Triplets, hydrogen adduct radicals and radical anions of benzil and 2,2'-dichlorobenzil

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Abstract. From flash photolysis data of benzil and 2,2'-dichlorobenzil, the role of conformeric triplets in the formation of hydrogen adduct radicals has been discussed. The planar relaxed triplet absorbing at 470 nm is less efficient in forming a hydrogen adduct radical as compared to its puckered conformeric partner. Among the hydrogen donors, triethyl amine and isopropanol, the former is more efficient in converting puckered triplets and less efficient in the case of planar conformers. Absorptions of radicals and radical anions of 2,2'-dichlorobenzil appear at 355 nm and 460 nm respectively. These are blue-shifted as compared to those of the parent compound benzil appearing at 370 nm and 540 nm, respectively. This blue-shift has been discussed in terms of steric hindrance due to ortho-substitution.

Keywords. Laser flash photolysis; triplet and radical conformation; radical anions; aromatic α-dicarbonyls.

1. Introduction

Recent investigations on dicarbonyl compounds reveal many interesting properties in their triplet and radical states (Hayon *et al* 1972; Arnett and McGlynn 1975; Fang *et al* 1978; Encinas and Scaiano 1979; Roy *et al* 1980; Griller *et al* 1981). Flash photolysis of benzil ($C_6H_5COCOC_6H_5$), one of the representative dicarbonyls, shows two conformic triplets (Dasmohapatra *et al* 1987). One conformer, present in a rigid glassy matrix and emitting green phosphorescence, is assumed to be of puckered geometry, while the other, which emits yellow phosphorescence and is present in molten media, is taken to be the planar conformer. The hydrogen adduct radical and radical anion formation have also been studied. The benzil radical anion appears in two conformeric forms. One form absorbs at 540 nm generated in alcoholic media by acid dissociation of hydrogen adduct radicals and is described as the planar conformer. The other one is generated from triplets directly by addition of electrons from bases. They appear in media of high dielectric constant such as acetonitrile, dimethylformamide etc. and are assumed to have puckered conformation (Dasmohapatra *et al* 1987). Involvement of at least three triplet levels to form hydrogen adduct radicals of benzil has been demonstrated from the magnetic field effect by Datta and Chowdhury (1990). Investigations on another dicarbonyl, α-naphthil ($C_{10}H_7COCOC_{10}H_7$) shows equilibrium between two triplets and two geminate

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radical pairs. Out of two α-naphthil triplets one is inert towards hydrogen donors and does not form hydrogen adduct radicals (Sen *et al* 1991). On the whole, the photochemistry of dicarbonyl compounds appears to be complicated because of the presence of two conformeric triplets and the involvement of more than one triplet state. In the present case, results of our investigations on benzil and its derivatives are analysed to understand the mechanism of hydrogen adduct formation.

2. Experimental

2.1 *Preparation of the aromatic α-dicarbonyls*

Benzil (BDH) was recrystallized from ethanol before use. The 2,2'-dichlorobenzil, 4,4'-dichlorobenzil and 4,4'-dimethylbenzil (Hodgson and Rosenberg 1930; Klein 1941) were prepared by benzoin condensation from the respective benzaldehydes followed by air oxidation. Finally they were purified and recrystallised from ethanol. Isopropanol, *n*-heptane and triethyl amine were purified following standard methods (Vogel 1978).

2.2 *Apparatus*

The laser flash photolysis set-up has been described earlier (Manna *et al* 1991). The set-up consists of an Nd: YAG Laser from Spectra Physics, USA, model DCR 11. The third harmonic ($\lambda = 355$ nm) separated by prism harmonic was used for excitation. The instrument has a time constant of 0·2 to 0·5 μs and uses a tungsten halogen lamp as the monitoring source. The decay kinetics and traces were captured on 100 MHZ digital storage oscilloscope model 4072 of Gould Inc., UK, after averaging 8–10 shots. Absorption and emission spectra were recorded on a Shimadzu Spectrophotometer model UV-VIS-NIR 365 and Spex Spectrofluorimeter model Fluorolog F 111 AI. The working solutions were made oxygen-free by passing dry nitrogen in a quartz cuvette fitted with a septum for 25–30 minutes.

