

## SOLVENT SHIFT AND EXCITED STATE GEOMETRIES OF BENZIL

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(Received April 25, 1985)

### Summary

The room temperature and low temperature absorption and emission spectra corresponding to the "relaxed" and "unrelaxed" excited states of benzil are reported. It is observed that while the spectra corresponding to the unrelaxed state exhibit an appreciable blue shift in an alcoholic solvent compared with those in a hydrocarbon solvent, there is no such shift for emissions originating from the relaxed state. The lack of a solvent shift for relaxed emission furnishes additional evidence that the relaxed state has a trans-planar geometry with a zero dipole moment, while the unrelaxed form must be skew in both singlet and triplet excited states.

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### 1. Introduction

The photorotomerism of diaromatic  $\alpha$ -dicarbonyls has been the subject of several recent studies [1 - 12]. Of these, benzil has received the greatest attention. It is now well established that the skew bimolecule benzil, whose two benzoyl units are at an angle of about  $72^\circ$  in the ground state [12], on excitation in fluid media "relaxes" to a trans-planar geometry in which the  $-\text{CO}-\text{CO}-$  dihedral angle is  $180^\circ$ . There have been several attempts to ascertain the excited state geometry of benzil. Bera and coworkers [3, 4] "forced" benzil to take up a trans-planar geometry by doping it into *trans*-stilbene and observed that the emission spectra of such a trans-planar benzil are remarkably similar to those of benzil in solution. This led them to suggest that the geometry of benzil in the relaxed excited state is trans planar. More recently, Kohler and Loda [9] doped benzil into di-benzyl and observed similar phenomena. Morantz and Wright [7] adopted a different strategy. They compared spectra of benzil with those of other compounds with known excited state geometries. They observed that the emission spectra of benzil in fluid media resembles very closely those of biacetyl and mesityl, which are known to have a trans-planar geometry, and hence

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they concluded that the relaxed excited state of benzil is trans planar. Later, Arnett and McGlynn compared the spectra of a number of  $\alpha$ -dicarbonyls and concluded that they emit from a more-or-less coplanar geometry. A more recent electron nuclear double resonance (ENDOR) study also indicated that the excited state of benzil is nearly trans planar [13, 14].

It is evident that in the unrelaxed skew excited state benzil has an appreciable dipole moment, as in this geometry the two  $>C=O$  dipoles are at an angle of about  $72^\circ$ . However, in the relaxed trans-planar geometry, the two  $>C=O$  dipoles cancel each other out resulting in a zero dipole moment. It is well known that in an  $n-\pi^*$  transition an electron is transferred from a non-bonding molecular orbital (MO) centred around the oxygen atom of the  $>C=O$  group to a  $\pi^*$  MO embracing the oxygen and carbon atoms. This leads to a partial charge transfer from oxygen to carbon and offsets, at least partially, the electron deficiency created around the carbon atom owing to the higher electronegativity of the oxygen. This leads to  $n,\pi^*$  excited states which are less polar and have dipole moments less than in the corresponding ground state. Thus, when a carbonyl compound is placed in a polar solvent, the excited state is less stabilized by solvent-solute interaction compared with the ground state, and the result is a blue shift of the absorption and emission spectra in polar solvents (e.g. alcohol) relative to those in non-polar solvents (e.g. methylcyclohexane). It occurred to us that, since the unrelaxed and relaxed excited states have such different dipole moments, they should have different solvent shifts. Thus, in order to see whether solvent shifts lend additional support to the proposed excited state geometries of benzil, we have compared the spectra of relaxed and unrelaxed excited states of benzil in alcohol and in methylcyclohexane.

## 2. Experimental details

The experimental details have been described in our previous papers [1, 2]. The absorption and emission spectra were recorded using Cary 17D and Perkin-Elmer MPF 44B spectrophotometers respectively. The unrelaxed fluorescence in a rigid matrix was obtained by a box-car gating technique using a Moletron UV-1000 nitrogen laser and a PAR box-car.

## 3. Results and discussion

The absorption and emission characteristics of benzil are summarized in Figs. 1(a) - 1(d). The absorption (Fig. 1(a)) is at 387 nm in alcohol and at 397 nm in methylcyclohexane. The blue shift of 10 nm is consistent with the  $n \rightarrow \pi^*$  character of the transition. The absorption spectrum is similar to that of benzaldehyde which indicates that the two benzoyl units are essentially non-interacting [7], as expected for a skew geometry.

