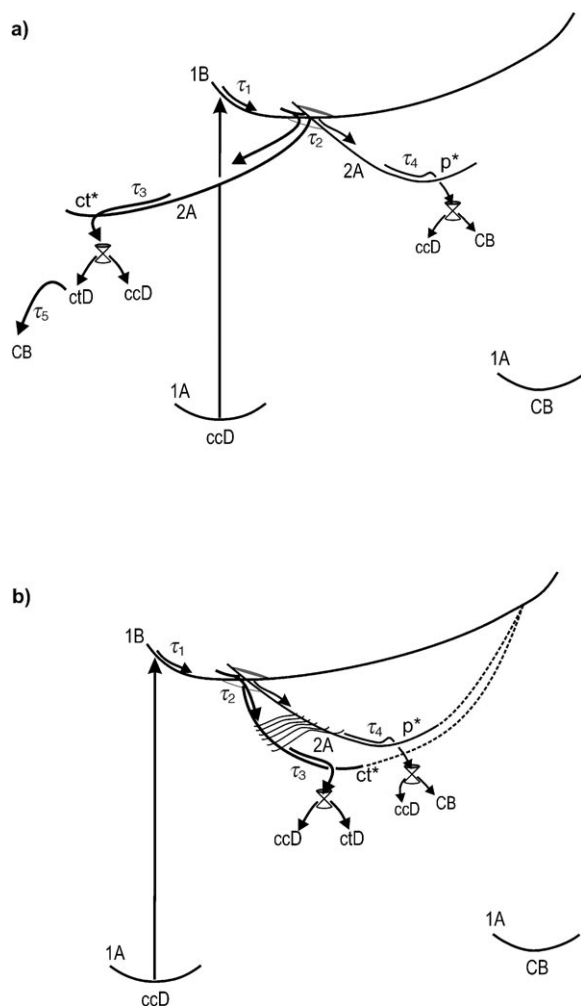
Figure 1. Potentials and pathways for reactions of the *cis,cis*-dienes (ccD) CHD and COD. After excitation, the wave packet first travels along Franck–Condon active coordinates (τ_1) and then within τ_2 leaves to the 2A surface via a conical intersection, where it then branches to two valleys. The two minima ct* and p* are then left within τ_3 and τ_4 via conical intersections to the ground state of the observed products. To avoid overloading, the ground-state reaction ctD→CB (time constant τ_5, left margin in Figure 1a) is omitted in Figure 1b. The diene experiment[17] alone cannot distinguish between the cases a and b; in the latter, the geometries at ct* and p* are assumed to be similar, so that both minima should also be accessible from the cyclobutene (CB) side. The drawing does not indicate that according to calculation,[13] all products (ccD, ctD and CB) are accessible from both minima and corresponding CIs, though with different bias.

Table 1. Time constants τ_i (fs) determined for BCH6 and BCO7. Error limits are standard deviations of τ_i determined in 10 separate runs.				
	τ_1	τ_2	τ_3	τ_4
BCH6	< 30	44 ± 4	50 ± 4	180 ± 20
BCO7	$30^{[a]}$	$30^{[a]}$	53 ± 3	?

[a] $\tau_1 + \tau_2 = 60 \pm 6$ fs. The error limits for the individual constants could not be determined.

potential surfaces (see also the discussion of the assignment in the Supporting Information). To do so, it is convenient to start with the scheme of potential surfaces, which has been applied to many photochemical pericyclic reactions[3] including the two isomeric dienes[17] (see Introduction and Figure 1). Initial excitation populates the one-electron excited $\pi\pi^*$ state (symmetry designation 1B), which is then depleted to the two-electron excited 2A state via a 1B/2A conical intersection. From a 2A minimum (or minima), the molecule then passes to the ground state (S_0) of the product(s) and the reactant, again via conical intersection(s). The energies of the observation windows (locations L_i on the potentials) can be estimated from three properties of the signals: Decreasing electronic energy drastically reduces the ionization probability (*signal intensity*) and raises the *order of ionization*; the latter is determined from observing the signal on variation of the probe intensity. Since the total energy is conserved during relaxation, vibrational excess energy is released, and ionization of such a hot molecule gives rise to a hot ion that fragments before detection; the *degree of fragmentation* is thus also a measure of the electronic (or vibrational excess) energy of an individual L_i.