3. Results and discussion

The phosphorescence of benzil changes colour from green to yellow on melting the alcoholic glass. The phosphorescence spectra of benzil has been shown in figure 1. The peak of the green emission is around 525 nm and on melting it shifts to 565 nm. At room temperature the 565 nm emission can be observed by scrupulously driving out oxygen with dry nitrogen. The unchanged position of the excitation band of green and yellow emission indicates that the change occurs in the excited state and not in the ground state. Oscillograms (inset in figure 1) show similar decay of yellow phosphorescnce at 565 nm and triplet–triplet absorption at 470 nm and also the similar decay of green phosphorescence at 525 nm and triplet–triplet absorption at 490 nm. In figure 2, benzil and 2,2'-dichlorobenzil in a rigid glassy matrix of isopropanol having green phosphorescence show triplet–triplet absorption peaks around 490 nm and 485 nm, respectively. On melting the glass, these peaks shift to 470 nm for benzil and 465 nm for 2,2'-dichlorobenzil with an additional weak absorption in the region of 350 nm. In fact this weak absorption at 350 nm has enough
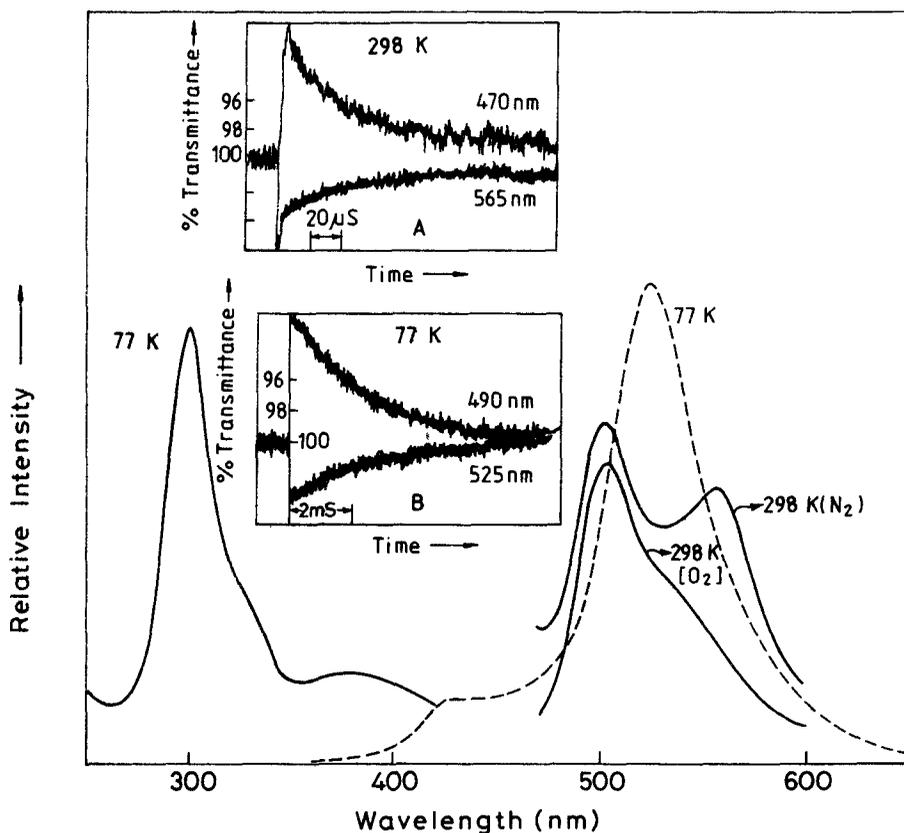
Figure 1. Excitation (———) and phosphorescence at 77 K (- - - -), phosphorescence and fluorescence at 298 K in presence of air (O_2, ———), and after passing dry N_2 through the solution (N_2, ———), of benzil (1.0×10^{-4} M) in isopropanol. Oscillogram A: Similar decays at 298 K of triplet–triplet absorption at 470 nm and yellow phosphorescence at 565 nm. Oscillogram B: Similar decays at 77 K of triplet–triplet absorption at 490 nm and green phosphorescence at 525 nm.

extinction coefficient to compensate for the ground state bleaching, hence it is not weak in the usual sense. The oscillograms show decay of triplet–triplet absorption at 470 nm and of yellow phosphorescence at 560 nm.

