J. Phys. Chem. A **2009,** *113,* 5061–5065 **5061**

Photoinduced Ring-Opening of a Photochromic Dihydroindolizine Derivative Monitored with Femtosecond Visible and Infrared Spectroscopy[†]

Omar F. Mohammed,[‡,§,∥] Saleh A. Ahmed,[§,⊥] Eric Vauthey,[*,∥] and Erik T. J. Nibbering[*,‡]

Max Born Institut für Nichtlineare Optik and Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany, Department of Chemistry, Faculty of Science, University of Assiut, Assiut, Egypt, Chemistry Department, Faculty of Science, Taibah University, 30002-A 1-Madena Al-Mounwara, Saudi Arabia, and Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Received: December 19, 2008

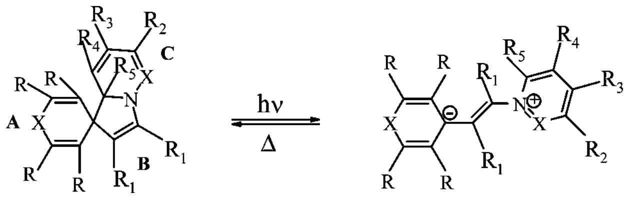
We present results of a femtosecond spectroscopy study of the ring-opening dynamics of the photochromic compound trimethyl-1′*H*-spiro[fluorene-9,1′-pyrrolo[1,2-*b*]pyridazines]-2′,3′,6′-tricarboxylate (also known as dihydroindolizine and abbreviated as DHI) in solvents of different polarities. We follow the ring-opening dynamics of photoexcited DHI by probing the transient response in the visible region between 450 and 700 nm, as well as in the fingerprint region between 1100 and 1800 cm^{-1}. We conclude that photoexcited DHI converts into the ring-opened betaine isomer while remaining in the electronic excited state. Subsequent electronic excited-state decay on a time scale of 40−80 ps results in regeneration of ground-state DHI (0.75−0.9 quantum yield) or betaine photoproduct, the exact value for DHI quantum yield recoveries and rates being solvent dependent.

1. Introduction

Design of photochromic switches is an active area of research,[1−3] because new routes in molecular synthesis are crucial for devices that operate at the molecular and supramolecular levels.[3,4] In particular, extensive research has been devoted to the study of molecules whose physical properties can reversibly be switched using light. Such compounds provide a high lateral resolution and short switching times, in addition to having an almost instant verification of written data and photooptical technology,[4−6] due to their bistable nature with different absorption spectra. Furthermore, thousands of switching cycles (great fatigue resistance) can consecutively be repeated without any sign of degradation, even in the presence of molecular oxygen.[7] In this category of photochromic switches, the superior photophysical properties of spiroheterocyclic molecules, that is, spiropyrans, spirooxazines, chromenes, and dihydroindolizines, provide great promise in the area of photonic materials.[1,8,9] For instance, dihydroindolizines (DHIs) and tetrahydroindolizines (THIs), first reported on by Hauck and Dürr in 1979,[10] have been applied in applications as diverse as ophthalmic lenses, data storage photoswitches, dental filling materials,[11,12] IR-sensitive photoswitchable materials,[13,14] and DNA markers.[15]

DHIs undergo a photoinduced change of color in solutions and in polymer matrices when exposed to UV radiation or direct sunlight exposure. They return to the initial state when the illumination ceases, normally via a thermal pathway (Scheme 1). The photochromic behavior of DHIs is based on a reversible pyroline ring-opening, induced by light, that converts a colorless form (usually named the “closed form”) to a colored form (betaine form). The thermal back reaction, the 1,5-electrocyclization, from the ring-open betaine to DHI shows rates extending from milliseconds to several weeks[11,13,14] depending on the nature of the substituents in the three DHI regions (A, B, and C; see Scheme 1).

