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Photoisomerization and Relaxation Dynamics of a Structurally Modified Biomimetic Photoswitch

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S Supporting Information

ABSTRACT: Recent experimental and theoretical studies on *N*-alkylated indanylidene pyrroline Schiff bases (NAIP) show that these compounds exhibit biomimetic photoisomerization analogous to that in the chromophore of rhodopsin. The NAIP compounds studied previously isomerize rapidly and often evolve coherently on the ground-electronic surface after reaction. We present the results of transient electronic absorption spectroscopy on dMe-OMe-NAIP, a newly synthesized NAIP analogue that differs from other NAIP compounds in the substituents on its pyrrolinium ring. Following excitation with 400 nm light, dMe-OMe-NAIP relaxes from the electronic-excited state in less than 500 fs, which is slower than in other analogues, and does not show the prominent oscillations observed in other NAIP compounds. A reduction in the amount of twisting between the rings caused by removal of the methyl group is likely responsible for the slower isomerization. Measurements of varying viscosity and structure suggest that intramolecular processes dominate the relaxation of nascent photoproducts.

1. INTRODUCTION

Photoisomerization usually begins by displacing molecules far from their equilibrium geometry in an electronically excited state, and they undergo a substantial change in configuration as they subsequently evolve in the excited state. Ultrafast lasers allow careful investigation of the role of nuclear motion in such reactions, which are ubiquitous in a wide variety of biological and materials engineering applications.^{1–8} Complementary theoretical studies have also advanced toward prediction of photoisomerization rates and yields by including the effect of passage through a conical intersection.^{9–12}

One particularly interesting class of compounds for photoisomerization is the *N*-alkylated indanylidene pyrroline Schiff bases (NAIP).^{13–16} These compounds, designed to mimic the behavior of chromophores in rhodopsin,^{17,18} undergo extremely rapid *cis*–*trans* isomerization upon exposure to ultraviolet light. A distinguishing feature of these charged compounds is that the photoisomerization substantially changes their permanent dipole moment.¹⁴ Olivucci and various collaborators and co-workers have demonstrated the speed and efficacy of photoisomerization in NAIP compounds,^{13,15} which move to the conical intersection with the ground state within a few hundred femtoseconds of excitation. Upon reaching the conical intersection, they isomerize with yields between 20% and 40% and, after passing through the conical intersection, form the isomer or restore the original molecule in nonequilibrium states that persist for tens of picoseconds.¹³

Haacke and co-workers observed marked oscillations in the time evolution of the nascent photoisomerization products in a zwitterionic NAIP analogue (ZW-NAIP)¹³ and identified them as coherent wavepacket motion on the ground-electronic state of the relaxing molecules. The frequencies obtained from the Fourier transform of these oscillations suggest that they come from torsional motion both about the reactive bond and within the five-membered rings adjacent to the reactive bond. Recent work by Olivucci, Haacke, and co-workers suggests that this motion is quite similar to the torsional motion of the chromophore in bovine rhodopsin,¹⁹ which allows the chromophore to isomerize efficiently in a tightly constrained pocket of the protein.²⁰

Here, we present transient electronic absorption spectra that reveal the dynamics of a rather simple NAIP compound, dMe-OMe-NAIP. Figure 1 shows the structure of dMe-OMe-NAIP along with a sketch of the potential energy curves along which the isomerization reaction proceeds. The key structural difference between dMe-OMe-NAIP and the previously investigated OMe-NAIP¹⁵ and other NAIP compounds is the absence of a methyl group on the pyrrolinium ring where the charged nitrogen resides, a change that appears to alter the torsional potential. Figure 1 also shows the excitation and probe transitions we use to interrogate the system. After exciting

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Figure 1. Schematic diagram of the S_0 and S_1 potential energy surfaces of dMe-OMe-NAIP along the isomerization coordinate between the *E* and *Z* isomer. A photon at $\lambda_{\text{excitation}} = 400$ nm excites the *E* isomer to S_1 , after which the excited dMe-OMe-NAIP evolves through the conical intersection to either form *Z*-dMe-OMe-NAIP or reform *E*-dMe-OMe-NAIP.

dMe-OMe-NAIP to the S_1 state, we monitor the reaction by detecting stimulated emission (SE) and excited-state absorption (ESA) from S_1 , transient absorption (TA) of newly formed, vibrationally excited products, and depletion of ground-state absorption of unexcited molecules. We also measure the rates of these processes in solvents with varying polarity and macroscopic viscosity to explore the effects of the environment on the time scale of reaction and relaxation. Our results establish the rates of the excited-state reaction and ground-state vibrational relaxation of dMe-OMe-NAIP.

