Interaction of a Hindered Piperidine Stabilizer with Hydroxy-Substituted Aromatic Carbonyl Compounds in the Photostabilization of Polypropylene

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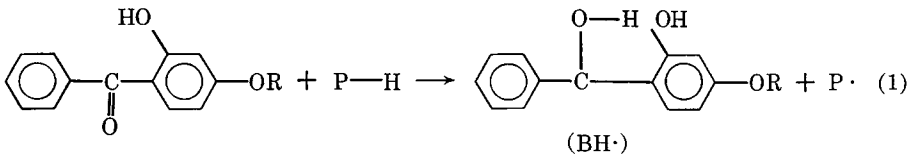
Synopsis

The effect of a hindered piperidine compound, Bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate on the photostability and light-stabilizing performance of hydroxy-substituted benzophenone and anthraquinone compounds in polypropylene film has been examined using three different light exposure units. The stabilizing effects observed were found to be highly dependent on the utraviolet content (300–340 nm) of the light source. In the absence of this utraviolet component the hindered piperidine compound inhibited the photolysis of all the hydroxy-substituted compounds, whereas in its presence no protective effect was observed. In fact, direct absorption of ultraviolet light was found to be totally ineffective in photostabilizing the polymer. The protective effects were associated with the ability of the hindered piperidine compound to destroy the hydroperoxides formed during processing. This was confirmed by the observation of no protective action with unsubstituted benzophenone and anthraquinone through both steady-state and laser flash-photolysis experiments. A further novel protective effect was observed when the hindered piperidine molecule was linked to the anthraquinone chromophore in the 2-position to the carbonyl group. In this case photoprotection is associated with an intramolecular excited-state quenching process.

INTRODUCTION

The interaction of hindered piperidine compounds with other ultraviolet stabilizers in polyolefins is currently a topic of considerable scientific and technological interest.[1–7] While a number of hindered piperidines are excellent light stabilizers, ultraviolet absorbers such as the 2-hydroxybenzophenones and 2-hydroxyphenylbenzotriazoles are often used to enhance their performance in certain applications. However, recent work by the authors[6,7] has shown that while hindered piperidine compounds protect these ultraviolet absorbers, the effective does not lead to synergism. For the 2-hydroxybenzophenones for example, there are essentially two mechanisms through which they may react on light exposure in the polymer. The first mechanism involves a hydrogen atom abstraction process by the excited triplet benzophenone to give a ketyl radical:



(1)

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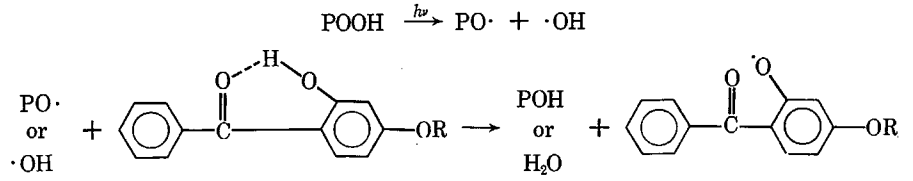
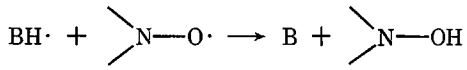
where R = H or n—$C_8H_{17}O$. For the 2-hydroxy derivative this reaction will have a very low quantum yield, since radiationless deactivation through photoenolization is predominant.[8]

The second mechanism involves abstraction of the hydrogen atom from the *ortho* hydroxy group by alkoxy or hydroxyl radicals produced in the photolysis of hydroperoxides:



(2)

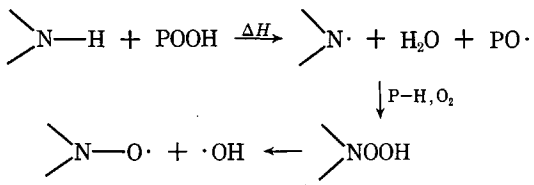
On the basis of these two processes there are two mechanisms of protection by the hindered piperidine compounds. The first involves regeneration of the 2-hydroxybenzophenone by reaction of the ketyl radical (BH·) formed in reaction (1) with a nitroxy radical:[6]



