

Efficient ultraviolet-light energy dissipation by an aromatic ketone†

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Experimental evidence on the efficiency of 2,2',4,4'-tetramethoxybenzil for UV-light energy dissipation is provided. This non-phenolic aromatic ketone has a low energy triplet which quickly decays to the ketone ground state, thus avoiding the generation of undesirable reactive species.

Compounds showing an optimal ultraviolet (UV) spectral performance and low capacity as photosensitisers can dissipate UV-light energy, thereby protecting living organisms and materials from the harmful effects of UV radiation of sunlight.¹ These compounds, termed photostabilisers, can provide photoprotection by competitive energy absorption of UV photons. They should have an efficient mechanism for light energy dissipation, *i.e.* exceptionally low quantum yield of photochemical reaction,^{2–4} bypassing potential reactive triplet excited states. However, their triplet excited state can be generated by means of energy transfer from an electronically excited triplet donor.⁵ As a consequence, those compounds show a diminished photoprotective capacity.

Aromatic ketones are good UV-absorbers, but they are usually photolabile due to an enhanced spin–orbit coupling between the $\pi\pi^*$ and $n\pi^*$ states, resulting in an efficient singlet–triplet intersystem crossing. In addition, the usually high energy of their triplet excited state allows them to photosensitise the transformation of many compounds by triplet energy transfer.⁶

Moreover, the triplet excited state can efficiently abstract hydrogen *via* a direct hydrogen abstraction process (from good hydrogen donors such as methanol and alkanes) or *via* a coupled electron–proton transfer process (fenol and indoles); in both cases, reactive radicals are generated. Furthermore, aromatic ketone triplets can promote degradation of materials due to photosensitised generation of singlet oxygen.⁷

Herein, we report the photophysics and the photostability of 2,2',4,4'-tetramethoxybenzil (TMBZ,⁸ Chart 1). The results demonstrate that this aromatic ketone efficiently dissipates UV-light energy due to the extremely short lifetime of its

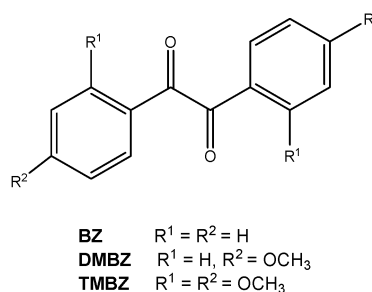


Chart 1 Structures of the benzils.

triplet excited state, which rapidly decays back to the ground state. For comparison, the photobehaviour of analogous compounds, benzil (BZ) and 4,4'-dimethoxybenzil (DMBZ), is included.

There is much evidence demonstrating that, in the solid state,⁹ in solution, and in the gas phase, benzil has a skew structure, in which the phenyl rings are nearly coplanar with the carbonyl groups and the two benzoyl units lie in planes approximately at right angles. Similarly, the *para*-substituted analogue 4,4'-dimethoxybenzil (DMBZ) possesses a structure with almost planar benzoyl groups (carbonyl phenyl ring dihedral angle of 4.21°).¹⁰ X-Ray analysis of crystals of a sample of 2,2',4,4'-tetramethoxybenzil showed that it also possesses a skewed structure in the solid state (Fig. S1 and S2 in ESI†).‡ A similar arrangement of molecular planes to that of TMBZ has been found for most benzil derivative structures containing at least one non-substituted *ortho* position (see data in ESI†).

The absorption spectrum of BZ was performed in dimethylformamide (DMF), methanol, and acetonitrile (Fig. 1 and Fig. S3 in ESI†). In acetonitrile, it shows a weak signal at around 370 nm and a strong band at 260 nm (Fig. 1).¹¹ These bands are ascribed to the S₁($n\pi^*$) and S₂($\pi\pi^*$) transitions, respectively. The low molar absorption coefficient of the band at 370 nm indicates its forbidden character. By comparison, *para*-alkoxybenzils have also one absorption band in the ultraviolet (see Fig. 1 for DMBZ), while *ortho*- and *meta*-substituted analogues exhibit two main peaks.¹² The UV spectrum of TMBZ consists of two main peaks at 275 nm and 310 nm in acetonitrile (Fig. 1).¹³ The excitation spectrum (measured at the maximum emission wavelength, λ_{em}) confirmed that the emission band ($\lambda_{max} = 550$ nm, see below) is not related to the strong absorption at λ_{max} *ca.* 310 nm (π,π^* transition) but to a weak absorption located close to 370 nm which is partially overlapped by the high-intensity

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† Electronic supplementary information (ESI) available: X-Ray data for TMBZ and additional UV-visible spectra. CCDC 743200. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915792a