The ionization probability from L_1 is highest, and the degree of fragmentation smallest, so that τ_1 can be assigned to the departure from the Franck–Condon region. Accordingly, the next step (τ_2) will be the transition to the 2A surface. This is supported by the fragmentation patterns (see Supporting Information): Whereas the parent ion is the dominant signal from L_1 and L_2, it completely disappears on leaving L_2 (as generally observed in pericyclic photochemical reactions[3]). In fact, ionization of the (two-electron excited) 2A state will not lead to the ion ground state but to a one-electron excited state. This will not only raise the order of ionization and decrease the signal intensity (as observed, see Supporting Information) but also enhance fragmentation. An early example of this proposed scheme and assignment was the electrocyclic ring opening of 1,3-cyclohexadiene.[21,22] Very recently this assignment was independently confirmed by detection of the transient photoelectron spectra (including the time constants) from the 1B and 2A states of this molecule.[23]

For the dienes CHD and COD,[17] we found that L_3 and L_4 have the same order of ionization and degree of fragmentation, indicating that they must have a similar energy. We concluded that they are populated from the same preceding location (L_2) in a branched process, and that, because L_3 and L_4 are kinetically distinct, there cannot be any fast exchange of populations between these locations. The relative L_3 and L_4 signal intensities then reflect the branching ratio.[20] In fact, on com-

Table 1 lists the time constants found for the two cyclobutenes. The constant τ_1 for BCH6 could not be directly measured; a nonvanishing τ_1 is only assumed by analogy to BCO7 and in order to match the scheme of potential energy surfaces (see below). If there is any contribution to the BCO7 signals with a time constant 53 fs $< \tau <$ ca. 120 fs (which would be τ_4), its amplitude is too small to be established in view of the properties of the pump laser pulse.

The lifetimes τ_i can be attributed to locations (observations windows) L_i on the potential surfaces. They are also associated with different mass spectra (fragmentation patterns), ionization probabilities and orders of ionization, and these properties help to assign the L_i to different locations or regions on the

paring COD with CHD these intensities just change proportionally to the branching ratio between *cis–trans* isomerization and ring closure, as defined by the relative quantum yields of the two processes in these compounds. The assignment was further confirmed by observation of a hot ground-state process (time constant τ_5, Figure 1a) following depletion of L_3, whose rate was found for both molecules to agree acceptably with the rates[24] of known thermal reactions of the strained ctD isomer of the dienes: ring closure[24] and *cis–trans* isomerization.[25] This all suggests that departure from L_3 leads to ctD; thus L_3 was assigned to the ct* minimum on the 2A surface and L_4 to the p* minimum (Figure 1).

For the cyclobutene BCH6, we now find again the same order of ionization and a similar degree of fragmentation for L_3 and L_4, but different signal intensities (see Supporting Information). Again, we can infer a branching process, populating two 2A minima. With BCO7, no signal from L_4 could be detected. Unfortunately, the branching ratios for BCH6 and BCO7 are not known, so that we cannot compare them with the variation of signal intensities. It was also not possible to detect the very weak signals from S_0, due to the mentioned properties of the pump laser tail. However, it is most interesting to compare the L_3 and L_4 lifetimes for the cyclobutenes to those of the dienes. If Figure 1b applies, L_3 and L_4 should be the common minima (ct* and p*) for the forward and backward reactions. Table 2 shows this comparison.

Table 2. Comparison of the time constants τ_3 and τ_4 (in fs, error limits 5–10%) for the cyclobutenes BCH6 and BCO7 with those of the isomeric dienes CHD and COD.

	$\tau_3(CB)/\tau_3(ccD)$	$\tau_4(CB)/\tau_4(ccD)$
BCH6/CHD	48/50	180/286
BCO7/COD	53/53	?/118

Obviously the lifetimes τ_3 are identical for each of the isomeric pairs, that is, $\tau_3(CB) = \tau_3(ccD)$, whereas $\tau_4(BCH6) = 0.63 \times \tau_4(CHD)$. Here, one should realize that the long τ_4 for the diene suggests that there is a (small) barrier for leaving p* towards the CI, so that the higher initial energy from the CB side would be expected to accelerate this process, resulting in a shorter τ_4 from the CB side than from the diene side. The shorter τ_3 implies that a barrier for departure from this region of the surface must be much smaller, resulting in essentially equal τ_3 values from the CB and diene sides. The signal from the L_4 observation window (p*) of COD was much weaker (about 10 times) than with CHD, consistent with the nine times less favorable branching ratio.[17] If this L_4 window is also disfavored on starting from the cyclobutene side, it is not surprising that a τ_4 could not be detected from BCO7, considering the poor signal-to-noise ratio in the tail of the short-wavelength pump pulse.

