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Unraveling Ultrafast Dynamics of the Photoswitchable Bridged Dithienylethenes Under Structural Constraints

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Excited state dynamics of constrained photochromic benzodithienylethenes were addressed by considering the bridging with polyether chains (from $x=4$ to 6 units) at the ortho and meta positions of the aryl group, noticed DTE- o_x and DTE- m_x , through time-resolved absorption spectroscopy supported with (TD)-DFT calculations. The photochromic parameters and geometrical structures of these series are discussed. A Novel photocyclization pathway via triplet state evidenced recently (Hamdi *et al.*, Phys. Chem. Chem. Phys. 2016, 18, 28091-28100.) is largely dependent on the length and the position of the polyether chain. For the first time, by comparing the two series, we revealed, for the DTE- o_x series, an interconversion not only in the ground state but also between the triplet states of the anti-parallel and parallel open form conformers.

INTRODUCTION

During the last few decades, diarylethenes (DAEs), for which photochromism is due to the reversible photoinduced transformation between an open form (OF) and a closed form (CF), have become one of the most important organic photoswitches used in various hot topic fields: DAEs are used to modulate fluorophore features,¹ magnetic properties,² electrochemical properties,³ metallic ion complexation⁴ for examples. More recently, DAEs have been used to obtain shape light sensitive crystals⁵ or photoresponsive supramolecular assemblies.⁶ Exhaustive list of fundamental or industrial applications related to DAEs are covered by excellent books.⁷ Among DAEs, dithienylethenes (DTEs) belong to the most used photochromic compounds because of their high fatigue-resistant property and the thermal stability of both CF and OF isomers.⁸ Upon UV irradiation, DTEs undergo efficient photocyclization ($\phi_{cycl} \sim 0.2-0.5$) and less efficient photoreversion reactions ($\phi_{rev} \sim 0.01$).⁹ For photocyclization reactions, the quantum yield was thought to be limited to 0.5 explained by the coexistence, in equal proportions, of two isomers presenting either a parallel (P) or an anti-parallel (AP) conformation,

only the latter being photoactive.⁸⁻¹⁰ Overcoming this inherent limitation was the focus of various research projects relying on a purposed designed synthetic approach¹¹ or specific excited state reactivity.¹² As a matter of fact, thoughtful rationalization for photoswitching processes is highly desired to further improve the efficiencies of DTEs. Considerable efforts have been developed worldwide to explore the excited state topologies of DTEs (or DAEs) via advanced optical spectroscopies and quantum chemical calculations.¹³

In recent years, we have undertaken several studies to thoughtfully investigate the photoswitching processes of different series of bridged DAEs¹⁴ or DTEs molecules,^{13e,14-15} combining ultrafast spectroscopies, chemometrics data treatment and (TD)-DFT calculations. Indeed, by blocking the molecule in a given conformation, the comparison of bridged vs free analogs allows to distinguish the photochemistry of the AP conformer from the photophysics of P one (AP and P conformers are characterized by a rapid interconversion in the ground state and present similar absorption spectra). By this way, we have reported in 2010 two photocyclization pathways for cyano-substituted DAEs,¹⁴ results confirmed recently by advanced *ab-initio* calculations.¹⁶ Similarly, the ultrafast excited state and reaction dynamics of a series of inverse bridged DTEs have been fully understood in solution¹⁷ and in the gas-phase.^{15a} In particular, we were able to prove that the systems photocyclized directly from the Franck-Condon region (~ 120 fs) and not from the first relaxed excited state. Finally in 2016, due to its primordial place in the literature,¹⁸ we have reinvestigated the normal dithienylethene 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene called later DTE together with its bridged analog¹⁹ called DTE- m_5 (DTE with a polyether bridged substituted at the meta position of the terminal phenyl rings). At first glance, DTE- m_5 was thought to block the molecule in the AP ideal conformation. Instead, we discovered that UV photoexcitation of ground state DTE- m_5 molecules gave birth to two triplet states, 3P and 3AP with distinct intersystem crossing (ISC) and relaxation process characteristic times. Furthermore, we found that the structural constraint opened up a new

