Activation of aliphatic C-H bonds by tetracyanobenzene photosensitization. A time-resolved and steady-state investigation.

Stefano Protti,[a] Maurizio Fagnoni,[a] Sandra Monti,[b] Julien Réhault,[c] Olivier Poizat[d] and Angelo Albini[a]

[a] PhotoGreen Lab, Department of Chemistry, University of Pavia, V.le Taramelli 12, 27100 Pavia, Italy.

[b] Istituto per la Sintesi Organica e la Fotoreattività (ISOF-CNR), Via P. Gobetti 101, I-40129 Bologna, Italy.

[c] Physikalisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland.

[d] Laboratoire de Spectrochimie Infrarouge et Raman-LASIR, (UMR 8516 du CNRS), Université des Sciences et Technologies de Lille, Bat C5, 59655 Villeneuve d'Ascq Cedex, France.

**Corresponding Author, e-mail: angelo.albini@unipv.it, , tel.: +390982987316, fax: +390382987323*

SUPPORTING INFORMATION

1. UV-Vis absorption and emission spectra of TCB

2. Femtosecond absorption spectra of photoexcited TCB under different conditions and kinetic analyses of obtained data

1. UV-Vis absorption and emission spectra of TCB

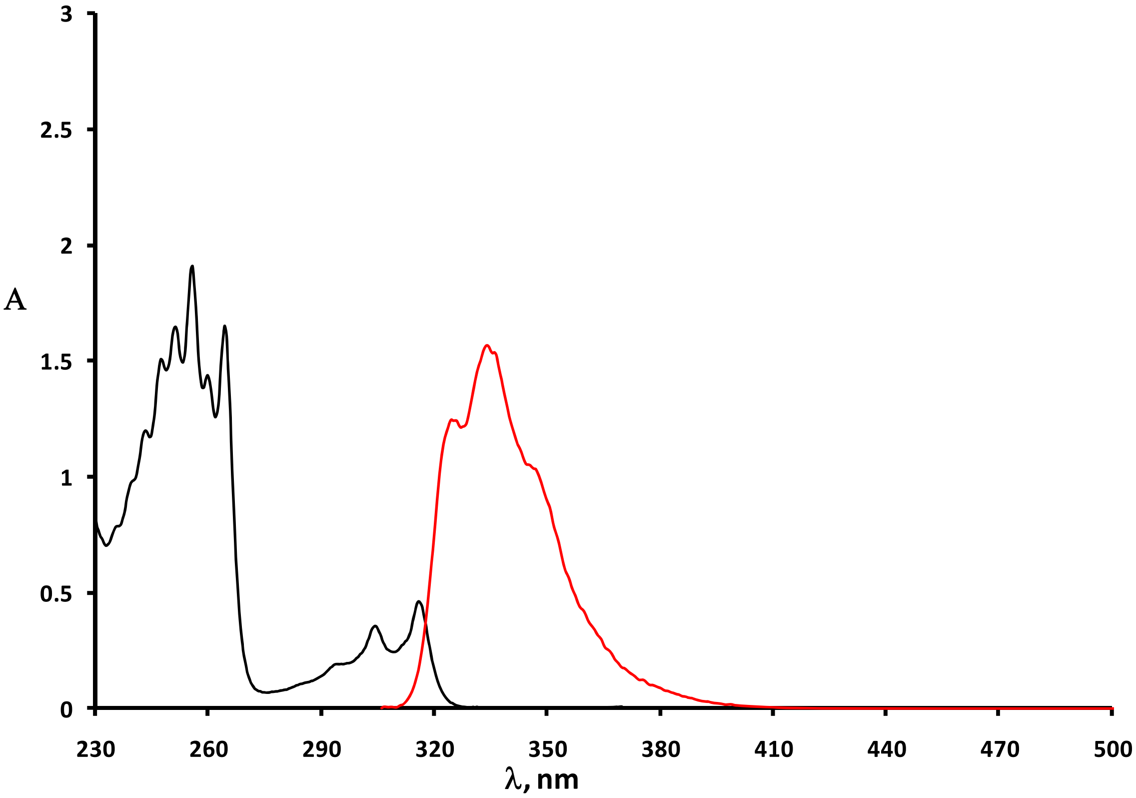

Fig. S1. UV-Vis absorption (black) and emission (red) spectra of a 1.25 x 10^{-4} M solution of TCB in MeCN. Cell path 1 cm.

