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Transient Spectroscopic Study of a Non-Kekulé Molecule Generated by Photochemical γ-Hydrogen Abstraction of Ethyl 4-Formyl-1,3-dimethylpyrazole-5-carboxylate

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The dynamics of photochemical hydrogen-atom abstraction in ethyl 4-formyl-1,3-dimethylpyrazole-5-carboxylate (EFDPC) has been studied by femtosecond through microsecond time-resolved absorption techniques in different solvents at room temperature. The photoreaction initiates within the time period of the excited singlet state (S_1) lifetime and gives transient photoproduct with $\lambda_{max} \sim 580$ nm. The transient absorption spectra are consistent with that obtained in the steady state after the photolysis of EFDPC at cryogenic temperature in various glassy matrixes, as well as in a solid sate. The photoproduct was a non-Kekulé molecule of zwitterionic form resulting from γ-hydrogen abstraction by an excited formyl group followed by a very short-lived intermediate singlet 1,4-biradical, which is identical to that of tetramethyleneethane (TME) biradical. The photoproduct exists for a few microseconds in solution before the reverse reaction occurs to come back to the original compound. The density functional theory (DFT) calculations have also been made to elucidate the energetics along the reaction pathway, the geometrical conformation of the intermediate, and the final photoproduct.

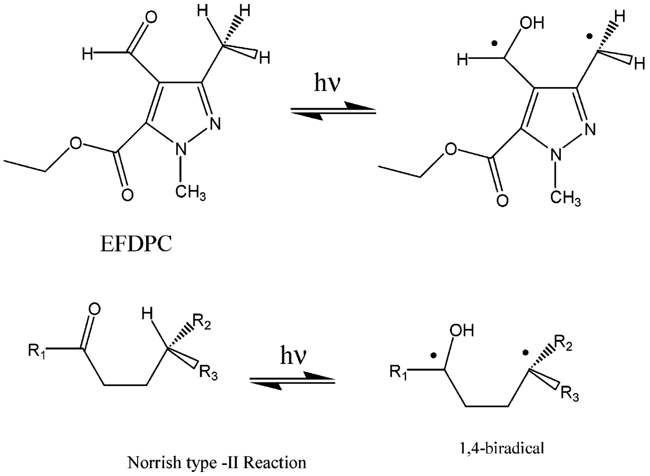
1. Introduction

A photochromic (PC) reaction has a switching activity at the molecular level whereby the molecular structure of photochromic molecules change photochemically and reversibly together with their optical as well as electronic properties upon irradiation with quanta of appropriate energy. The two isomers differ in geometrical and electronic structures with consequent change not only in the color but also in refractive indices, dielectric constants, oxidation/reduction potentials, and other physical/chemical properties. The PC reaction is expected to serve as the basic principle for creating new and next-generation photochemical materials. In modern technology, PC materials are relevant candidates for optoelectronic devices, such as optical memories, photooptical switching, and display.[1−5]

Photochemical hydrogen abstraction is a fundamental reaction in excited organic molecules and is useful not only for organic synthesis but also for various applications in materials science. The photochemical H-abstraction in π-conjugated molecules has been especially fruitful for creating new functional photochemical materials[1,6] to show photochromism, energy relaxation, and many other interesting physical and chemical properties.

Recently, we found that ethyl 4-formyl-1, 3-dimethylpyrazole-5-carboxylate (EFDPC) shows remarkable photochromism in its solid state: a prominent color change from colorless to reddish purple ($\lambda_{max} \sim 580$ nm) upon UV irradiation and thermal reverse (in several days at room temperature or short time at melt) without loss of starting material.[7] Upon photoirradiation, infrared absorption peaks ($\nu = 1725$ and 1682 cm^{-1}) due to the stretching mode of two carbonyl groups in EFDPC decrease and one new peak ($\nu = 1700$ cm^{-1}) appears,[7] suggesting that there is no prominent carbonyl stretching mode in the colored photochromic product. In contrast, it seemingly has no change upon UV irradiation in its solution phase. The structure of EFDPC is shown in Scheme 1 and is similar to that of the ketones with γ-hydrogen atoms to show the Norrish type II reaction. Because of the structural similarity, intramolecular γ-hydrogen abstraction can easily occur from the n,π* state of EFDPC when the cyclic six-membered transition state is not precluded by structural constraint.[8] The 1,4-biradical of EFDPC found as a result of hydrogen abstraction is a non-Kekulé molecule, a family of the 1,4-biradical of tetramethylenethane (TME). In general, the PC reactions that take place in the crystalline state frequently differ from those occurring in solution

SCHEME 1: Schematic Representation of Ethyl 4-Formyl-1,3-dimethylpyrazole-5-carboxylate (EFDPC) with Comparison to General Norrish Type II Reaction