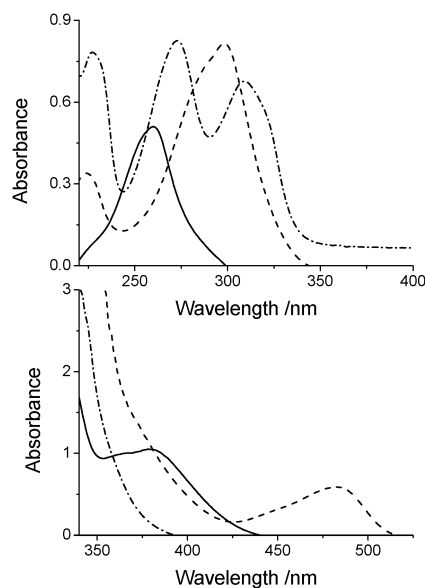


Fig. 1 UV-Vis spectra in acetonitrile of BZ (—), DMBZ (---) and TMBZ (---): (up) 42 μM (BZ), 74 μM (DMBZ), 75 μM (TMBZ) and (down) 1.4 mM (BZ), 1.6 mM (DMBZ), 1.0 mM (TMBZ).

π, π^* band. This absorption can be safely assigned to the n, π^* transition by comparison with that of BZ (Fig. S4 in ESI†).

It has been reported that benzil photoabsorption and emission spectra are consistent with a mechanism involving molecular reorientation,^{14,15} *i.e.* photoexcitation of benzil causes a change from its normal skew configuration into one in which the dicarbonyl system becomes coplanar while it is in the excited singlet state. As a consequence photoemission (both fluorescence and phosphorescence) takes place from this configuration. In the emissive states (S_1 and T_1 of $n\pi^*$ nature), the carbonyl groups are in a coplanar *trans* orientation and the phenyl groups are out of the dicarbonyl plane.

The emission spectra ($\lambda_{\text{exc}} = 320$ nm) of BZ in acetonitrile consists of a fluorescence band ($\lambda_{\text{max}} = 500$ nm) and a phosphorescence band ($\lambda_{\text{max}} = 560$ nm) attributed to the relaxed near *trans*-planar form of BZ (Fig. 2). Similarly, the corresponding DMBZ emission maxima are located at *ca.* 500 nm and 550 nm (Fig. 2). The emission yield decreased in the order $\text{BZ} \gg \text{DMBZ} > \text{TMBZ}$ (see Fig. 2, samples with the same absorbance $A = 0.1$, $\lambda_{\text{exc}} = 320$ nm). From the TMBZ phosphorescence spectrum an energy of *ca.* 53 kcal mol⁻¹

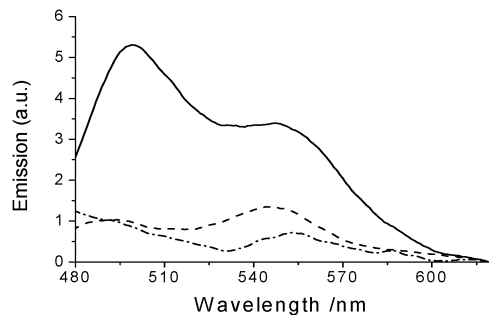


Fig. 2 Emission spectra of BZ (—), DMBZ (---) and TMBZ (---) in CH_3CN ($\lambda_{\text{exc}} = 320$ nm, $A_{320} = 0.1$).

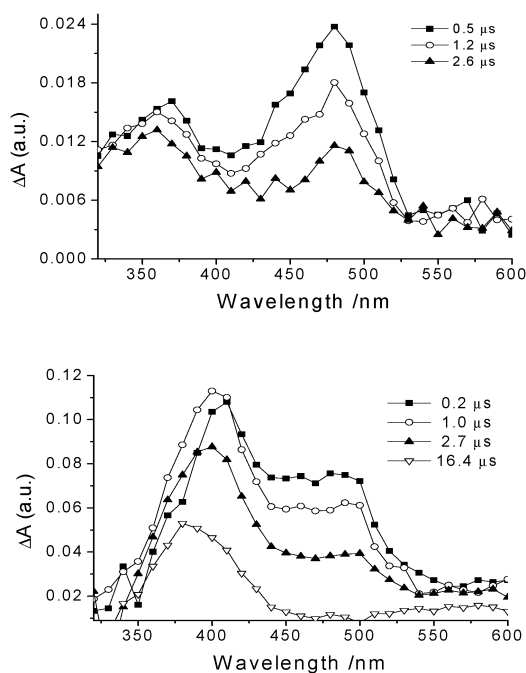


Fig. 3 Transient absorption spectra of BZ (top) and DMBZ (bottom) in deaerated DMF ($\lambda_{\text{exc}} = 355$ nm, $A_{355} = 0.3$).

was estimated for its lowest-lying triplet excited state. This value is similar to that already reported for BZ and DMBZ.¹⁴