(3)

The nitroxy radical is produced during thermal or photooxidation of the hindered piperidine compound.[1-7]

The second mechanism involves destruction of the hydroperoxides by the hindered piperidine compound to give a nitroxy radical via the following stoichiometric reaction scheme:[1,6]



(4)

To establish more clearly the mode of protection of hindered piperidine compounds we have examined in detail the interaction of one important commercial compound, Bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate with a number of hydroxy-substituted benzophenone and anthraquinone compounds. This will enable us to establish not only whether the position of substitution is important, e.g., hydrogen-bonded or non-hydrogen-bonded to the carbonyl group, but whether these stabilizing effects extrapolate to other chromophoric systems. Further, to resolve the relative importance of mechanisms (3) and (4) we have examined the above systems using two quite different polychromatic light exposure units. One employs a filtered xenon/Hg source which is very rich in ultraviolet (UV) light in the 300–340 nm range while the other exhibits virtually no emission in this region and employs a fluorescent Hg/W source (see Fig. 1 later). In the first exposure unit direct absorption of UV light by the hydroxy compounds will occur and hence photoreaction through mechanism (1) is expected to dominate. All the hydroxy derivatives exhibit high absorption in this

wavelength region and their spectra are well documented.[6,9,10] In the second unit a photoinduced reaction is expected to dominate through mechanism (2). To confirm the involvement of a photosensitized reaction we have also exposed some of the samples to a fluorescent lamp which emits an intense UV line at 365 nm only. The experimental results clearly demonstrate the dependence of reactions (1) and (2) on the UV content of the light sources.

Finally, in this work we have discovered an interesting reaction between 2-hydroxyanthraquinone and the hindered piperidine compound which leads to a powerful stabilizing process on the anthraquinone chromophore.

EXPERIMENTAL

Materials

Polypropylene powder containing no commercial additives was supplied by I.C.I. (Plastics and Petrochemicals Division) Ltd., U.K. Samples of light stabilizers 2-hydroxy-4-*n*-octoxybenzophenone (U.V. 531) and Bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate (Tinuvin 770) were supplied by American Cyanamid Co., New Jersey, and Ciba-Geigy Corp., Basel, Switzerland, respectively. Samples of hydroxy-substituted anthraquinones and benzophenones and 2-piperidinoanthraquinone were supplied by the Fine Chemicals Service of I.C.I. Ltd., Manchester, U.K. Anthraquinone, benzophenone, and quinine sulfate were purchased from Hopkin & Williams Ltd., U.K. All the compounds except quinine sulfate were recrystallized from "Analar" ethanol until their melting points were in agreement with the literature values. The compound 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy was purchased from Eastman Kodak Company, New York.

All the additives were solvent blended into polypropylene powder at 0.1% w/w concentration using dichloromethane. The solvent was allowed to evaporate at room temperature overnight. Films 200 μm thick were then prepared by pressing the powder between sheets of aluminum foil at 200°C for 1 min. The films were then quench cooled in cold water.

Irradiation Units

All the films were exposed in a Microscal apparatus, Microscal Ltd. (London) utilizing a 500 W high pressure Hg/tungsten fluorescent source at Manchester Polytechnic and in a SEPAP 70:07 unit utilizing a 1000 W xenon/Hg lamp at the Universite de Clermont II. Both units operate at low relative humidities of less than 20% and 50°C.

Films were also exposed in front of a Phillips fluorescent TL20 W lamp. Figure 1 compares the spectral distribution of all three light sources. While the 1000 W xenon/Hg lamp is expected to be considerably more intense than the 500 W Hg/W source it is seen to posses intense UV lines at 313 and 333 nm both of which are absent in the spectrum of the Hg/W source. The Phillips TL20 W fluroescent lamp emits only a broad emission line at 365 nm (half-width ~30 nm).