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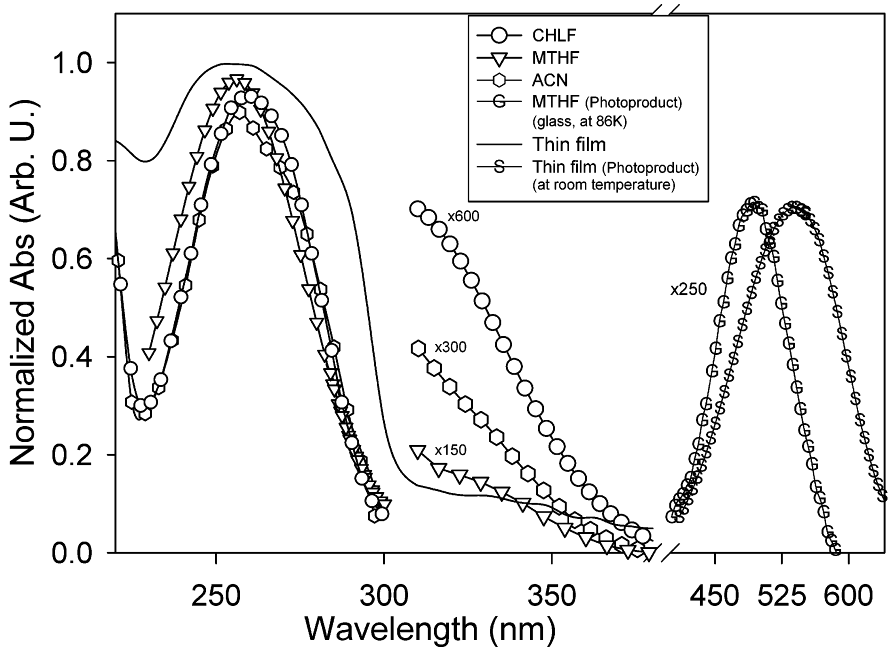


Figure 1. Steady-state absorption spectra of EFDPC at room temperature in different solvents and in a thin film and absorption spectrum of the photoproduct at 86 K in MTHF and at room temperature in a thin film.

phase:[9−12] for example, intermolecular reactions take place easier in a solid state than in a solution state. In this circumstance, understanding the solution phase photoreaction, reactive intermediates, reversibility property of photoproduct of EFDPC, and the determination of the involved reaction mechanism are worthy and interesting topics. Transient absorption spectroscopy is a technique used to gain information about the time evolution of excited species created in a sample upon photoexcitation. There may be several different excited-state species present simultaneously in the photoexcited sample: singlet and triplet states, zwitterionic states, and biradicals. All of them are possible along with reversible photochromic reactions. Each one of these has its own characteristic absorption spectrum. Thus probe photons of different energies will be absorbed by different species present.

In the present study, we have investigated the femtosecond through microsecond transient spectroscopic properties of photochromic EFDPC in solution. TD-DFT has also been used to estimate the geometrical conformations of the intermediate and final photoproduct.

2. Experimental Section

Details of synthesis and solid-state photochromic properties of EFDPC have been described elsewhere.[7] All solvents, diethyl ether (DEE), chloroform (CHLF), acetonitrile (ACN), methanol (MeOH), and 2-methyltertahydrofuran (MTHF), used were of spectroscopic grade (Kishida Chemicals) and were dried over molecular sieves 4A (Kishida Chemicals).

The absorption spectra (steady state) were recorded on a Hitachi U-3210 and a Shimadzu DR8000 spectrometer equipped with an Oxford DN1704 variable-temperature cryostat. The temperature was monitored with a Pt thermocouple. Sample solutions for low-temperature experiments were degassed by three freeze−pump−thaw cycles. Photoirradiation was performed with Ushio-USH-500D super-high-pressure mercury arc-lamp through a focusing lens and cutoff filters (Toshiba UV310 and IRA-25S). For all transient studies 2 mm quartz cell was used with the solution concentration of 0.04−0.08 M.

The laser system used for femtosecond transient absorption spectroscopy consisted of a hybridly mode-locked, dispersion-compensated femtosecond dye laser (Coherent Satori 774) that was pumped by a continuous wave (cw) mode-locked Nd:YAG laser (Coherent Antares76S).[13] The output of the dye laser was amplified to an energy of ∼400 μJ at a center wavelength of 710 nm by a regenerative amplifier system (Continuum RGA60 and PTA60) with repetition rate of 10 Hz. The second harmonic (∼355 nm) obtained by a 1 mm BBO crystal was used as an excitation pulse. A remaining fundamental pulse was focused into a 1 cm water cell to generate white-light continuum as probe and reference pulses. The system response function of pump−probe method was estimated to be ∼200 fs fwhm. The signal was analyzed by a computer controlled ICCD detector (Princeton Instruments, ICCD-576-G) at each optical delay using a translation stage (Sigma Koki, STM-500X). A temporal dispersion of the white-light continuum was corrected for the transient absorption spectra. The pump pulse energy for this configuration was of 20 μJ with a beam diameter 0.6 mm. For microsecond transient absorption spectroscopy we have used a Q switched nanosecond Nd:YAG laser (LOTIS TII, Model LS-2134, Belarus) as the pump source and synchronized xenon flash lamp as the probe pulse with a gated ICCD detector (ICCD-576-G). All solutions used for transient spectroscopy were deoxygenated by N_2 bubbling and allowed to keep a little N_2 pressure inside the cell during the studies.

The density functional theory (DFT) and time dependent DFT (TD-DFT) calculations were carried out using a Gaussian 98 program suite[14] at the B3LYP level of theory and a 6-31G* basis set. Geometries were fully optimized followed by frequency calculation. Energies were corrected with zero-point energies. For ZINDO calculations, the CAChe program package[15] was used.