These observations and comparisons provide sufficient evidence for the idea that the transient intermediates L_3 and L_4 are common to both the forward and backward reactions, corresponding to the previously identified ct* and p* minima on

the 2A surface. An equality $\tau_3(CB) = \tau_3(ccD)$ for two isomer pairs and the expected reduction in τ_4 are unlikely to be accidental. Figure 2 shows how the paths from the ccD and CB sides merge in the ct* and p* minima. As shown in the following, this model can explain quite a number of observations in cyclobutene and diene photochemistry, which were not satisfactorily understood before.
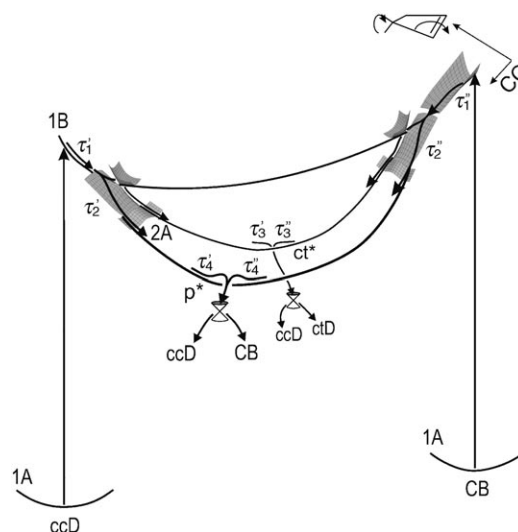

Figure 2. Suggested relaxation paths for the forward and backward reactions. For brevity, the drawing uses τ_i' instead of $\tau_i(ccD)$ and τ_i'' instead of $\tau_i(CB)$. After excitation of the cyclobutene (CB), the wave packet is accelerated not only along a CC stretch coordinate but also along a conrotatory coordinate, twisting the C=C bond and the CH_2 groups (across the initial valley; the indicated coordinate is a superposition of a conrotatory and disrotatory motion, so that only one CH_2 group is twisted). In branching (during τ_2'') at the first conical intersection, the initial conrotatory momentum drives part of the wave packet to the ct* channel, although this path is energetically disfavored by the Woodward–Hoffmann rules. Departure from the two valleys (that are separated by a ridge) then occurs in practically the same time as if the wave packets had arrived from the diene (ccD) side.

Paths on the Potential Surfaces and Violation of the WH Rules

As already said, the relative strengths of the signals attributable to ct* and p* in part reflects the branching ratio and in part the ratio of ionization probabilities; the latter was estimated to be about 10:1, starting from CHD.[17,20] In fact, if we assume a 1:1 branching in analyzing the BCH6 results, we obtain a very similar value (7:1) from the intensity ratio of the strongest signal (mass 79) from ct* and p*. This suggests that starting from BCH6*, passage through the ct* channel competes nearly equally with that through the p* channel. The former involves net conrotatory (anti-WH) motion, so we must consider what causes the molecule to decay in that direction.

Upon $\pi\pi^*$ excitation of CB, the initial relaxation will follow [within $\tau_1(CB)$] the Franck–Condon active coordinates. Giving in to the π-antibonding properties of this state, the molecule will then elongate and twist the C=C bond (as indicated in Figure 2) and to some extent also pyramidalize these carbon

