



Photoprocesses of bis-diaminobenzylidenecyclobutanone upon nanosecond laser excitation

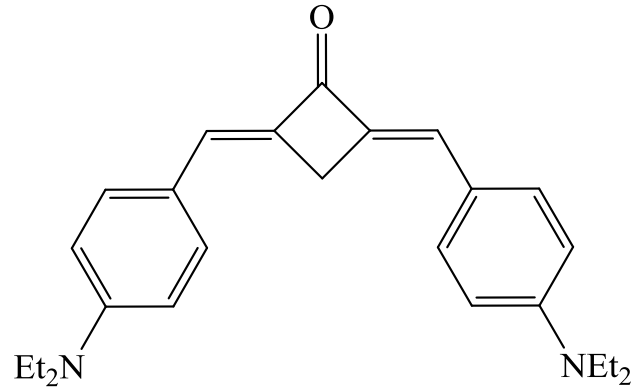
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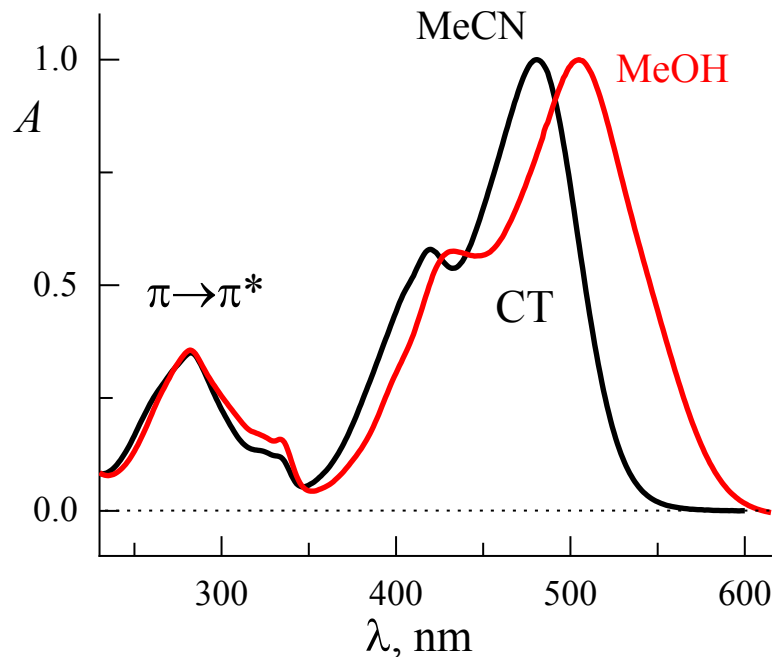
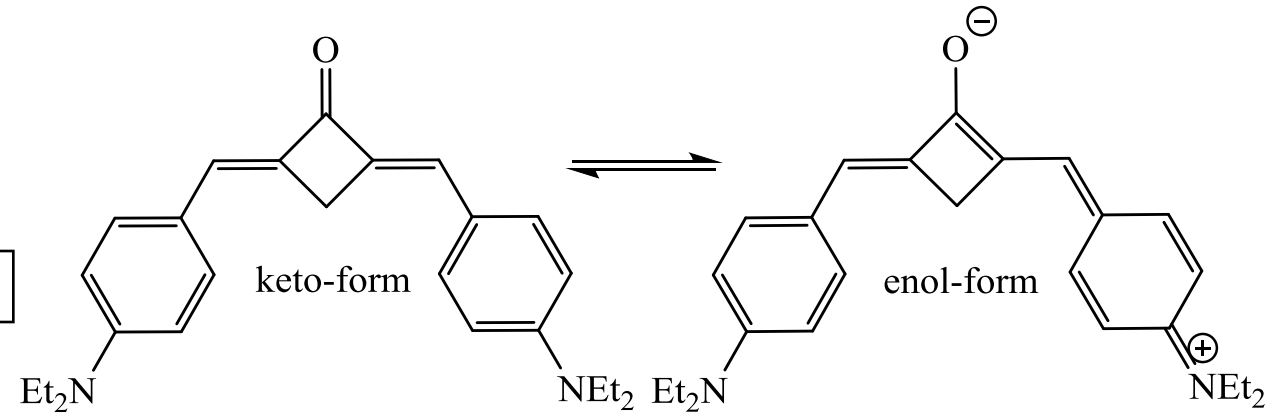
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Absorption



2,4-bis-(diethylaminobenziliden)cyclobutanone (**DACB**)



The band at 210-350 nm in absorption spectrum is due to $\pi \rightarrow \pi^*$ transition which is typical for aromatic ketones. The band at 480-600 nm is assigned to the charge transfer (CT) state of the carbonyl group.