2. EXPERIMENTAL APPROACH

We use 0.5 mJ of 800 nm light from a Ti:Sapphire regenerative amplifier to generate the excitation and probe pulses for this study. This instrument is a sister to one described previously²¹ and uses similar data acquisition routines. A 0.1 mm β -barium borate crystal doubles the frequency of a portion of the light to produce a 1 μ J ultraviolet excitation pulse, and a half-wave retarder sets the polarization of the excitation beam at the magic angle (54.7°) relative to that of the probe in order to avoid effects of orientational anisotropy. We focus a small portion of the laser fundamental into a 3 mm CaF_2 substrate to produce a broad, ultraviolet–visible continuum spanning wavelengths from 350 to 600 nm for probing the system. A parabolic mirror collimates the continuum, and a neutral density filter splits it into probe and reference beams. A retroreflector on a computer-controlled delay stage in the probe line sets the delay between excitation and probe pulses.

A flow cell composed of a Teflon spacer compressed between two calcium fluoride windows contains the sample. The spacer thickness determines the optical path-length and is usually 1 mm. A peristaltic pump circulates the sample through the cell, refreshing the volume rapidly enough to avoid spurious signals from photoproducts. A parabolic mirror with a focal length of 100 mm focuses the probe into the sample, and a lens with a focal length of 250 mm focuses the excitation pulse at a small angle to the probe. A home-built spectrometer disperses the probe and reference pulses onto a pair of matched, 1024-channel photodiode arrays. Using a pair of fast shutters, we

collect and integrate series of probe and reference pulses, with and without the excitation pulse present, and average five exposure pairs, each composed of 150 accumulated laser pulses, for each data point. This averaging generally yields noise on the order of 1 mOD across the entire measured spectrum.

Conveniently, in most solvents, we observe Raman scattering from the C–H stretch of the solvent in our transient spectra when the excitation and probe pulses coincide. The time evolution of this feature is a measure of the instrument response function, which we typically find to have a Gaussian profile with 110 fs full-width at half-maximum. The continuum probe pulse is slightly chirped in time, with wavelengths at either extreme of the useful range separated by about 200 fs. We use solvents as purchased from Sigma-Aldrich and prepare solutions of dMe-OMe-NAIP with an optical density between 0.8 and 1.0 OD at 400 nm.

Preparation of dMe-OMe-NAIP (see Scheme 1) started with the known indanone derivative **1** and the commercially

Scheme 1

available N-protected lactam (**A**). The lithium enolate of **A** added to the BF_3 -activated²² carbonyl group of **1** gives the corresponding aldol **2**, as described by Rossi Paccani et al.²³ The latter compound provided **3** by spontaneous dehydration in CHCl_3 followed by a one-pot formation of a polyconjugated aldimine by reduction, cleavage of the *N*-Boc group, and condensation.²⁴ The free base **3** provided the dMe-OMe-NAIP target through N-quaternarization performed with methyl triflate. A NOSEY measurement indicated the geometry of the exocyclic double bond. The correlation between the signals of CH_2 at $\delta = 3.29$ – 3.35 ppm and of the hydrogen at the C8' of the indane ring at $\delta = 7.50$ ppm as well as between the signals of CH_3 at $\delta = 1.61$ ppm and of the aldiminic hydrogen at $\delta = 10.24$ ppm clearly identified the *E* geometry.

3. RESULTS AND DISCUSSION

Figure 2 shows a contour plot of the transient absorption of dMe-OMe-NAIP in methanol after excitation at 400 nm. We assign the four prominent features in analogy to the analysis of the related zwitterionic compound by Briand et al.¹³ The small, positive feature at early times is a signature of excited-state absorption (ESA) from S_1 to some higher-energy state S_n . Our excitation pulse reduces the population of the ground-state dMe-OMe-NAIP, producing a negative transient signal, the ground-state bleach (GSB), which appears between 350 and 400 nm. Stimulated emission (SE) from S_1 gives rise to the short-lived negative feature between 450 and 600 nm, the long-wavelength edge of the useful range of our continuum probe. We assign the strong, positive feature centered at 435 nm to transient absorption (TA) from vibrationally excited molecules after passage through the conical intersection. Our results agree qualitatively with studies on related molecules.^{13,15}

Figure 2. Contour plot of the transient spectrum of dMe-OMe-NAIP in methanol after excitation at 400 nm. The labels mark the prominent stimulated emission, transient absorption, excited state absorption, and ground-state bleach features described in the text.