atoms. The twist deformation belongs to the a_2 symmetry type and is thus conrotatory; depending on the relative signs, pyramidalization of the two sp^2 carbon atoms can be either b_1-symmetric (disrotatory) or a_2-symmetric. Twisting also distorts the σ backbone, raising the CH_2–CH_2 single bond out of plane ("ring puckering", Figure 2). This distortion permits interaction of the σ with the π orbitals, bringing orbital symmetry effects into play; essentially, the WH rules are switched on only after a delay [i.e. during $\tau_2(CB)$],[6,26] after the ring-puckering distortions are activated. The "WH forces" (or the interactions of the orbitals considered in the WH rules) cause a downward slope, emanating out the front of the drawing plane in Figure 2, favoring disrotation. After branching, probably near the 1B/2A CI, a steep disrotatory valley leads to p* and a less steep conrotatory one to ct*. Nevertheless, if the initial conrotatory momentum generated by the C=C bond twist is strong enough as the branching is approached, the molecule may resist falling into the disrotatory valley. One might expect this resistance to be greater in the less-strained system BCO7, and indeed the results suggest a prevailing population of the ct* channel in this derivative, which can be compared to the similar populations of the ct* and p* channels in BCH6.

In quantum chemical calculations of the *initial* reaction pathway from (unsubstituted) CB*, Ben-Nun and Martínez found only b_1 pyramidalization and a_1 distortions and concluded that disrotatory motions dominate excited-state decay from its very earliest stages.[27] If this were the case, the formation of anti-WH products of substituted CBs could not be explained. Earlier high-level calculations by Negri et al. found, however, that the ππ* state is unstable towards two conrotatory distortions, a_2 pyramidalization and ring puckering (involving C=C torsion).[28] The same work also re-analyzed the previous resonance Raman data[29] and found strong activity in exactly these two a_2 modes. From resonance Raman spectra one can generally deduce the coordinates of the initial motion after excitation. Negri et al. concluded that the decay of CB* is initiated with twisting of the C=C bond, a process that is typical of simple aliphatic alkenes.[2] On the other hand, activity was also found in at least one b_1 mode,[28] consistent with Figure 2 and the idea that some of the excited molecules are able to choose a disrotatory decay path. That is, the resonance Raman spectrum indicates that unsubstituted CB also enters into both the WH and anti-WH paths. It would clearly be of considerable interest to check whether both types of products are formed from suitably deuterium labeled CB. It is worth noting that an excited conjugated diene experiences a much gentler slope towards twisting than monoolefins; polyenes with more than two conjugated double bonds even have a planar S_1.[30]

We thus suggest that it is the momentum of the C=C twist that is responsible for competitive selection of the anti-WH valley, even though the slopes would disfavor it. This mechanism finds support in the observation that formation of anti-WH products is substantially reduced in cyclobutenes in which double-bond torsion is hindered by the presence of an adjoining ring.[31] This suggests that the mechanism and considerations of this work can be applied generally to diene/cyclobutene systems.

We hence replace all three suggested mechanisms of Scheme 2 by our model, which is depicted in Figure 2. The present results are incompatible with the adiabatic model of Scheme 2c to the extent that it would require complete traversal of the 1B surface from CB* to ccD* without falling through the first funnel. Although Figure 2 and Scheme 2a both show an early branching from ccD*, there is a fundamental difference which explains the formation of anti-WH products; in the mechanism of Figure 2, both channels are also accessible from CB*. This accessibility must have to do with a geometric similarity of p* and ct*. Such a similarity was indeed predicted,[12–15] and was the basis for the suggestion that branching to WH and anti-WH products occurs at the last IS (Scheme 2b). Our experiment provides no evidence whether this late branching occurs in addition to that at the first CI. These calculations[12,13] only investigated the 2A and 1A surfaces with their intersections and could therefore not find the early branching at the 1B/2A CI.

Figure 2 is based on a geometric similarity of p* and ct*. Such a similarity of (*s-cisoid* and *s-transoid*) 2A minima and of the corresponding CIs was predicted by calculations mainly of unsubstituted butadiene.[13–15,32] It would be desirable to check whether both minima still exist in the cyclic systems discussed here, since the steric constraints are expected to differ for the two structures.

