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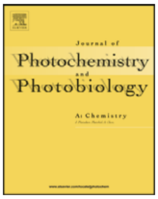

Laser induced optoacoustic spectroscopy of benzil: Evaluation of structural volume change upon photoisomerization

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ABSTRACT

The *cis*-skew to *trans*-planar photoisomerization of benzil in the photoexcited state was studied by laser-induced optoacoustic spectroscopy (LIOAS) in a series of normal alkane solvents at room temperature. The structural volume change due to the photoisomerization process has been estimated and compared with the same calculated from the optimized skew and *trans* structures. The magnitude of the structural volume change is estimated to be 22.9 ± 1.2 mL/mol. This study reveals that an expansion in volume occurs during the photoinduced isomerization process. In non-polar alkane solvents, the estimated volume change has been argued to be free from electrostrictional contribution.

1. Introduction

Benzil has been, perhaps, the most studied 1,2-dicarbonyl compound for the last few decades [1–11]. The most interesting photoreaction of the compound is the so called *cis-trans* photoisomerization. Photoisomerization about the double bond is a fundamentally important phenomenon considering the fact that this process is responsible for our vision, where such a phototransformation occurs between rhodopsin and isorhodopsin [12,13]. Study of these processes from different angles is thus very important. Benzil is also a very good triplet state sensitizer and a photoinitiator for several photochemical reactions. From crystallographic and theoretical studies, the *cis*-skew configuration of benzil is known to be the most stable form in the ground state (S_0). The dihedral angle, i.e., the angle between the two-carbonyl moieties is estimated to be nearly 111° in the crystalline state and 98° in the solution state [14,15]. In the triplet state (T_1), however, a photoisomerization takes place from the *cis*-skew to a *trans*-planar configuration [4,5,11,16]. Dual phosphorescence of benzil has been reported in the frozen or semi-frozen matrix corresponding to its unrelaxed and relaxed geometries [4,5]. The triplet photophysical behavior of benzil has been schematically represented in Scheme 1.

In the solution phase benzil is only poorly fluorescent ($\Phi_f = 0.0013$) at room temperature [17]. Moreover, for the aromatic diketones, the nonradiative singlet to triplet intersystem crossing is reported to be extremely efficient. The corresponding rate constant (k_{isc}) is very high; sometimes leading to the triplet quantum yield to be unity. Thus, $k_{isc} \gg k_f$, where k_f is the rate constant of fluorescence [18]. For benzil itself Φ_T is reported to be 0.92 [17] making the unrelaxed *cis*-skew S_1 state of benzil short-lived which is readily converted to the corresponding unrelaxed *cis*-skew T_1 state. Phosphorescence can be observed from this state ($\lambda_{max} = 530$ nm) only in a rigid matrix at 77 K. However, in solution phase, phosphorescence at $\lambda_{max} = 530$ nm does not exist at room temperature and this state relaxes promptly to a *trans*-planar conformation [4]. A glance at the optimized structures of the skew and the *trans* conformations of benzil indicates an intrinsic volume change due to photointerconversion. The photothermal technique, viz., laser induced optoacoustic spectroscopy (LIOAS) or photoacoustic calorimetry (PAC) is the most convenient way for the determination of the volume changes associated with such a photoprocess [19–25]. The partial molar volume of a dissolved species in solution is determined by three factors [26]: (i) The intrinsic size of the species as determined by its van der Waals radius, (ii) The interaction of the species with the solvent to cause electrostriction and (iii) the interaction of the species with all the solute species, including itself. The third factor is less important in dilute solutions, and the contribution from (i) is usually accepted to be independent of the solvent and the concentration. The second factor has a complex concept.

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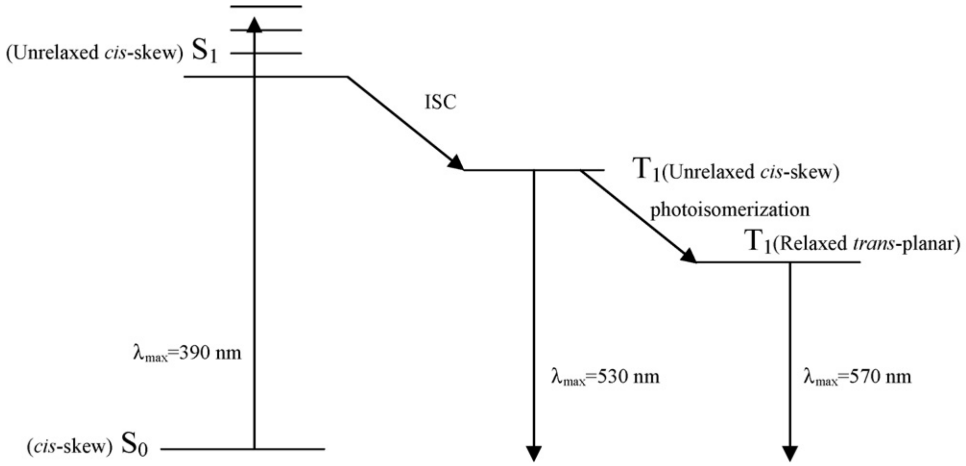


Scheme 1. Schematic representation of triplet photophysical behavior of Benzil.