SCHEME 1: General Schematic Representation of the Light-Induced Ring-Opening Process of DHIs with the Three Regions A, B, and C



Understanding the structural events of photoinduced dynamics of the ring-opening of DHIs may enable an even more targeted subsituent design for applications such as photoinduced electron transfer for artificial solar energy storage.[16,17] Because of the ultrafast nature of the primary events of ring-opening of DHIs, new femtosecond probing techniques providing structural information may be of great use. Typically ultrafast UV/vis spectroscopy has been used in the investigation of the photoswitching dynamics.[18,19] Here, however, the large electronic absorption bands, often strongly overlapping, provide minor insight into the transient structure of these compounds. Instead, with ultrafast vibrational spectroscopy, despite the lower absorption cross sections of molecular vibrations and potential overlap with solvent bands, key structural information can be obtained from vibrational marker modes.[20] Recently, several of us have explored the photoinduced ring-opening dynamics of spiropyrans using femtosecond mid-infrared spectroscopy, where vibrational marker modes reveal a solvent-dependent quantum yield for internal conversion,[21,22] the occurrence of different product isomers,[23] as well as sequential formation of these merocyanine isomers.[24] The method of following the evolution of vibrational

---

[†] This work constitutes part XIII in a series by S. A. Ahmed.

* Corresponding authors. E-mail: nibberin@mbi-berlin.de (E.T.J.N.); eric.vauthey@unige.ch (E.V.).

[‡] Max Born Institut für Nichtlineare Optik and Kurzzeitspektroskopie.

[§] University of Assiut.

[∥] University of Geneva.

[⊥] Taibah University.

10.1021/jp811248u CCC: $40.75

marker modes has also been applied in a study of the photophysics of indolylfulgimides[25−28] and photoswitchable polypeptide compounds containing azobenzene as chromophore.[29,30] Here, we present results on the photoinduced ring-opening of DHI measured with ultrafast mid-IR spectroscopy. We will use femtosecond electronic and vibrational spectroscopy to elucidate the initial stages of isomerization dynamics upon photoexcitation of a particular DHI (with a five-membered ring with R = benzyl, $R_1 = R_2 = R_3 = R_4 = R_5 = COOCH_3$, and X = N). We will derive excited-state lifetimes of photoexcited DHI, electronically excited-state betaine, and the conversion rates and yields into ground-state DHI and the ground-state betaine product isomer appearing within several tens of picoseconds.

2. Experimental Section

Photochromic dihydroindolizine (DHI) (trimethyl-1′*H*-spiro-[fluorene-9,1′-pyrrolo[1,2-*b*]pyridazines]-2′,3′,6′-tricarboxylate) was synthesized via electrophillic addition reaction of spirocyclopropene to 3-carboxymethylpyridazine[12] in dry ethereal solution at room temperature under dry nitrogen atmosphere in the absence of light for 72 h (TLC-controlled using CH_2Cl_2 as eluent). The reaction product was 2 times further purified by column chromatography on silica gel using CH_2Cl_2 as eluent. After recrystallization from ether, the product resulted as yellow needles in 46% yield.

The perdeuterated solvents acetonitrile (ACN-d_3) and dichloromethane (DCM-d_2) were obtained from Deutero GmbH (99.8% deuteration grade), while the other solvents tetrachloroethene (TCE), dichloromethane (DCM), and acetonitrile (ACN) were purchased from Merck (p.a.). All solvents were used without further purification. Sample solutions were circulated through a flow cell consisting of 1 mm thick BaF_2 windows separated by a 50 μm thick Teflon spacer, to guarantee that for every laser shot a new sample volume was excited. All experiments were performed at room temperature (23 ± 2 °C).