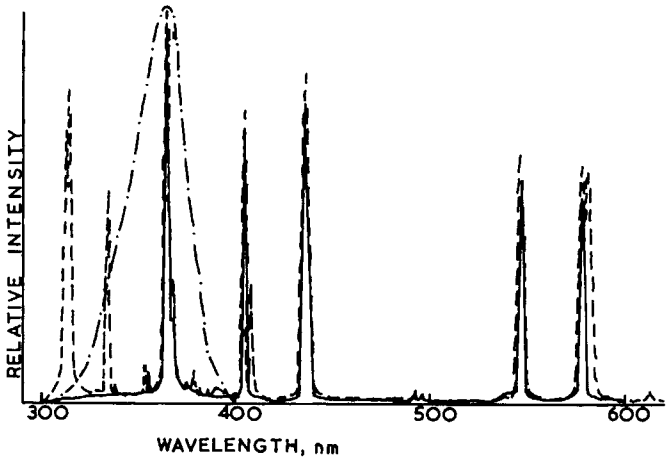


Fig. 1. Comparison of the spectral distribution of the 500 W fluorescent Hg/Wo source (—), 1000 W xenon/Hg source (- - -), and Phillips TL 20 W fluorescent lamp (—.—.).

Rates of Photooxidation

Rates of photooxidation of the polymer films were monitored by infrared using the well-established carbonyl index method.[1–3,5–7] Spectra were recorded using Perkin–Elmer spectrometers models 457 (Manchester Polytechnic) and 682 (Universite de Clermont II).

UV-Visible Absorption Spectra

Spectra were recorded at both institutions using a Perkin–Elmer spectrophotometer model 554.

Laser Flash Photolysis

Flash photolysis experiments were obtained using a neodymium laser set-up at Kelsterton College, North Wales, U.K. After doubling the frequency twice, the wavelength of excitation was 265 nm.

Fluorescent Measurements

Fluorescence spectra were recorded using a double-beam Perkin–Elmer spectrofluorimeter model MPF-3L. Quantum yield measurements were obtained using quinine sulfate as a standard (ϕ_f = 0.55).[11] The quinine sulfate was purified as described earlier.[12]

RESULTS

Microscal Exposure Results

The light stabilities of all the polypropylene films exposed in the Microscal unit are compared in Table I. The data shown are embrittlement times and these were found to correspond with a carbonyl index value of 0.06 units. Comparing

TABLE I
UV Embrittlement Times for Polypropylene Films in the Microscal and SEPAP Units

Additives (0.1% w/w each)	Embrittlement times (h)	
	Microscal	SEPAP
Control	100	25
Benzophenone	40	18
Benzophenone + Tinuvin 770	440	400
U.V.531	1630	80
U.V.531 + Tinuvin 770	3300	300
4-Hydroxybenzophenone	80	8
4-Hydroxybenzophenone + Tinuvin 770	1270	130
2-Hydroxybenzophenone	175	25
2-Hydroxybenzophenone + Tinuvin 770	2000	200
Anthraquinone	24	18
Anthraquinone + Tinuvin 770	240	190
1-Hydroxyanthraquinone	155	8
1-Hydroxyanthraquinone + Tinuvin 770	3100	180
2-Hydroxyanthraquinone	120	8
2-Hydroxyanthraquinone + Tinuvin 770	1000	80
Tinuvin 770	2720	270

the data it is seen that as expected both benzophenone and anthraquinone are powerful photosensitizers. The presence of the hindered piperidine compound inhibits the photosensitizing action and these results essentially confirm our earlier findings.[7] The hindered piperidine compound, Tinuvin 770, is, again, as expected, more effective than U.V.531, but together they are clearly antagonistic. Comparing 4-hydroxybenzophenone with the 2-hydroxy derivative it is seen that while the former is a weak sensitizer, the latter is surprisingly only a weak stabilizer. Clearly, the presence of the 4-*n*-octoxy group in U.V. 531 plays a vital role in the achievement of high stability and will be discussed later. Both 1-hydroxy and 2-hydroxyanthraquinones are also only very weak stabilizers. While the presence of Tinuvin 770 gives good protection with all these hydroxy derivatives, it is seen that strong antagonism is displayed in all but one case. In this case 1-hydroxyanthraquinone is synergistic with Tinuvin 770.