Overlapping features that each evolve differently complicate the analysis of the reaction and relaxation dynamics of excited dMe-OMe-NAIP. Figure 3 schematically shows the evolution of the system along the reaction coordinate and the times associated with that evolution. Immediately after excitation, in region one (1), the ground-state bleach and excited-state absorption appear within our instrument response time. After a

Figure 3. Schematic representation of the relaxation of dMe-OMe-NAIP after excitation at 400 nm. The vertical arrows show the various probe wavelengths and the processes they interrogate, including the ground-state bleach (GSB), excited-state absorption (ESA), stimulated emission (SE), and transient absorption (TA). The gray arrows indicate the progression of the excited molecules along the S_1 and S_0 potential energy surfaces. The quantum yields of 75% for the *E* isomer and 25% for the *Z* isomer marked on the figure come from measurements using high performance liquid chromatography to determine the relative amounts of each isomer.

short time, $\tau_{R,SE}$, the excited molecules evolve to a region favorable for stimulated emission, identified as region two (2). The molecules then progress to region three (3), where we no longer measure absorption to the higher lying excited states, and then continue toward the conical intersection, identified as region four (4). The times for the decay of the excited-state absorption and stimulated emission, $\tau_{D,ESA}$ and $\tau_{D,SE}$, correspond to this progression toward the conical intersection. After molecules pass through the conical intersection to form vibrationally excited products, in region five (5), the transient absorption from vibrationally excited dMe-OMe-NAIP rises with a time constant $\tau_{R,TA}$. Finally, the vibrationally energized molecules relax, resulting in the decay of the transient absorption and recovery of the bleach on the time scales $\tau_{D,TA}$ and τ_{GSB} , which are comparable. Because the absorption spectra of the *E* isomer and *Z* isomer are very similar, we cannot distinguish them in the transient absorption.

The following discussion describes the dynamics that we infer for dMe-OMe-NAIP on the S_1 and S_0 surfaces after excitation at 400 nm, and Table 1 summarizes the results of

Table 1. Time Constants Measured at Various Wavelengths for dMe-OMe-NAIP in Methanol, Hexanol, and Acetonitrile^a

	methanol	hexanol	acetonitrile
$\lambda_{\text{probe}} = 530 \text{ nm}$			
$\tau_{R,SE}$	$130 \pm 50 \text{ fs}$	$170 \pm 40 \text{ fs}$	$200 \pm 100 \text{ fs}$
$\tau_{D,SE}$	$300 \pm 30 \text{ fs}$	$325 \pm 30 \text{ fs}$	$290 \pm 30 \text{ fs}$
$\lambda_{\text{probe}} = 430 \text{ nm}$			
$\tau_{R,TA}$	$1.0 \pm 0.2 \text{ ps}$	1 ps^b	1 ps^b
$\tau_{D1,TA}$	$1.3 \pm 0.2 \text{ ps}$	$1.1 \pm 0.2 \text{ ps}^c$	$0.9 \pm 0.1 \text{ ps}^c$
$\tau_{D2,TA}$	$6.6 \pm 0.2 \text{ ps}$	$7.7 \pm 1.1 \text{ ps}^c$	$9.5 \pm 1.4 \text{ ps}^c$
$\lambda_{\text{probe}} = 385 \text{ nm}$			
$\tau_{D,ESA}$	$200 \pm 30 \text{ fs}$	$250 \pm 60 \text{ fs}$	$280 \pm 60 \text{ fs}$
$\tau_{D1,GSB}$	$2.3 \pm 0.2 \text{ ps}$	$1.1 \pm 0.2 \text{ ps}^c$	$1.2 \pm 0.6 \text{ ps}$
$\tau_{D2,GSB}$	$15 \pm 4 \text{ ps}$	$12 \pm 2 \text{ ps}^c$	$12 \pm 3 \text{ ps}$

^aThese time constants accurately describe the evolution of the system across the measured spectrum. In some cases, multiple scans were averaged to obtain stable fits, and uncertainties reported are estimates based on the fitting. ^bThe fit constrains the rise time constant to this value in the biexponential fit. ^cUncertainty estimated to 15%.

fitting of the observed signals to this relatively simple picture. As Figure 2 shows, there are regions in which signals from the different processes do not interfere with each other, and we use them to extract time constants, as described in the Supporting Information. These time constants describe the evolution of the signal at all the wavelengths we observe, as confirmed by using them to fit the signal at a total of 12 different wavelengths between 380 and 560 nm, a range that encompasses the contour plot of Figure 2. Here, we use three representative wavelengths to illustrate the behavior, but the Supporting Information shows all of the data and the corresponding fits. The time constants described below and reported in Table 1 fit all of these data within the precision of the measurements and only the amplitudes of the different components vary among the wavelengths. Some, but not all, of the transient absorption data clearly have two decay times. In order to model the data consistently, we fit the signal with double-exponential decay in all cases, as described below and in the Supporting Information.