We performed a femtosecond transient absorption spectroscopy by initiating the photoreaction with electronic pump at 400 nm and probing with white light. The 400 nm pulses were produced by frequency-doubling of the fundamental output of a standard 1 kHz Ti:sapphire amplified laser system. The details of the system are described elsewhere.[31]

Femtosecond infared spectroscopy was performed after triggering the reaction with electronic pump pulses tuned at 400 nm. The pump pulses were produced by second-harmonic generation of the fundamental output of the Ti:sapphire amplified laser system operating at 800 nm. The pump pulse energy on the sample was in the range of 2−4 μJ with a pulse duration of 55 fs and a focal spot diameter of 500 μm. Tunable mid-IR probe pulses (200−300 fs duration) were generated by difference frequency mixing of signal and idler pulses from a near-infrared optical parametric amplifier.[32] The probe and the reference pulses, split off by a ZnSe wedge, were spectrally dispersed in a grating spectrometer and recorded simultaneously in a single-shot detection using a liquid nitrogen cooled double array (2 × 32 pixels) of MCT (HgCdTe) detectors. Spectrally resolved absorbance changes in the mid-IR have been recorded with a spectral resolution of 2−7 cm^{-1}. Synchronous chopping of the pump pulses was used to eliminate long-term drift effects. The transient IR spectra were recorded at magic angle between the 400 nm pump pulses and the mid-IR probe pulses. The whole pump−probe setup was purged with nitrogen to avoid spectral and temporal reshaping of the mid-IR pulses by the absorption of water vapor in air. The time resolution was determined to be 200 fs based on cross-correlation measurements between 400 nm pump and IR-probe pulses and on estimations of group velocity mismatch between both pulses.

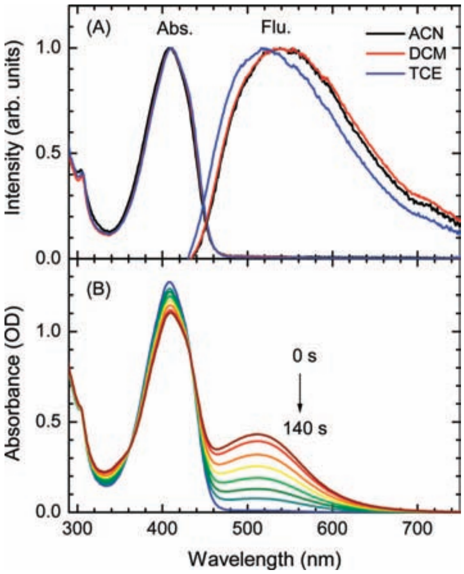


Figure 1. Steady-state absorption and emission spectra of DHI in ACN, DCM, and TCE (A), and thermal recovery of the closed form (B), recorded with 20 s time steps after irradiation with cw 400 nm light of the closed form for 60 s duration.

3. Results

Figure 1a shows the electronic absorption and fluorescence spectra of DHI dissolved in TCE, DCM, and ACN. The closed form of DHI prevails in all solvents used in this study, as indicated by the electronic band located at 410 nm, which does not show an observable solvent shift going from nonpolar TCE to polar ACN. The electronic emission on the other hand shows a significant solvent dependence, with a peak position at 515 nm in TCE, and 545 nm for both DCM and ACN. More importantly, the lack of mirror symmetry between absorption and emission spectra is indicative of substantial structural rearrangements accompanied by charge redistributions upon photoexcitation of the closed form. From the larger shift of the emission band in ACN, a larger dipole moment in the emissive state than in the ground state can be derived.

Irradiation of the DHI closed form at 400 nm induces a transformation into the open betaine form, as is evidenced by the changes observed in the electronic absorption spectra after 60 s of irradiation (Figure 1b). A new band located at longer wavelengths (515 nm peak position) appears under steady-state irradiation conditions and is assigned to the open betaine isomer because of the larger conjugation as compared to the closed form. The betaine band disappears when the UV irradiation is halted. The presence of three isosbestic points (at 306, 360, and 435 nm) indicates that the thermal back reaction of betaine to the closed form follows a precursor−successor relationship.

Figure 2 shows the transient electronic response of DHI in ACN measured in the visible region between 450 and 700 nm. Within time resolution two bands are observed, located at 470 and 620 nm. These bands decay with a 42 ± 6 ps time constant, and a transient band centered at 590 nm emerges with the same time constant.