3. Results and Discussion

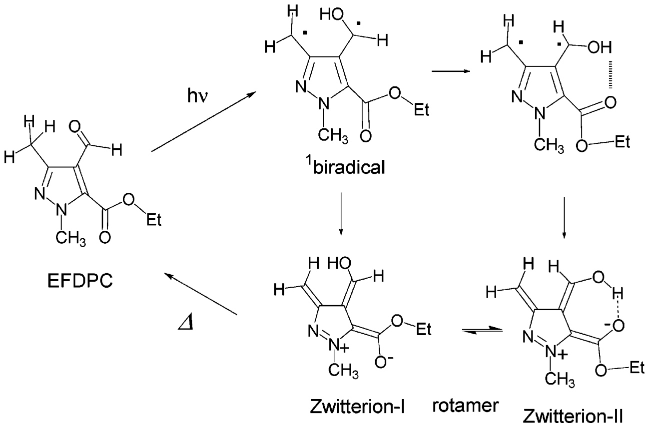
3.1. Steady-State Absorption Spectra of EFDPC. Ground-state absorption spectra of EFDPC have been recorded in different solvents at 298 K and in solid state, a cast film prepared from chloroform solution onto quartz substrate. Figure 1 depicts the absorption spectra of EFDPC in solution of varying solvent polarities. The recorded spectra show two distinct bands: one

TABLE 1: Temperature- and Matrixes-Dependent Absorption Peaks of the Photoproduct (PP) of EFDPC

matrix	temperature (K)	photoproduct λ_{max} (nm)	η/η_{3MP}[a]
EPA[b]	85−107	497	5.5×10^{-2}
	120	slowly disappear ($t_{1/2} = 6$ min)	
EM[c]	89−93	500	1.7×10^{11}
	123	511	
	134 to 143	disappear	
MTHF[d]	86	495	6.9×10^{5}
	101	504	
	137	slowly disappear ($t_{1/2} = 2$ min)	
MC-IP[e]	90	no color change	1.1×10^{-2}

[a] Ratio of viscosity of different glass matrixes to the viscosity of 3-methylpentane at 77 K. [b] EPA: ether:isopentene:ethanol 5:5:2. [c] EM: ethanol:methanol 1:1. [d] MTHF: 2-methyltetrahydrofuran. [e] MC-IP: methylcyclohexane:isopentane 1:3.

SCHEME 2: Photochemical H-Abstraction Reaction Mechanism of EFDPC



is a strong absorption band at around 256 nm and another is very weak shoulder band at around 330 nm. The extinction coefficient of higher energy band is higher than 10 000 M^{-1} cm^{-1} whereas the lower energy band has an extinction coefficient of ∼ 25 M^{-1} cm^{-1} at 330 nm. No detectable solvatochromic effect was observed for both the bands. On the basis of the extinction coefficient values we easily assigned the higher energy band to be $\pi-\pi^*$ ($S_2 \leftarrow S_0$) and lower one to be of $n-\pi^*$ ($S_1 \leftarrow S_0$)[16] in nature. The absorption spectrum of the thin film of EFDPC is very similar to that in solution with respect to peak position, but 256 nm band is rather broad. Upon UV irradiation (∼350 nm) onto the film, the color of the film was changed. Initially, the film was colorless and after UV irradiation by 10 s the color of the film became reddish purple. This color lasts for several days if the film is kept in a dark place, and the color disappears on heating the film to 330 K without loss of starting materials. Upon UV irradiation onto the film (Figure 1) a new band could be observed at 550 nm with little decrease in intensity of the 256 and 330 nm bands. This phenomenon is the characteristic of photochromic reaction of EFDPC. We assigned this new band as the absorption band of photoproduct. It is pertinent to mention here that at room temperature in solution EFDPC does not show any color change upon UV irradiation, neither in polar nor in nonpolar solvents.

Upon UV irradiation (∼350 nm) on EFDPC at 86 K in an MTHF matrix, an intense red purple color appeared with a broad and structureless band peaking at 495 nm. Figure 1 shows one representative absorption spectrum of the photoproduct of EFDPC at 86 K in an MTHF glass after UV irradiation. On warming to 104 K, the peak position is shifted to 504 nm without any change of intensity, and on further warming over 120 K, disappearance of the colored species ensured.

In other organic glassy media, such as diethyl ether−isopentane−ethanol (5:5:2, EPA) and ethanol−methanol (1:1, EM), similar behaviors were observed except the positions of λ_{max}, and the temperatures showing decay of the colored species were slightly different to each other. Table 1 summarizes these cryogenic experiments at steady state.

The shift of absorption maximum upon warming could be attributed to the conformational change from an initial conformation of the photoproduct. The temperature of the thermal extinction of the colored species strongly depends on the hardness of matrix. Speculating the hardness of the matrixes from the relative viscosity of various matrixes at 77 K, the hardness at cryogenic temperature is in the order of EM > MTHF ≫ EPA> MP. The relaxation of thermal distinction of the photoproduct is inverse in the order of hardness. Retrieving the stability of the photoproduct in crystalline solid, these results prevail that the color photoproduct lasts permanently only in restricted geometry at low temperature or in solid state at room temperature.

Not only the survival temperatures but also the apparent absorbance of the colored species obeyed the order of hardness of the matrixes. These results are combined with the fact that for photoreaction as well as to have a stable photoproduct, EFDPC is required to be in highly constrained environment. As the temperature increases, glass matrixes start becoming softer, offering an inadequate rigid environment to the probe EFDPC within it, which results in no photoreaction (no color change) or very fast reversible reaction.

Thus, the photoproduct could not be monitored by steady-state spectroscopic technique in a soft medium, like in solution. EFDPC contains three γ-hydrogen atoms and a nearby carbonyl group at the end of a six-membered ring, which opens the possibility of hydrogen atom abstraction process via a six-membered transition-state, Norrish type II.[17−20] This type II reaction needs strict geometric requirement between abstracted and abstracting atoms.[21] So, this easy going color change of EFDPC upon UV radiation in solid-state and low-temperature glass matrixes could be involved with the hydrogen abstraction process producing stable photoproduct.

