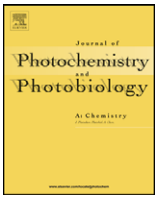
Journal of Photochemistry and Photobiology A: Chemistry 198 (2008) 256–261

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



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

Alok Chakrabarty [a], Pradipta Purkayastha [b], Nitin Chattopadhyay [a,*]

[a] Department of Chemistry, Jadavpur University, Calcutta 700 032, India
[b] Department of Chemistry, Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India

ARTICLE INFO

Article history:
Received 5 December 2007
Received in revised form 3 March 2008
Accepted 2 April 2008
Available online 11 April 2008

Keywords:
Laser induced optoacoustic spectroscopy
Photoacoustic calorimetry
Benzil
Photoisomerization
Structural volume change

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.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

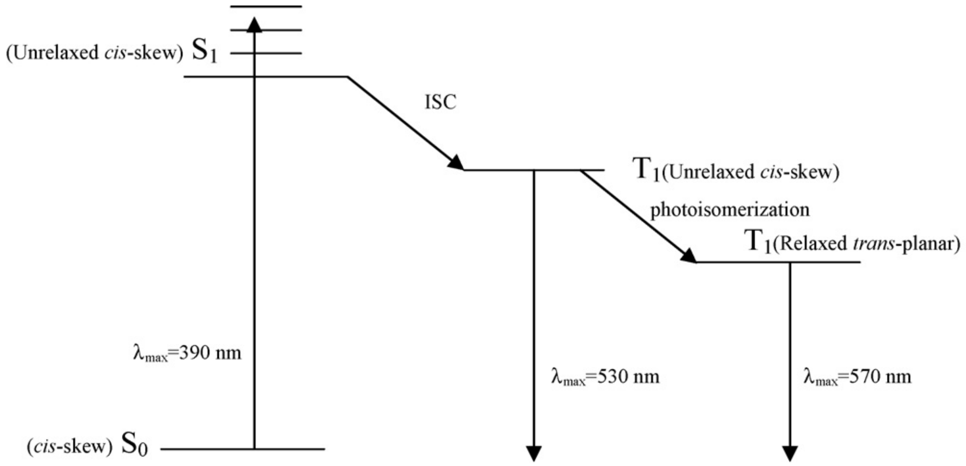
Benzil has been, perhaps, the most studied 1,2-dicarbonyl compound for the last few decades [1–11]. The most interesting photoreaction of the compound is the so called *cis-trans* photoisomerization. Photoisomerization about the double bond is a fundamentally important phenomenon considering the fact 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.

---

* Corresponding author. Fax: +91 33 24146266.
E-mail address: pcnitin@yahoo.com (N. Chattopadhyay).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.04.001



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.

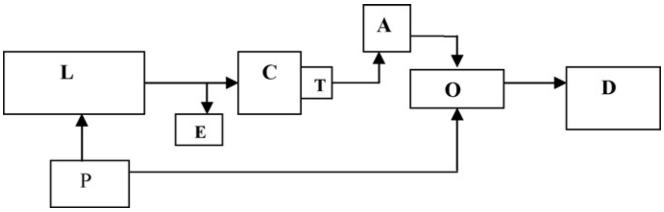
Information can be gathered simply by measuring the LIOAS (or PAC) signal from the sample in relation to that from a suitable reference [19,24]. The reference, in ideal case, releases all its absorbed energy as heat promptly without passing through other photophysical/photochemical routes like fluorescence,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

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

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.

2. Experimental

2.1. Materials

Benzil and 2-hydroxy benzophenone (HBP) were procured from Aldrich and recrystallized from methanol. The purity of the samples was checked by absorption and/or fluorescence measurements (HBP is nonfluorescent). Normal alkanes, namely, pentane (PEN), hexane (HEX), heptane (HEP), octane (OCT), decane (DEC), dodecane (DOD), and hexadecane (HEXD), were of highest purity available from Aldrich and they were used as received.

2.2. Instruments and software

Shimadzu MPS 2000 absorption spectrophotometer and Spex fluorolog-2 spectrofluorimeter were used for the absorption and emission spectral studies respectively at room temperature. LIOAS apparatus has been schematically described above. The 355 nm excitation laser pulse was provided by the third harmonic of a INDI-40 Nd:YAG laser system from Spectra Physics (USA) operating at 10 Hz repetition rate. Laser energy was measured by laser energy meter FieldMax-II fitted with energy sensor J8LP-4 (both from Coherent). The pressure wave generated was detected by piezoelectric transducer (2.25 MHz, from Panametrics). The signal was amplified by an ultrasonic preamplifier (Panametrics-5076) and stored by a digital oscilloscope (Tektronix-2012). The signal data was then transferred to a computer and analyzed there. Calculations on benzil were performed on semi-empirical basis using the commercial package Hyperchem 6.0.