The time-resolved spectra of benzil and 2,2'-dichlorobenzil in isopropanol show triplet–triplet absorption of benzil at 470 nm and of 2,2'-dichlorobenzil at 465 nm. At $3.5\,\mu$s the absorption of the hydrogen adduct radical of benzil appears in the 370 nm region and of its dichloro derivative in isopropanol in the 355 nm region (figure 3). The growth of hydrogen adduct radical absorption of benzil at 370 nm corresponds well with the decay of triplet–triplet absorption at 470 nm as shown in the oscillogram. After $80\,\mu$s only absorption due to the hydrogen adduct radical is present. In hydrocarbon media, e.g. in *n*-heptane, the addition of the hydrogen donor, triethyl amine, generates the hydrogen adduct radical. After a shorter time period of $2\,\mu$s, the triplet, along with the radical, is present showing absorption peaks at 470 and 370 nm, respectively (figure 4). In contrast to isopropanol medium, there is no prominent radical growth in the hydrocarbon medium corresponding to the decay
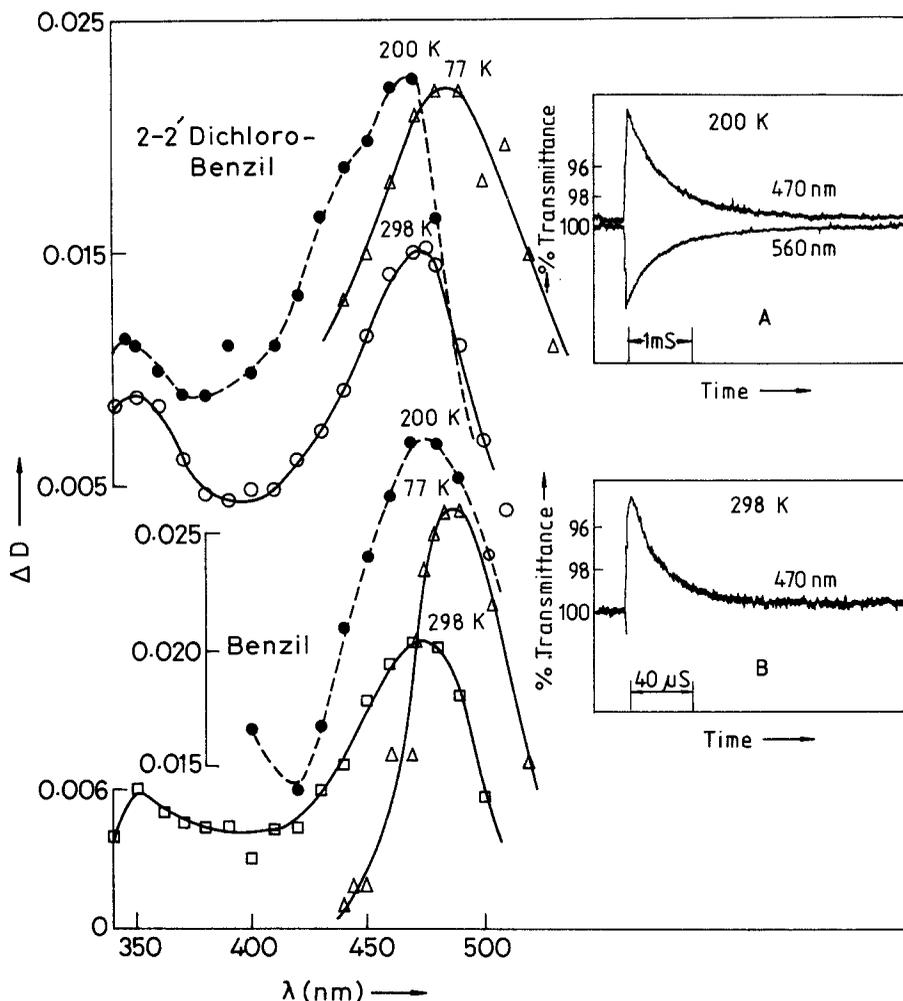
Figure 2. Triplet–triplet absorption of benzil $(1.0 \times 10^{-4} \text{M})$ and 2,2'-dichlorobenzil $(5.0 \times 10^{-4} \text{M})$ in n-heptane at 298 K and in isopropanol at 200 K and 77 K. Oscillogram A: Similar decays of triplet–triplet absorption and phosphorescence at 200 K of benzil in isopropanol. Oscillogram **B**: Triplet–triplet absorption decay at 470 nm of benzil in n-heptane at 298 K.