The rates of photolysis of all the benzophenone and anthraquinone compounds are shown in Figures 2 and 3, respectively. Here the decrease in absorbance of each compound at a particular absorption maximum is plotted against exposure time. Both figures exhibit a number of interesting features. First, in agreement with our earlier work,[6,7] it is seen that while the presence of Tinuvin 770 does not inhibit the photolysis of benzophenone and anthraquinone, it does protect U.V. 531. The initial increase in absorption of the U.V. 531 is due to aggregation of the stabilizer molecules; an effect quite common with dyestuffs.[13] Second, the inhibitory effect of Tinuvin 770 also occurs with the simpler 2- and 4-hydroxybenzophenones (Fig. 2) and 1-hydroxyanthraquinone (Fig. 3). Clearly, the position of substitution and the effect of intramolecular hydrogen bonding is unimportant here.

The third and certainly one of the most interesting results is the interaction between 2-hydroxyanthraquinone and Tinuvin 770. Here, both compounds reacted in dichloromethane to give an orange-red crystalline product which is almost certainly the 2-substituted hindered piperidinyl derivative of anthra-

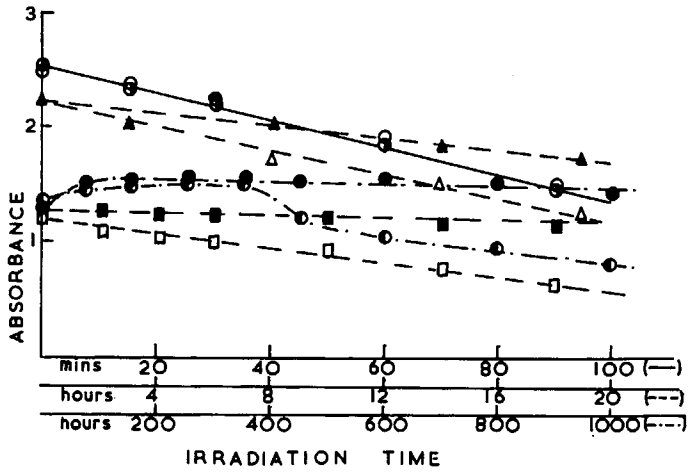
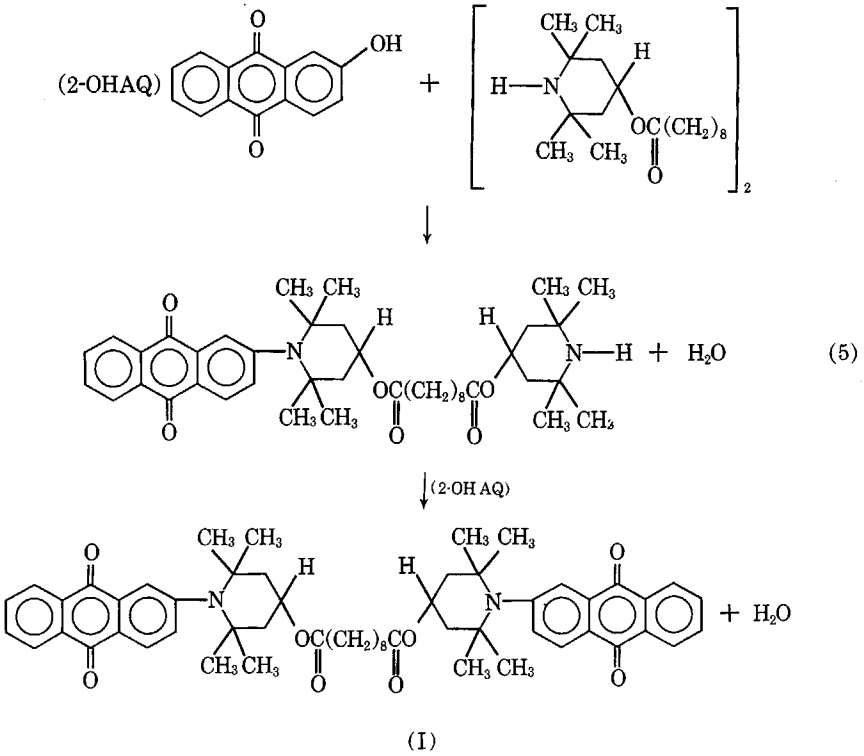