3.2. Femtosecond Transient Absorption Study. To obtain insight into the reaction process in solution, we have measured femtosecond transient absorption spectra for the EFDPC system in several solvents with increasing polarities on excitation at 355 nm. We have checked that photoreaction occurred upon excitation at 355 nm. However, the basic features of differential transmission spectra as a function of delay replicate in all solvents studied, diethyl ether, chloroform, acetonitrile, and methanol. Figure 2 shows the transient absorption spectra of EFDPC obtained with excitation at 355 nm in chloroform. A broad transient absorption band at 625−645 nm appeared immediately after the excitation is attributable to the absorption spectrum of the singlet 1,4-biradical generated by γ-hydrogen abstraction to the nearest excited formyl group with analogy to recent literature.[22] Zewail et al. have shown that the rate of hydrogen atom transfer in the Norrish type II reaction for various kinds of carbonyl compounds is on the order of 70−90 fs to form the 1,4-biradical followed by cyclization or fragmantation reaction.[23,24] The formation of the biradical is very similar in our case (Scheme 2) and the hydrogen atom transfer in EFDPC could be of similar time constant. Calculating photon flux density with the pump pulse energy of 20 μJ at 355 nm and

TABLE 2: Solvent Dependent Transient Spectroscopic Properties of EFDPC[a]

solvent	$E_T(30)$[b] (kcal/ mol)	λ^1_{abs} (nm) at 0.2 ps	λ^2_{abs} (nm) (fwhm) at 3 ns	λ^3_{abs} (nm) (fwhm) at 3 ns	λ_{abs} (nm) at 3 ns	S_1 decay time (ps)	rise time of PP (ps)	decay time of PP (μs)	rel yield ($\Delta OD_{\lambda^{max,100ps}}/OD_{355nm}$)
DEE	35.0	625 ± 3	538 ± 5 (88 ± 5)	615 ± 5 (57 ± 5)	580 ± 3	4.0 ± 0.5	4.0 ± 0.5	6.8 ± 0.5	0.05
CHLF	39.1	630 ± 3	552 ± 5 (85 ± 5)	606 ± 5 (56 ± 5)	571 ± 3	4.9 ± 0.5	4.5 ± 0.5	7.0 ± 0.5	0.044
ACN	45.6	623 ± 3	491 ± 5 (108 ± 5)	552 ± 5 (87 ± 5)	560 ± 3	1.5 ± 0.5	1.0 ± 0.5	5.6 ± 0.5	0.037
MeOH	55.0		575 ± 5 (119 ± 5)	625 ± 5 (67 ± 5)	600 ± 3			3.0 ± 0.5	0.025

[a] λ^2_{abs} and λ^3_{abs} are peaks resolved by band shape analysis. The numericals in parentheses are full widths at half-maximum of individual Gaussian function. PP is photoproduct. [b] From ref 32.

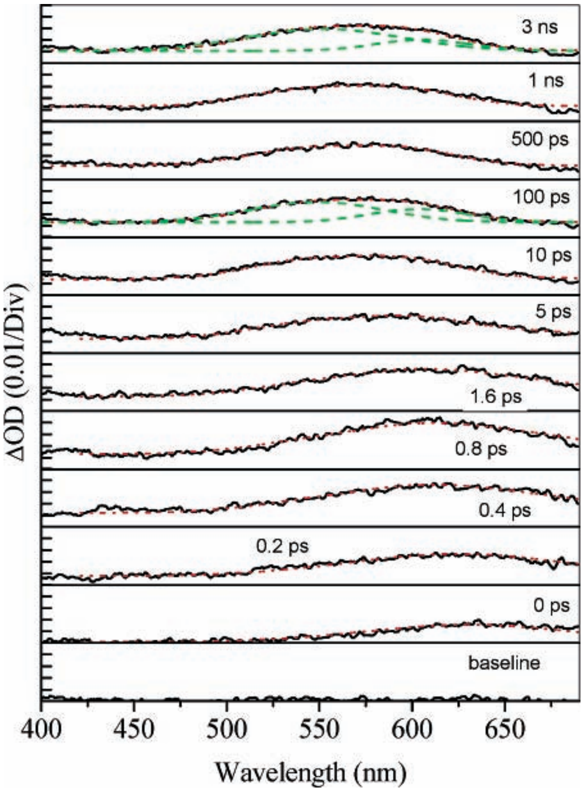


Figure 2. Transient absorption spectra of EFDPC at room temperature in chloroform. The red dotted line is the simulated transient absorption spectra and the green dashed lines are the two resolved Gaussain bands found by band shape analysis.

assuming 100% conversion efficiency from EFDPC to the 1,4-biradical, we have calculated the molar extinction coefficient to be ~3000 M^{-1} cm^{-1}. The molar extinction coefficient and peak position of the 1,4-biradical of EFDPC is very similar to those of the singlet 1,4-biradical of furan, thiophene, and pyrrol derivatives.[25] Considering the ultrafast hydrogen transfer (less than 100 fs), which is far below the system response function (~200 fs), we exclude the possibility of the assignment of this band to be the $S_n \leftarrow S_1$ absorption. This initial 625−645 nm band then apparently starts shifting toward blue, which includes the change of spectral shape with delay time till a few picoseconds. Finally, the shape of the spectral structure and the peak position are fixed (after a few tens of picoseconds) with a flat absorption maximum at 520−600 nm depending on the solvents. As shown later, this spectrum detected at longer delay time is in good agreement with the microsecond transient absorption spectrum. The band appearing at a longer delay with a peak maximum at 520−600 nm is assigned to be the absorption spectrum of the photoproduct. The minimum energy conformational geometry of this photoproduct has been determined by TD-DFT and it is of zwitterionic form (vide infra). From the Gaussian-type band shape analysis we find two well-resolved peaks under the envelope of this delayed absorption band (Table 2) and the peak height of those two hidden bands remain constant for all the delays, even if in the microsecond region too. These two hidden peaks may be due to the possible isomeric forms (rotamer) of the photoproducts, which supports our findings of two closely lying energetic conformations from semiempirical calculation (vide infra). The other possibility of having these two peaks in delayed transient absorption spectra could be the vibrational progression of the photoproduct. But it can be ruled out, as we found that the energy difference of these two bands strongly depends on the solvent polarity. In the intermediate time region (0.2 ps to a few picosecond), the spectrum shifts from the longer to shorter wavelength region with time. Assuming the possible origins of those two bands, the spectra in the intermediate time region were analyzed by a weighted superposition of the two bands, a single Gaussian peak for the absorption band at 0.2 ps and two Gaussian peaks for absorption at 100 ps where no further spectral change was detected and no contribution of the absorption of the singlet 1,4-biradical was found, which is given by

