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Photochemical formation of thiirene and thioketene in 1,2,3-thiadiazoles with phenyl substituents studied by time-resolved spectroscopy[†]

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Photochemistry of 4-phenyl-1,2,3-thiadiazole (PT) and 4,5-diphenyl-1,2,3-thiadiazole (DPT) in solution was studied at room temperature using UV-vis and IR transient absorption spectroscopies (λ_{ex} = 266 nm). Ultrafast techniques show a very fast rise (<0.3 ps) of thiirene and thioketene species, formed from 1,2,3-thiadiazoles in the singlet excited state. The remarkable unimolecular stability of thiirenes in solution is observed. On a millisecond time scale thiirenes with phenyl substituents undergo an intermolecular reaction (dimerization of thiirene–thioketene complexes) leading to 1,3-dithiole derivatives.

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1. Introduction

The compounds 1,2,3-thiadiazoles and their derivatives make an important class of molecules in organic synthesis^{1,2} and medicinal chemistry,² and their rich photochemistry has been studied by chemical, physical, and computational methods.³ The light irradiation of 1,2,3-thiadiazoles can result in molecular nitrogen extrusion and formation of intermediates such as thiirenes and thioketenes. Both species have been directly characterized in numerous studies in cryogenic matrices.³⁻⁸ Hypothetical intermediacy of 1,3-diradicals and thiocarbenes as precursors of thiirenes or thioketenes is not clear.³ The mechanistic details of the photoreaction have been recently studied by time-resolved spectroscopy for 4-methyl-5carboethoxy-1,2,3-thiadiazole (MCT) in solution phase (Scheme 1).⁹ When extrusion of molecular nitrogen from 1,2,3thiadiazole takes place, the structure immediately collapses to thiirene. Thioketene is formed in a hetero-Wolff rearrangement, possibly in a concerted process without intervention of thiocarbene.9

We choose to study 4-phenyl-1,2,3-thiadiazole (PT) and 4,5diphenyl-1,2,3-thiadiazole (DPT) precursors. The advantage of phenyl substituents over simpler groups should be the presence of red-shifted electronic transitions of intermediates facilitating their detection with time-resolved UV-vis spectroscopy. The aim of our study was to check if Scheme 1, initially proposed for MCT, can be also applied for other derivatives of 1,2,3-thiadiazoles and be a generalized scheme for such type of compound. Additionally, to the best of our knowledge, thiirenes with phenyl substituents have never been observed. The question is how phenyl substituents will affect thiirene formation and its unimolecular stability. On the basis



Scheme 1 Thiirene and thioketene formation upon photolysis of 1,2,3-thiadiazoles.

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of the studies in cryogenic matrices, electron-withdrawing groups ($CO_2C_2H_5$, CO_2CH_3 , CH_3CO , CF_3) have been proposed to stabilize the ring, by lowering the π -electron density on the carbon–carbon double bond in thiirenes.³ Indeed, methyl, carboethoxy-thiirene has been found to present a high unimolecular stability, as its decay in acetonitrile was caused by dimerization on a millisecond time scale.⁹

Photochemistry of PT and DPT has been already studied. The redistribution of a ¹³C label has been examined for 4-phenyl-[¹³C]-l,2,3-thiadiazole. Upon photolysis ($\lambda > 230$ nm in benzene or methanol) the position of a ¹³C label was completely retained in thioketene, implying that thiirene could not have been its precursor, in agreement with the proposed Scheme 1.^{10,11} The thioketene intermediates have been characterized by a weak electronic transition in the visible range $(\lambda_{\text{max}} = 624 \text{ nm}, \log \varepsilon = 2.5 \text{ for DPT}, \lambda_{\text{max}} = 596 \text{ nm for PT})$, at wavelengths below 300 nm, stronger electronic transitions are located.¹² Thioketenes possess a convenient IR marker $(\nu_{C=C=S}$ stretching vibration, in dichloromethane at 1725 cm⁻¹ for DPT, in trichlorofluoromethane at 1745 cm⁻¹ for PT).¹²⁻¹⁴ The main photoproduct of PT and DPT photolysis in benzene solution has been identified as 1,3-dithiole, while a small yield of 1,4-dithiine has been observed for DPT.^{15,16}



Stable photoproducts from photolysis of DPT and PT.