Fig. 2. Change in absorbance vs. irradiation time in the Microscal unit for (○) benzophenone and (◑) benzophenone + Tinuvin 770 (251 nm); (◐) U.V.531 and (●) U.V.531 + Tinuvin 770 (325 nm); (△) 4-hydroxybenzophenone and (▲) 4-hydroxybenzophenone + Tinuvin 770 (300 nm); (□) 2-hydroxybenzophenone and (■) 2-hydroxybenzophenone + Tinuvin 770 (255 nm) in polypropylene film (~ 200 μm thick). All additives were 0.1% w/w.

quinone produced through the following condensation reaction:



Under the concentration conditions employed in this work reaction scheme (5) would go to completion to give the product Bis[*N*-(2-anthraquinonyl)2,2,6,6-

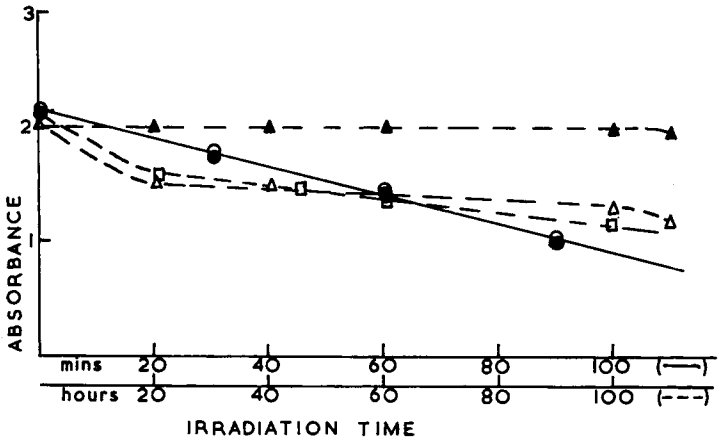


Fig. 3. Change in absorbances vs. irradiation time in the Microsal unit for (○) anthraquinone and (●) anthraquinone + Tinuvin 770 (252 nm); (△) 1-hydroxyanthraquinone and (▲) 1-hydroxyanthraquinone + Tinuvin 770 (250 nm), and (□) Bis[*N*-(2-anthraquinonyl)2,2,6,6-tetramethyl-4-piperidinyl] sebacate (250 nm) in polypropylene film (~ 200 μm thick). All additives were 0.1% w/w.

tetramethyl-4-piperidinyl] sebacate. This reaction is well known and occurs readily at room temperature between 2-chloro- or 2-hydroxyanthraquinones and piperidine to give 2-piperidinoanthraquinone.[14] In the case of Tinuvin 770 steric hinderance by the bulky methyl groups would inhibit the reaction with 1-hydroxyanthraquinone. Figure 4 shows that the visible absorption spectrum of the product (I) above matches very closely that of 2-piperidinoanthraquinone in chloroform.

