

The Photochemistry of 1-Benzoyl-2-naphthol and 6-Hydroxybenzanthrone and their Effect on the Rate of Photo-oxidation of Polypropylene

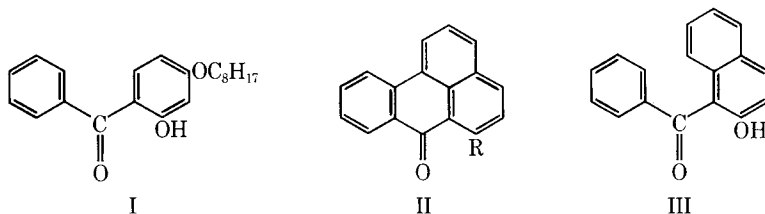
P. BENTLEY and J. F. MC KELLAR, *Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire, England*

Synopsis

A comparison of the effect of two structurally similar additives, 1-benzoyl-2-naphthol and 6-hydroxybenzanthrone, on the rate of photo-oxidation of polypropylene under conditions of simulated daylight shows that while 6-hydroxybenzanthrone acts as a prodegradant, 1-benzoyl-2-naphthol is a light stabilizer. Examination of the spectroscopic and photochemical properties of 1-benzoyl-2-naphthol indicates that in fluid solution the photoexcited stabilizer is probably deactivated within the singlet manifold. In glassy solvents at 77°K, on the other hand, triplet formation does occur, but only in molecules in which the intramolecular hydrogen bond of the 1-benzoyl-2-naphthol is disrupted.

INTRODUCTION

It is well known that light stabilizers of the 2-hydroxybenzophenone type, such as Cyasorb UV 531(I), owe their high light stability to the presence of an electron donating group ortho to, and capable of hydrogen bonding with, the oxygen atom of a carbonyl group.¹⁻³ One might expect therefore, by analogy, that 6-hydroxybenzanthrone (II, R = OH) or 6-aminobenzanthrone (II, R = —NH₂) should also possess high light stability.



However, in practice, both 6-hydroxy- and 6-aminobenzanthrone have relatively poor light stability but, interestingly, 6-anilinobenzanthrone (II, R = —NPh) is exceptionally light stable.⁴

The high light stability of both 2-hydroxybenzophenone and 6-anilinobenzanthrone is associated with the fact that, following light absorption, they are rapidly deactivated within the singlet manifold, thus reducing the possibility of photochemical reaction.²⁻⁷ In contrast, 6-hydroxy- and 6-aminobenzanthrone are deactivated much more slowly.⁴⁻⁶

In expecting high light stability from 6-hydroxy- and 6-aminobenzanthrone, we assume that (a) the ortho substituents will enhance the rate of deactivation following light absorption and therefore improve light stability when substituted in a naphthalene, rather than a phenyl ring; and (b) that rapid deactivation can occur when the molecule is rigid. The first of these assumptions has been examined in an earlier paper.⁸ Concerning the second assumption, our spectroscopic work⁵ suggests that the 6-hydroxy- and 6-aminobenzanthrones are planar molecules which possess considerable molecular rigidity due to the substituent at the 6-position being firmly held by intramolecular hydrogen bonding. In the case of 6-anilinobenzanthrone, on the other hand, molecular rigidity is lost due to the free rotation of the phenyl ring of the anilino group. This "loose bolt" effect⁹ could, to some extent, explain the facile deactivation of 6-anilinobenzanthrone. Likewise, Heller^{3,10} has proposed that deactivation of the lowest excited singlet state of 2-hydroxybenzophenone derivatives is enhanced by free rotation of the hydroxyphenyl group. In agreement with this suggestion, it has recently been reported¹¹ that 1-benzoyl-2-naphthol (III) can stabilize polypropylene toward light, indicating that this compound, unlike 6-hydroxybenzanthrone, must have relatively good light stability. In order to further examine the effect of molecular rigidity on these compounds, we have therefore examined the photochemical behavior of 6-hydroxybenzanthrone and 1-benzoyl-2-naphthol (III) and compared their effectiveness as light stabilizers for polypropylene.

EXPERIMENTAL

Materials Used

1-Benzoyl-2-naphthol and 6-hydroxybenzanthrone were prepared from 2-naphthyl benzoate by methods described in reference 12. The 1-benzoyl-2-naphthol was purified by crystallization twice from ethanol followed by vacuum sublimation mp 139–140° (lit.¹² 137–9°). 6-Hydroxybenzanthrone was purified by four successive crystallizations from hexane to give yellow needles mp 178–9° (lit.¹² 176°).

The polypropylene powder used was obtained from I.C.I. Plastics Division and contained no additives.