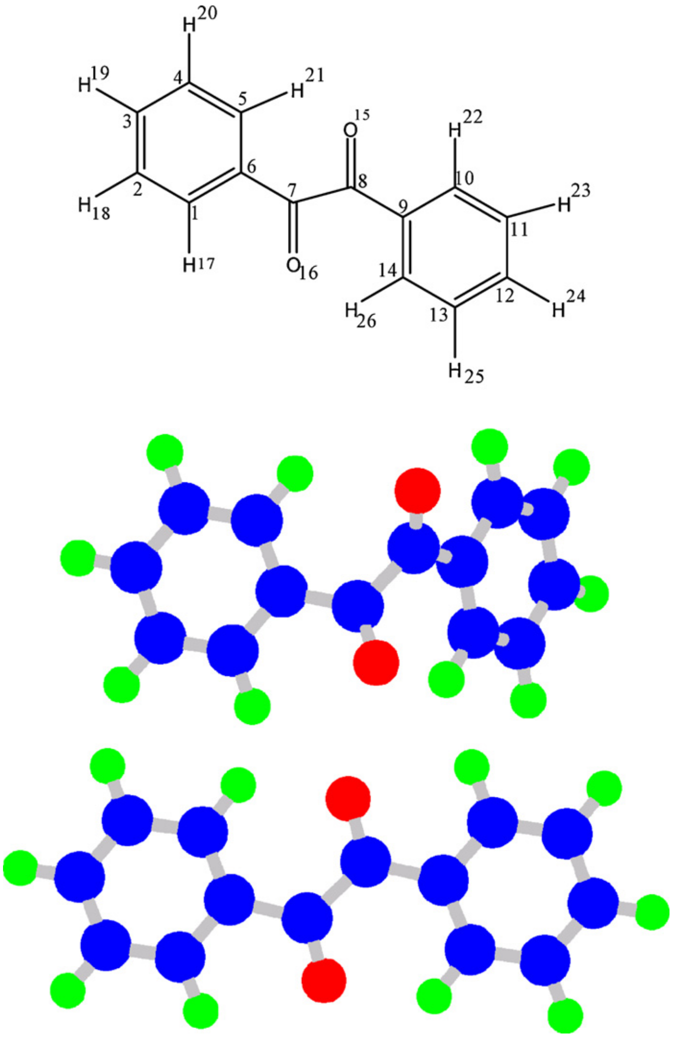
2.3. Methods

HBP was used as a calorimetric reference (α, fraction of absorbed energy coming out as heat, $= 1.0$). In each alkane solvent three solutions of benzil and HBP were prepared with absorbance values of 0.08, 0.10 and 0.12. Each solution was degassed by bubbling ultrapure nitrogen gas for 15 min. The gas was made saturated with the solvent before its entry to the solutions under examination. The prepared solutions were excited by the third harmonic (355 nm) of the Nd:YAG laser. The fluence-normalized LIOAS signal intensity ratios (H_S/H_R) were determined for the three solutions in a particular solvent and the average value was calculated. The diameter of the laser beam was set with a pinhole of 1 mm diameter. The range of laser energy used spanned within 0–20 μJ to avoid any biphotonic process or ground state depletion. The ultrasonic sound wave was detected with transducer attached to the wall of the high neck quartz cuvette with 1 cm optical path length. Vacuum grease was used between the wall of the cuvette and the transducer face to avoid the disturbances coming out of the interference of the layer of air trapped therein. Average of 64 signals was stored in the oscilloscope. The fluorescence quantum yields of benzil in alkanes were determined taking quinine sulphate solution in 0.1 N sulphuric acid as a reference ($\Phi_f = 0.54$).