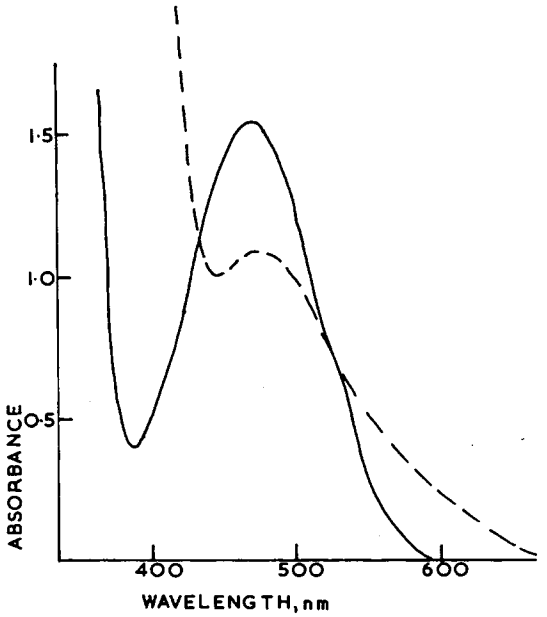


Fig. 4. Absorption spectrum of 2-piperidino anthraquinone (——) compared with that of Bis[N-(2-anthraquinonyl)2,2,6,6-tetramethyl-4-piperidinyl] sebacate (- - -) in chloroform (~ $10^{-4}M$).

SEPAP Exposure Results

The light stabilities of all the polypropylene films exposed in the SEPAP unit are also shown in Table I. Comparing the data with those in the Microscal unit it is seen that many of the results are quite conflicting. First, it is seen that all the hydroxy derivatives except U.V.531 and 2-hydroxybenzophenone are powerful photoinducers; even more powerful than benzophenone and anthraquinone. This must clearly be due to the strong overlap between the absorption spectra of the hydroxy compounds (Fig. 5) and the UV emission lines in the wavelength region 300–340 nm. Again the role of the 4-substituted *n*-octoxy group is extremely important, but under these exposure conditions the performance of the U.V. 531 compared to the control is reduced from a factor of 16 in the Microscal unit to only 4 in the SEPAP unit. The performance of Tinuvin 770 is also considerably reduced relative to the control, and antagonism is observed with the hydroxy-substituted compounds. One unexplainable result is the synergism between benzophenone and Tinuvin 770.

The rates of disappearance of all the compounds were found to be completely unaffected by the presence of Tinuvin 770 in the SEPAP unit.

Examples of this are shown in Figure 6 for 2-hydroxybenzophenone and U.V.531. It is interesting to note that in both exposure units the rate of disappearance of U.V.531 is considerably slower than 2-hydroxybenzophenone. Throughout the exposure periods employed here there was no evidence of additive migration to the surface of the polymers. The spectral changes observed were photochemical.

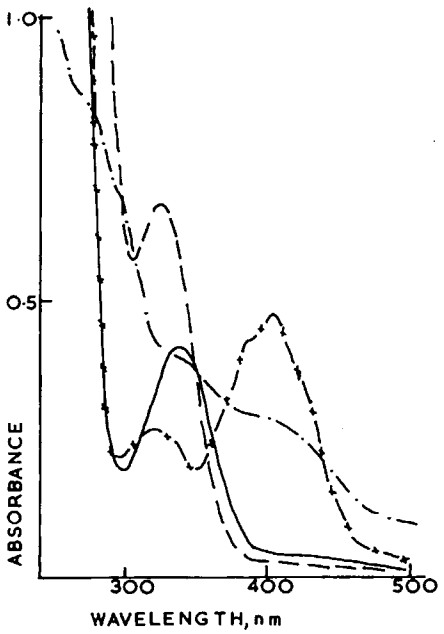


Fig. 5. Absorption spectra of (——) 2-hydroxybenzophenone, (- - -) U.V.531, (-·-) 2-hydroxyanthraquinone, and (—X—X) 1-hydroxyanthraquinone in polypropylene film (~ 200 μm thick).