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Electronic Supplementary Information (ESI) available: additional stationary transition spectra; and DFT calculations.

photocyclization pathway via ^3AP at about 10% extent. Because triplet species of DAEs have been more and more investigated recently,²⁰ we decided to examine the photoreactivity-structure relationship for a complete series of bridged DTEs consisting of the parent molecule with an additional polyether chain of different length substituted at the meta (DTE- m_4 , DTE- m_5 , DTE- m_6) or the ortho (DTE- o_5 , DTE- o_6) positions with respect to the phenyl rings. Still combining femtosecond/nanosecond absorption spectroscopy, DFT calculations, and NMR techniques, we will evidence, for the first time, a triplet state interconversion process $^3\text{AP} \leftrightarrow ^3\text{P}$. In addition, we will show the large dependency of the triplet photocyclization pathway yield to the length of the polyether chain.

Scheme 1: Normal DTE, DTE- o_x and DTE- m_x bridged series. ϕ_1 and ϕ_2 are the dihedral angles between thiophene and phenyl rings.

EXPERIMENTAL AND THEORETICAL METHODS

Stationary techniques.

All bridged DTEs were synthesized by Takeshita *et al.*²¹ and the preparations are detailed in the previous work concerning DTE- m_5 .¹⁹ Chloroform (CHCl_3) solvent (spectroscopic grade, Sigma-Aldrich) was used as received. The steady state absorption spectra were measured with a CARY 100bio absorption spectrometer. ^1H -NMR spectra in CDCl_3 , to determine AP/P ratio, were recorded on Bruker Avance-300 (300 MHz). The photocyclization and photoreversion yields have already been published for DTE²² and were determined in this work for all the molecules according to usual procedure.²¹

Transient absorption techniques.

Our nanosecond transient absorption spectroscopy setup has been described elsewhere.²³ Briefly, a third harmonic pulse (355 nm) of a Nd:YAG laser with ca. 1 mJ output energy and 5 ns pulse width was used as excitation light and a pulsed Xe lamp was utilized as probe light. Transient absorption spectra were obtained from the transient absorption decays recorded at various wavelengths by sampling the absorbance changes for different given delay-times.¹⁹

Femtosecond time-resolved experiments were performed using a pump-probe spectrometer²⁴ based on Ti:sapphire laser system (Coherent Mira-900-D oscillator and Libra-S regenerative amplifier) delivering 800 nm, 1 mJ and 90 fs pulses with a repetition rate of 1 kHz. The pump pulses tuned at 320 nm were generated by frequency quadrupling the output of a Quantronix Palitra OPA pumped at 800 nm and the energy at the sample was about $2 \mu\text{J}$ (0.2 mJ cm^{-2}). Note that, we choose to excite the molecule far from the maximum of absorption localized near 270 nm to avoid short-time 2-photon absorption signal coming from the solvent. The probe pulses were obtained by focusing $1 \mu\text{J}$, 800 nm pulses into a 1 mm thick CaF_2 plate to generate a white light continuum. The pump-probe polarization configuration was set at the magic angle (54.7°). Transient absorbance was obtained by comparing signal and reference spectra with and without pump pulses for different delay-times. The delay-time between the pump and probe was varied up to 0.5 ns using an optical delay line. Sample solutions ($\sim 10^{-3} - 10^{-5} \text{ mol dm}^{-3}$, OD = 1 at the pump wavelength) were circulated in a cell equipped with 200 μm thick CaF_2 entrance window

and having 2 mm optical path. During measurements, the solution was circulated and was irradiated by a CW Xe lamp visible light to prevent the accumulation of CF. In this configuration, for 320 nm excitation, the instrumental response function determined by fitting the stimulated Raman transient pic of acetonitrile was determined to be 180 fs. All the transient spectra presented in this paper are GVD corrected according to the typical extrapolation method²⁵ (the temporal chirp over the white-light 350-800 nm range was about 400 fs). The characteristic times deduced from kinetics are obtained by fitting the data with the result of a multiexponential function convolved with a Gaussian pulse mimicking the pump-probe cross-correlation function (FWHM: 180 fs).