2. Femtosecond absorption spectra of photoexcited TCB under different conditions and kinetic analysis of obtained data

Global kinetic analysis of the transient absorption data was performed using the commercial SPECFIT/32^{TM} program, based on the publications of A. Zuberbühler at the University of Basel, Switzerland (see refs. RS1 and RS2). The program can model the chemical kinetics of a system on the basis of multiwavelength spectrophotometric measurements performed as a function of time. Factor analysis of 3D data (absorbance, wavelength, time) is performed by singular value decomposition (SVD) for the determination of the principal spectral components that contribute in the explored wavelength window. Best fitting to a (multi)exponential kinetic model is performed by the least squares method using the Leverberg-Marquardt algorithm. The analysis affords the rate constants and the separated principal spectral components. Relative error of fit and DW parameter are used as criteria for reliability of the results. In kinetic simulations the rate constants were fixed.

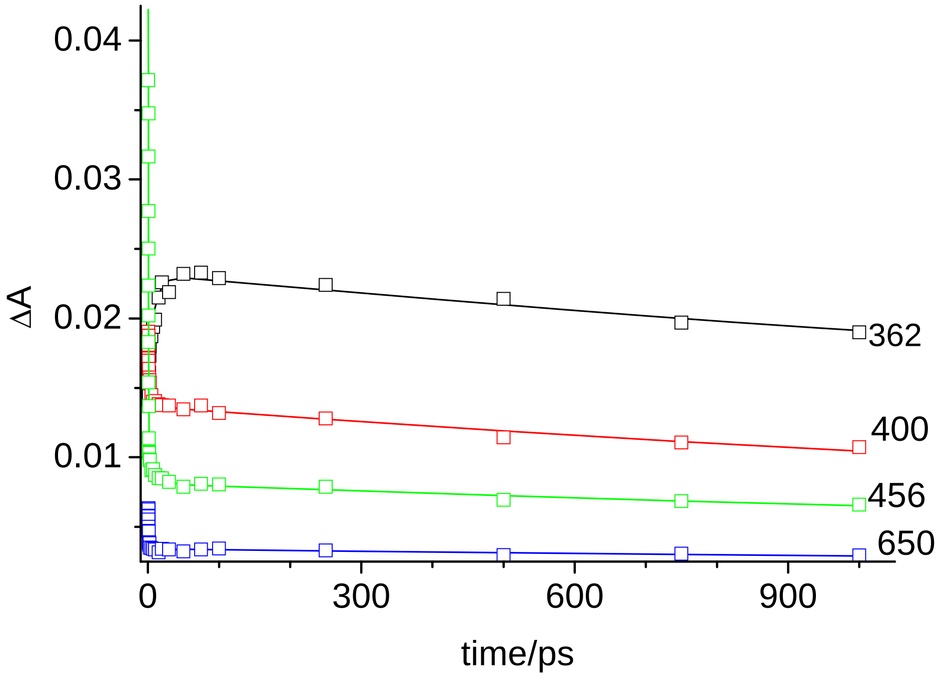

Figure S2. Reproduction of absorbance changes (symbol, exptl; line, calcd) at key wavelengths in the time window 0.650 ps -1 ns observed in TCB 7×10^{-4} M in neat MeCN, upon excitation of at 266 nm with a 70 fs laser pulse. The time constants were from Table S1 and the transient spectra were those in Figure 1a of the main text.

Transient absorption data of TCB 7×10^{-4} M, excited by a 70 fs laser pulse at 266 nm in presence of 0.5 M cyclohexane, from spectra taken at 13 different delays in the time window 50 ps-1.5 ns and in the wavelength range 350-550 nm were globally fitted with a monoexponential model ($A \rightarrow B$ with rate constant k_4). The k_4 value, representing the pseudo first order rate constant for the decay of $^1TCB_s$ (A) to $TCB^{-\cdot}$ (B), was optimized as $(5.7\pm0.3) \times 10^8$ s^{-1}, relative error of fit = 0.4%, Durbin-Watson Factor = 1.4. The starting concentration of $^1TCB_s$ was taken as 7×10^{-6} M, equal to the concentration of the excited molecules, i.e. the earlier relaxation processes were assumed to occur with unitary efficiency . The absolute $\varepsilon\times\Phi$ spectra of the A and B components were retrieved and are shown below.

