

Supplemental data

Caption of figures:

Figure A. Photoisomerization of **6**. (a) Insert: photoisomerization of a 2-methylpentane (MP) solution of *E*-**6** at 273K with >280 nm light (0, 40, 80, 160, 320, 640 and 1280 sec, curves 1-7). Figure a: the above irradiated solution was cooled to 80K and irradiated with >280 nm light and spectra recorded at 0, 160, 320, 640, 1280, 2560 and 5120 sec of irradiation (curves 1-7). Figure b: The difference spectra from those of part a. Insert, the absorption spectra of the photoproduct before (curve 1) and after (curve 2) warming to 273K and re-cooling to 80K.

Figure B. Photoisomerization of isomers of **7**. (a) Irradiation of trans-**7** in MP at 273K (0, 10, 20, 40, 80, 160, 320, 640, and 1280 sec, curves 1-9); (b) the above mixture was cooled to 80K and irradiated with >280 nm light (0, 80, 160, 320, 640, 1280 and 2560 sec, curves 1-7) with >310 nm light. Insert in (a): changes in absorbance at 300 nm of the trans (triangles) and at 307 nm of the cis (circles) during irradiation at 80K. Insert in (b): effect of warming on the absorption spectrum of the photoproduct. Absorption spectra of trans-**7** in the dark (curve 1), photoproduct from trans-**7** produced at 273K (curve 2), photoproduct from curve 2 produced at 80K (curve 3), and the sample after warming and re-cooling to 80K (curve 4). All four spectra were measured at 80K.

Figure C. Photoisomerization of isomers of 2,2',4,4'-tetramethylstilbene **8**. (a) Changes in UV absorption spectra during irradiation (>280 nm) of cis-**8** in MP glass at 80K (0, 160, 320, 640, 1280, 2560, 5120, and 10240 sec, curves 1-8). The absorption spectrum of trans-**8** is also shown (curve 9); (b) the difference spectra ( $t - t_0$ ) of part a. Insert: changes of absorbance at 316 nm during irradiation of the trans (circles) and the cis (triangles) isomers in low temperature glass showing the low reactivity of the trans.

Figure D. Photoisomerization of *trans*-**11**. (a) Difference spectra from irradiating an iP solution of *trans*-**11** at 273K with >310 nm light,  $t = 60, 180, 360, 600, 840, 1320, 1800$  and 2520 sec. (b) Difference spectra from low temperature (80K) irradiation of the final mixture of part a with light >310 nm,  $t = 60, 240, 480, 720, 960, 1200, 1680, 2160$  and 2640 sec. Insert in (a): absorbance changes at 293 nm during irradiation at 273K (triangles) and at 252 nm during irradiation at 80K (squares). Insert in (b): absorption spectra of the photoproduct before (green) and after (red) warming up at re-cooling to 80K.