Thiirenes with phenyl substituents have not been characterized in the literature, but the intermediacy of diphenyl-thiirene has been considered in the photoreaction of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one in benzene (Scheme 2).^{17,18}

In this paper, results of transient absorption IR and UV-vis spectroscopies, supported by calculations, show that the ultrafast processes (<0.3 ps) lead to formation of thiirene or thioketene from the initially photoexcited 1,2,3-thiadiazole, allowing us to propose a general photo-dynamic scheme. To our best knowledge, this work is the first report on detection and characterization of thiirenes with phenyl substituents.

2. Experimental

PT (4-phenyl-1,2,3-thiadiazole) and DPT (4,5-diphenyl-1,2,3thiadiazole) were provided by Cayman Chemical Company. Diphenylacetylene, tetraphenyl-thiophene, acetonitrile (spectroscopic grade), chloroform (spectrometric grade), deuterated acetonitrile- d_3 (99.8 atom% D), deuterated methanol- d_1 (99.5 atom% D) and deuterated chloroform-d1 were purchased from Sigma-Aldrich and used without further purification. The ultrafast infrared laser system and broadband UV-vis femtosecond transient absorption set-up have been described elsewhere.¹⁹⁻²¹ The pump pulse energy was about 3 µJ (IR detection) and 10 µJ (UV-vis) at the sample position. The sample concentration was adjusted for an optical density of 1.0 at the excitation wavelength. A sample volume of 2 mL (IR) and 50 mL (UV-vis) was continuously circulated through the sample cell to ensure that the fresh sample was photoexcited. The entire set of pump-probe delay positions was repeated at least three times, to ensure data reproducibility. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces were analyzed by fitting to a sum of exponential terms. Convolution with a Gaussian response function was included in the global fitting procedure. The instruments response was approximately 300 fs (fwhm). All experiments were performed at room temperature.

The nanosecond UV-vis transient absorption system has been described elsewhere.²² Samples were placed in a quartz cell (10 mm \times 10 mm) at concentrations adjusted for absorption of about 1 at 266 nm excitation wavelength. The influence of sample irradiation with UV xenon light (266 nm, bandwidth 10 nm, cell with a magnetic stirrer) on stationary absorption UV-vis spectra was also checked with a Jasco V-550 spectrometer. Stationary IR spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer.

NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer (¹H 500 MHz, ¹³C 125 MHz) or 300 MHz (¹H 300 MHz, ¹³C 75 MHz) equipped with a TXI or QNP probe using standard sequences (¹H, 1D-Noesy, ¹³C), 2D ¹H⁻¹³C HSQC (Heteronuclear Single Quantum Coherence), 2D ¹H⁻¹³C HMBC (Heteronuclear Multiple Bond Correlation). Data acquisition and processing were performed with Topspin 2.1 software (Bruker). Irradiation with 254 nm light in rotating quartz



Scheme 2 Hypothetical formation and decay of thiirenes.

NMR tubes (5 mm) was achieved at 295 K with a Bioblock Scientific VL-6LC lamp (12 W). Irradiation with 313 nm light was carried out directly in the NMR tube in a home-built apparatus with a 1000 W high-pressure Hg–Xe lamp equipped with two filters: Schott 11FG09 (259 < λ < 388 nm with λ_{max} = 330 nm, *T* = 79%), and interferential one (λ_{max} = 313 nm and *T* = 16%).

DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were used to verify that stationary points obtained corresponded to the energy minima. The calculated frequencies were scaled by a factor of 0.9614.²³ The electronic spectra were computed using time-dependent density functional theory of Gaussian 03 at the B3LYP/6-311+G(d,p) level, and 20 allowed electronic transitions were calculated.

3. Results and discussion

3.1. PT

The stationary UV-vis spectrum of PT in acetonitrile is shown in Fig. S1.[†] On the basis of TD-DFT calculations (Table S2[†]), we can assume that 266 nm excitation will generate a set of highly excited singlet states. Fig. 1a shows results for PT in acetonitrile recorded by ultrafast UV-vis transient absorption spectroscopy. Initially, a broad absorption band with a maximum at 380 nm is observed, which can be assigned to PT in the singlet excited state. This band undergoes a fast decay and at delays of few ps, a band peaking at 400 nm is found. We attribute the 400 nm band to the phenyl-thiirene on the basis of TD-DFT calculations using the PCM model (402.3 nm, $S_0 \rightarrow S_1$, f = 0.1271, Table S4⁺). In a 6–50 ps time window thiirene band narrowing is observed due to vibrational cooling, at longer delays up to 2 ns the thermalized thiirene absorption band does not change shape and intensity. Fitting of kinetics of UV-vis transient absorption at selected wavelengths 350, 400, 430, and 500 nm with a double-exponential function