3.1. Stimulated Emission. We begin a detailed analysis of the dynamics of dMe-OMe-NAIP by fitting the decay of the

stimulated emission signal beyond 480 nm, where, as Figure 2 shows, the contribution from the transient absorption is negligible. The blue circles in Figure 4 show the signal at 530 nm

Figure 4. (a) Overview of the time evolution of the isomerization reaction in methanol, highlighting the relaxation of the system after passage through the conical intersection. (b) Detailed view of the early time dynamics of dMe-OMe-NAIP at 385 nm (GSB and ESA), 430 nm (SE and TA), and 530 nm (SE). Each set of open circles corresponds to a set of data from a single scan. Solid lines are fits to the data, as described in the text.

nm. This trace and all others presented below are the average over 20 pixels of the diode array, corresponding to about 6 nm. We convolute the instrument response function with eq 1,

$$A_{SE}(1 - e^{-t/\tau_{R,SE}})e^{-t/\tau_{D,SE}} \quad (1)$$

which describes an exponential rise followed by an exponential decay, to fit the time evolution of the stimulated emission.

The best fit yields a time constant for the rise of $\tau_{R,SE} = 130 \pm 50$ fs and a time constant for the decay of $\tau_{D,SE} = 300 \pm 30$ fs. The uncertainty is the standard deviation of the values we obtain from fitting 29 scans of the time evolution measured throughout several days of data collection. The uncertainty in the rise component is comparatively large because the rise time is close to our 110 fs instrument response. As Figure 4b shows, our fit does not reproduce the negative component at very early times. This feature is not present in pure solvent but appears with the same magnitude regardless of NAIP concentration and appears to be an artifact, such as a coherent response in a contaminated cell window. Our value for $\tau_{D,SE}$ of 300 fs in dMe-OMe-NAIP is twice as long as that of related compounds such as ZW-NAIP, in which the stimulated emission decays in 150 fs,^{13,15,25} and we do not observe the biexponential decay of stimulated emission seen in OMe-NAIP.¹⁵ In the case of dMe-OMe-NAIP, the stimulated emission is not obscured by strong transient absorption in the same spectral region that appears in related compounds.

The lifetimes we observe suggest that the exchange of a methyl group for a hydrogen in dMe-OMe-NAIP alters the torsional potential enough to produce a substantially different excited-state residence time compared to related compounds. In OMe-NAIP, the pyrrolinium ring twists to relieve steric strain, especially in the dominating *Z* form. Figure 5 shows

Figure 5. Computed equilibrium structures of the *E*-isomer of dMe-OMe-NAIP and *Z*-isomer of OMe-NAIP in methanol (B3LYP/6-31G* level with the PCM continuous solvation model to simulate the solution environment (ref 26)). These calculations illustrate the qualitative differences between the two structures. However, the inclusion of a chloride counterion and the use of an implicit solvent model accounting for hydrogen bonding give different values of the OMe-NAIP twisting angle. Nonetheless, the angle is always larger than 10° (ref 15). The time constant for the decay of stimulated emission ($\tau_{D,SE}$), which reflects the time scale of motion on the excited state, is about twice as large in dMe-OMe-NAIP as in OMe-NAIP.

equilibrium structures of the *E*-isomer of dMe-OMe-NAIP and the *Z*-isomer of OMe-NAIP in methanol calculated using B3LYP/6-31G* with a PCM continuous solvation model.²⁶ The pretwisting of OMe-NAIP by more than 15° toward a favorable geometry for isomerization, which is absent in dMe-OMe-NAIP, should favor isomerization in the electronically excited state. Olivucci and co-workers have documented this effect by mapping the excited state potential energy surface driving the relaxation of simple protonated Schiff bases from the Franck–Condon region of their excited states.²⁷ Their calculations show that pretwisting, which increases the helicity about the reactive bond, accelerates the excited-state relaxation by increasing the coupling between the initially populated stretching mode and the isomerization mode.²⁷ A potentially countervailing factor is the greater mass of the methyl group, which could slow the isomerization. The shorter excited-state lifetime in the case of OMe-NAIP indicates that acceleration by pretwisting outweighs the effect of the change in mass on the pyrrolinium ring.