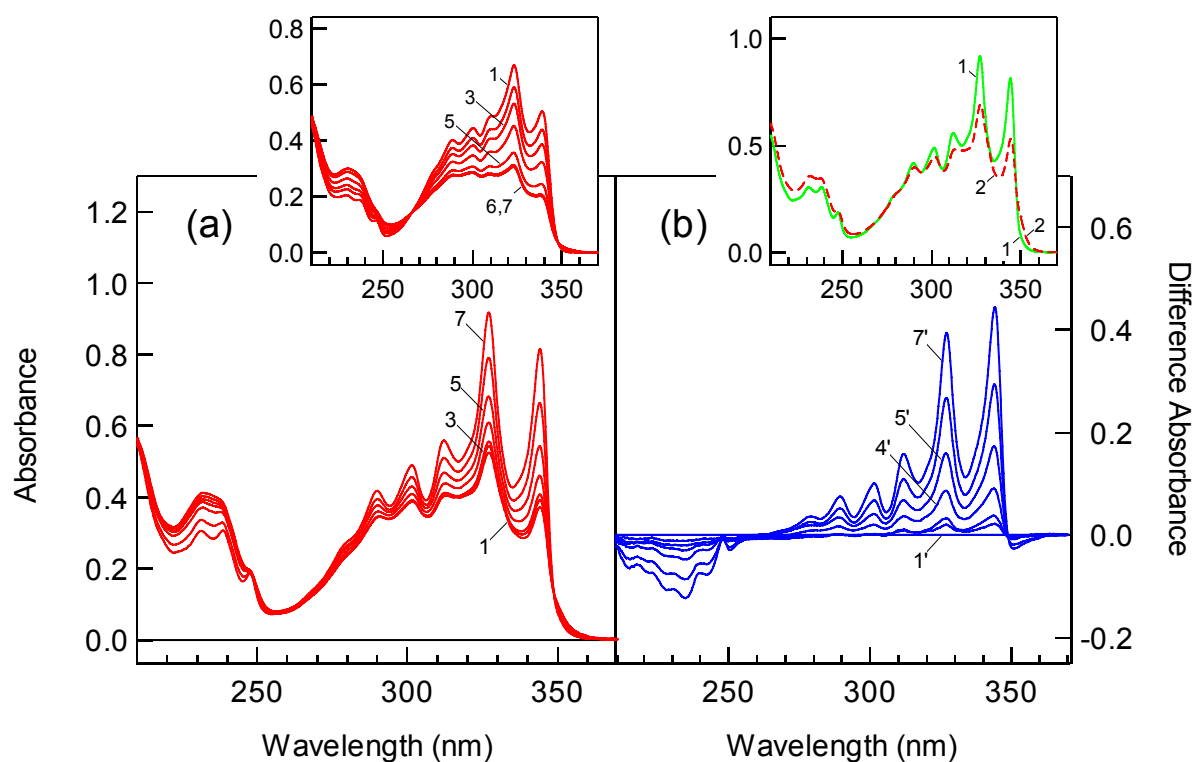


Figure A

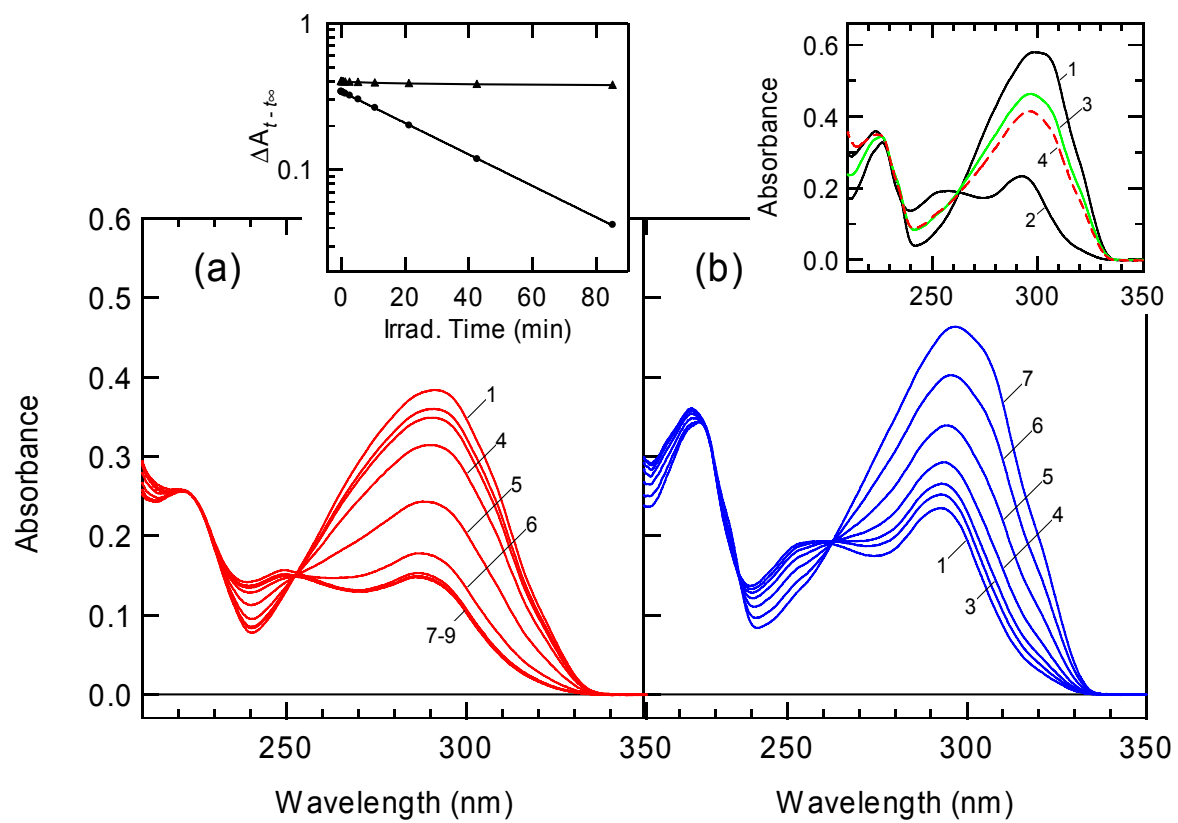


Figure B