The steady-state IR absorption spectra of DHI in the fingerprint region from 1150 to 1900 cm^{-1} dissolved in TCE, DCM-d_2, and ACN-d_3 are depicted in Figure 3a. Many of the

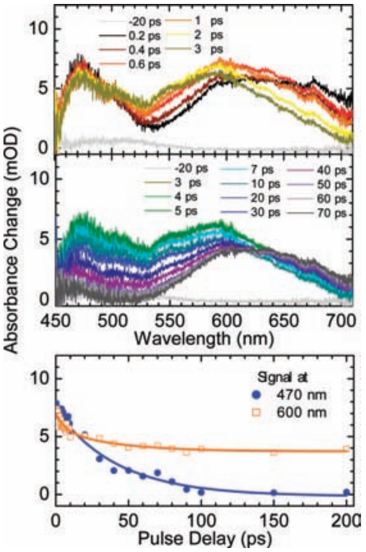


Figure 2. Transient electronic spectra of DHI in ACN, recorded at specific pulse delays, showing the excited-state absorption consisting of two bands of excited-state *Z*-betaine formed within time resolution (A), and the conversion into a single band indicative of *Z*-betaine in the electronic ground state at long pulse delays (B). From the signals a conversion rate can be deduced using an exponential fit with a time constant of 42 ps (C).

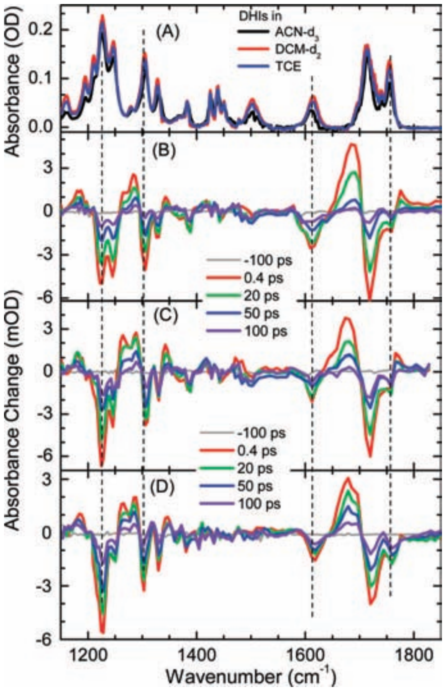


Figure 3. Steady state of DHI in ACN-d_3, DCM-d_2, and TCE (A). Transient spectra of DHI at different pulse delays after 400 nm laser excitation in ACN-d_3 (B), in DCM-d_2 (C), and in TCE (D).

IR-active vibrations of DHI in the electronic ground state are present as bleach (decreased absorbance) signals in the transient IR spectra of DHI upon electronic excitation at 400 nm shown in Figure 3b−d. These bleach signals as well as the transient absorbance signals appear within temporal resolution of 200 fs. Apart from minor changes in the width of the transient vibrational bands, no pronounced solvent dependence was found on spectral position or magnitude, with the exception of the pattern between 1200−1300 cm^{-1}, which may be indicative of overlap effects between ground-state bleach and product signals, whose magnitude is solvent dependent (vide infra).

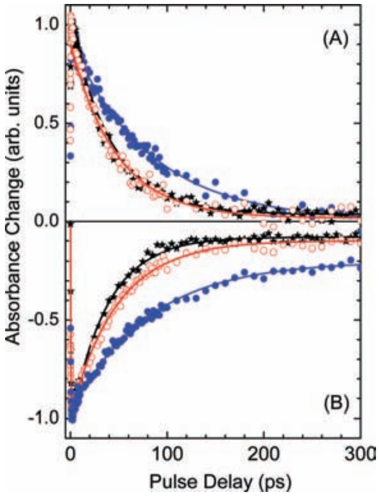


Figure 4. Normalized measured transient response for the DHI extracted at 1690 cm^{-1} (A) and 1720 cm^{-1} (B) as a function of pulse delay (symbols) and fits (solid lines) in ACN-d_3 (★), DCM-d_2 (red ○), and in TCE (blue ●) after 400 nm excitation.