Theoretical Calculations

All the calculations have been performed using the Gaussian 09 package²⁶ within the Density Functional Theory (DFT) and Time-Dependent (TD-DFT) frameworks, to model the ground-state (GS) and excited state (ES) properties, respectively.

In the course of the GS and ES geometry optimizations, we used the ωB97XD range-separated hybrid (RSH) functional²⁷ combined with the 6-31G (d) atomic basis set. Contrary to conventional hybrid functionals, RSHs are known to avoid inconsistencies for ES geometries and this computational strategy was successfully applied in a previous study to investigate the structural properties of DTEs.¹⁹ All the geometry optimizations have been carried out in CHCl_3 , applying the Polarizable Continuum Model (PCM)²⁸ to quantify the impact of the environment. Both the GS and ES geometry optimizations have been carried out in the equilibrium limit using the linear-response (LR) PCM scheme. For the lowest triplet state exploration (T_1), the unrestricted formalism was considered, and the spin-contamination was systematically checked.

The optical properties have been determined using vertical TD-DFT calculations computed by the LR-PCM scheme in its non-equilibrium limit. At that stage, we have used the CAM-B3LYP/6-311+G(2d,p) methodology. We have previously demonstrated that this computational scheme is able to reproduce accurately the absorption wavelength $\lambda_{\text{abs}}^{\text{max}}$ of bridged DTEs.¹⁹

RESULTS AND DISCUSSION

Influence of ortho and meta positions on the structure, the quantum yields, the torsion angle and the absorption spectra.

Fig. 1 shows the absorption spectra of OF and CF of DTE, DTE- m_x and DTE- o_x respectively, in chloroform solution. All the theoretical and experimental photochromic parameters together with AP:P proportion (from NMR experiments) are listed in Table 1. As seen in Fig. 1, ortho linked polyether bridges affect more strongly the optical properties of the molecules compared to the meta analogs in the sense that both CF and OF species are concerned. Indeed, as seen in Table 1, for DTE- m_x series, $\sim 2 \text{ nm}$ and $\sim 15 \text{ nm}$ bathochromic shifts (in comparison with DTE) are reported for the OF and CF respectively. In the meantime, for DTE- o_x series, $\sim 25 \text{ nm}$ hypsochromic shifts are reported for both species. Thus to stress efficient structural constraint to both AP and P conformers, polyether bridge has to face the well-known flexibility of OF (ground state AP-P equilibrium). Because, molecular orbitals responsible for OF/CF absorption bands are localized on the photochromic core and delocalized on the phenyl rings, the large spectral shifts reported so far have to be correlated with the torsion angle between the thiophene and the phenyl ring planes (see ϕ_1 and ϕ_2 in scheme 1). Indeed, in the case of 1,2-bis(2-methyl-5

Table 1: Calculated and experimental photochromic parameters of DTE, DTE- m_x and DTE- o_x series in c chloroform.

	Calculated values									Experimental values				
	r_{cc} (Å)			Average torsion angle difference / DTE (°) ^a			λ_{abs}^{max} (nm)			λ_{abs}^{max} (nm)		Quantum Yields		% ^d
	AP	P	CF	AP	P	CF	AP	P	CF	OF	CF	Φ_{cycl}^b	Φ_{rev}^c	
DTE	3.78	4.00	1.53	0	0	0	266	267	527	273	575	0.46	0.015	48 52
DTE- m_4	3.70	3.92	1.53	8	1	11	268	263	526	274	590	0.29	0.026	35 65
DTE- m_5	3.88	3.95	1.53	7	9	9	277	263	513	272	580	0.36	0.015	42 58
DTE- m_6	4.22	4.09	1.53	8	9	8	267	275	527	273	576	0.43	0.014	44 56
DTE- o_5	4.30	4.24	1.53	37	56	80	259	254	508	256	550	0.41	0.056	48 52
DTE- o_6	5.36	4.17	1.53	13	23	58	247	248	490	257	550	0.37	0.055	41 59

^a $(|\phi_1 - \phi_1(DTE)| + |\phi_2 - \phi_2(DTE)|)/2$; values for torsional angles see Table S.1; ^b @ 313 nm; ^c @ 517 nm; ^d from NMR experiment.