3.2. Ground-State Bleach and Excited-State Absorption. Figure 4 also shows a detailed view of the time evolution of the ground-state bleach recovery feature at 385 nm, where the contribution from both stimulated emission and transient absorption are negligible, as black circles. There are two positive features at very early times. Because the first is also apparent in pure methanol, we assign it to a coherent response in the solvent or cell window, and we assign the second positive

feature to excited-state absorption at this wavelength. We convolute the instrument response function with eq 2,

$$A_{TA} e^{-t/\tau_{D,ESA}} - (A_{1,GSB} e^{-t/\tau_{D1,GSB}} + A_{2,GSB} e^{-t/\tau_{D2,GSB}}) \quad (2)$$

which describes the decays of the excited-state absorption and ground-state bleach, to fit the time evolution at 385 nm. Unlike the case for stimulated emission, this convolution describes the early time dynamics of the bleach recovery well. Our fits give values of $\tau_{D,ESA} = 200 \pm 30$ fs for the decay of the excited-state absorption, and $\tau_{D1,GSB} = 2.3 \pm 0.2$ ps and $\tau_{D2,GSB} = 15 \pm 4$ ps for the recovery of the ground-state bleach. These time constants fit the dynamics well across the entire feature.

The behavior we observe on the S_1 surface is different for the excited-state absorption signal at 385 nm and the stimulated emission signal at 530 nm. Because the excited-state absorption rises immediately, we conclude that as soon as molecules arrive in the Franck–Condon region of S_1 , the transition probability for the $S_n \leftarrow S_1$ absorption is quite good. The excited molecules must move to a different part of the upper surface before the stimulated emission becomes favorable. As the excited molecules move toward the conical intersection, the energy gap for stimulated emission becomes quite small, and we no longer detect the stimulated emission.¹³ Thus, the stimulated emission decay lifetime, $\tau_{D,SE}$, is a measure of the time scale on which the excited dMe–OMe–NAIP evolves from a region of the surface favorable for emission to the conical intersection, as shown in Figure 3.

3.3. Transient Absorption. The time evolution of the transient absorption from vibrationally excited molecules at 430 nm, shown as red circles in Figure 4, is more complicated than that of the other features. At this wavelength, there is also a contribution from the stimulated emission. We convolute the instrument response function with eq 3,

$$A_{SE}(1 - e^{-t/\tau_{R,SE}}) e^{-t/\tau_{D,SE}} + (A_{1,TA} e^{-t/\tau_{D1,TA}} + A_{2,TA} e^{-t/\tau_{D2,TA}})(1 - e^{-t/\tau_{R,TA}}) \quad (3)$$

which combines eq 1 for the evolution of the stimulated emission and a similar expression for the transient absorption, to fit this signal. We constrain $\tau_{R,SE}$ and $\tau_{D,SE}$ to the values obtained from fits at 530 nm and find $\tau_{R,TA} = 1.0 \pm 0.2$ ps, $\tau_{D1,TA} = 1.3 \pm 0.2$ ps, and $\tau_{D2,TA} = 6.6 \pm 0.2$ ps. Because the time scales of the rise and first decay of the transient absorption are similar, fitting these processes is more complicated. The Supporting Information details the fitting process and shows that these time constants are accurate across the entire transient absorption spectral region.

The growth of the transient absorption is substantially slower than the decay of the stimulated emission and excited-state absorption. The 1 ps growth is a measure of the time required for molecules to populate the Franck–Condon active region of the ground-electronic state after excitation at 400 nm. This growth includes both the residence time on S_1 and the time it takes the excited molecules to pass through the conical intersection and evolve to a region of S_0 where the electronic excitation that we observe as transient absorption is favorable. The decay of the transient absorption reflects the time required for energy to flow out of Franck–Condon active modes and into low-energy modes of both the relaxing molecule and the surrounding solvent.