In solution the ketocyanine dyes exist in equilibrium between enol- and keto-form that depends on the solvent properties. The keto-form dominates mostly in aprotic solvents; whereas in proton-donating solvents the keto-form presents as charge-separated (enol-) form of dyes.

Fig. 1. Absorption spectra of DACB in acetonitrile and methanol.

Flash photolysis

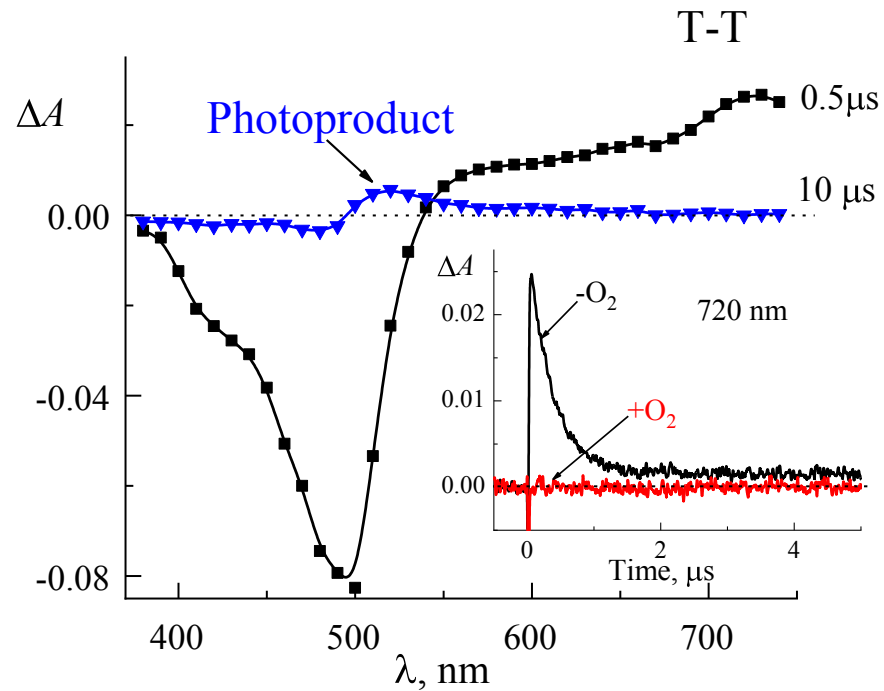


Fig. 3. Transient absorption spectra of DACB in oxygen-free acetonitrile at 0.5 and 10 μs after the laser pulse (354 nm). Insert: decay kinetics of oxygen-free and air-saturated solution at 720 nm.

Upon laser pulse irradiation of oxygen-free solutions of DACB in acetonitrile, short-lived reversible changes in absorption were observed. The short-lived band at 720 nm is due to T-T absorption, whereas in air-saturated solutions the shortening of the lifetime was observed. The absorption band at 520 nm belongs to stable photoproduct.

Laser irradiation of oxygen-free solution in methanol resulted in an increase of the lifetime of the triplet from 3,5 μs in acetonitrile to 15 μs in methanol and expected photoproduct was not observed.