-(4-methoxy-phenyl)-3-thienyl)perfluorocyclopentene²⁹ and in the case of a diarylethene bearing carboxyl groups at ortho, meta and para positions in the single-crystalline phase³⁰, similar bathochromic shifts were explained by the increase of the torsion angle. To confirm this hypothesis, we have optimized the structure of the different DTE series (Fig. 2) within the DFT framework. The energy difference between TD-DFT and experimental absorption wavelengths (Table 1) is smaller than 0.19 eV which validates our computational scheme.

Thus, from the calculated values of the two torsion angles (see Table S.1), an average has been computed and compared with the value computed for the parent molecule DTE, for the AP, P and CF species. As shown by Table 1, for the DTE- m_x series, the moderate bathochromic shift (0-15 nm) is correlated to the small torsion compared to DTE (<11°) while for the DTE- o_x series, the stronger bathochromic shifts, ~25 nm for OF and CF, arise from the larger modification of the torsional angles (between 13° and 80°). Therefore, we can conclude that polyether bridges are more effective when substituted in ortho position compared to meta position inducing probably some drastic changes for excited states topologies.

Consequently, quantum yields for photoswitching processes are also directly affected by the structural constraints. First, concerning the photocyclization yield (see Table 1), polyether bridges seem to change significantly the AP-P balance compared to the unbridged analog DTE: along the serie (DTE- m_4 , m_5 and m_6) the rise of P population (+25 %, +12%, + 8 %) corroborates the decrease of the ring closing efficiency (-37%, -22%, -7%). Furthermore, DTE- m_4 is the only molecule to display an increase of photoreversion yield (+73%) compared to DTE- m_5 and DTE- m_6 . Both effects are probably related to the shorter length of polyether bridge that should affect the overall topological points; in other words, when the bridge is too long, it cannot affect the photochemistry of the molecule anylonger. For the DTE- o_x series, the most important observation concerns the increase of the photoreversion yields from ~0.15 to ~0.55 concomitantly with the ~25 nm hypsochromic shift of the CF spectra. This effect is probably related to a diminution of the well-known potential barrier standing between CF* and OF* excited states. Closer inspection of the optimized structures of the P, AP and CF conformers (see Fig. 2) shows that in the case of DTE- o_5 (see Fig. 2) and DTE- o_6 (see Fig. S.11), the distance between the reactive carbons r_{cc} in Table 1 is much larger than in the other compounds. Probably, this distended conformation is responsible for the singularity distinguishing ortho and meta series. Following our previous paper¹⁹ dealing with DTE and DTE- m_5 , an investigation of the photophysics of the P conformer and photochemistry of the AP and CF conformers will allow to rationalize the differences between the different series.

Fig. 1: Normalized Absorption spectra of the CF and OF for DTE, DTE- m_x and DTE- o_x molecules in chloroform. Offset of 0.05 OD are applied for bridged molecules.

Fig. 2: DFT optimized structures at the ω B97XD/6-31G(d) level for the CF, AP and P of (top) DTE- o_s , (down) DTE- m_s . The polyether chain is represented by tube model without hydrogen. All optimized structures are presented in Figure S.11 and Figure S.12.

Photophysics of triplet states (Nanosecond regime)

Nanosecond transient absorption spectra of DTE- m_5 recorded in chloroform, in the 350-700 nm spectral domain, for uncolored solution purged with N_2 following 320 nm laser excitation are shown in Fig. 3 (top) while kinetics are shown in Fig. 3 (down). The overall molecules presented in this study display similar transient data (see Fig. S.4 and Fig. S.5) and precise assignments have been made in the past (see Fig. 3 and Fig. 4 of reference¹⁹). The kinetics at 440 nm can be fitted by a tri-exponential function (see characteristic times τ_5 , τ_6 and τ_7 in Table 2): the characteristic time τ_5 and τ_6 are attributed to the 3AP and 3P triplet states and τ_7 (related with a so-call X species) may describe the dynamics of polyether chain in the ground state. In addition, the 580 nm band corresponds to the CF signal. We determined the extent of CF coming from 3AP using the diminution of ΔA plateau value @ 580 nm (easily seen on kinetics) upon O_2 bubbling inside the solution. The photocyclization pathway via the triplet state is more efficient for DTE- o_5 , DTE- m_5 and DTE- m_4 (20%, 10% and 10% respectively) compared to DTE- o_6 and DTE- m_6 (5% and 3.5 % respectively).