of triplets. This fact indicates that hydrogen adduct radical generation follows different routes, the conversion of the 470 nm absorbing triplet to a hydrogen adduct radical is one of them, and this conversion seems to be less efficient in a hydrocarbon medium. It is also to be noted that in isopropanol the initial hydrogen adduct radical absorption is much higher as compared to that which would have occurred with the 470 nm triplet alone. The addition of triethyl amine in isopropanol solutions of benzil and 2,2'-dichlorobenzil produces corresponding radical anions. In figure 5 time-resolved spectra show the presence of triplets and radicals at a time just after the laser flash and later at the time of the growth of radical anion absorption of benzil at 540 nm and of 2,2'-dichlorobenzil at 460 nm from their respective hydrogen adduct radicals. The oscillogram at 470 nm for 2,2'-dichlorobenzil shows the initial triplet–triplet
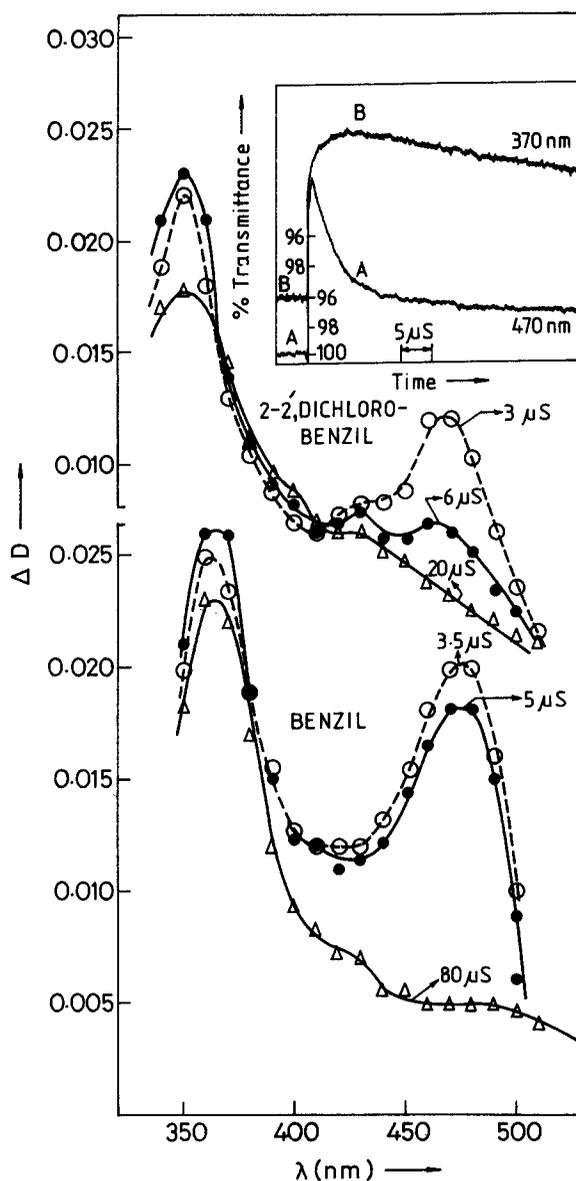
Figure 3. Time-resolved spectra of flash-excited benzil (1.0×10^{-4} M) showing coupled growth and decay at 370 and 470 nm, and of 2,2'-dichlorobenzil at 355 and 465 nm, respectively, in isopropanol. Oscillogram: Trace A at 470 nm shows initial rapid decay of triplet–triplet absorption followed by long-lived radical; trace B shows initial growth followed by decay at 370 nm of benzil radical (1.0×10^{-4} M) in isopropanol.