3. Results and discussion

3.1. Calculation

The geometry of the benzil molecule was optimized in the ground state using semi-empirical AM1 method [32,33]. AM1–SCI (singly excited configuration interaction) was performed to get the energy (E_g) and dipole moment in the ground state and the transition energies ($\Delta E_{i\rightarrow j}$), and dipole moments of different excited states. All the singly excited configurations (>100 configurations) have been taken care of within an energy window of 13 eV from the ground state. $\Delta E_{i\rightarrow j}$ corresponds to the excitation of an electron from the orbital ϕ_i (occupied in the ground state) to the orbital ϕ_j (unoccupied in the ground state). The total energy of the excited state (E_j) was then calculated as $E_j = E_g + \Delta E_{i\rightarrow j}$. The CI wavefunction has been used to generate orbitals and one-electron density matrices, which were used to calculate the dipole moments of the excited states of benzil. The nature of the electronic transitions has been determined from the individual eigenvectors. The planes containing the phenyl rings have been oriented about the backbone containing the dione group from 0° to 180°. It is well established that in the ground state (S_0) benzil exists in a *cis*-skew conformation where the central bond between the two carbonyl moieties is twisted at an angle close to 100 degree and in the excited singlet (S_1) and triplet state (T_1) it exists in *trans*-planar conformation with an angle of nearly 180°. We have calculated the potential energies of different electronic states of benzil as a function of the torsion angle between 6 and 9 (Scheme 3) from 0° to 180°. Calculation of the energies of different electronic states of benzil was done for an understanding of the stable skew and *trans* conformers. However, since the entire potential energy curves are not essential considering the objective of the present work, we restrain us from presenting them here.



Scheme 3. Numbered general structure and skew and *trans* configurations of Benzil.

Since the optimized *cis*-skew and *trans*-planar forms of benzil are far from being spherical we calculated the volumes of these optimized conformations considering them to be cylindrical (Scheme 3). Calculation of the volume of the *trans* form is rather easy from its regular shape (planar). The skew isomer, however, has a bent structure making the volume calculation not so trivial. We have taken the values of radius and length of the cylinder from the optimized structure at the specified dihedral angles considering the various possibilities and calculated the most realistic volume of the *cis*-skew form. For both the isomers, the length of the cylinder was taken from H19 to H24 and the diameter ($2r$) of the cylinder from H18 to H20 (Scheme 3). For the *cis*-skew isomer the length is obtained as 9.78 Å and for the *trans* one it is 11.72 Å. Diameter for both the isomers is calculated to be the same and it is 4.32 Å. The required volumes were calculated from these dimensions. Since in the excited state benzil undergoes relaxation from *cis*-skew to *trans*-planar form [4], we have subtracted the volume of *cis*-skew configuration from the *trans*-planar one. The volume change per mole of benzil is found to be positive and is equal to 17.13 mL/mol. As expected, the optimized structures suggest an increase in the volume for the skew → *trans* photoisomerization.

3.2. LIOAS study

Optoacoustic signals of the sample (benzil) and the calorimetric reference (HBP) were recorded varying the laser energy from 0 to 20 μJ. The plots of first maximum of the LIOAS signal versus laser energy were found to be linear in all the solvents. This linearity confirms non-occurrence of any biphotonic process or ground state depletion of the compounds under study [34,35]. Fig. 1 presents a set of these plots for the sample and the reference. Typical LIOAS signals of benzil and the reference is shown in Fig. 2.

The photoacoustic or LIOAS signal from the sample comprises of the contribution of prompt heat released by the sample and any volume change associated with the photoprocess within the heat integration time. But for the reference HBP, the signal depends only on the prompt heat released multiplied by the thermal expansivity of the solvent. Thus, for HBP, $\alpha = 1.0$. The sample signal might have an extra contribution from the structural volume change (ΔV_R) associated with the photoisomerization process and does not depend on the expansivity of the solvent. The two volume terms in Eq. (1) can be separated by photothermal measurements as a function of the thermoelastic parameter ($c_p\rho/\beta$) of the medium [19,22,31].

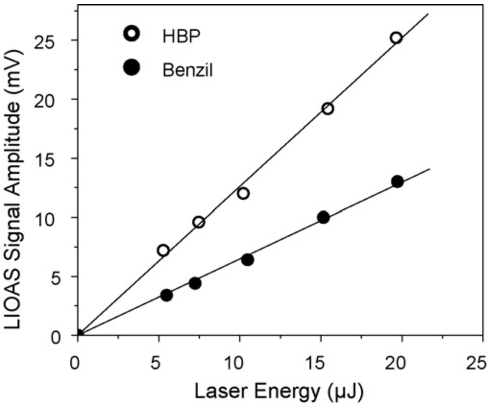


Fig. 1. Energy dependence of the LIOAS signal amplitude for benzil and HBP in *n*-octane at room temperature. Absorbance of the solutions were 0.1 and $\lambda_{exc} = 355$ nm.