Fig. 3: (top) Microsecond time-resolved absorption spectra of DTE-m₅ in chloroform under N₂ atmosphere after laser excitation at 320 nm. **(down)** Kinetics recorded at 580 nm and 440 nm under N₂ (bleu curve) and O₂ saturated (red curve) atmosphere. The characteristic time constants derived from multiexponential fitting procedure are also given in the figure.

Table 2: Lifetimes deduced from multiexponential fitting of transient kinetics obtained from the laser-flash photolysis experiment for DTE, DTE-m_x and DTE-o_x molecules. % of CF coming from triplet pathway (deduced from quenching experiment).

	Lifetime (μs)			% ³ AP → CF
	τ ₅ (³ AP)	τ ₆ (³ P)	τ ₇ (X)	
DTE	25.5 (4) (20%)	2.55(3) (80%)	...	0
DTE-m ₄	12.5(5) (17%)	2.10(1) (70%)	38(2) (13%)	10
DTE-m ₅	11.6(3) (55%)	1.65(4) (35%)	43(1) (10%)	10
DTE-m ₆	8(2) (35%)	1.70 (2) (40%)	42(5) (25%)	3.5
DTE-o ₅	6 (1) (25%)	1.3(5) (20%)	52(2) (55%)	20
DTE-o ₆	10(5) (35%)	1.5(1) (28%)	47(2) (37%)	5

To rationalize the photocyclization pathway via the triplet state (³AP → CF), additional DFT calculations have been performed including triplet state species. In the energy diagram of Fig. 4, the energies of the ground and triplet states are given as a function of the distance between the reactive carbons (r_{cc}). With those diagrams, one can compute the distance difference between CF and ³AP topological points (Δr_{cc}). We found that more efficient triplet photocyclization molecules have smaller Δr_{cc} values between ³AP and CF: for example, DTE-o₅ (2.09 Å) and DTE-m₅ (1.60 Å) values are almost two times smaller compared to DTE-o₆ (4.38 Å) and DTE-m₆ (2.53 Å). Moreover, in the case of DTE-o₆, the triplet state is oriented in the improper molecular coordinate direction (Δr_{cc} positive instead of negative) explaining the low quantum yield. Concerning, the lifetimes of ³P

(~2 μs) and ³AP (~10 μs) reported on Table 2, if the former is unaffected compared to DTE, the latter is divided by a factor going from 2 (DTE-m₄) to 4 (DTE-o₅). In this last case, the percentage of CF emanating from ³AP is assessed to reach a maximum of ~20 %. This experimental result is corroborated by the minimum energy gap between ³AP and CF. Finally, it is worth to note that the extent of the X species, assigned in our previous paper to be conformational relaxation of CF,³¹ is enhanced for ortho series for which additional hydrogen bonding is reported between polyether bridge and photochromic core.

As an important conclusion from nanosecond regime, if some specificities are noticed for the ortho series (enhancement of conformational relaxation), the main ³P and ³AP photophysics behavior remains similar for both series. We will see that in the femtosecond regime, this statement is no longer true.

Fig. 4 Relative energies of the S₀ and T₁ states for the DTE-o₅ (blue), DTE-m₅ (green) and DTE-o₆ structures (red) calculated at PCM (CHCl₃)-ωB97XD/6-31G(d). The energy of the most stable S₀ P conformer is considered as the energy reference. ΔE represents the energy gap between the ³AP and ³P.

Photocyclization of AP conformer (Femtosecond regime).