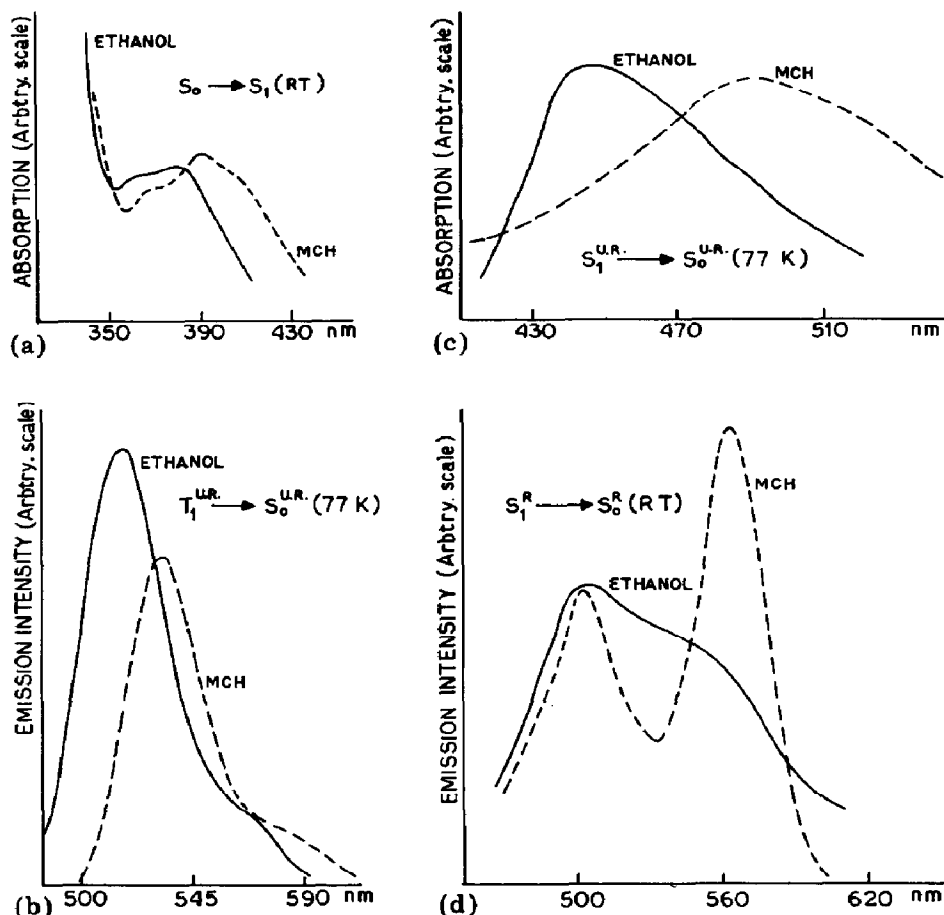


Fig. 1. (a) Absorption spectra of benzil in methylcyclohexane (MCH) and ethanol; (b) phosphorescence emission from the unrelaxed excited state of benzil in methylcyclohexane and alcoholic glassy matrices at 77 K; (c) fluorescence emission from the unrelaxed excited state in glassy matrices; (d) fluorescence emission from the relaxed excited state at room temperature.

At 77 K in a rigid glass, in which the molecule cannot undergo conformational relaxation, benzil exhibits an intense green phosphorescence with  $\lambda_{\max} = 515$  nm in alcohol and  $\lambda_{\max} = 530$  nm in methylcyclohexane (Fig. 1(b)). In rigid media, the phosphorescence must originate from a skew geometry which is essentially the same as that in the ground state. It is apparent that the unrelaxed phosphorescence also exhibits a blue shift of about 15 nm.

The unrelaxed fluorescence is difficult to produce. High spin-orbit coupling, a low S-T interval and consequently a large intersystem crossing efficiency render the  $S_1$  state of benzil very short lived, and hence the time-integrated fluorescence from the unrelaxed state is low. In fact, at 77 K the green phosphorescence completely masks the fluorescence. The elusive unrelaxed fluorescence may, however, be detected if one recognizes that the instantaneous intensity of the fluorescence is high; if one uses a time

window much shorter than the low temperature lifetime of the phosphorescence, one can separate out the unrelaxed fluorescence from the total emission. In a previous paper [1], we have discussed how the unrelaxed fluorescence of benzil can be detected. The unrelaxed fluorescence in alcohol and methylcyclohexane is given in Fig. 1(c). The maximum is located at 445 nm in alcohol and at 490 nm in methylcyclohexane. Thus, there is a large blue shift for unrelaxed fluorescence also.

When the rigid glass is allowed to melt, the intense green phosphorescence (at 515 nm in alcohol and 530 nm in methylcyclohexane) switches over to a yellow phosphorescence with  $\lambda_{\text{max}} = 565$  nm in both solvents. In a previous paper [2], we have shown that the new band at 565 nm is due to the relaxed triplet. From the time-resolved study of the new band at 565 nm, we were able to follow the dynamics of the geometry change in the excited triplet of benzil [2]. As the temperature of the medium is raised, another peak begins to grow in on the higher energy side. In methylcyclohexane at room temperature, two distinct peaks are observed, one at 505 nm and the other at 565 nm. On aeration, the peak at 565 nm is quenched, while the other remains undiminished in intensity. This led Arnett and McGlynn [8] to suggest that the peak at 505 nm is due to the relaxed singlet and that at 565 nm is due to the relaxed triplet. In alcohol, the peak at 565 nm is easily detected at low temperatures (145 - 195 K), while at room temperature the peak at 505 nm dominates. The important point to note is that in fluid media, in both alcohol and methylcyclohexane, the fluorescence is at 505 nm and the phosphorescence is at 565 nm (Fig. 1(d)). The lack of a solvent shift cannot be due to a  $\pi, \pi^*$  state, as the  $\pi, \pi^*$  states of benzil are much higher in energy than the unrelaxed fluorescence and phosphorescence. The lack of a solvent shift suggests that the state from which the emission originates and the state at which it terminates have equal dipole moments. Such a situation is surprising because, as discussed earlier, the  $n, \pi^*$  excited state must be less polar than the ground state. Only a trans-planar geometry for both the relaxed  $S_1$  state and its corresponding  $S_0$  state, and the consequent cancellation of  $>C=O$  dipole moments, can explain the lack of a solvent shift. Thus, our solvent-effect studies have substantiated earlier claims [1 - 4, 7, 8] that the relaxed  $S_1$  and  $T_1$  states of benzil have a trans-coplanar geometry, while unrelaxed  $S_1$  and  $T_1$  states have a skew configuration. In fact, in a recent study [11], Fessenden *et al.* measured the dipole moment of benzil in the relaxed triplet state using a microwave dielectric absorption change technique and they found that the dipole moment in the relaxed triplet is indeed zero. Their technique, however, is incapable of investigating the dipole moment of the singlet state, as is revealed in the present study.

### Acknowledgments

The work has been done under the Department of Science and Technology project SERC 23(IP-2)/81-STP II. We thank Dr. D. S. Ray for helpful discussions.

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