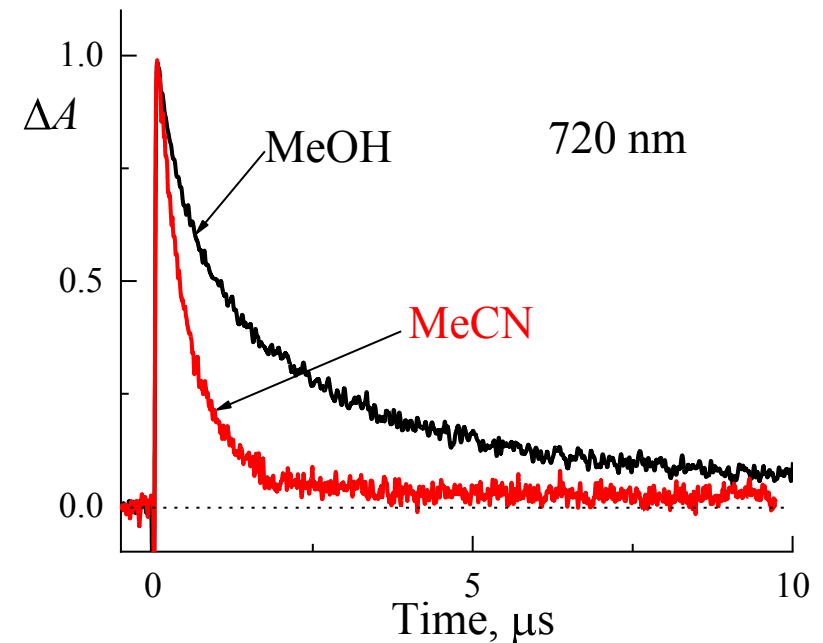


Fig. 4. Decay kinetics of triplet of DACB in MeOH and in MeCN at 720 nm.

T-T Energy transfer

The decreasing of DACB triplet lifetime in the presence of tetracen as a triplet energy acceptor was found.. The appearance of the T-T absorption of tetracen at 460 nm confirmed the energy transfer.

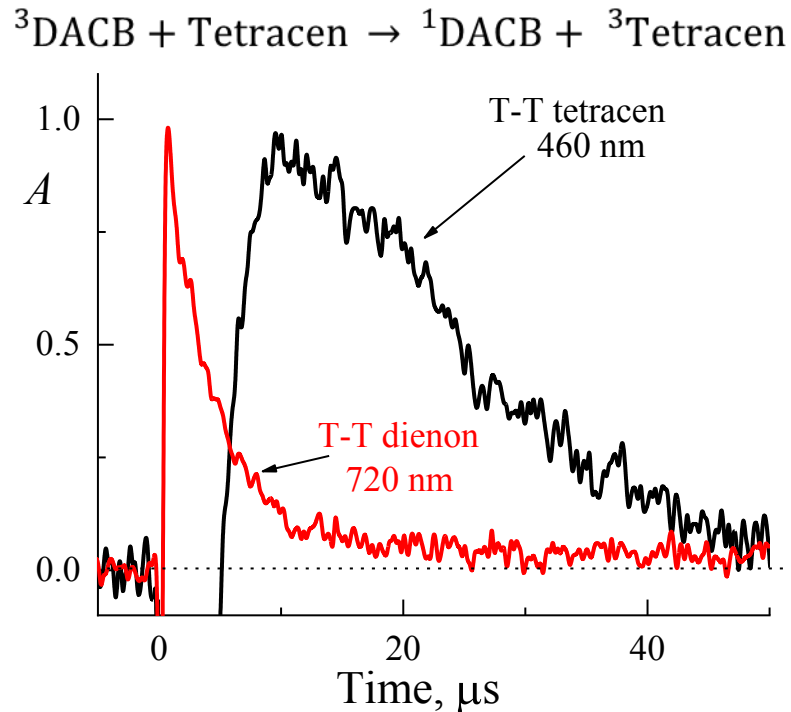
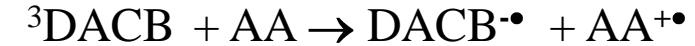


Fig. 5. The decay kinetics of DACB triplet at 720 nm. The kinetics of formation and decay of tetracen triplet at 460 nm in MeCN.