Transient absorption spectra of chloroform solutions of DTE-o₅ (right) and DTE-m₅ (left) (for DTE-o₆, DTE-m₄ and DTE-m₆ respectively see Fig. S.8) recorded in the 350-700 nm spectral range within four time-windows (-1-0.18, 0.24-0.9, 1-7 and 10-500 ps), following 320 nm excitation are shown in Fig. 5. Global fitting of transient signals with four-exponential (DTE-m_x) or three-exponential (DTE-o_x) functions, convoluted with a Gaussian profile simulating the pump-probe correlation function are shown in supporting information (see Fig. S.7, Fig. S.9 and Fig. S.10). The characteristic times obtained for DTE, DTE-m_x and DTE-o_x are gathered in Table 3. As a matter of fact, the interpretation of the data obtained for the complete series DTE-m_x and DTE-o_x (DTE-m₅ and DTE-o₅ presented in Fig. 5) strongly relies on the discussion published in our previous work for DTE and DTE-m₅¹⁹ but some differences arise for the ortho-series.

For short delay-times (-1-0.18 ps), the transient absorption spectra exhibit two absorption bands peaking around 380 nm and 460 nm, these two bands were attributed to the Excited States Absorption (ESA) of S₁ states within the Franck-Condon (FC) region of both AP and P conformers noticed respectively S₁^{FC}(AP) and S₁^{FC}(P). In the second panel (0.24-0.9 ps) for DTE-m₅, meanwhile the ESA signal of P conformer seems to be constant, the band peaking at 380 nm

decreases while a new band rises at ~ 580 nm (max of CF absorbance) with a characteristic time τ_1 of about 110-160 fs for bridged DTE series (see Table 3). By referring to previous work, this characteristic time is unambiguously attributed to the ultrafast photocyclization via the S_1 FC state.^{16,31} Besides photocyclization, there is the parallel relaxation of the AP conformer from the FC region to the relaxed excited singlet state noticed $S_1^{\text{rel}}(\text{AP})$. It is worth to note that τ_1 is always higher compared to the unbridged analog which suggests that the polyether chain pulls apart the reactive carbons. Concerning DTE-o5, the photocyclization related spectral signature is extremely weak and the ESA band (near 420 nm) of the P conformer substantially decreases suggesting an Internal Conversion (IC) toward the ground state.

In the third panel (1-7 ps), substantial differences between meta and ortho series still occur. For DTE-m₅ (left), an ESA band peaking near 460 nm decreases with a characteristic time $\tau_2 = 0.40$ ps. This evolution is attributed to the relaxation of the FC state of the P conformer ($S_1^{\text{FC}}(\text{P}) \rightarrow S_1^{\text{el}}(\text{P})$). In the meantime, for DTE-o₅, such kind of evolution is missing in accordance with the IC of P conformers, previously reported, which is therefore the main relaxation pathway of P excited state conformers.

Finally, for pump-probe delay-times higher than 10 ps (panel 4), one can observe for DTE-m₅ a weak decrease of the 360 nm band attributed to $S_1^{\text{rel}}(\text{AP})$ together with the decay of the 420 nm band attributed to $S_1^{\text{rel}}(\text{P})$. Two characteristic times of 1.3 ps and 70 ps for DTE-m₅ have been deduced from the fitting procedure; the shorter time is attributed to the Inter-System Crossing (ISC) of the AP conformer ($S_1^{\text{rel}}(\text{AP}) \rightarrow {}^3\text{AP}$) while the longer one is ascribed to the ISC of the P conformer ($S_1^{\text{rel}}(\text{AP}) \rightarrow {}^3\text{AP}$). In the meantime, as logically expected, a unique decay is reported for DTE-o₅, which is related with the ISC of the AP conformers. In brief, for the meta- series, both ${}^3\text{AP}$ and ${}^3\text{P}$ triplet states are produced while only the ${}^3\text{AP}$ is observed for the ortho- series.