Sample Preparation

The required amount of stabilizer was dissolved in a minimum of diethyl ether, and the solution was stirred with polypropylene powder (1 g). After evaporation of the solvent, the powder was pressed between aluminum sheets at 200°. Control films were prepared by stirring the polypropylene with ether and subsequently pressing into films in the same way.

Light Stability Tests

The films were irradiated in a Xenotest 150 apparatus under conditions of simulated daylight. The black-body temperature of the irradiated surfaces was 45°, and the effective humidity¹³ was 40%.

The extent of photo-oxidation of the films was monitored by measuring the ratio of infrared absorption at 1720 cm^{-1} (due to carbonyl group formation) to that at 1890 cm^{-1} .¹⁴ The time taken to embrittlement, i.e., when the film cracked on simple flexing, was also noted.

Flash Photolysis Measurements

The laser nanosecond flash photolysis apparatus is described elsewhere.⁶ The solutions used had an absorbance of ca. 1.8 at the incident wavelength (347 nm) corresponding to a concentration of 0.4 mole/m^3 and 0.6 mole/m^3 for 1-benzoyl-2-naphthol in benzene and methanol, respectively, and to a concentration of 0.2 mole/m^3 for 6-hydroxybenzanthrone in benzene or methanol.

The microsecond flash photolysis equipment is similar to that described by Allen and McKellar.¹⁵ The quartz photolysis cells were 200 mm long and had optically flat end windows. Transient absorption was recorded on Ilford

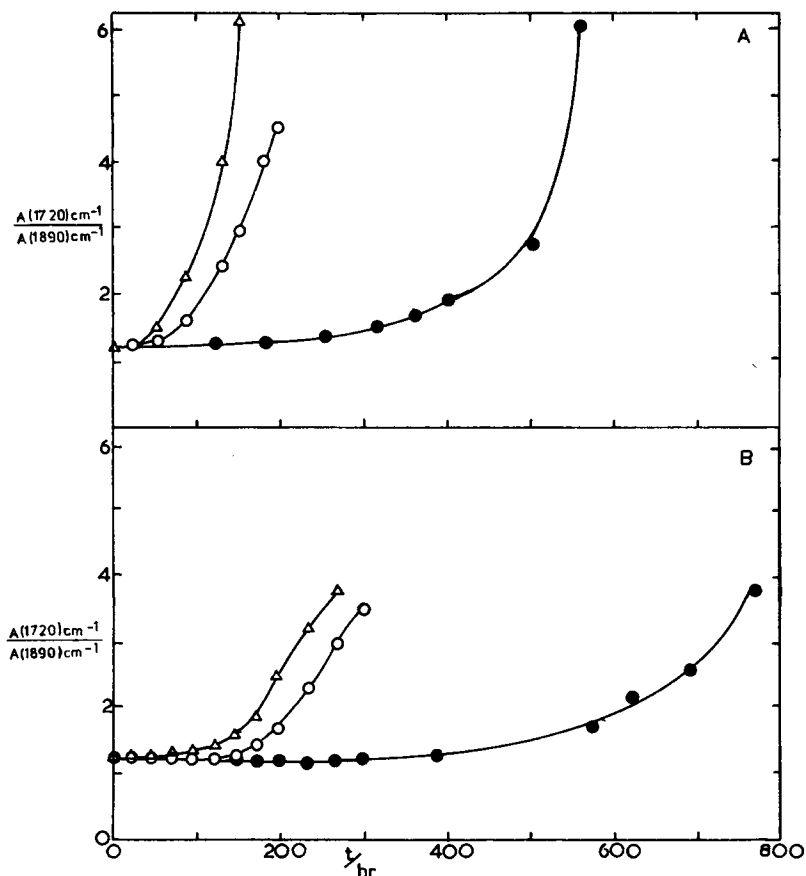


Fig. 1. Effect of light on the carbonyl index of polypropylene films containing 0.1% (A) and 0.5% (B) 1-benzoyl-2-naphthol (●-●), 6-hydroxybenzanthrone (Δ-Δ), and no additive (○-○). The data obtained in (A) and (B) were obtained in independent experiments and were carried out with lamps of slightly different light intensity.

TABLE I
Effect of Additives on the Photodegradation of Polypropylene Film^a

	Time to embrittlement, hr	
	Run 1 (0.1% Additive)	Run 2 (0.5% Additive)
Control	180	220
1-Benzoyl-2-naphthol	500	680
6-Hydroxybenzanthrone	120	140

^a Runs 1 and 2 are independent experiments and were carried out with xenon lamps of slightly different light intensity.

HP3 photographic plates which are sensitive to light of wavelengths shorter than ca. 600 nm.