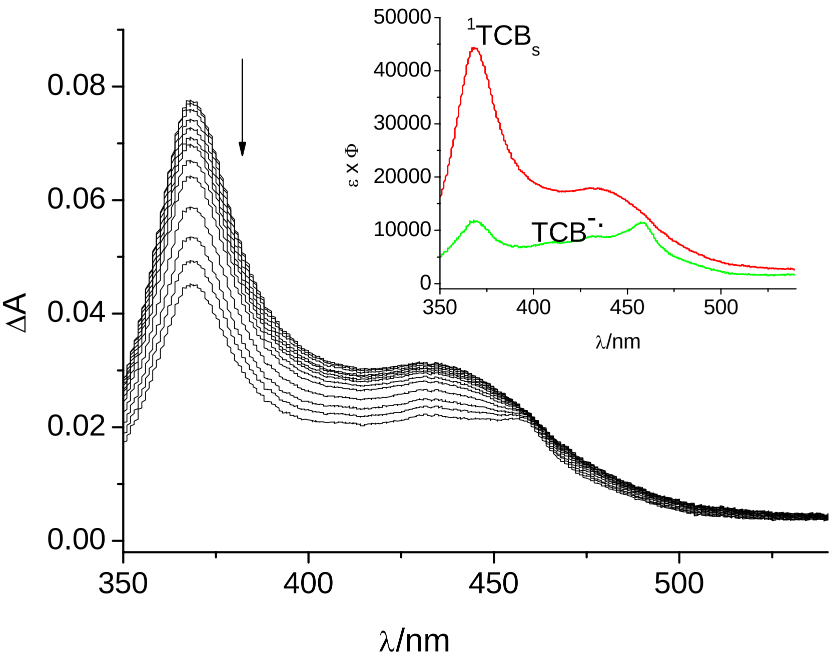

Figure S3. Difference spectra evolution of TCB in MeCN 7×10^{-4} M in presence of 0.5 M cyclohexane, upon 70 fs laser excitation at 266 nm, in the time window 50 ps-1.5 ns. Inset: $\varepsilon\times\Phi$ spectra of the involved intermediates calculated with pseudo first order rate constant $k_4 = (5.7 \pm0.3)\times10^8$ s^{-1}. Initial concentration of $^1TCB_s$ was assumed as 7×10^{-6} M . See details of the fs measurements in the Experimental.

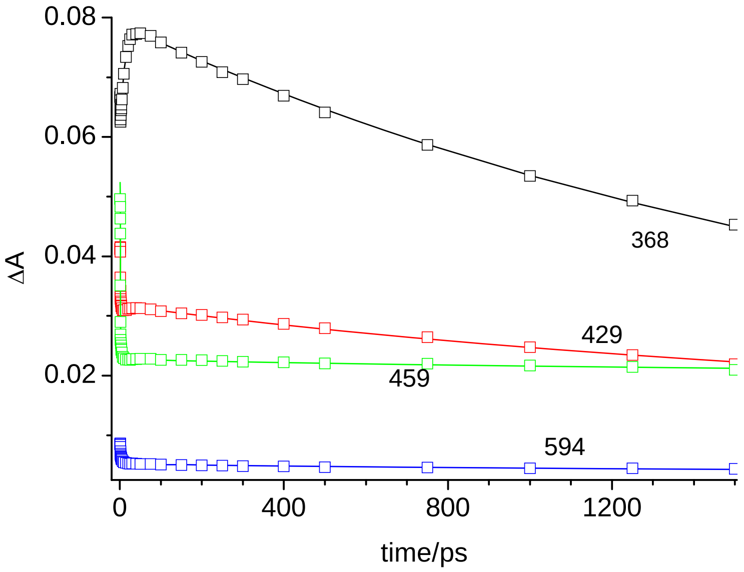

Figure S4. Reproduction of absorbance changes (symbol, exptl; line, calcd) at key wavelengths in the time window 0.65 ps -1.5 ns upon excitation of TCB 7×10^{-4} M in MeCN in presence of 0.5 M cyclohexane, at 266 nm with a 70 fs laser pulse, with the time constants of Table S1 and the spectra of Figure 2a of the main text.