absorption followed by growth of radical anion absorption. At 350 nm, the oscillogram shows the decay of the hydrogen adduct radical absorption which corresponds to the growth of radical anion at 470 nm followed by its decay. The inefficiency of triethyl amine in converting triplets absorbing at 470 nm to radicals has also been noted in isopropanol, otherwise triplet–triplet absorption would not be present where triethyl
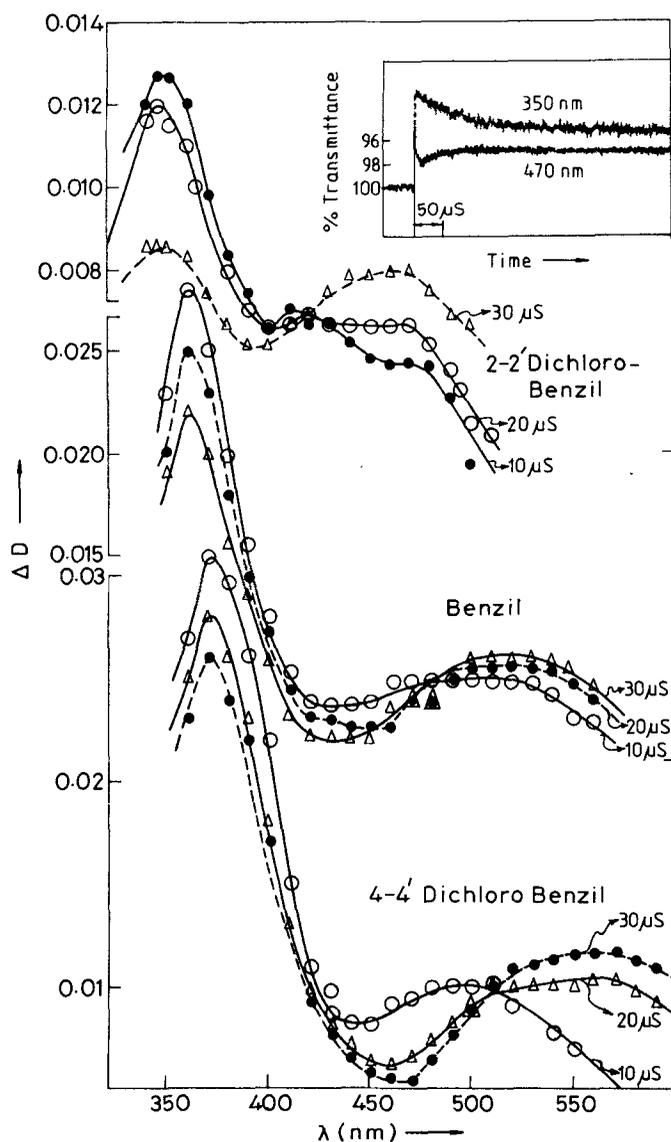
Figure 4. Time-resolved spectra of flash-excited benzil ($1\cdot0 \times 10^{-4}$ M) with triethyl amine ($1\cdot0 \times 10^{-5}$ M) and 2,2′-dichlorobenzil ($5\cdot0 \times 10^{-4}$ M) with triethyl amine ($1\cdot0 \times 10^{-5}$ M) in *n*-heptane. Oscillogram: Trace A, initial triplet–triplet absorption followed by slow decay of radicals at 470 nm; trace B, the small growth followed by decay of radicals of benzil at 370 nm ($1\cdot0 \times 10^{-4}$ M) with triethyl amine ($1\cdot0 \times 10^{-5}$ M) in *n*-heptane.

amine concentration is sufficient to form radical anions (oscillogram in figure 5). The suggested reaction mechanism might be as follows.

$$^{3}Bz_{I} \rightarrow {}^{3}Bz_{II}(470\,nm), \tag{1}$$

$$^{3}Bz_{I} + RH \rightarrow {}^{3}(Bz_{I}\ldots H - R) \rightarrow Bz^{\bullet}H + R^{\bullet}, \tag{2}$$

$$^{3}Bz_{II} + RH \rightarrow {}^{3}(Bz_{II}\ldots H - R)\left\{\begin{array}{l}\rightarrow Bz^{\bullet}H + R^{\bullet}, \qquad (3)\\ \rightarrow Bz + RH. \qquad (4)\end{array}\right.$$