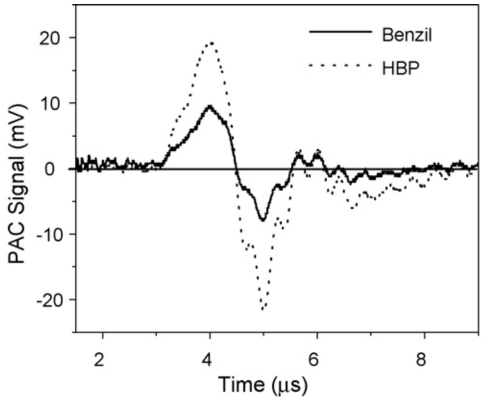


Fig. 2. Typical LIOAS signals of benzil (solid line) and HBP (dotted line) in *n*-octane at room temperature. Absorbance of both the solutions was 0.1 and the laser energy was 15 μJ.

As already mentioned, ΔV_R is assumed to be temperature independent, while ΔV_{th} is a function of temperature. ΔV_R is zero for the reference compound. Thus the amplitude of the photoacoustic response of HBP will be given by

$$H_R = k[\Delta V_{th}] = k\alpha E_\lambda \beta/(c_p\rho) \tag{2}$$

where, E_λ is the excitation energy per absorbed mole of photons. Since for HBP, $\alpha = 1$, so Eq. (2) reduces to,

$$H_R = k[\Delta V_{th}] = kE_\lambda \beta/(c_p\rho) \tag{3}$$

But for the sample benzil, both the contributions remain and hence the amplitude of the photoacoustic signal is given by

$$H_S = k[\Delta V_{th} + \Phi_R \Delta V_R] = k[\alpha E_\lambda \beta/(c_p\rho) + \Phi_R \Delta V_R] \tag{4}$$

where, Φ_R is the photoisomerization quantum yield of benzil in the excited triplet state. When the sample solution has the same absorbance as that of the reference solution, the ratio of Eqs. (4) and (3) will give,

$$(H_S/H_R) = \alpha + (\Phi_R \Delta V_R/E_\lambda)(c_p\rho/\beta) \tag{5}$$

where (H_S/H_R) is the fluence-normalized optoacoustic signal of benzil (H_S) with respect to that of HBP (H_R). Thus, a plot of (H_S/H_R) versus the thermoelastic parameter of the alkane solvents, $(c_p\rho/\beta)$, should be linear. The values (H_S/H_R) were determined in each *n*-alkane solvent with three different values of absorbance (0.08, 0.10, and 0.12) and the mean values are recorded. The structural volume change per mole (ΔV_R) is determined from the slope of this plot. The plot is given in Fig. 3.

The slope is found to be positive (6.82×10^{-5} mL/J) reflecting that there occurs a volume expansion due to the photoisomerization of benzil. E_λ is 3.37×10^5 J/mol at the excitation wavelength 355 nm. The experimental value of ($\Phi_R \Delta V_R$) is thus obtained as 22.9 ± 1.2 mL/mol. At room temperature one does not observe the phosphorescence (530 nm) from the unrelaxed triplet state indicating that the photoisomerization process is extremely efficient at ambient temperature. Taking $\Phi_R \approx 1$, ΔV_R comes out to be 22.9 ± 1.2 mL/mol. The experimental LIOAS data and thermoelastic parameters of the solvents are tabulated in Table 1. It is pertinent to mention here that the effect of variation of the fluorescence quantum yield of benzil in the alkane solvents on (H_S/H_R) has been neglected after it was verified to be inappreciable [31].

Apart from the intrinsic reaction volume change (ΔV_i), the estimated ΔV_R term includes another term ΔV_{el} which is the volume change due to the electrostatic interaction (electrostriction) between the solute and the solvent molecules [19,22,31]. Thus,