Previous evidence was based on product analysis. It was found in several cases that the *cis–trans* ratio in the products is the same, whether photolysis started from an *s-cis* fixed diene or from its isomeric cyclobutene.[8,9,33] This finding would be compatible with Scheme 2b (late branching in a common IS) or Scheme 2c (adiabatic ring opening). To explain this finding in our scheme (Figure 2), one must assume that the branching is the same in the two 1B/2A conical intersections. Such an assumption may not seem compelling from the outset. However, it was repeatedly found that the first (1B/2A) and second (2A/S_0) intersections have similar branching spaces (cyclohexadiene,[6] polyenes[30]), so that the two 1B/2A intersections should also resemble each other in their branching. However, in our scheme (Figure 2) deviations from the ideal of equal *cis–trans* ratios can occur. Perhaps even one of the molecules studied here provides an example. The product ratio *cis,cis*-COD/*cis,trans*-COD is 2.5 when *cis,cis*-COD is excited,[18,34] whereas it is 1.3 if BCO7 is the reactant;[9,35] see in this context also the discussion on p. 220 of ref. [18]. Our mechanism is hence compatible with more observations than Schemes 2b and c.

Conclusions

In the end, cyclobutene breaks the WH rules because of the anti-WH momentum acquired in the Franck–Condon region due to (conrotatory) torsion of the C=C bond, an excited state process that is common to most alkenes.[2] Whereas such a distortion is in fact necessary for interactions between the σ and π orbitals to start to develop and "turn on" the WH rules, the momentum it creates diverts some molecules into a second (anti-WH) portion of the potential energy surface that they share with the isomeric diene—that for *cis–trans* isomerization.

This momentum can certainly only have an effect if the difference in the slopes of the WH and anti-WH paths, as well as the barrier separating them, is small enough in the early region. Presumably, these small differences result from the geometric similarity of the distortions involved in ring opening/closure and *cis–trans* isomerization, as calculated in refs. [12–15] and [32]. Momentum effects have already been suggested in ref. [12] and in another theoretical study of electrocyclic reactions of ccD and CB.[36] It is interesting to note that the photochemical ring opening of 1,3-cyclohexadiene, which displaces six electrons and is therefore conrotatory, is not expected to suffer from similar effects. The motions required for its ring opening and *cis–trans* isomerization of its isomer (*Z*-1,3,5-hexatriene) differ considerably,[6,37] and a WH-conforming (conrotatory) initial C=C torsion is easily feasible, as always if more than one double bond is present. More generally, one can also state that the WH rules have a very wide applicability and that the rare exceptions (such as the photochemical ring opening of cyclobutenes) can be understood on the basis of special features of the potentials.

Experimental Section

The bicyclic cyclobutenes BCH6 and BCO7 were prepared by photolysis of the corresponding cyclic alkenes CHD and COD in *n*-pentane and purified by semi-preparative gas chromatography (see Supporting Information). This reduced the content of diene impurity to $\leq 0.1\%$.

The pump pulses (196 nm, 150 fs, 10^9 W cm^{-2}) were generated from a titanium–sapphire laser system combined with an optical parametric generator and various nonlinear frequency conversions. The fundamental of the laser (805 nm, 45 fs, $1–3\times10^{13}$ W cm^{-2}, polarization 55° versus the pump) served for probing by ionization after a variable delay. Using pressures of $10^{-7}–10^{-4}$ mbar at 20 °C, the yields of the parent M$^+$ and two fragment ions (M$^+$−15, M$^+$−28) were determined in a time-of-flight mass spectrometer. These signals were simulated by sums of exponentials, with convolution of the pump and probe pulses where necessary (i.e. at short times), in order to determine time constants. The latter represent lifetimes of observation windows, that is, locations on the potential surfaces. Relative energies of these locations can be estimated from the order of ionization on varying the probe intensity. Details of the setup and evaluation are given elsewhere.[22,38]

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[11] Instead of S$_1$ minima, we indicate the S$_1$/S$_0$ conical intersections (CIs); they are the regions where the paths can branch.

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[20] The calculated small energy difference between ct* and p*[13],[14] is consistent with the observed higher ionization probability of ct*. The calculated barrier between ct* and p*[13],[14] is, however, too small to explain why ct*/p* population exchange cannot compete with relaxation down to S$_0$ within τ_3 and τ_4. The calculated (small) barriers for the latter processes[13],[14] are consistent with the observed decay times within the accuracy of calculation. The longer τ_4 suggests that departure from p* requires a (minor) activation energy, whereas *cis–trans* isomerization from ct* is barrierless. For details (also why we exclude a ct*→p* process), see ref. [17] and the Supporting Information.

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