The low fluorescence quantum yield of benzil is mainly due to the close proximity of the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ excited states, favouring singlet–triplet intersystem crossing. Transient absorption experiments (Nd:YAG, 355 nm, 10 ns pulse) were performed to compare the spectral features of BZ triplet with that of TMBZ triplet. Fig. 3a shows that the BZ spectra in DMF have two peaks at 360 nm and 480 nm. The peak at 480 nm is attributed to the triplet–triplet absorption of BZ¹⁶ (lifetime of 2 μs). In a weak hydrogen donor solvent, such as acetonitrile, the absorption at 360 nm would be ascribed mainly to the benzoyl radical arising from carbonyl α -cleavage. However, BZ ketyl radicals, absorbing in the same region, would also be generated in methanol or DMF.^{17,18} For comparison, the transient absorption spectra of DMBZ in DMF showed two bands at λ_{max} 490 nm and 400 nm (Fig. 3b). The former can be assigned to the DMBZ triplet, while the latter should be attributed to *para*-methoxybenzoyl and DMBZ ketyl radicals. Interestingly, even in a hydrogen-donor solvent such as methanol, no transients were detected in the case of TMBZ (see Fig. S5† for results in acetonitrile).¹⁹

In the case of BZ, intersystem crossing from the singlet excited state to the triplet excited state is virtually complete in fluid solution.²⁰ Formation of a fast-decaying triplet excited state could be responsible for the non-detection of any transient after laser irradiation of TMBZ. Therefore, triplet photosensitization experiments were carried out using 2-benzoylthiophene ($E_T = 63$ kcal mol⁻¹)²¹ and benzophenone ($E_T = 69$ kcal mol⁻¹)²² as the triplet photosensitisers. Indeed, both triplet excited states were quenched²³ but no transients were detected in either case.

In addition, TMBZ failed to produce pyrene triplet ($E_T = 48$ kcal mol⁻¹)²² *via* triplet–triplet photosensitization

in acetonitrile. These results are of high relevance in the context of the photoprotecting capacity of TMBZ. In fact, upon prolonged irradiation ($300 < \lambda < 360$ nm, 3 h) of an air-equilibrated DMF solution of tryptophan methyl ester (Trp-Me, 10 mM) and TMBZ (10 mM), no photoproducts were detected by GC-MS analysis. By contrast, BZ photosensitised Trp-Me transformation.

Therefore, TMBZ appears to possess the features for an efficient dissipation of UV-light energy *via* the collaborative action of different processes, such as (i) competitive energy absorption of UV photons, (ii) fast-decay of its triplet excited state to the ground state, and (iii) energy transfer to its low energy excited triplet state, which quickly dissipates the energy.

The different behaviour between BZ and TMBZ could be explained if we take into account that while benzil possesses rotationally flexible freedom around the adjacent bonds to the carbonyl groups, which allows a relatively long-lived triplet excited state with the relaxed *trans*-planar conformation, steric hindrance caused by the methoxy groups at the *ortho*-position of the TMBZ could derive in a short-lived triplet.

Steady-state irradiation studies using different light sources (A: $360 < \lambda < 300$ nm and B: $380 < \lambda < 320$ nm) concurred with the above-mentioned results. Thus, BZ underwent considerable photodegradation, mainly in DMF, both in the presence and in the absence of oxygen (Fig. S6 in ESI†). By contrast, TMBZ remained unchanged under the same conditions (Fig. S6 in ESI†). Even GC-MS analysis confirmed TMBZ photostability (no photoproducts were detected in DMF (10 mM), acetonitrile (10 mM), methanol (1 mM), see Fig. S7 in ESI†). In addition, no photoproducts were detected after three hours irradiation of TMBZ in toluene.

In summary, the fast decay of the triplet excited state of TMBZ to the ground state allows efficient light-energy dissipation, which avoids (i) its photodegradation, and (ii) its being an efficient triplet photosensitiser. In addition, the low-energy of the TMBZ lowest-lying excited states converts this broadband UV-absorber into a light energy sink for many excited molecules. All these facts make TMBZ a promising UV-absorber with excellent properties to inhibit the photodegradation of (bio)molecules and materials.

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Notes and references

† *Crystal data for TMBZ*: colourless prism grown by evaporation of CH_2Cl_2 , $0.38 \times 0.22 \times 0.20$ mm size, monoclinic, $P2_1/c$, $a = 8.4629(17)$, $b = 11.351(2)$, $c = 18.242(4)$ Å, $\beta = 113.15(3)^\circ$, $V = 1611.2(7)$ Å³, $Z = 4$, $\rho_c = 1.362$ g cm⁻³, $\mu = 0.103$ mm⁻¹,

$\theta_{\text{max}} = 32.34$, Mo-K α ($\lambda = 0.71073$ Å), ω -scan, diffractometer Oxford Gemini, $T = 120(2)$ K, 32 390 reflections collected, 5476 independent reflections ($R_{\text{int}} = 0.0431$), multi-scan absorption correction ($T_{\text{min}}/T_{\text{max}} = 0.949/0.980$), direct primary solution, refinement on F^2 (SHELXS-97, SHELXL-97, G.M. Sheldrick, U. of Göttingen, 1997), 221 refined parameters, Methyl groups hydrogen atoms refined as rigid, others riding, $R_1[I > 2\sigma(I)] = 0.0382$, $wR_2(\text{all data}) = 0.0946$.

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