Microsecond transient absorption data of DTE-o₅ (see Table 2), indicated unambiguously the presence of the triplet state of both AP and P conformers ($\tau_1 = 1.3$ μs and $\tau_2 = 6$ μs) which seems incoherent with the femtosecond absorption data conclusions. The only way to face this contradiction consists of relying on an interconversion at the triplet manifold for the ortho series, i.e. ${}^3\text{AP} \leftrightarrow {}^3\text{P}$. To confirm this assumption, theoretical calculations have been performed for DTE-m_x and DTE-o_x molecules with optimized ${}^3\text{AP}$ and ${}^3\text{P}$ structures. As shown by Fig. 4, in the case of DTE-o₅, the energy level difference between ${}^3\text{AP}$ and ${}^3\text{P}$ is 5 times lower ($\Delta E = 1.8$ Kcal/mol) than the one calculated for DTE-m₅ ($\Delta E = 10$ Kcal/mol). This feature indicates a possible lower energy barrier between the ${}^3\text{AP}$ and ${}^3\text{P}$ and the large feasibility of a rapid interconversion ${}^3\text{AP} \leftrightarrow {}^3\text{P}$ in the case of DTE-o_x compared to DTE-m_x.

Table 3. Characteristic times deduced from the global fitting method applied to femtosecond transient absorption data for DTE, DTE-m_x and DTE-o_x open form UV excitation.

	$\tau_1(\text{ps})$	$\tau_2(\text{ps})$	$\tau_3(\text{ps})$	$\tau_4(\text{ps})$
DTE	0.10(2)	0.20(5)	1.0(1)	55(10)
DTE-m ₄	0.11(3)	0.21(2)	40(6)	140(30)
DTE-m ₅	0.19(1)	0.40(5)	1.3(1)	70(1)
DTE-m ₆	0.15(7)	0.23(2)	3.3(5)	43(7)
DTE-o ₅	0.16(1)	0.32(1)	1.2(1)	...
DTE-o ₆	0.16(1)	0.35(1)	2.9(2)	...

Fig. 5: Femto-picosecond time-resolved absorption spectra of DTE-m₅ (left) and DTE-o₅ (right) in chloroform ($\sim 10 \mu\text{M}$) using 320 nm excitation wavelength. The transient data are separated into four distinct temporal windows. All spectra are corrected from the GVD. The time constants derived from multiexponential fitting procedure convolved with a 180 fs Gaussian instrumental response function are reported in the figure.

Fig. 6: Proposed photophysical and photochemical mechanisms including characteristic times for DTE- o_x (red) and DTE- m_x (blue) deduced from time resolved experiments. The molecular coordinate (horizontal axe) can be either carbene-carbene distance or dihedral angles difference.

CONCLUSION

Following our previous exploration of the DTE photoreactivity, distinguishing AP photocyclization from P photophysics, we have investigated a series of bridged DTEs substituted with a polyether chain at the meta- and ortho- positions of the phenyl rings. For the DTE- m_x molecules ($x=4-6$), AP conformers within FC region photocyclize rapidly (110-190 fs) and decay within a parallel pathway to give rise to the relaxed S_1 state. The latter state, following an ISC mechanism, gives rise to a triplet state (1.3-40 ps) of short lifetime ($\sim 2 \mu s$). In the meantime, the excited P conformers undergo an ultrafast IC (200-400 fs) followed by an ISC (40-140 ps). Note that the effect of constraints is clearly noticed for DTE- m_4 through faster photocyclization and much slower ISC process. Concerning the DTE- o_x molecules ($x=4-6$), the AP conformers photochemistry mimics the meta- analogs: photocyclization (160 fs) and ISC (1.2-3 ps) dominate the excited state electronic relaxation. Meanwhile, the P conformers undergo IC directly to the ground state without any production of S_1 relaxed state (and subsequent ISC). Despite this finding, the presence of a triplet state for the P conformer can be rationalized by a rapid interconversion at triplet state manifold. To the best of our knowledge, this is the first time that such excited state equilibrium is emphasized for DTE. The modifications of excited states topology being responsible for the new P conformers photophysics as well as the photocyclization via the triplet route, it appears relevant to undertake advanced multireference calculations to pave the way to the control of DTE excited states. Such theoretical efforts are presently undertaken in our laboratories.

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