$$F(\lambda)_t = aG_1(\lambda)_{0.2ps} + b\{G_2(\lambda)_{100ps} + G_3(\lambda)_{100ps}\} \qquad (1)$$

where $F(\lambda)_t$ is the fitting function at arbitrary time t. $G_i(\lambda) = y_0^i + (A_i/w_i\sqrt{\pi/2})e^{-2(x-x_c^i)^2/w_i^2}$ is the Gaussian function, i = 1, 2, 3, and a and b are the amplitude parameters of 0.2 and 100 ps components, respectively. The y_0 is the offset value, A is the amplitude, w is the full width at half-maximum, and x_c is the peak position of the corresponding Gaussian function. The values of A_i, w_i, and $x_c{}^i$ were determined from the band shape analysis. Here we have used $A_1 = 2.50$, $A_2 = 1.28$, $A_3 = 0.97$, $w_1 = 112$ nm, $w_2 = 85$ nm, $w_3 = 56$ nm, $x_c{}^1 = 631$ nm, $x_c{}^2 = 552$ nm, and $x_c{}^3 = 606$ nm, respectively. All the spectra starting from 0.2 ps to 3 ns could be simulated well as a sum of two components by a nonlinear least-squares fitting method. Figure 2 also shows the comparison of simulated and experimental spectra, in which the simulated spectra corresponds well to the experimentally found absorption spectra.

From the simulation results we found that as delay time increases, contribution of the first component a decreases and the magnitude of b increases. Figure 3 illustrated the change of a and b as a function of time, which suggests that the decay of the first absorption (625−640 nm band) was accompanied by the concomitant growth of the absorption with a peak maximum at 530−600 nm. The decay time and the growth time of the intermediates are very similar, which suggests that the photoproduct is directly formed from the singlet 1,4-biradical. The time constant of the formation of final photoproduct is less than 10 ps, which has been summarized in Table 2 for different solvents.

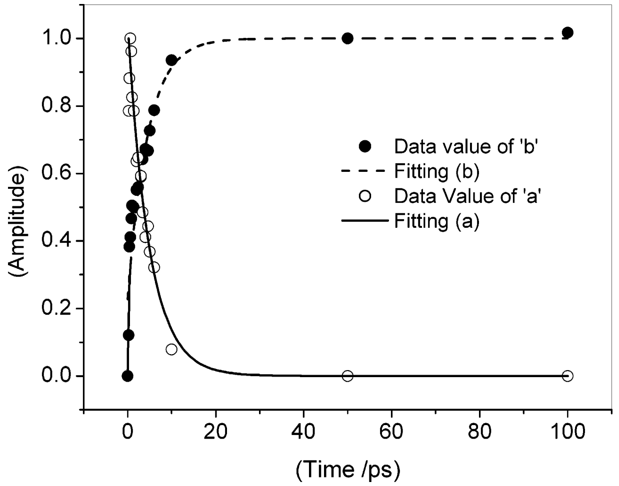


Figure 3. Decay and rise curves of the amplitude of *a* and *b* in eq 1 as a function of time.

The relative yield (ratio of differential OD of the transmission spectra at peak position on 100 ps delay to the ground-state OD at 355 nm) of the photoproduct in different solvents was observed and is listed in Table 2. The yield of the photoproduct decreases with increasing solvent polarity, which indicates that specific configuration of the EFDPC facilitates the photoreaction. As we discussed earlier, specific geometric configuration is one of the important requirements for the hydrogen atom abstraction reaction. In a polar solvent, the interaction between EFDPC and the surrounding solvent molecules is appreciably higher than that in a nonpolar solvent, which hinders the freedom of the molecular configuration and consequently may have less probability of hydrogen atom transfer. In solution, hydrogen atom transfer occurs immediately and it produces the 1,4-biradical just after the excitation at 355 nm, as indicated previously. Hence, the decay time of parameter *a* is defined as the lifetime of the singlet 1,4-biradical, which is on the order of ~4 ps (Table 2), and the growth time of the parameter *b* is the formation time of relatively stable zwitterionic photoproduct.

It is well documented that hydrogen abstraction is very sensitive to structural factors relating to the distance and orientation of the target hydrogen atom relative to the oxygen n orbital.[8] Thus abstraction is expected to be most facile when the hydrogen atom approaches the carbonyl group with maximum overlap with the nonbonded atomic orbital of oxygen. Hence, unlike in the solid state, in solution, reactants are free to explore alternative conformation and react via geometry of approach, which favors ultrafast hydrogen transfer reaction to occur.