.

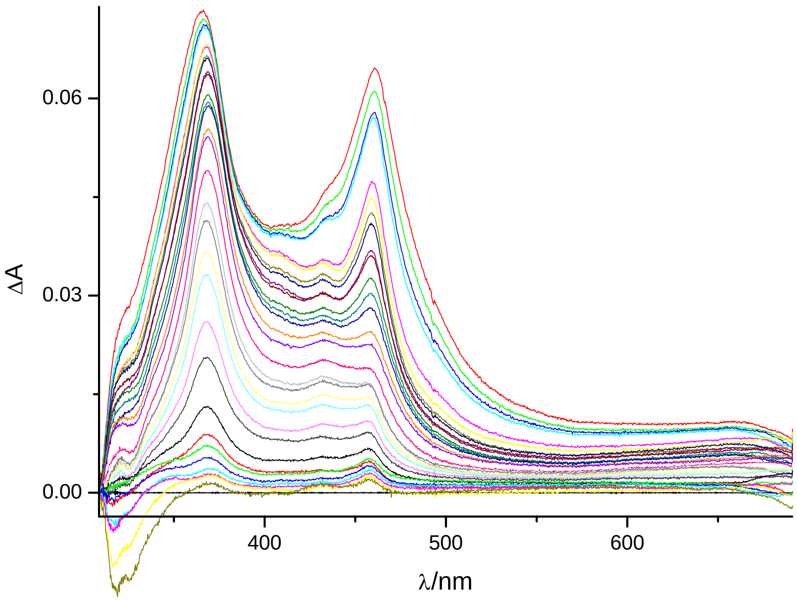

Figure S5. Difference spectra evolution of TCB in MeCN 7×10^{-4} M in presence of 0.5 M 1,4-dioxane, upon 70 fs laser excitation at 266 nm, in the time window 0.65 ps-2 ns. See details of the fs measurements in the Experimental. Notice that a negative signal under 350 nm causes distortions of the spectral profiles at long delays.

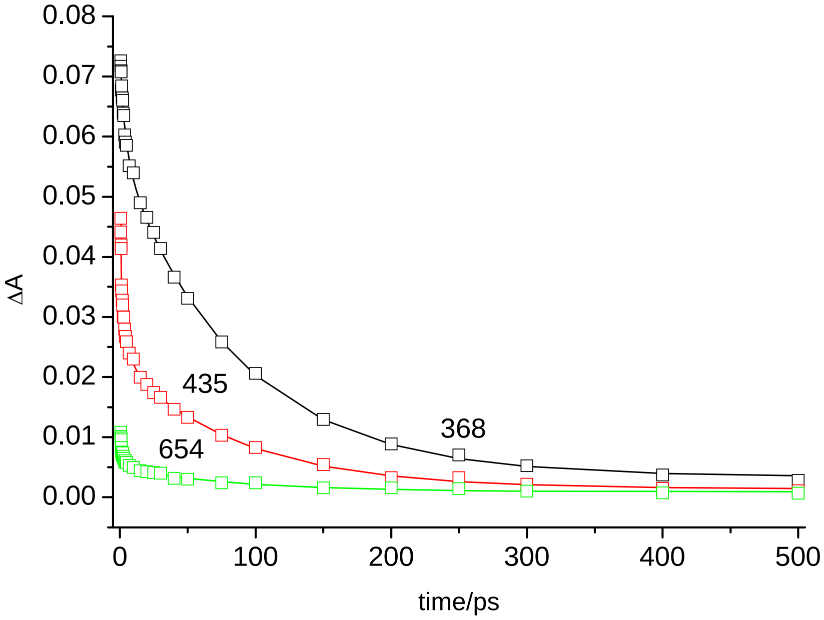

Figure S6. Reproduction of absorbance changes (symbol, exptl; line, calcd) at key wavelengths in the time window 0.65 ps -500 ps of TCB 7×10^{-4} M in MeCN in presence of 0.3 M 1,4-dioxane, upon excitation at 266 nm with a 70 fs laser pulse, with the time constants of Table S1 .