Electron transfer

Photoreduction of DACB by ascorbic acid (AA)



Photooxidation of DACB by *para*-nitroacetophenone (*p*-NAP)

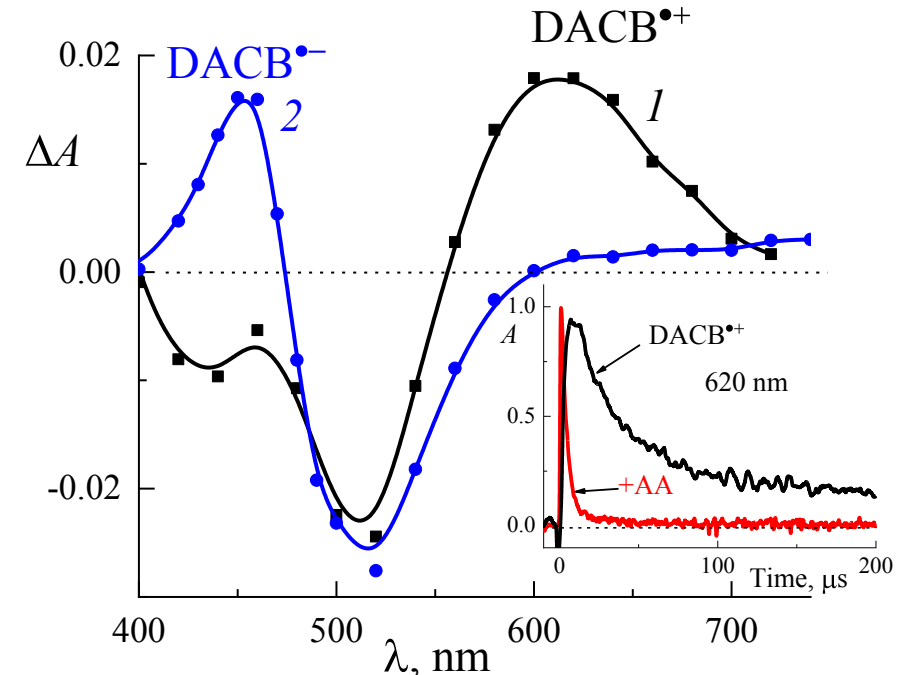
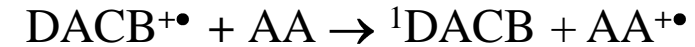
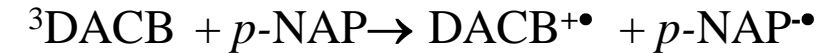


Fig. 6. Transient absorption spectra of DACB ($1 \cdot 10^{-4}$ mol/L) in oxygen-free methanol in the presence of both ascorbic acid ($5 \cdot 10^{-4}$ mol/L) (1) and *p*-NAP ($2 \cdot 10^{-5}$ mol/L) (2) at 20 μs after the laser pulse. Inset: decay kinetics of $\text{DACB}^{\bullet+}$ in the absence and presence of AA ($5 \cdot 10^{-5}$ mol/L) at 620 nm.

The DACB was found to participate in the redox photoreaction proceeding via the transient species as the dye triplet, both radical anion ($\tau = 3 \cdot 10^{-4}$ s) and radical cation ($\tau = 5 \cdot 10^{-5}$ s).

Photoproduct formation

Continuous irradiation

Upon irradiation of a DACB solution in toluene with light varied in the range 420-480 nm, the changes in the absorption spectrum associated with the formation of a photoproduct were observed. However, subsequent irradiation of the photoproduct at (>515 nm) resulted in the restoration of the principal absorption band.