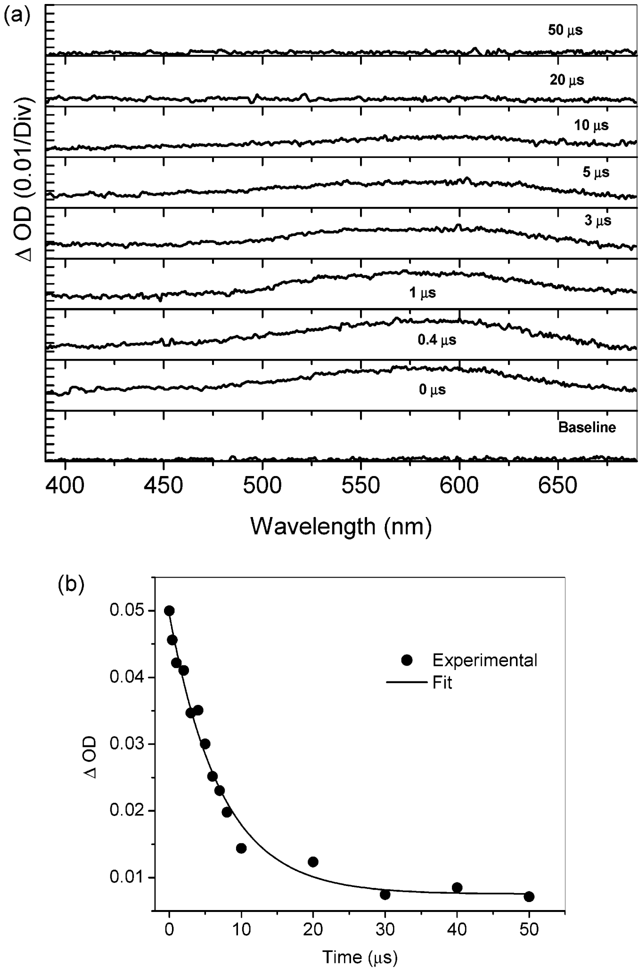


Figure 4. (a) Microsecond transient absorption spectra of EFDPC at room temperature. (b) Change of ΔOD at 580 nm with time.

3.3. Microsecond Transient Absorption Spectra. To determine the relaxation process of the photoproduct, we have observed microsecond transient absorption spectra of EFDPC in various solvents. In each case the microsecond transient absorption shows very similar spectral profile as observed at longer delay time (~3 ns) in femtosecond transient absorption study. A broad absorption band with a peak maximum at 530−600 nm arises just after the excitation. This absorption band is composed of two well-resolved Gaussian bands and the ratio of these two peak heights remains constant for all delays, whereas the total intensity of the absorption spectra decreases with time. After a few tens of microseconds the absorption spectrum is completely extinct. Figure 4a exhibits the transient absorption spectra of EFDPC in chloroform as a function of delay in microsecond order. We have plotted the change of ΔOD at the peak position as a function of time (Figure 4b), which shows the single-exponential decay with characteristic decay time of ~6 μs (Table 2). This long decay time again confirms that the photoproduct is not of biradical nature but is of zwitterionc form, which is also well supported by TD-DFT calculation. As of today no evidence was found where the singlet 1,*n*-biradical has such a long lifetime. The lifetime of the singlet biradical reported elsewhere is very short, and the maximum longer lifetime is found to be of few nanoseconds.[26] Furthermore, this single-exponential decay suggests that very fast equilibrium exists between two isomers. In protic solvents like in methanol, the decay is relatively faster than that in aprotic solvent and is caculated to be 3 μs, which could be explained by a possible hydrogen bonding interaction with photoproduct. Thus, the photochromic reaction in solution is a completely reversible process, and the zwitterionic photoproducts last only a few microseconds before reverse hydrogen transfer to regenerate the ground-state aldehyde, i.e., the starting material EFDPC.

To compare the reaction pathways in glass matrixes and in solution, we calculated the activation energies both at room temperature and low temperature. At the low temperature (120 K) in MTHF matrix EFDPC shows a strong red-violet color upon 350 nm excitation and the color fades up to 50% within 2 min after photoexcitation is switched off. Assuming this 2 min as the half-lifetime of the photoproduct, we calculated the activation energy (E_a) from the Arrhenius equation to be 6−7 kcal/mol when the Arrhenius constant A is $\sim 10^{10}$ s^{-1}. Similarly, at room temperature, taking the lifetime of the photoproduct as 6 μs, the calculated activation energy is 6.7 kcal/mol. These

TABLE 3: Calculated (TD-DFT) Total Energies (au) Vibrational Zero-Point Energies (au) and Relative Energies (kcal/mol) of the Stationary Structures and Absorption Peaks (ZINDO/TD-DFT)

	EFDPC				Zwitterionic photoproduct			
conformer	in/out	out/in	in/in	out/out	in/out	out/in	in/in	out/out
energy[a]	−685.3581	−685.3469	−685.356	−685.3517	−685.2846	−685.2935	−685.2826	−685.2889
ZPE[a]	0.208538	0.207902	0.20857	0.208162	0.208263	0.208673	0.208292	0.208556
relative energy[b]	0	6.6	1.3	3.7	0	−5.28	+1.31	−2.5
singlet transition/nm (ZINDO)	358	341	295	348	473	528	491	488
	296	278	281	284				
	281	264	244	273				
	229	226		235				
singlet transition/nm (TD-DFT)	357	347	275	353	460	532	474	495
	276	267	254	270				
	254	260		263				
		246		253				

[a] In Hartrees. [b] Relative energies (kcal/mol) were calculated at the level of B3LYP/6-31G* and include scaled zero-point vibrational energies (scaling favctor is 0.9806).

