Phosphorescence from the Second Triplet State of Benzil and a Related Compound

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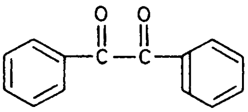
Benzil, which adopts a near-planar *cisoid* geometry on excitation in an ethylene glycol glass, and 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-10,11-dione, which has a rigid near-planar *cisoid* conformation, phosphoresce from the second triplet state.

In recent years the emission characteristics of benzil (**1**) have been studied in order to elucidate its geometries in excited states. It is known that, depending on the solvents and temperature, (**1**) has near-planar *transoid* or skewed structures in these excited states.[1-3] Earlier work has provided evidence for the existence of a near-planar *cisoid* geometry for (**1**) in the triplet state in an ethylene glycol glass.[4]

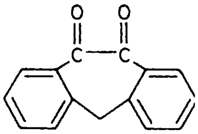
Here we report the phosphorescence from the second triplet state of benzil relaxed to *cisoid* geometry after excitation and of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-10,11-dione ('bridged benzil') (**2**) which has a rigid near-planar *cisoid* conformation.

The latter molecule (**2**) shows dual phosphorescence depending on the excitation wavelength. The emission spectra presented in Figure 1 are of phosphorescence, because very weak and structureless fluorescence appears around 470 nm at room temperature in an aerated solution and cannot be observed under the present experimental conditions using a rotating sector. A relatively weak phosphorescence band is observed at 530 nm when (**2**) is excited to the S_1 state,† whereas excitation to the S_2 state‡ causes phosphorescence emission in a much shorter wavelength region (peaks at 402, 427, and 450 nm) with a high efficiency [the intensity in Figure 1 spectrum (A) has been amplified by a factor of 10]. The longer-wavelength phosphorescence is regarded as the normal emission from the first triplet state (T_1) because the excitation spectrum monitored at 530 nm corresponds to the first absorption band at 440 nm (n–π^* $S_1 \leftarrow S_0$ transition). Conversely, the shorter-wavelength phosphorescence consisting of three peaks appears at the shorter wavelength side of the first absorption band. The excitation spectrum for this phosphorescence corresponds well to the second absorption band at 273 nm (π–π^* $S_2 \leftarrow S_0$ transition). The appearance of this dual phosphorescence is not solvent dependent. These results indicate that the phosphorescence observed in the short wavelength region arises from the second triplet state (T_2) which is populated from the S_2 state by efficient intersystem crossing. From the two peaks of the T_1 and T_2 phosphorescence (402 and 530 nm), the T_1–T_2 energy separation is *ca.* 6010 cm^{-1}.

Turning now to the phosphorescence of (**1**), it was found previously[4] that (**1**) has both a *cisoid* geometry and a *transoid*



(**1**)



(**2**)

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† The maximum of the weak n–π^* absorption band is at 440 nm.

‡ The maximum of the strong π–π^* absorption band is at 273 nm.

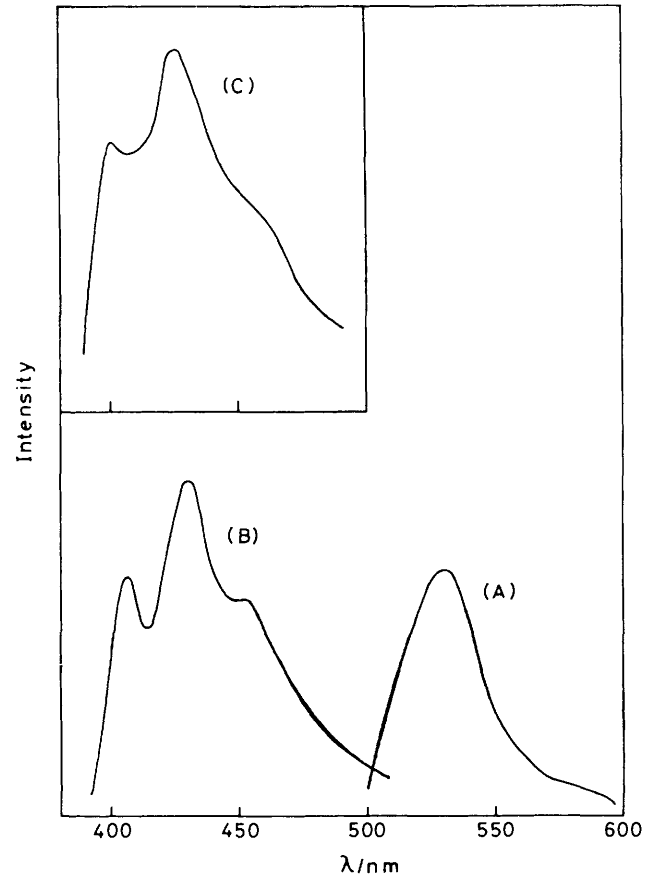

Figure 1. Phosphorescence spectra at 77 K; (**2**) in methylcyclohexane, (A), excitation at 430 nm, conc. 5×10^{-3} M (intensity × 10); (B), 290 nm, 5×10^{-5} M; and (C) of (**1**) in ethylene glycol, 316 nm, 1.0×10^{-4} M.

geometry in the triplet state when polyhydric alcohols, *e.g.*, ethylene glycol, are employed as solvent matrices. The phosphorescence spectrum of *cisoid* (**1**) is similar to the T_2 phosphorescence of (**2**). This indicates that the excited molecules of (**1**) which relax to *cisoid* geometry from the skewed structure have π-electronic energy levels similar to those of excited (**2**), and thus emit the T_2 phosphorescence. Because the formation of the *cisoid* excited state is necessary for the T_2 phosphorescence of (**1**), specific matrices,[4] in which the solvent molecules have two hydrogen atoms which can form hydrogen bonds with (**1**), must be used in contrast to those used for (**2**).

In view of Kasha's rule, emission from the T_2 state is an anomalous event. However, several compounds have been reported to give this unusual emission.[5] In these reported compounds, the T_1–T_2 energy separation is so small that the thermal repopulation of the T_2 state from the T_1 state is possible at appropriate temperatures. The T_2 emission is accounted for by this repopulation. In the present case such thermal repopulation is unlikely, because the T_1 and T_2 states are significantly separated and the phosphorescence measurements are carried out at 77 K. We therefore believe that the phosphorescence presented here is a novel type of T_2 phosphorescence whose origin needs to be clarified.

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