Luminescence Measurements

Luminescence measurements were performed on Perkin-Elmer MPF-4 and Baird-Atomic Fluorispec 100E instruments. The emission monochromator-photomultiplier combination of the instruments was calibrated by means of compounds whose corrected emission spectra have been accurately determined by earlier workers.¹⁶ The excitation source-excitation monochromator combination of the instruments was calibrated using quinine sulfate [(1-10) × 10⁻³ mole/m³] in sulfuric acid (500 mole/m³), and rhodamine B (8000 g/m³) in ethylene glycol, as optically dilute and optically dense quantum counters, respectively.¹⁷

Fluorescence quantum yields were determined by the relative method¹⁷ using quinine sulfate in dilute sulfuric acid as standard. The fluorescence quantum yield of quinine sulfate was assumed to be 0.55.^{17,18}

Phosphorescence quantum yields were also determined by the relative method. In this case, phenanthrene was used as standard with an assumed phosphorescence quantum yield of 0.105 in E.P.A. (ether:2-methylbutane: ethanol, 5:5:2 by vol) at 77°K.¹⁹ In the case of the phosphorescence quantum yield measurements on 1-benzoyl-2-naphthol, excitation was carried out at 334 nm where the intermolecular and intramolecular hydrogen-bonded forms have almost the same absorption coefficient. Consequently, and error due to a change in the relative proportions of the two forms on cooling would be negligible.

Phosphorescence lifetimes were determined with the Baird-Atomic instrument by rapidly shutting off the exciting light and monitoring phosphorescence decay on a high-speed chart recorder.

RESULTS AND DISCUSSION

Figure 1 shows that the rate of formation of carbonyl groups on irradiation of polypropylene is effectively inhibited by 1-benzoyl-2-naphthol while it is accelerated by 6-hydroxybenzanthrone. Similarly, the flex tests show that while 1-benzoyl-2-naphthol stabilizes polypropylene, 6-hydroxybenzanthrone acts as a prodegradant (Table I).

Since 1-benzoyl-2-naphthol-stabilized films are colorless, suitable deriva-

tives of this compound could be developed that may be of interest as commercial light stabilizers. A thorough literature search produced only one previous report of the stabilizing effect of 1-benzoyl-2-naphthol, or close derivatives, on light-sensitive polyolefins.¹¹ Films containing 6-hydroxybenzanthrone, on the other hand, are bright yellow in color. On irradiation, the color had markedly faded within approximately 50 hours. Thus, if 6-hydroxybenzanthrone, or suitable derivatives, were to be used in a prodegradant capacity,¹⁴ the user would have ample warning of the imminent self-destruction of the substrate. The loss of color from the films containing 6-hydroxybenzanthrone (which did not appear to be due to migration of the additive to the films surface) shows that the sensitizing ability of 6-hydroxybenzanthrone must be associated with its poor light stability.⁴

In order to understand these interesting and opposite effects of 1-benzoyl-2-naphthol and 6-hydroxybenzanthrone on the light stability of polypropylene, we must consider their behavior in the polymer in the light of their spectroscopic and photochemical properties. For example, the magnitude of the absorption coefficient of the long-wavelength absorption band of 1-benzoyl-2-naphthol (Fig. 2) shows that its lowest excited singlet state, like that of 6-hydroxybenzanthrone,⁵ is $\pi\pi^*$ in nature. However, on increasing solvent polarity, the long wavelength absorption maximum of 1-benzoyl-2-naphthol moves to shorter wavelengths. This effect is caused by either partial or com-

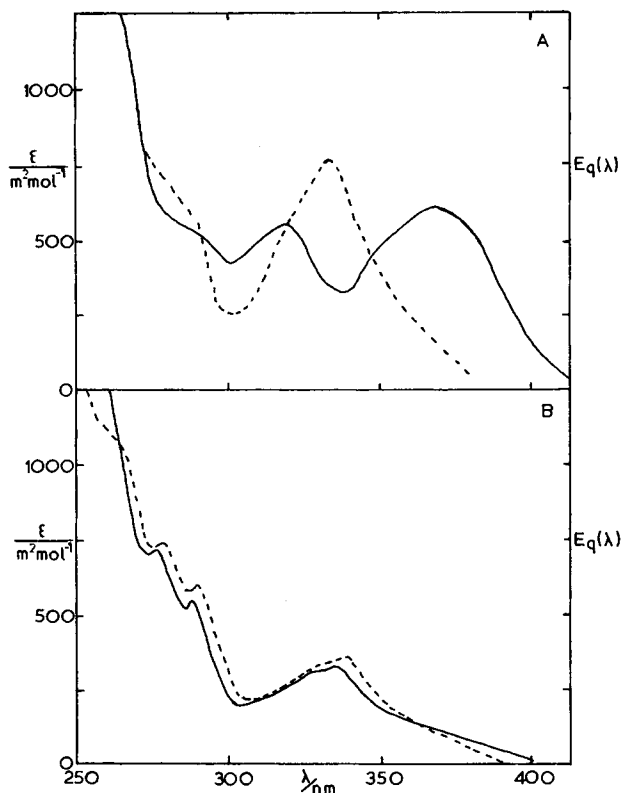


Fig. 2. Electronic absorption spectrum at 298°K (—) and corrected phosphorescence excitation spectrum at 77°K (- -) of 1-benzoyl-2-naphthol in 2-methylbutane (A) and EPA (B).