The solute molecules or ions exert repulsive forces on the solvent molecules at close separations and attractive forces at longer distances. For ionic solute, the attractive forces get importance resulting into a contraction of the solvent molecules by electrostriction. This contribution is important and often so large that it completely overrides the intrinsic volume component [20,27]. The complex concept of electrostriction can be avoided by using non-polar solvents and molecules with low dipole moment. Fessenden et al. showed that benzil has a very low dipole moment in the triplet state [28]. In a study on the photoconversion of 2′,3′-dihydro-6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indole] to its open merocyanin form in a series of aerated cycloalkanes, Williams et al. [29] have mentioned about the contribution of a small electrostriction to the volume change. Understandably, use of non-polar alkane type solvents reduces the influence of electrostriction on the measured volume changes of the compounds. Herbrich and Schmidt [30] explained the contribution of electrostriction to the volume change due to photoisomerization and the thermoelastic parameter of the solvent for *n*-alkanes at 25 °C. They have assigned this to be the reason why reaction volumes and enthalpies determined by PAC in the series of *n*-alkanes are generally free of electrostriction contributions. According to them, the structural volume changes are directly obtained from this process and the overall reaction enthalpies are obtained only after an appropriate correction.

A thorough discussion of this newly developed photothermal technique is available in a classic review article of Braslavsky and Heibel [19]. The working principle can be extracted as follows. The very fast non-radiative deactivation of a photoexcited fluorophore leads to the release of a reasonable amount of heat to the solvent molecules surrounding it. Dissipation of the released heat through the solvent is a much slower process resulting in a heating effect in the microscopic region. This leads to an adiabatic volume expansion of the solvent molecules present in the immediate vicinity of the excited fluorophore. This is known as thermoelastic expansion, which in turn, generates a shock wave and eventually develops an acoustic wave. A high frequency transducer picks up the ultrasonic acoustic signal which is then amplified and fed to a digitizer and finally to a computer. Scheme 2 gives a schematic diagram of our PAC set-up.

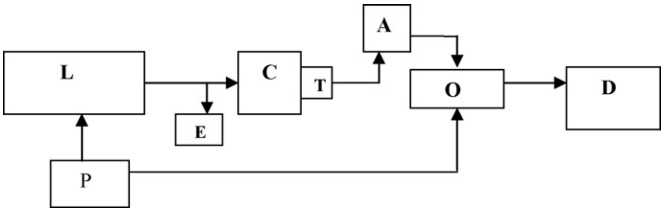
Information can be gathered simply by measuring the LIOAS (or PAC) signal from the sample in relation to that from a suitable reference [19,24]. The reference, in ideal case, releases all its absorbed energy as heat promptly without passing through other physical/photochemical routes like fluorescence, phosphorescence, photoreaction etc.

PAC or LIOAS yields information about the volume changes associated with an excited state photoprocess. There are two possible contributions to the volume change associated with a photoinduced reaction in solution: (a) the change in intrinsic reaction volume (ΔV_R) and (b) the expansion of the medium upon release of the heat (ΔV_{th}) [19]. The LIOAS signal produced by the pressure waves contains both the components, i.e,

$$\text{LIOAS signal} = k[\Delta V_{th} + \Delta V_R] \tag{1}$$

ΔV_R is independent of the thermoelastic properties of the medium, at least to the first approximation [31]. ΔV_{th}, however, depends on the thermoelastic parameter ($c_p\rho/\beta$) of the solution (c_p is the specific heat capacity at constant pressure, $\beta = 1/V(\partial V/\partial T)_p$, the volume expansion coefficient and ρ, the density of the solution = density of solvent for dilute solutions). k is a constant carrying the geometrical and instrumental signatures. One can separate the two volume effects from the LIOAS measurements as a function of the thermoelastic parameters of a series of solvents having grossly similar solvent properties.

In the present study, we have measured the LIOAS signals of benzil in a series of *n*-alkane solvents and have determined the structural volume change for the *cis*-skew → *trans*-planar photoisomerization process. The *n*-alkane solvents have been chosen to vary the thermoelastic parameters. As mentioned above, use of alkane solvents provides the additional advantage of removing the electrostrictional volume effect. The volume change obtained from the experiment was in agreement with the value calculated from the optimized *cis*-skew and the *trans*-planar conformations of the molecular system.



Scheme 2. A schematic diagram of the LIOAS set-up. P: laser power supply unit, L: Nd-YAG laser, E: energy meter, C: quartz cuvette, T: transducer, A: preamplifier, O: oscilloscope, and D: computer.