Experiments probing the relaxation of molecules in solution prepared with specific amounts of vibrational energy via infrared excitation reveal similar time scales for relaxation.^{28–36} The biexponential decay of the transient absorption and ground-state bleach recovery points to relaxation of subsets of excited molecules with varying strengths of coupling to low-energy, dissipative molecular and solvent modes.³⁶ The slow component of the transient absorption decay is faster than that of the bleach recovery. The bleach-recovery time of $\tau_{D2,GSB} = 15 \pm 4$ ps reflects complete vibrational relaxation, but the decay of the transient absorption of $\tau_{D2,TA} = 6.6 \pm 0.2$ ps corresponds only to molecules losing enough energy from Franck–Condon active modes to disappear from our detection window.

The strong oscillatory signal due to coherent motion in related molecules is much less apparent, perhaps indeed absent, from the transient absorption response in dMe–OMe–NAIP. As discussed above, electronically excited dMe–OMe–NAIP persists twice as long as ZW–OMe–NAIP and OMe–NAIP. This longer time scale for electronic relaxation results in dephasing of the coherent motion about the reactive coordinate.

3.4. Solvent Dependence. We have also measured transient electronic spectra of dMe–OMe–NAIP dissolved in acetonitrile and hexanol to explore the influence of solvent viscosity. Although both solvent molecules are quite polar, the absence of an OH group in acetonitrile should change the interaction with the charged center of dMe–OMe–NAIP. Hexanol is both more viscous and has many more vibrational modes than methanol. Figure 6 shows the transient signal in the three solvents at the wavelengths we have discussed above, and all of the fits for these solvents are in the Supporting Information. For the most part, the behavior in acetonitrile and hexanol is quite similar to that in methanol. The lifetimes in Table 1 for excited state absorption and stimulated emission, which reflect motion on the electronically excited state, are identical within our experimental uncertainty for the three solvents we studied.

The strong covariance between times for the rise and first decay of the transient absorption complicates the analysis of the relaxation of the nascent photoproducts in hexanol and acetonitrile. We fix the rise of the transient absorption to 1.0 ps, its value in methanol. Because the electronic dynamics are similar in the three solvents, we expect the time scale of electronic relaxation to be similar, and we perform the same analysis as we use in methanol. Just as in that solvent, the time constants we extract from the fits accurately describe the relaxation across the entire transient absorption feature. In all three solvents, the time constant for the first decay of the transient absorption is about the same within the uncertainty of the measurements. This insensitivity to solvent identity suggests that the initial vibrational relaxation is an intra-molecular process that transfers energy from modes that have good Franck–Condon factors to modes that have poorer ones. The time for the second, slower decay varies among the solvents, being slower in acetonitrile than in methanol or hexanol. It seems likely that the vibrational relaxation rate in the primary alcohols is faster because of attractive forces between the hydroxyl group of the solvent and the cation in dMe–OMe–NAIP that strongly couple the solvent and solute. The recovery of the ground-state bleach, probed at 385 nm, behaves similarly to the decay of the product transient absorption, and the times for the complete repopulation of the ground state are similar in methanol, hexanol, and acetonitrile.

Figure 6. Time evolution of the transient absorption of dMe-OMe-NAIP at three different wavelengths, (a) 530 nm, (b) 430 nm, and (c) 385 nm, in methanol (black), hexanol (red), and acetonitrile (blue) after excitation at 400 nm. For hexanol and acetonitrile, the points are the average of six scans. For methanol, the points are from one scan. In all cases, the solid gray lines are fits to the data, as described in the text and Supporting Information.

4. CONCLUSIONS

We have measured the transient electronic absorption spectra of dMe-OMe-NAIP, a modified NAIP analogue, after excitation at 400 nm. The dynamics of dMe-OMe-NAIP are quite similar to those of two closely related compounds, ZW-NAIP and OMe-NAIP, and we use the experimental results of Briand et al.¹³ and Sinicropi et al.¹⁵ on those molecules to guide our analysis. The progression of excited dMe-OMe-NAIP along S_1 toward the conical intersection is slower than in ZW-NAIP and OMe-NAIP, whose excited state dynamics are quite similar to each other. Although all three molecules have excited-state lifetimes of only a few hundred femtoseconds, the analogue without the methyl group lives about a factor of 2 longer. The dMe compound does not have a twist between the rings that is prominent in OMe-NAIP, and the longer lifetime of dMe-OMe-NAIP suggests that the out-of-plane distortion shortens the lifetime. The longer lifetime for dMe-OMe-NAIP, perhaps in conjunction with differences in the torsional potential resulting from changes in the structure, strongly attenuates the oscillatory signals observed in ZW-NAIP.

■ ASSOCIATED CONTENT

Supporting Information

Transient data and fits to those data at 12 different wavelengths. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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