In contrast, marked differences are found in the dynamics of the transient vibrational bands and in the magnitude of the bleach recovery. Figure 4 shows the dynamics of the positive band at 1690 cm^{-1} and the negative bleach signal at 1720 cm^{-1}. The fitting results of these bands in the C═O stretching region are typical for the other bands monitored in the fingerprint region. The decay rate of the 1690 cm^{-1} band fits with a monoexponential function in all solvents we used. The values are 76 ± 7, 47 ± 5, and 43 ± 3 ps in TCE, DCM-d_2, and ACN-d_3, respectively. The bleach refill rate also appears to be solvent dependent, and the values found (80 ± 2, 49 ± 3, and 42 ± 1 ps in TCE, DCM-d_2, and ACN-d_3, respectively) are, within experimental error, identical to the decay constants of the bands showing positive transient absorbance. From this we learn that the state generated by photoexcitation (species I) decays to some extent back to DHI ground state. Whereas most of the strong transient absorbance bands decay to zero value, the bleach signals only recover partially, showing a clear solvent dependence. From this observation, we learn that the quantum yield of DHI ground-state recovery is 0.75 ± 0.05, 0.88 ± 0.05, and 0.90 ± 0.05 in TCE, DCM-d_2, and ACN-d_3, respectively, from which we derive that the product formation is not the most important relaxation channel after electronic excitation of DHI in these solvents. The magnitude of bleach recovery scales with the steady-state fluorescence intensity, that we have found to be more than a factor of 2 higher in TCE than in ACN (data not shown). The remaining bleach persists for pulse delays beyond 500 ps, the maximum scanning value of our delay stage.

At specific frequency positions, we have observed positive transient absorbance bands persisting for pulse delays up to 500 ps. These IR-active bands are located at 1290, 1345, 1360, 1419, 1465, 1477, and 1570 cm^{-1}. We assign these bands to the product isomer formed after photoexcitation of DHI. For most of these bands, we have not been able to resolve a time-dependent rise, due to substantial spectral overlap with either the DHI bleach signals or the strong transient bands that appear within time resolution. Figure 5 shows the dynamics observed for one particular band, located at 1165 cm^{-1}, that is an exception to this. The data show the spectral evolution of the transient change of IR absorption bands in the frequency range between 1100−1200 cm^{-1} during the first 300 ps in DCM-d_2. It is clear that the bleaching band at 1140 cm^{-1}, the decay of the transient band at 1117 cm^{-1}, and the delayed appearance of

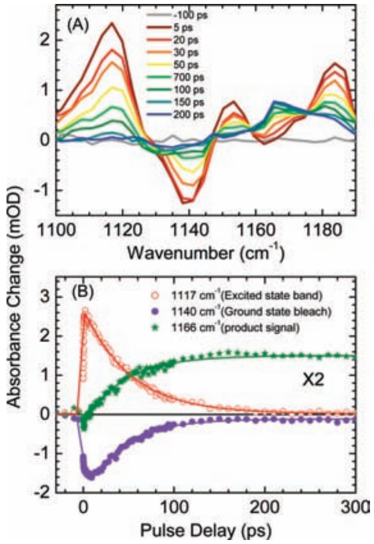


Figure 5. (A) Transient absorbance difference spectra of DHI measured at different pulse delays after 400 nm excitations, showing the appearance of the positive band (product band) at 1165 cm^{-1}, ground-state bleach at 1140 cm^{-1}, and the decay of the transient band at 1117 cm^{-1}, and (B) the dynamics of the three transient bands.

the band at 1165 cm^{-1} have the same dynamics. The presence of isosbestic points at 1175 and 1158 cm^{-1} strongly suggests that the 1165 cm^{-1} band is indicative of a state (named species II) populated sequentially from the state initially generated by photoexcitation (named species I) that has marker modes appearring within time resolution.