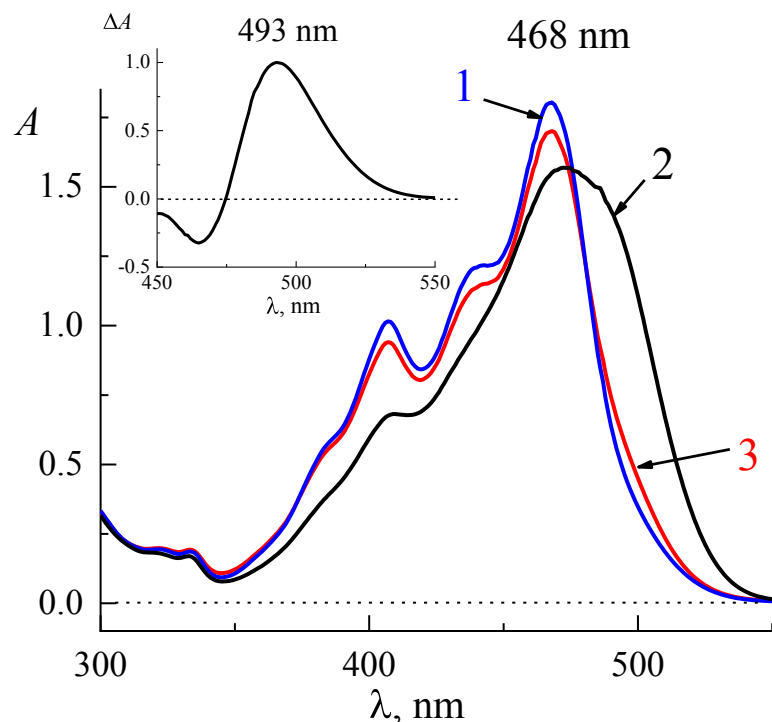


Fig. 7. Absorption spectra of DACB in toluene before (1) and after (2) irradiation at 420 - 480 nm, and as well as after subsequent irradiation at >515 nm (3). Inset: the difference absorption spectrum between spectra 2 and 1 (absorption spectra of photoproduct)

Pulse laser irradiation

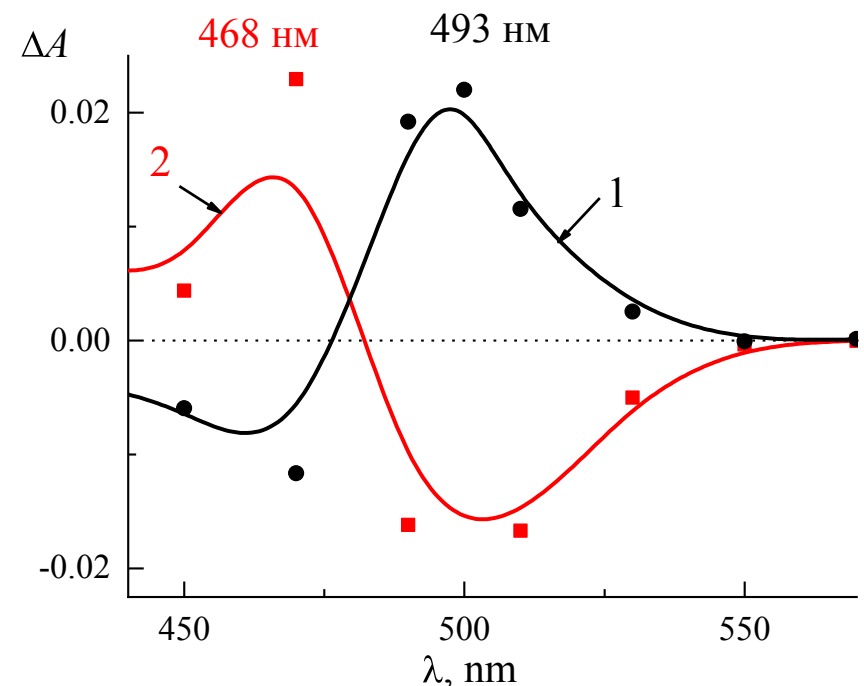


Fig. 8. Transient absorption spectra of DACB in toluene at 3 μs after laser pulse at 354 nm (1) and at subsequent laser pulse at 532 nm (2).

The laser irradiation at 354 nm resulted in the formation of a stable product at 493 nm. The subsequent laser irradiation at 532 nm in the absorption region of the photoproduct gives rise to formation of the initial diene at 468 nm.

Conclusion

1. 2,4-bis-(diethylaminobenziliden)cyclobutanone undergoes intersystem crossing with triplet lifetimes is 3.5 – 15 μ s.
2. The triplet-triplet energy transfer between 2,4-bis-(diethylaminobenziliden)cyclobutanone and tetracen was established.
3. Dienone is involved in the redox photoreaction which occurs via several intermediates such as the dye triplet, the radical anion ($\tau = 3 \cdot 10^{-4}$ s), and the radical cation ($\tau = 5 \cdot 10^{-5}$ s)
4. Upon both continuous and the laser pulse irradiation the formation of long-lived product was observed that demonstrating the photoinduced conversion into the initial dienon.

Acknowledgements

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