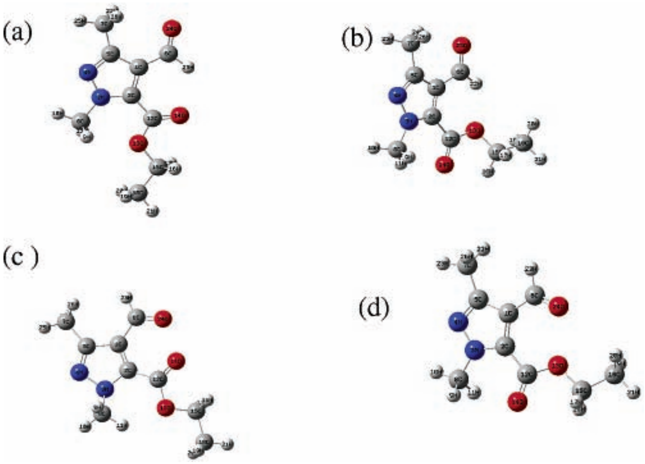


Figure 5. Optimized structure of four conformers of EFDPC: (a) in/in; (b) in/out; (c) out/in; (d) out/out.

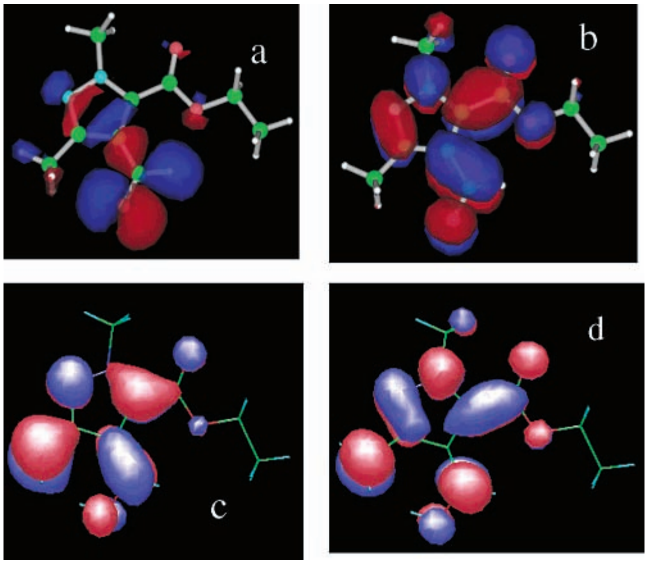


Figure 6. HOMO and LUMO orbitals at the B3LYP/6-31G* level of theory of the in/out conformer of both EFDPC and the photoproduct: (a) HOMO of EFDPC; (b) LUMO of EFDPC; (c) HOMO of the photoproduct; (d) LUMO of the photoproduct.

results imply that photochromic reaction pathway both at room temperature and at low temperature are the same.

3.4. Time Dependent Density Functional Theory (TD-DFT) Calculation for the Spectral Simulation. At first we investigated the conformation of the starting material, EFDPC, by the DFT calculations at the B3LYP/6-31G* level. There are four energetically closely lying conformers resulting only from the orientation of two carbonyl moieties. We define a conformer as in/out, where an oxygen atom in the formyl group orients to the adjacent methyl and that in the ester orients opposite to the adjacent formyl group, is the most stable and is the same configuration as in crystals.[7] The other three conformers are in/in, where an oxygen atom in the formyl group orients to the adjacent methyl and that in the ester orients toward the adjacent formyl group, out/in, where an oxygen atom in the formyl group orients opposite to the adjacent methyl and that in the ester orients toward the adjacent formyl group, and out/out, where an oxygen atom in the formyl group orients opposite to the adjacent methyl and that in the ester orients opposite to adjacent formyl group (Figure 5). Table 3 shows the energies of the corresponding conformers. Out of those (four) possible conformers in/out conformation is most stable with a favorable geometric relationship for H-abstraction between the abstracting carbonyl group and the abstracted γ-hydrogen atom. The first and the most important parameter, *d*, the distance between carbonyl group and the γ-hydrogen atom H(26)−O(23), is 2.7931 Å, which is very near the sum of the van der Waals radii of oxygen and hydrogen.[27] The second parameter, the angle (C═O- - -H) C(6)−O(23)−H(26) is 99.40°, a good value lying between 90 and 120°. The third parameter ω, the dihedral angle by which the γ-hydrogen atom lies outside the mean plane of the carbonyl group is calculated to be 18°. Because the n-orbitals of oxygen lie in this plane, the ideal value of ω is expected to be zero. So, in this case γ-hydrogen is a little bit out of the plane of carbonyl group.

Figure 6a,b depict the HOMO and LUMO orbitals of the in/out conformer of EFPDC. The HOMO and LUMO exhibit a molecular orbital coefficient mainly on the carbonyl group adjacent to the γ carbon. This suggests that the first excited singlet is involved with carbonyl group and it could be confirmed by the low molar extinction coefficient, i.e., weak absorption band at 330 nm in steady-state absorption spectra. We have calculated the absorption spectra for four conformers of EFDPC and for the in/out conformer the calculated spectra are relatively consistent with experimental spectra in respect of peak position and oscillator strength. Figure 7 shows the transition of the peak position of calculated absorption spectra of four conformers of EFDPC.