convolved with the instrument response function (IRF, fwhm 300 fs) yields a time-constant <300 fs and a longer one in the range 1.5-4.7 ps (Fig. S2[†]). The short component can be assigned to the lifetime of PT in the excited state, the slower one to the vibrational relaxation of nascent thiirene species. In nanosecond transient absorption studies, the thiirene band at 400 nm is also clearly observed at a delay time of 0.1 ms (Fig. 1b). On a ms time scale, the thiirene absorption band undergoes a decay, which is accompanied by a rise of a new band peaking at 350 nm and an isosbestic point at 385 nm is observed. This 350 nm absorption band corresponds to a persistent photoproduct, on the basis of stationary UV-vis absorption studies performed for irradiated solution (λ = 266 nm, Fig. S1[†]). This stable photoproduct band can tentatively be assigned to 2-benzylidene-4-phenyl-1,3-dithiole by analogy to the results reported by Kirmse and Horner (product characterized by a maximum at 354 nm with log ε = 4.33 in dioxane,¹⁵ and at 244 nm with log ε = 4.34) and in agreement with TD-DFT calculations (Tables S6 and S8⁺). To confirm the identification of the persistent product, ¹H NMR measurements were performed for an irradiated solution of PT in benzene-d₆ (λ = 254 nm). Two types of new signals appeared at 6.60 and 5.83 ppm, and at 6.54 and 5.93 ppm, with the same rate of formation (Fig. S3[†]). They were assigned to the *cis* and trans 1,3-dithiole isomers.



1,3-dithiole isomers formed upon photolysis of PT.

FT-IR measurements were also performed for the irradiated solution ($\lambda = 266$ nm) of PT in deuterated acetonitrile (Fig. S4[†]). The IR spectrum of persistent photoproducts agrees with reported IR frequencies for both isomers of 2-benzylidene-4-phenyl-1,3-dithioles (1565s, 1550m, 1480m and 1430s cm⁻¹, recorded in KBr),²⁴ in fair agreement with theoretical predictions (Tables S5 and S7[†]).



Fig. 1 Time-resolved UV-vis transient absorption spectra recorded for PT in acetonitrile after photoexcitation at 266 nm in (a) 0–100 ps (b) 0.1–90 ms time windows.



Fig. 2 Time-resolved IR transient absorption spectra recorded for PT in deuterated acetonitrile (a) and methanol MeOD (b), after photoexcitation at 266 nm.



Fig. 3 Time-resolved UV-vis transient absorption spectra recorded for DPT in acetonitrile after photoexcitation at 266 nm in (a) 0–20 ps (b) 1.3–150 ms time windows.

Since thiirene-thioketene dimerization leads to 1,3-dithiole photoproducts,⁹ one can expect to observe thioketene absorption in time-resolved studies. Phenyl-thioketene is known to show an absorption band at 596 nm measured in dichloromethane¹² at $T \sim 80$ °C (Table S10[†]). However this absorption band is weak $(n \rightarrow \pi^*$ electronic transition), and we failed to detect it in UV-vis time-resolved experiments. For thioketene detection a suitable method is the time-resolved IR spectroscopy. Phenyl-thioketene is expected to show a strong IR transition at about 1745 cm⁻¹ on the basis of the literature¹² and calculations (1739 cm⁻¹, Table S9⁺). Experiments using 266 nm excitation with IR detection for PT in acetonitrile-d₃ were performed to detect thicketene species. Fig. 2a shows that at initial delays, a positive band is present at about 1660 cm⁻¹ which can be assigned to the vibrationally hot thioketene. This species undergoes vibrational relaxation as confirmed by band-narrowing and the spectral frequency up-shift of the initial positive IR band, over a 100 ps time window (Fig. 2a). The hot thicketene shows a significant band area at early times (~1.8 ps), so RIES (rearrangement in the excited state) might be an important channel for thioketene generation. The RIES has been proposed as an important reaction channel for diazo carbonyl compounds on the basis of the significant IR band area of photoproduced hot ketene species at early delays (~1 ps), and by the observation of a "nontrappable carbene" route to rearranged products.^{25,26} Thioketenes are formed with a similar yield in CH_3OD (Fig. 2b), so this result favours an RIES process under the assumption that hypothetical thiocarbonyl carbene species can be efficiently trapped by the solvent despite the competition of a fast hetero-Wolff rearrangement process.