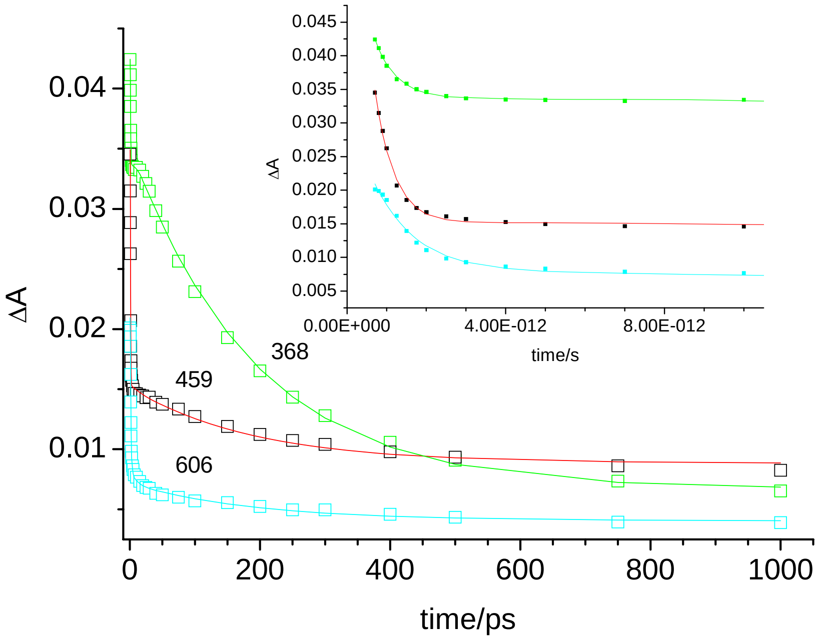

Figure S7. Reproduction of absorbance changes (symbol, exptl; line, calcd) at key wavelengths in the time window 0.70 ps – 1 ns of TCB 7×10^{-4} M in MeCN in presence of 0.2 M TEA, upon excitation at 266 nm with a 70 fs laser pulse, with the time constants of Table S1. Inset: time window 0.70 ps-10 ps.

Table S1. Kinetic parameters of absorbance changes upon 266 nm excitation of a 7×10^{-4} M solution of TCB in MeCN, analysed with a multiexponential function.

Additive	k_1 (τ_1)	k_2 (τ_2)	k_3 (τ_3)	k_4 (τ_4)
None	2.25×10^{12} s^{-1} (440 fs)	9.0×10^{11} s^{-1} (1.1 ps)	1.0×10^{11} s^{-1} (10 ps)	2.5×10^{8} s^{-1} (~4 ns)
Cyclohexane 0.5M	1.65×10^{12} s^{-1} (606 fs)	6×10^{11} s^{-1} (1.7 ps)	8.7×10^{10} s^{-1} (11 ps)	5.7×10^{8} s^{-1} (1.7 ns)
Dioxane 0.3M	2.13×10^{12} s^{-1} (470 fs)	1.94×10^{11} s^{-1} (5.2 ps)	1.15×10^{10} s^{-1} (87 ps)	
TEA 0.2 M	1.9×10^{12} s^{-1} (526 fs)	1.05×10^{12} s^{-1} (0.95 ps)	1.2×10^{11} s^{-1} (8.3 ps)	5.9×10^{9} s^{-1} (170 ps)

References

RS1. Harald Gampp, Marcel Maeder, Charles J. Meyer, and Andreas D. Zuberbühler "Calculation Of Equilibrium Constants From Multiwavelength Spectroscopic Data I. Mathematical Considerations", Talanta, 1985, 32, 95-101.

RS2. Harald Gampp, Marcel Maeder, Charles J. Meyer, and Andreas D. Zuberbühler "Calculation Of Equilibrium Constants From Multiwavelength Spectroscopic Data II. SPECFIT: Two User Friendly Programs In BASIC And Standard FORTRAN 77", Talanta, 1985, 32, 257-264.