Next we investigated the energetics for the photoproduct by DFT calculations. As shown in the Scheme 2, the photoproduct can take both the biradical (open shell) and zwitterionic (closed shell) singlet states. This biradical form belongs to the same group as the tetramethyleneethane (TME) diradicals. The TMEs

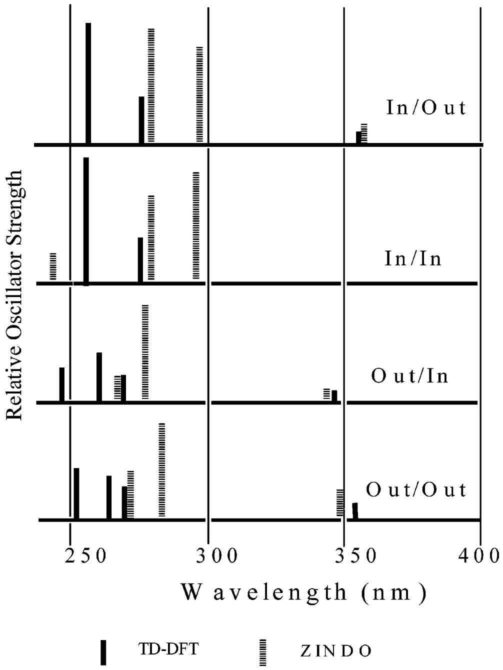


Figure 7. Calculated absorption peak positions with relative oscillator strengths of four conformers of EFDPC.

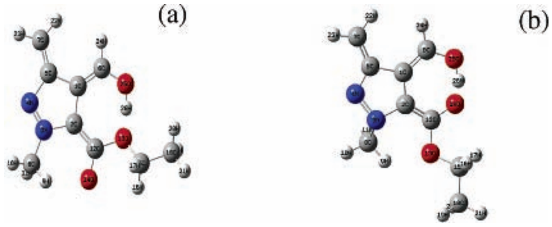


Figure 8. Optimized structure of two energetically closely lying conformers of photoproduct: (a) out/out; (b) out/in.

substituted with O, S, and NH atoms are known to be singlet open shell states lying slightly below triplet states.[28−30] Generally, in the heterocyclic series of singlet biradicals[29,30] derived conceptually from the disjointed biradical TME, the first-order perturbative interaction[29,31] between the lone-pair orbital of the heteroatom and the nonbonding molecular orbital of the C_s symmetric TME increases the energetic preference for the singlet in the order of O or S < NH,[29] and this has been exemplified elsewhere.[22] Thus, the energy gap between the singlet and triplet 1,4-biradical of EFDPC is expected to be larger in the ground state. These electron-donating substituents also stabilize the zwitterionic state. In fact, our DFT calculations (B3LYP/6-31G*) show that the zwitterionic singlet state is more stable than the triplet state of the biradical by 15.8 kcal mol^{-1} at the in/out conformation. Due to a problem arising from spin contamination we could not obtain the energetics of the singlet biradical of the photoproduct. We supposed that the singlet state of the biradical may lie below the triplet state; however, such large energy gap (15.8 kcal mol^{-1}) is not expected between the singlet and triplet states of the biradical.

Thus only the zwitterions at various conformations were considered for spectral simulations of the photoproduct. As shown in Table 3, out/out and out/in conformers (Figure 8) are energetically closely lying and more stable among the four conformers. We speculated these two conformers coexist in solution. The existence of these two species are in good agreement with the experiment of transient spectroscopy in solution.

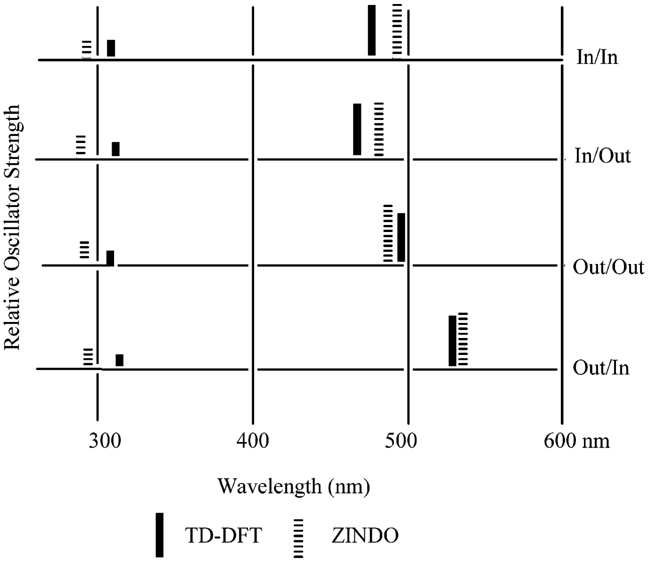


Figure 9. Calculated absorption peak positions with relative oscillator strengths of four conformers of photoproduct.

ZINDO-1 and TD-DFT calculations were performed on four zwitterionic conformers and Figure 9 shows the transition of the peak position of calculated absorption spectra of four conformers. For both cases (ZINDO and TD-DFT) the calculated electronic absorption spectra show a new absorption peak on the red side of the lowest energy absorption band of the starting material EFDPC. These results are qualitatively consistent with experimentally found absorption spectra of the photoproduct. Figure 6c,d portray the HOMO and LUMO orbitals of in/out conformer of the zwitterionic conformer. The most notable feature of these HOMO and LUMO are the appearance of the orbitals mostly exclusively on the pyrazole ring. This is precisely the species that shows a new absorption band in photoproduct.

4. Conclusion

We explored the photochemical reaction mechanism of EFDPC in solution, where the reaction initiated through hydrogen abstraction. On photoexcitation a very fast H-atom abstraction occurs in the excited singlet state of EFDPC followed by the formation of the singlet 1,4-biradical. After that, within ∼4 ps this biradical decays to bring about a singlet zwitterion with an absorption maxima around ∼580 nm. The non-Kekulé π-system of colored photoproduct resembles that of zwitterionic form. The resultant photoproduct is unstable in solution and it exists for few microseconds in two isomeric forms before reverse hydrogen transfer takes place to regenerate the ground-state aldehyde, i.e., the starting material EFDPC. Due to this fast back-reaction no color change was observed in solution by UV photolysis.

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