Here $^{3}Bz_{I}$ and $^{3}Bz_{II}$ represent two different conformeric benzil triplets. The $^{3}Bz_{II}$ is the triplet absorbing at 470 nm and RH is a hydrogen donor like isopropanol or triethyl amine. In step (1), the change of conformation from puckered to planar has already been discussed in connection with phosphorescence colour change from green to yellow and triplet–triplet absorption change from 490 to 470 nm in benzil (485 to 465 nm in 2,2′-dichlorobenzil). The oscillogram in figure 1 supports this

Figure 5. Time-resolved spectra of benzil ($1{\cdot}0 \times 10^{-4}$ M), 2,2'-dichlorobenzil ($5{\cdot}0 \times 10^{-4}$ M), and 4,4'-dichlorobenzil ($1{\cdot}0 \times 10^{-4}$ M) in presence of triethyl amine in isopropanol ($5{\cdot}0 \times 10^{-5}$ M). Oscillogram: traces show the initial presence of triplets at 470 nm, followed by growth and decay of radical anions, and the initial decay of hydrogen adduct radicals at 350 nm followed by long decay of radical anions of 2,2'-dichlorobenzil ($5{\cdot}0 \times 10^{-4}$ M).

phenomenon. Step (2) is perhaps the most efficient route for hydrogen adduct radical formation. Hydrogen adduct radical formation, (3) seems to be less efficient and it is almost ineffective for the hydrogen donor triethyl amine. Addition of triethyl amine to a large extent makes step (2) exceedingly efficient in comparison to step (1) when only hydrogen adduct radical absorption is noticed and no triplet–triplet absorption at 470 nm. The inefficiency of $^3Bz_{II}$ in reacting with the hydrogen donor

has also been noticed in the case of α-naphthil where the relaxed triplet is inert to either triethyl amine or isopropanol (Sen *et al* 1991).

The decay kinetics of benzil triplets ($^3Bz_{II}$) above the melting point of isopropanol (187 K) has been found to follow first order with activation energies of 28·0 and 48·0 kJ/mol for benzil and 2,2'-dichlorobenzil, respectively. The hydrogen adduct radical and the radical anion follow second-order decay kinetics; at 25°C the respective decay rate constants for benzil are $7·0 \times 10^4 \, \varepsilon^{-1} \, mol^{-1} \, s^{-1}$ at 370 nm (radical decay) and $8 \times 10^3 \, \varepsilon^{-1} \, mol^{-1} \, s^{-1}$ at 540 nm (radical anion decay), whereas these values for 2,2'-dichlorobenzil are $3 \times 10^4 \, \varepsilon^{-1} \, mol^{-1} \, s^{-1}$ at 355 nm (radical decay) and $2·5 \times 10^3 \, \varepsilon^{-1} \, mol^{-1} \, s^{-1}$ at 460 nm (radical anion decay).

Spectra of the hydrogen adduct radical and the radical anion of 2,2'-dichlorobenzil are blue-shifted as compared to those of benzil and appear at 355 and 460 nm respectively (in case of benzil they are at 370 and 540 nm). Chloro-substitution is not the cause for such a large blue-shift because in 4,4'-dichlorobenzil, they appear at 370 and 560 nm, respectively; in the case of 4,4'-dimethylbenzil also these bands are not shifted much and appear at 370 and 540 nm (Dasmohapatra *et al* 1987). Thus spectral shift depends not so much on the nature of substitution as on the position of substitution. A similar blue-shift has also been noted in case of mesitil(2,2',4,4',6,6'-hexamethylbenzil) where hydrogen adduct radical absorption occurs at 390 nm and radical anion absorption occurs at 400 nm (Dasmohapatra *et al* 1987). In mesitil, the ortho-positions are occupied by methyl groups. Thus ortho-substitution causes the blue-shift in hydrogen adduct radical and radical anion spectra. This is perhaps due to loss of π conjugation as ortho-substitution sterically hinders the molecule from becoming planar.

Acknowledgement

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