4. Discussion

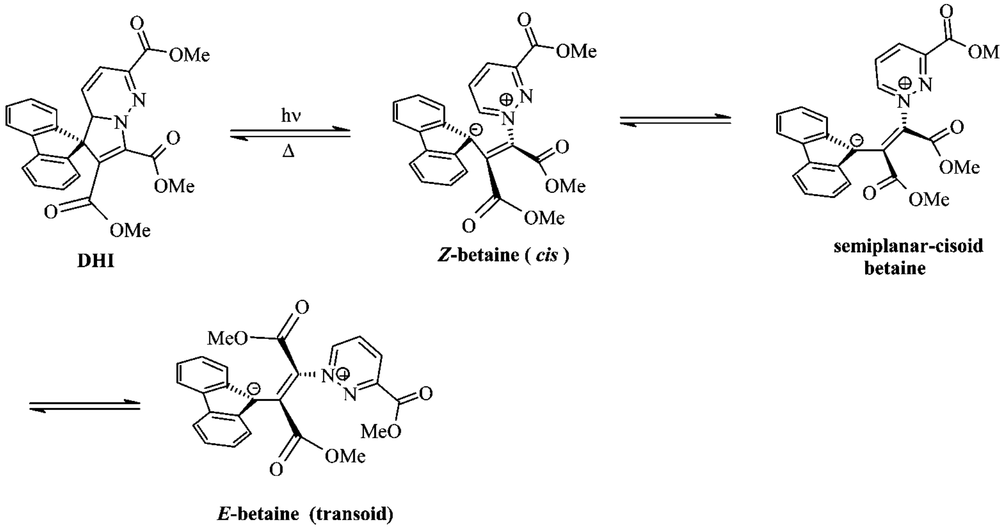
Previous work on the photoinduced DHI−betaine isomerization has shown that the mirror symmetry between absorption and emission spectra only holds for DHI derivatives at low temperatures.[33] At room temperature, however, this symmetry does not persist, indicating strong structural rearrangements in the electronic excited state. On the basis of the strong frequency downshift, and the fact that a more polar state emerges, it has been concluded that photoexcitation of DHI leads to ring-opening to a betaine isomer in the electronic excited state.[33−35] The emission lifetimes have been found to be in the subnanosecond time range. For the DHI explored in the current study, we have a strong argument, based on the similarity of the emission spectra recorded here and those reported by Bleisinger et al.,[33] that ring-opening occurs in the electronic excited state. The electronic excited-state lifetime has not been reported until now, but is expected to have a value between 30 and 700 ps.[34,35] In contrast, rearrangements between different betaine isomers and conversion of the betaine forms back into DHI take place on nano- to microsecond time scales.

Ring-opening directly upon photoexcitation (or at least within our time resolution of 200 fs) is consistent with both of the observed emission spectra, the transient visible spectra and the transient IR spectra. The emission spectra indicate that the fluorescence emitting species should be different from the closed DHI form. The transient electronic spectra show that the initial species, which should be structurally different from DHI, while being in the electronic excited state, has excited-state absorption bands at 470 and 590 nm. The decay of these bands correlates with the electronic excited-state decay, which can be assigned to the electronic excited state of *Z*-betaine (Scheme 2), the first betaine isomer directly formed after ring-opening of DHI. The transient infrared spectra show a multitude of fingerprint bands appearing within time resolution, only to change on a time scale of 40−80 ps (actual value solvent dependent), which then should be assigned to the excited-state decay of the ring-opened *Z*-betaine form. After fluorescence emission, the fate of the molecule is either to return to the "closed" DHI form, being the major relaxation channel of excited molecules, or to betaine photoproduct.

Recent femtosecond infrared experiments on spiropyrans have revealed that upon UV photoexcitation of the spiropyran molecules an ultrafast subpicosecond internal conversion process to the closed ground state dominates[21,22] with merocyanine product formation being solvent dependent.[23,24] Ring-opening of dihydroazulenes,[19] and of fulgimides,[26,27] has been shown to occur on picosecond time scales, although for the latter faster components have been reported.[28] Photoinduced ring-closure on picosecond time scales has in addition been reported for bis(thienyl)cyclopentenes.[18]

In the current work, the C=O stretching region reveals structural detail on the nature of the excited-state betaine species formed from photoexcitation of DHI, which is understood to have a ring-opened *Z*-betaine structure. The C=O stretching