Femtosecond UV-vis and IR data show the presence of two competitive ultrafast reaction channels in the 1,2,3-thiadiazole excited state: formation of thiirenes and thioketenes. Note that the interpretation of time-resolved UV-vis and IR data for PT is analogous as for MCT.⁹

3.2. DPT

The extra phenyl group in DPT shifts the stationary UV-vis absorption band to longer wavelengths in comparison to that of PT. On the basis of TD DFT calculations (Table S12[†]) we can assume that 266 nm excitation results in formation of a highly excited state of DPT. Ultrafast UV-vis transient absorption measurements were performed for DPT in acetonitrile (λ_{exc} = 266 nm). At early delays a broad positive absorption band peaking at 380 nm is observed, corresponding to DPT in the singlet excited state (Fig. 3a). At longer delays a 440 nm absorption band is present, which can be assigned to diphenyl-thiirene on the basis of TD DFT calculations using the PCM model (strong transition at 482.1 nm, $S_0 \rightarrow S_1$, Table S14[†]). Analysis of kinetic traces at 380, 445 and 500 nm reveals that the best fits are found using a biexponential function

convoluted with the instrument response function (Fig. S5⁺). The fast component determined is close to IRF (~300 fs), the second component varies from 6 to 17 ps and depends on the wavelength. These two components reflect the short lifetime of DPT in the excited state and vibrational cooling of the diphenyl-thiirene, respectively. Results of nanosecond photolysis at 266 nm (Fig. 3b) reveal that in a 150 millisecond time window thiirene decay at 440 nm is accompanied by a rise of the new band at 350 nm. This 350 nm band can be assigned to a 1,3dithiole stable photoproduct on the basis of the reported absorption band with a maximum at 347 nm and log ε = 4.38 in benzene,¹⁵ and TD DFT calculations predicting a strong $S_0 \rightarrow S_3$ transition at 362.5 nm (Table S16[†]). Stationary UV-vis absorption spectra were recorded for fresh and irradiated solutions (at 266 nm, 3 min) of DPT in acetonitrile (Fig. 4). Interestingly, with no further UV irradiation, we can observe the evolution of UV-vis absorption spectra in a 30 minutes time window and the initial yellow colour of the irradiated solution disappears. There is a decay of bands at 440 nm and 270 nm (both correspond to thiirenes, Table S14⁺), and a gentle rise at 300 nm. The rising band at about 300 nm can be assigned to tetraphenyl-1,4-dithiine (in agreement with TD DFT calculations predicting a strong $S_0 \rightarrow S_3$ transition at 307.1 nm, f = 0.3132, Table S18,[†] and a reported shoulder at 310 nm in chloroform²⁷) or tetraphenyl-thiophene (its absorption spectrum is shown in Fig. S6[†]). The latter scenario can be proposed by analogy to thiirene-thiirene dimerization observed for an MCT precursor.9 The process of thiirene decay can be described by a second order reaction, the kinetic trace at 440 nm is shown in the inset of Fig. 4. Moreover, examination of UV-vis absorption spectra of irradiated DPT solution reveals a weak contribution of diphenyl-acetylene, confirmed by a characteristic band at 279 nm (Fig. 4 and S6⁺). One can assume that diphenyl-acetylene is formed upon UV-irradiation



Fig. 4 Absorption UV-vis spectrum of DPT in acetonitrile (solid black curve). UV-vis spectra (colored dashed curves) were recorded at different delays for solution irradiated with 266 nm (3 min). The inset shows the linearity of kinetic trace of 1/absorbance traced at 440 nm.