$\Delta V_R = \Delta V_i + \Delta V_{el}$. One could expect an appreciable electrostriction of the solvent around the probe, if a highly polar triplet were formed. For benzil, however, the case is not like that [28]. The dipole moments of the lowest triplet states corresponding to the two conformers are quite low (for the *trans* it is typically zero) and the solvents used are *n*-alkanes, having insignificant polarity. For alkane solvents, pressure derivative of solvent dielectric constant (ε) is linearly related with the thermoelastic parameters at room temperature [30]. Hence, photoacoustic measurements in a series of alkanes should produce reaction volumes bare of electrostatic contribution (vide infra). The volume change arising out of the electrostriction has thus been neglected considering it to be inappreciable on the above grounds [30,36]. Hence for benzil, the molar structural volume change is equal to the molar intrinsic volume change. The estimated value of 22.9 ± 1.2 mL/mol is in agreement with the value of 17.13 mL/mol calculated from the optimized geometries of the two conformers. It is apparent that the volume change should depend on the molecular system as well as on the photoprocess. Depending on these factors ΔV_R can be either positive (leading to an expansion) or negative (leading to a contraction). In their review article, Braslavsky and Heibel have discussed about the structural volume changes of a number of systems undergoing different types of photoreactions. Herman and Goodman estimated an intrinsic reaction volume expansion amounting to 5.6 ± 4.3 mL/mol for the *cis-trans* photoisomerization of stilbene [37]. Morais et al. [38] reported a volume contraction of 29 ± 7 mL/mol for the photoisomerization of another molecular entity, namely, tetraphenylethylene. This contraction was attributed to the formation of the twisted excited state. Wegewijs et al. [22] observed a total volume change of a donor-bridge-acceptor compound to be −40 ± 5 mL/mol, of which 15 mL/mol was the contribution from electrostriction. Exclusion of the electrostriction component, thus, led to an intrinsic volume change of −25 mL/mol. Churio et al. [20] measured a volume contraction to the extent of 29 ± 12 mL/mol for the photoisomerization of 3,3′-diethyloxadicarbocyanine iodide which they assigned to the contraction of the solvent coordination sphere around the cyanine cation due to the higher dipole moment of the photoproduct. Looking at various literature values for the reaction volume changes, our estimation appears reasonable. Thus result of our study reveals that the volume change for the photoisomerization of benzil is not so high. This is justified since neither any ring is produced nor any one is destroyed as larger volume changes are involved when rings are produced or destroyed in a photoreaction [39].

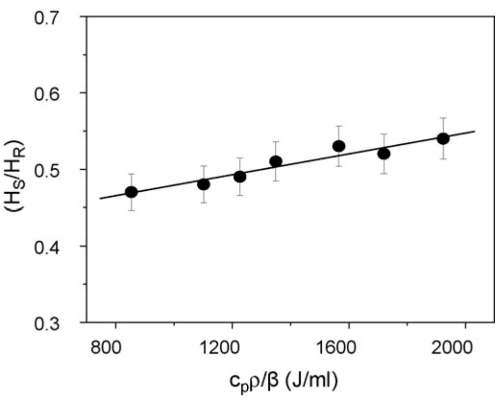


Fig. 3. Plot of fluence-normalized optoacoustic signal of benzil with respect to HBP (H_S/H_R) versus thermoelastic parameter of the alkanes ($c_p\rho/\beta$) at room temperature.

Table 1
LIOAS data of benzil and thermoelastic parameter ($c_p\rho/\beta$) in different *n*-alkanes

Solvent	$(c_p\rho/\beta)^a$ (J/mL)	(H_S/H_R)
Pentane	853.6	0.47
Hexane	1102.0	0.48
Heptane	1226.6	0.49
Octane	1349.8	0.51
Decane	1566.1	0.53
Dodecane	1720.6	0.52
Hexadecane	1924.6	0.54

[a] From ref. [31].

4. Conclusion

LIOAS study of benzil has been performed in a series of *n*-alkanes. From the fluence-normalized first maximum of the optoacoustic signal the volume change due to the photoisomerization process has been evaluated to be 22.9 ± 1.2 mL/mol. The value is consistent with the calculated value of 17.13 mL/mol considering the optimized geometries of the *cis*-skew and the *trans*-planar conformations. The experiment confirms that an expansion in volume results because of the skew → *trans* photoisomerization.

Acknowledgements

Financial supports from D.S.T., Government of India, through SERC (SR/S2/LOP-13/2004) and fast track (SR/FTP/CS-114/2005) projects are gratefully acknowledged. Thanks are due to Ms. Paramita Das for discussions.