SCHEME 2: Proposed Structures for Sequential Betaine Isomer Formation Induced by Ring-Opening upon UV Excitation of DHI



vibrations are marker modes to the changes in charge distribution in the molecule caused by photoexcitation. In the ground state of DHI, these C═O stretching modes of the CH_3OCO-side groups are located at 1714 and 1756 cm^{-1}. Upon electronic excitation, these bands are bleached, and new transitions at 1684 and 1775 cm^{-1} are found. The 1684 cm^{-1} feature may be composed of two transitions as the experimental data obtained in TCE suggest. The spectral feature is not similar to red-shifted extended absorption of so-called "hot" ground-state molecules that can be expected when ultrafast subpicosecond internal conversion would occur,[20,36] justifying our assumption that the 40−80 ps decay component is indicative of electronic excited-state decay. After this electronic decay, the excited-state vibrational bands and the ground-state bleaching components almost completely disappear, indicative of the large fraction of molecules returning to the closed DHI form. In addition, despite the smaller fraction of betaine product molecules, we conclude that the C═O stretching marker modes of the open betaine isomers have similar transition frequencies but somewhat smaller cross sections than closed DHI, as positive transient absorbance in this frequency range does not seem to persist beyond longer pulse delays. As such, subsequent rearrangement into *E*-betaine, which is present in the steady-state measurement of Figure 1, can only occur on much longer time scales beyond 1 ns.

5. Conclusion

We have shown that the primary events of isomerization dynamics of trimethyl-1′*H*-spiro[fluorene-9,1′-pyrrolo[1,2-*b*]pyridazines]-2′,3′,6′-tricarboxylate (also known as dihydroindolizine and abbreviated as DHI) can be probed with ultrafast electronic and vibrational spectroscopy. In the solvents used in this study, we observe that upon photoexcitation of the closed DHI isomer, ring-opening into the *Z*-betaine form occurs while being in the electronic excited state. Subsequent electronic excited-state decay with a 40−80 ps time constant results in the recovery of the closed DHI (with solvent dependent quantum yields ranging from 0.7 to 0.9) and of *Z*-betaine in the electronic ground state.

Acknowledgment. S.A.A. is highly indebted to Prof. Dr. H. Dürr, University of Saarland, Germany, and the partial financial support from Alexander von Humboldt foundation (AvH) and Taibah University. We are grateful for financial support of this work through a long-term mission fellowship of the Egyptian government (O.F.M.). This work was also supported by the Fonds National Suisse de la Recherche Scientifique through Project No. 200020-115942.

References and Notes

(1) Dürr, H.; Bouas-Laurent, H. *Photochromism-Molecules and Systems*; Elsevier: Amsterdam, 1990; p 1.

(2) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875.

(3) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789.

(4) Irie, M.; Masuhara, H.; Hayashi, K.; Mataga, N. *J. Phys. Chem.* **1974**, *78*, 341.

(5) Yamada, T.; Muto, K.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 6164.

(6) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2005**, *70*, 8180.

(7) Tomasulo, M.; Kaanumal, S. L.; Sortino, S.; Raymo, F. M. *J. Org. Chem.* **2007**, *72*, 595.

(8) Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639.

(9) Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751.

(10) Hauck, G.; Dürr, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 945.

(11) Tan, Y.; Ahmed, S. A.; Dürr, H.; Huch, V.; Abdel-Wahab, A. *Chem. Commun.* **2001**, 1246.

(12) Fromm, R.; Ahmed, S. A.; Hartmann, T.; Huch, V.; Abdel-Wahab, A. A.; Dürr, H. *Eur. J. Org. Chem.* **2001**, 4077.

(13) Weber, C.; Rustemeyer, F.; Dürr, H. *Adv. Mater.* **1998**, *10*, 1348.

(14) Andreis, C.; Dürr, H.; Wintgens, V.; Valat, P.; Kossanyi, J. *Chem.-Eur. J.* **1997**, *3*, 509.

(15) Gogritchiani, E.; Hartmann, T.; Palm, B. S.; Samsoniya, S.; Dürr, H. *J. Photochem. Photobiol., B* **2002**, *67*, 18.