TABLE II
Summary of Flash Photolysis and Luminescence Experiments

Experiment	1-Benzoyl-2-naphthol	6-Hydroxy-benzanthrone
Microsecond flash photolysis transients		
benzene	not observed	yes ^a
methanol	not observed	yes ^a
Nanosecond flash photolysis transients		
benzene	not observed	yes ^a
methanol	not observed	yes ^a
Fluorescence at 298°K		
hexane	not observed ($\phi_f < 10^{-5}$)	$\phi_f = 0.05 \pm 0.02$
methanol	not observed ($\phi_f < 10^{-5}$)	$\phi_f = 0.07 \pm 0.02^b$
Phosphorescence at 77°K		
2-methylbutane	$\phi_p = 0.03$	—
EPA ^c	$\phi_p = 0.15$ $\tau = 0.55 \text{ sec}$	$\phi_p = 0.009$ $\tau = 0.06 \text{ sec}$

^a Ref. 6.

^b Ref. 8.

^c Ether:2-methylbutane:ethanol = 5:5:2 by vol.

plete disruption of the intramolecular hydrogen bond, present in nonpolar solvents, by hydrogen bonding solvents such as ethanol²⁰ and is facilitated by the free rotation of the hydroxynaphthyl moiety. In the case of 6-hydroxybenzanthrone, on the other hand, the carbonyl and hydroxyl groups are held in close proximity by the carbon skeleton, and, accordingly, the long-wavelength absorption maximum of 6-hydroxybenzanthrone is unaffected by solvent polarity.⁵

Another difference between the two compounds is that, while 6-hydroxybenzanthrone exhibits relatively efficient fluorescence, fluorescence from 1-benzoyl-2-naphthol could not be detected in either hexane or methanol (Table II). The lack of fluorescence from 1-benzoyl-2-naphthol shows that

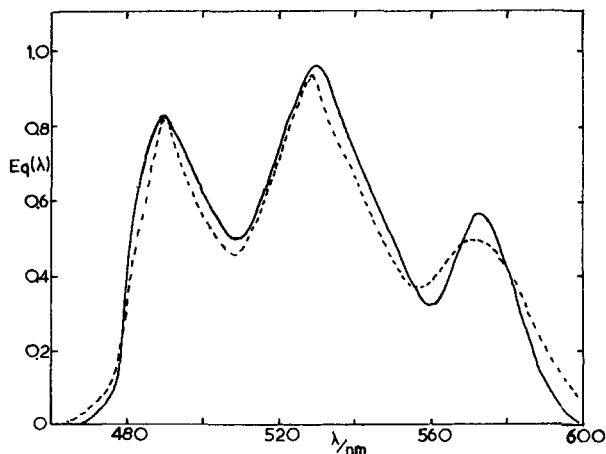


Fig. 3. Corrected phosphorescence spectrum of 1-benzoyl-2-naphthol in 2-methylbutane (—) and EPA (---) glass at 77°K.

the lowest excited singlet state is very short-lived. Rapid decay of the singlet state, however, does not appear to result in triplet formation, since, in contrast to 6-hydroxybenzanthrone, no transient absorption is observed on either microsecond or nanosecond flash photolysis. These observations suggest, therefore, that in fluid solution photoexcited 1-benzoyl-2-naphthol, like 2-hydroxybenzophenone, is rapidly deactivated within the singlet manifold.^{2,7}

In contrast to its behavior in fluid solution, the phosphorescence spectra (Fig. 3) show that 1-benzoyl-2-naphthol can undergo intersystem crossing to the triplet in rigid glass at 77°K. However, examination of the phosphorescence excitation spectra (Fig. 2) shows that only molecules in which the intramolecular hydrogen bond is disrupted achieve the phosphorescent state. In accordance with this observation, the phosphorescence quantum yield is considerably lower in 2-methylbutane than in EPA (Table II). Similar behavior is exhibited by 2-hydroxybenzophenone whose phosphorescence quantum yield is also solvent dependent.⁷ Finally, it is noteworthy that the phosphorescence from both 1-benzoyl-2-naphthol and 6-hydroxybenzanthrone is relatively long-lived, showing that in both cases the lowest excited triplet state, like the singlet, is $\pi\pi^*$ in nature.²¹

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