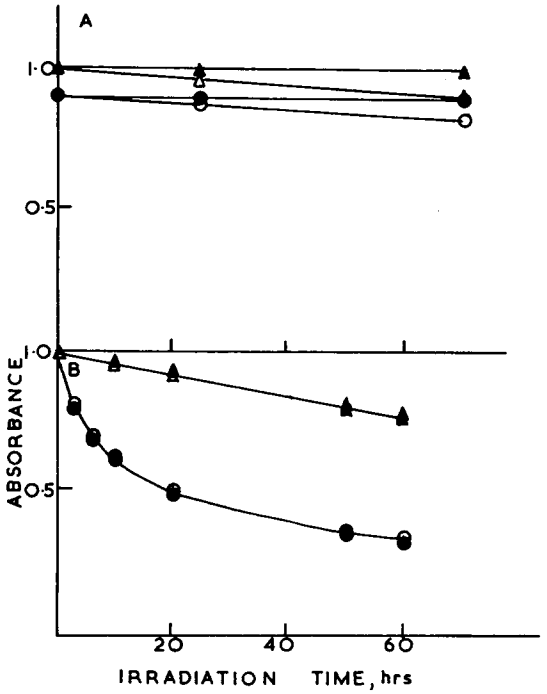


Fig. 6. Change in absorbance vs. irradiation time in (A) the Phillips TL20 W source and (B) SEPAP unit for (○) 2-hydroxybenzophenone and (●) 2-hydroxybenzophenone + Tinuvin 770 (340 nm); (△) U.V.531 and (▲) U.V.531 + Tinuvin 770 (325 nm) in polypropylene film (~ 200 μm thick). All additives were 0.1% w/w.

DISCUSSION

The results are evidently quite complex but apart from one or two anomalies a nubmer of important features arise which can account for the protective effects often displayed by hindered piperidine compounds in commercial polyolefins. The marked stabilizing effect of Tinuvin 770 on the photooxidation of U.V.531 in the Microscal is clearly due to its ability to destroy hydroperoxides through mechanism (4) and this is confirmed by the absence of a stabilizing effect in the SEPAP exposure unit. In the presence of strong UV light, in the 300–340 nm wavelength region, where the U.V.531 absorbs (Fig. 5) direct photolysis will occur [reaction (1)] whereas in its absence a photoinduced reaction will dominate [reaction (2)]. This conclusion is indicated by a further set of experiments carried out using a fluorescent lamp which emits a broad line at 365 nm. The results of this experiment are shown in Figure 6 where is it seen that the presence of Tinuvin 770 inhibits the photolysis of both 2-hydroxybenzophenone and U.V.531. The protective mechanism shown in reaction (3) would appear to be more important under conditions which involve direct photolysis, although from a comparison of the stabilizing effects its efficiency would appear to be lower. To exclude the slight possibility of any excited-state quenching by the amine or nitroxy radical we have also carried out some laser-flash photolysis experiments on anthraquinone and benzophenone in polypropylene film with and without a model nitroxy radical and Tinuvin 770. The results of this work are shown in Figure 7 where it is seen that neither the amine nor the nitroxy radical affected the transient absorptions produced on laser-flash photolysis of either carbonyl