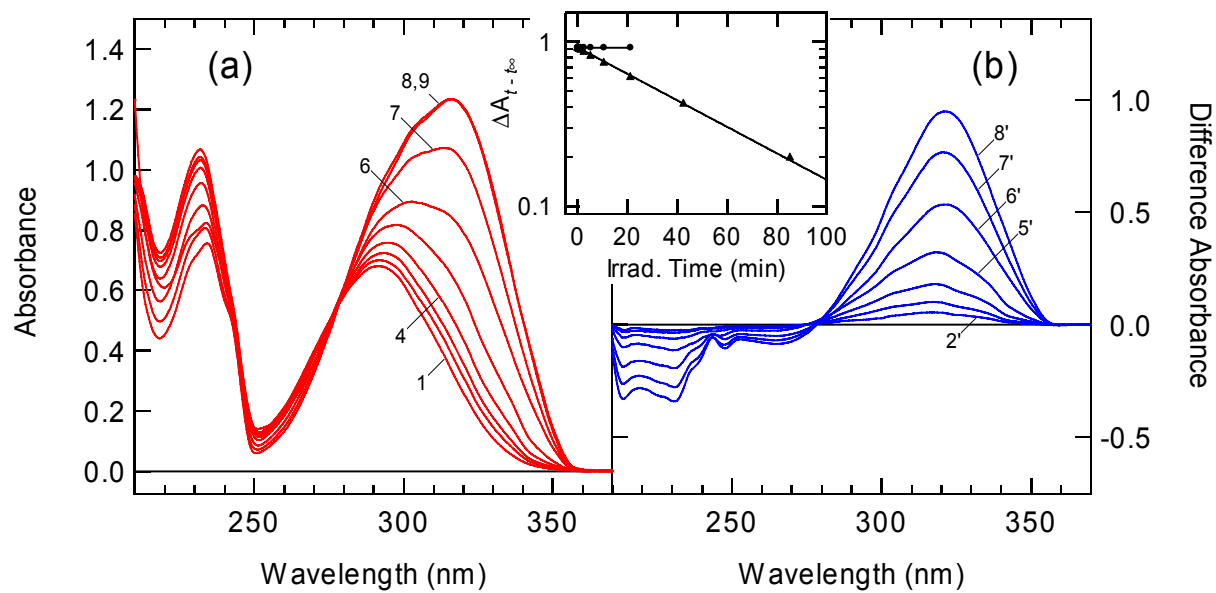


Figure C

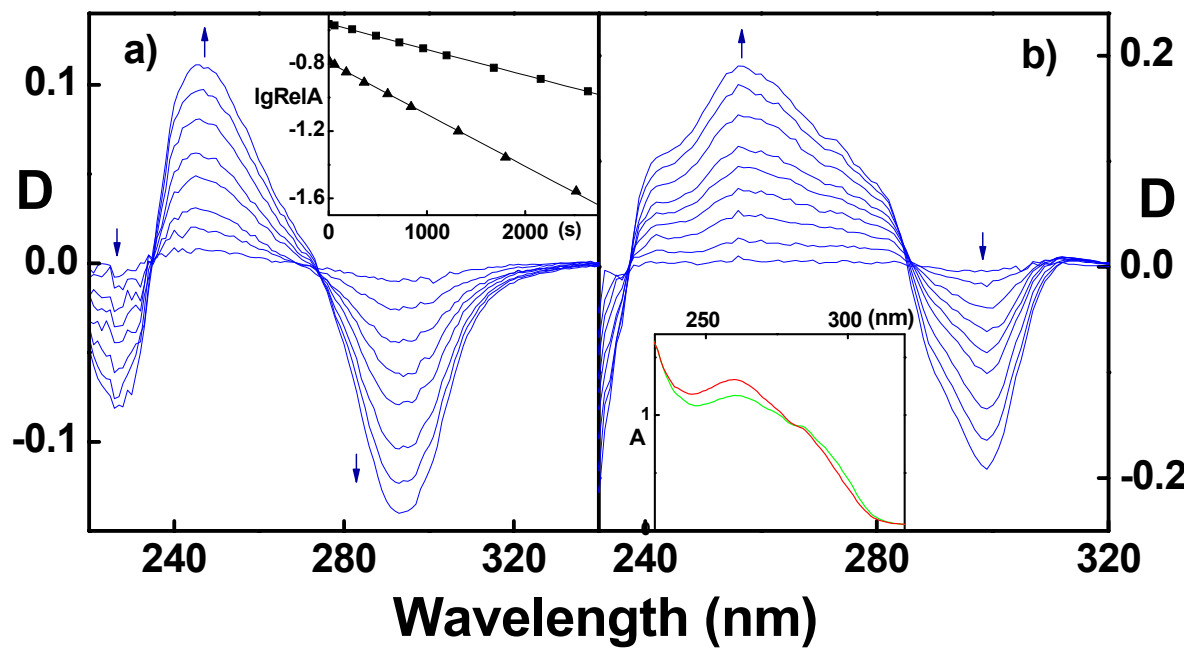


Figure D