References

[1] S.C. Bera, R. Mukherjee, M. Chowdhury, J. Chem. Phys. 51 (1969) 754–761.
[2] D.J. Morantz, A.J.C. Wright, J. Chem. Phys. 54 (1971) 692–697.
[3] I.Y. Chan, B.A. Heath, J. Chem. Phys. 71 (1979) 1070–1078.
[4] D.S. Ray, K. Bhattacharyya, S.C. Bera, M. Chowdhury, Chem. Phys. Lett. 69 (1980) 134–140.
[5] K. Bhattacharyya, D.S. Ray, M. Chowdhury, J. Luminescence 22 (1980) 95–101.
[6] K.K. Das, D. Majumdar, J. Mol. Struct. (THEOCHEM) 288 (1993) 55–61.
[7] Z. Pawelka, A. Koll, T.Z. Huyskens, J. Mol. Struct. 597 (2001) 57–66.
[8] N. Chattopadhyay, C. Serpa, M.I. Silva, L.G. Arnaut, S.J. Formosinho, Chem. Phys. Lett. 347 (2001) 361–395.
[9] A.K. Singh, D.K. Palit, J.P. Mittal, Chem. Phys. Lett. 360 (2002) 443–452.
[10] S. Lopes, A.G. Zavaglia, L. Lapinski, N. Chattopadhyay, R. Fausto, J. Phys. Chem. A 108 (2004) 8256–8263.
[11] J. Arnett, S.P. McGlynn, J. Phys. Chem. 79 (1975) 626–629.
[12] R.R. Birge, C.M. Einterz, H.M. Knapp, L.P. Murray, Biophys. J. 53 (1988) 367–385.
[13] R.W. Schoenlein, L.A. Peteanu, R.A. Mathies, C.V. Shank, Science 254 (1991) 412–415.
[14] C.J. Brown, R. Sadanaga, Acta Crystallogr. 18 (1965) 158–164.
[15] C.W.N. Cumper, A.P. Thurston, J. Chem. Soc. Perkin Trans. II (1972) 106–111.
[16] K. Bhattacharyya, M. Chowdhury, J. Photochem. 33 (1986) 61–65.
[17] A.A. Lamola, G.S. Hammond, J. Chem. Phys. 43 (1965) 2129–2135.
[18] B. Bonno, J.L. Laporte, Y. Rousset, Phys. Rev. B 43 (1991) 12767–12771.
[19] S.E. Braslavsky, G.E. Heibel, Chem. Rev. 92 (1992) 1381–1410.
[20] M.S. Churio, K.P. Angermund, S.E. Braslavsky, J. Phys. Chem. 98 (1994) 1776–1782.
[21] J.L.H. Jiwan, A.K. Chibisov, S.E. Braslavsky, J. Phys. Chem. 99 (1995) 10246–10250.
[22] B. Wegewijs, J.W. Verhoeven, S.E. Braslavsky, J. Phys. Chem. 100 (1996) 8890–8894.
[23] B. Wegewijs, M.N. Paddon-Row, S.E. Braslavsky, J. Phys. Chem. A 102 (1998) 8812–8818.
[24] J. Feitelson, D. Mauzerall, J. Phys. Chem. 100 (1996) 7698–7703.
[25] T. Gensch, C. Viappiani, S.E. Braslavsky, J. Am. Chem. Soc. 121 (1999) 10573–10582.
[26] S.D. Hamann, Rev. Phys. Chem. Jpn. 50 (1980) 147–168.
[27] R. van Eldik, T. Asano, W.J. Le Noble, Chem. Rev. 89 (1989) 549–688.
[28] R.W. Fessenden, P.M. Carton, H. Shimamori, J.C. Scalano, J. Phys. Chem. 86 (1982) 3803–3811.
[29] R.M. Williams, G. Klihm, S.E. Braslavsky, Helv. Chim. Acta 84 (2001) 2557–2576.
[30] R.P. Herbrich, R. Schmidt, J. Photochem. Photobiol. A: Chem. 133 (2000) 149–158.
[31] N. Chattopadhyay, M. Van der Auweraer, F.C. De Schryver, Chem. Phys. Lett. 279 (1997) 303–308.
[32] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 108 (1986) 8075–8086.

[33] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209–220, 221-264.
[34] N. Chattopadhyay, J. Rommens, M. Van der Auweraer, F.C. De Schryver, Chem. Phys. Lett. 264 (1997) 265–272.
[35] P. Van Haver, N. Helsen, S. Depaemelaere, M. Van der Auweraer, F.C. De Schryver, J. Am. Chem. Soc. 108 (1991) 6849–6857.
[36] M.A. Rodriguez, S.E. Braslavsky, J. Phys. Chem. A 103 (1999) 6295–6300.
[37] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 111 (1989) 1849–1854.
[38] J. Morais, J. Ma, M.B. Zimmt, J. Phys. Chem. 95 (1991) 3885–3888.
[39] E. Whalley, in: V. Gold (Ed.), Advances in Physical Organic Chemistry, Vol 2, Academic Press, London, 1964.