(16) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145.

(17) Terazono, Y.; Kodis, G.; Andreasson, J.; Jeong, G. J.; Brune, A.; Hartmann, T.; Dürr, H.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* **2004**, *108*, 1812.

(18) Hania, P. R.; Pugzlys, A.; Lucas, L. N.; de Jong, J. J. D.; Feringa, B. L.; van Esch, J. H.; Jonkman, H. T.; Duppen, K. *J. Phys. Chem. A* **2005**, *109*, 9437.

(19) De Waele, V.; Beutter, M.; Schmidhammer, U.; Riedle, E.; Daub, J. *Chem. Phys. Lett.* **2004**, *390*, 328.

(20) Nibbering, E. T. J.; Fidder, H.; Pines, E. *Annu. Rev. Phys. Chem.* **2005**, *56*, 337.

(21) Fidder, H.; Rini, M.; Nibbering, E. T. J. *J. Am. Chem. Soc.* **2004**, *126*, 3789.

(22) Rini, M.; Holm, A. K.; Nibbering, E. T. J.; Fidder, H. *J. Am. Chem. Soc.* **2003**, *125*, 3028.

(23) Holm, A. K.; Rini, M.; Nibbering, E. T. J.; Fidder, H. *Chem. Phys. Lett.* **2003**, *376*, 214.

(24) Holm, A. K.; Mohammed, O. F.; Rini, M.; Mukhtar, E.; Nibbering, E. T. J.; Fidder, H. *J. Phys. Chem. A* **2005**, *109*, 8962.

(25) Brust, T.; Draxler, S.; Malkmus, S.; Schulz, C.; Zastrow, M.; Ruck-Braun, K.; Zinth, W.; Braun, M. *J. Mol. Liq.* **2008**, *141*, 137.

(26) Koller, F. O.; Schreier, W. J.; Schrader, T. E.; Sieg, A.; Malkmus, S.; Schulz, C.; Dietrich, S.; Ruck-Braun, K.; Zinth, W.; Braun, M. *J. Phys. Chem. A* **2006**, *110*, 12769.

(27) Malkmus, S.; Koller, F. O.; Heinz, B.; Schreier, W. J.; Schrader, T. E.; Zinth, W.; Schulz, C.; Dietrich, S.; Ruck-Braun, K.; Braun, M. *Chem. Phys. Lett.* **2006**, *417*, 266.

(28) Heinz, B.; Malkmus, S.; Laimgruber, S.; Dietrich, S.; Schulz, C.; Ruck-Braun, K.; Braun, M.; Zinth, W.; Gilch, P. *J. Am. Chem. Soc.* **2007**, *129*, 8577.

(29) Hamm, P.; Helbing, J.; Bredenbeck, J. *Annu. Rev. Phys. Chem.* **2008**, *59*, 291.

(30) Ihalainen, J. A.; Bredenbeck, J.; Pfister, R.; Helbing, J.; Chi, L.; van Stokkum, I. H. M.; Woolley, G. A.; Hamm, P. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 5383.

(31) Duvanel, G.; Banerji, N.; Vauthey, E. *J. Phys. Chem. A* **2007**, *111*, 5361.

(32) Kaindl, R. A.; Wurm, M.; Reimann, K.; Hamm, P.; Weiner, A. M.; Woerner, M. *J. Opt. Soc. Am. B* **2000**, *17*, 2086.

(33) Bleisinger, H.; Scheidhauer, P.; Dürr, H.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Org. Chem.* **1998**, *63*, 990.

(34) Fromm, R.; Born, R.; Dürr, H.; Kannengiesser, J.; Breuer, H. D.; Valat, P.; Kossanyi, J. *J. Photochem. Photobiol., A* **2000**, *135*, 85.

(35) Fromm, R.; Ahmed, S. A.; Hartmann, T.; Huch, V.; Abdel-Wahab, A. A.; Dürr, H. *Eur. J. Org. Chem.* **2001**, 4077.

(36) Hamm, P.; Ohline, S. M.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519.

JP811248U