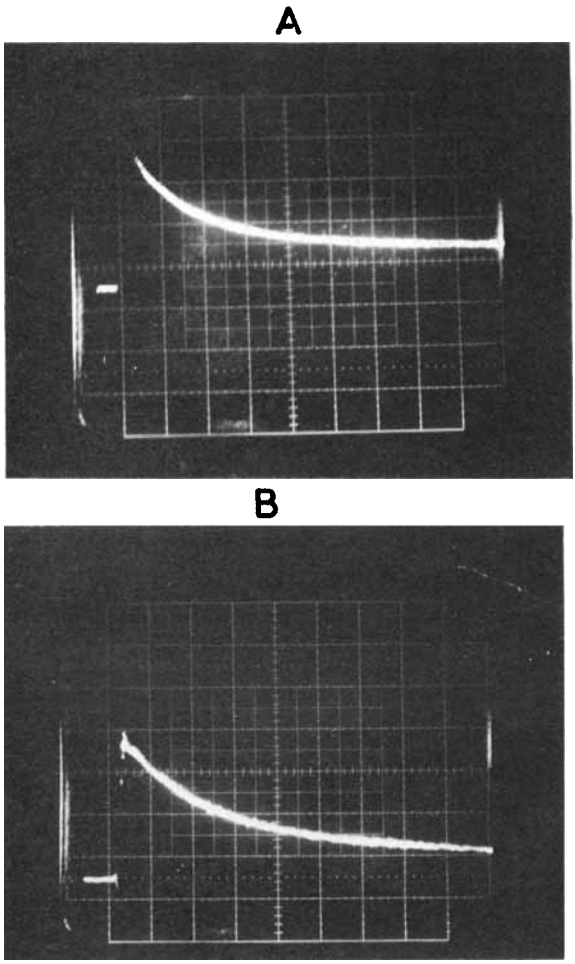


Fig. 7. End-of-pulse transient decays produced on laser photolysis (265 nm) of (A) anthraquinone and (B) benzophenone in polypropylene. Presence of Tinuvin 770 and nitroxy radical had no effect.

compounds with light of 265 nm excitation. The decay of both transients is virtually complete over a time scale of 10 μs. Both transients are well documented in the literature[15,16] and are evidently due to the corresponding triplets. Thus, on this very short time scale there is clearly no excited-state quenching.

The photostabilization action of U.V.531 in both the Microscal and SEPAP exposure units is extremely important; however, in the SEPAP unit where protection through direct absorption of the UV light would be expected, the stabilizing action of U.V.531 is considerably reduced.

Clearly, the direct absorption of UV light is insufficient to account for the marked stabilizing effect of U.V.531 compared to 2-hydroxybenzophenone in the Microscal unit. This suggests that the 4-*n*-octoxy group plays a vital role in stabilization. This is also confirmed by the fact that in the SEPAP unit U.V.531 is a photostabilizer and 2-hydroxybenzophenone has no effect. Thus, apart from acting as a link to prevent migration, the *n*-octoxy group is also believed to enhance the intramolecular hydrogen exchange between the carbonyl

and 2-hydroxy group,[9,17] this group would also enhance the lability of the hydrogen atom of the 2-hydroxy group and the antioxidant action of U.V.531.

Finally, another interesting aspect of the results is the high photostability of the Bis-anthraquinonyl derivative of Tinuvin 770 [structure I in reaction (5)]. An examination of the results in Figure 6 shows that the photolysis of the anthraquinone moiety in this derivative occurs at a much slower rate than anthraquinone itself and this is coupled with the effect of relatively high stability. Normally 2-substitution in anthraquinone leaves the carbonyl–carbonyl groups free for photoreaction. Although photoreactivity is suppressed by the introduction of low-lying charge-transfer singlet and triplet states,[18] 2-substituted anthraquinone derivatives normally exhibit very low light stability (on the 1, S, 0 scale they have a light fastness of less than one in all substrates),[18] and in many cases are powerful sensitizers.[9,18] An examination of the luminescence properties of this compound (I) showed that it was nonphosphorescent (77K) and virtually nonfluorescent ($\phi_f < 10^{-4}$) in the hydrocarbon solvent cyclohexane. The derivative 2-piperidinoanthraquinone has an experimentally measured fluorescent quantum yield of 0.2. The absence of any emission from the Bis-anthraquinonyl derivative of Tinuvin 770 correlates with its high light stability.

Deactivation of the excited singlet and triplet state of this molecule must occur through some type of intramolecular self-quenching process. One very likely possibility is that the two substituted anthraquinone moieties could quench each other by coiling back via the long aliphatic ester chain.

CONCLUSIONS

From the results it would appear that the protective effect of hindered piperidine compounds on 2-hydroxy-substituted aromatic carbonyl stabilizers is due to their ability to destroy hydroperoxides. Stabilizers based on 2-hydroxybenzophenone operate primarily as UV antioxidants since absorption of UV alone is ineffective for the achievement of high light stability.

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