of diphenyl-thiirene (Scheme 2). The FT-IR spectrum recorded on the UV irradiated solution of DPT in a deuterated solvent is less indicative (Fig. S7[†]), because it can be potentially assigned to four species: tetra-phenyl-thiophene, diphenylacetylene, 1,4dithiine and 1,3-dithiole derivatives. The first two compounds were proposed on the basis of a comparison of the spectra of photoproducts and the authentic samples (Fig. S7[†]); for tetraphenyl-1,4-dithiine the IR bands have been reported at 1485w and 1440w cm⁻¹;²⁷ for 4,5-diphenyl-2-(diphenylmethylene)-1,3dithiole the expected frequencies should be close to those reported for 2-benzylidene-4-phenyl-1,3-dithiole, i.e. 1565s, 1550m, 1480m and 1430s cm⁻¹ in KBr.²⁴ NMR spectra of the irradiated solution of DPT in deuterated benzene (C_6D_6 , λ = 254 or 313 nm) show a complex mixture of persistent photoproducts (Fig. S8⁺). Formation of diphenyl-acetylene and tetraphenyl-thiophene was confirmed by recording NMR spectra for the authentic samples in C_6D_6 (Fig. S8⁺). Presumably NMR data for the irradiated solution show also 4,5-diphenyl-2-(diphenylmethylene)-1,3-dithiole and phenyl(2-phenylethynyl)sulfane. The presence of the latter compound can be expected, since ethynyl mercaptan was observed in photolysis of simple 1,2,3-thiadiazoles (studies in a cryogenic matrix).⁵ For tetraphenyl-1,4-dithiine NMR data are known in deuterated chloroform,²⁷ however we have not detected such signals for the irradiated solution of DPT in CDCl₃.

The above proposed formation of 1,3-dithioles requires the presence of a thioketene precursor, which undergoes reaction with thiirenes. To detect the diphenyl-thioketene absorption band, the time-resolved IR spectroscopy was used. The diphenyl-thioketene absorption band is expected at $\sim 1725 \text{ cm}^{-1}$ on the basis of reported data in dichloromethane¹² and calculations (1719 cm⁻¹, Table S19[†]). The recorded time-resolved transient absorption spectra of diphenyl-thioketene in MeOD are shown in Fig. S9.[†] Similarly as for phenyl-thioketene, thermalized diphenyl-thioketene band intensity is not sensitive to solvent (chloroform vs. methanol). One can expect a gentle decrease in the quantum yield of molecular nitrogen extrusion for DPT compared to PT, since a more complex structure and a smaller $\Delta E(S_1-S_0)$ energy gap may facilitate the internal conversion process $(S_1 \rightarrow S_0)$. However, a substantial decrease in the absorption band amplitude of thermalized diphenyl-thioketene in comparison to that recorded for phenyl-thioketene (Fig. 2b and S9^{\dagger}) is observed (factor ~4). The calculations predict a similar IR oscillator strength for both species (Tables S9 and S19⁺). A lower yield of diphenyl-thioketene formation can be explained by a lower migratory ability of phenyl substituents, when compared to those of H in the Wolff rearrangement process. This is in line with the reported decrease in 1,3dithiole formation yield upon going from PT to DPT in benzene.³ Due to the reduced yield of reaction between diphenyl-thiirene and diphenyl-thioketene, one can expect that thiirenes undergo also other reactions (self-dimerization) confirmed by detection of tetraphenyl-thiophene. Moreover, large phenyl substituents slow down diffusion of thiirenes and exert steric effects on bimolecular reactions, so thiirenes are more exposed to secondary photolysis leading to diphenylacetylene



or phenyl(2-phenylethynyl)sulfane; this hypothesis requires further investigation.

4. Conclusions

The initial stages of photoreaction in 1,2,3-thiadiazoles can be described by a general Scheme 1. The results presented in this paper have shown for the first time the presence of thiirenes with phenyl substituents in solution. Surprising unimolecular stability of these thiirene species was observed, as their decay was caused by intermolecular processes of dimerization: thiirene-thioketene (PT, DPT) and thiirene-thiirene (DPT). The presence of one or two phenyl substituents in thiirene conveniently locates its absorption at ~400 and 440 nm in acetonitrile, respectively. Diphenyl-thioketene is formed at a lower quantum yield than phenyl-thioketene, because of lower migratory ability of phenyl substituents when compared to that of H in the ultrafast Wolff rearrangement process. Photolysis of PT leads to derivatives of 1,3-dithioles, for DPT, it results in a complex mixture of persistent products such as 4,5-diphenyl-2-(diphenylmethylene)-1,3-dithiole, tetraphenylthiophene, diphenyl-acetylene and presumably phenyl(2-phenylethynyl)sulfane.

In future, we would like to study the effect of *para* substitution in a phenyl ring on 1,2,3-thiadiazoles photochemistry, using electron-donating and electron-withdrawing substituents.

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