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Mechanisms of Singlet and Triplet Sensitized Decomposition of Bis(2-phenylbenzoyl) Peroxide

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Bis(2-phenylbenzoyl) peroxide (2-PhBPO) was found to decompose on singlet and triplet sensitized irradiations in benzene and carbon tetrachloride. The quantum yields were determined to be 0.48 and 0.43 on direct excitation and chrysene sensitization in benzene, respectively, and 0.62 and 0.60 on benzophenone and 3′-methoxyacetophenone sensitizations in carbon tetrachloride, respectively. The reaction mechanisms are discussed from the standpoint of the modes of bond cleavage.

Many organic peroxides have been known to decompose on heating[1] and on irradiation;[2] however, the mechanism for their photolyses has not been well understood.

Previously, dibenzoyl peroxide (BPO) was shown to decompose on direct irradiation and on singlet sensitization employing polycyclic aromatic hydrocarbons as sensitizers.[3–14] On direct and singlet sensitized photolyses BPO affords a moderate amount of phenyl benzoate, a geminate product,[12–14] in contrast with its thermolysis which produces a very low yield of the geminate product.[15,16] Through mechanistic investigations, it has been proposed that the direct and singlet sensitized irradiations of BPO result in simultaneous or successive cleavage of the peroxide linkage and carbon(carbonyl)-carbon(aromatic) bond to give a geminate pair of a benzoyloxyl and phenyl radicals which easily recombine into the geminate product,[14] whereas thermolysis of BPO is known to lead to homolytic cleavage of the peroxide linkage to give two benzoyloxyl radicals.[15,16]

In the course of extending the investigation on photochemistry of organic peroxides, bis(2-phenylbenzoyl) peroxide (2-PhBPO) was found to decompose on direct, singlet sensitized, and also triplet sensitized irradiation as well as thermolysis, the latter being known to give biphenyl-2,2′-carbolactone and 2-phenylbenzoic acid as main products.[17]

This paper describes the mechanism of photochemical decomposition of 2-PhBPO and discusses the modes of its bond cleavage depending on the reaction conditions.

Results

Products from Photochemical and Thermal Decomposition of 2-PhBPO. 2-PhBPO (0.02 mol/dm^3) was irradiated with 366-nm light at 20 °C without sensitizer in benzene and carbon tetrachloride, in the presence of chrysene (0.002 mol/dm^3) as a singlet sensitizer in benzene, and in the presence of benzophenone (0.02 mol/dm^3) as a triplet sensitizer in benzene and carbon tetrachloride. The irradiation was continued until the peroxide completely decomposed. As a control, 2-PhBPO (0.02 mol/dm^3) was thermolyzed in benzene at 80 °C and in carbon tetrachloride at 78 °C. The products are summarized in Table 1.

Effect of Temperature on the Products Arising from Thermolysis and Photolysis of 2-PhBPO. To examine the effect of temperature on the yields of products, 2-PhBPO (0.02 mol/dm^3) was irradiated in benzene in the absence of any sensitizer and in the presence of chrysene (0.002 mol/dm^3) and benzophenone (0.05 mol/dm^3) at 30 and 40 °C, and thermolyzed in benzene at 60 and 70 °C. The results are collected in Table 2 together with those at 20 °C (photolyses) and 80 °C (thermolysis).

Quantum Yields for Photochemical Decomposition of 2-PhBPO. Quantum yields, Φ, for decomposition of 2-PhBPO were determined at various concentrations of 2-PhBPO on direct irradiation in benzene with 313-nm

TABLE 1. YIELDS OF PRODUCTS IN PHOTOLYSIS AND THERMOLYSIS OF BIS(2-PHENYLBENZOYL) PEROXIDE (0.02 mol/dm^3) IN BENZENE AND CARBON TETRACHLORIDE (mol/mol PEROXIDE)

Product	Direct photolysis		Sensitized photolysis			Thermolysis	
			Chrysene	Benzophenone			
	In PhH	In CCl_4	In PhH	In PhH	In CCl_4	In PhH	In CCl_4
Biphenyl-2,2′-carbolactone	0.47	0.38	0.48	0.57	0.54	0.53	0.44
2-Phenylbenzoic acid	0.31	0.31	0.32	0.37	0.36	0.44	0.34
Biphenyl	0.36	0.06	0.31	0.31	0.02	0.50	0.03
o-Terphenyl	0.05	—	0.04	0.01	—	0.09	—
2-Chlorobiphenyl	—	0.17	—	—	0.05	—	0.35
Carbon dioxide	Not determined	0.49	0.33	0.10	0.16	0.50	0.44
Biphenyl moiety	1.19	0.92	1.15	1.08	0.97	1.56	1.16
CO_2 moiety	>0.78	1.18	1.13	1.04	1.06	1.47	1.22

Table 2. Temperature dependence of product yields in photolysis and thermolysis of bis(2-phenylbenzoyl) peroxide (0.02 mol/dm^3) in benzene (mol/mol peroxide)

Product	Direct photolysis			Sensitized photolysis						Thermolysis		
				Chrysene			Benzophenone					
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	60 °C	70 °C	80 °C
Biphenyl-2,2′-carbolactone	0.47	0.47	0.48	0.48	0.49	0.49	0.57	0.61	0.62	0.58	0.55	0.53
2-Phenylbenzoic acid	0.31	0.35	0.33	0.32	0.33	0.35	0.37	0.41	0.41	0.46	0.45	0.44
Biphenyl	0.36	0.38	0.39	0.31	0.30	0.31	0.13	0.15	0.16	0.35	0.44	0.50
o-Terphenyl	0.05	0.05	0.06	0.04	0.05	0.05	0.005	0.008	0.014	0.06	0.08	0.09

Table 3. Quantum yields for photochemical decomposition of bis(2-phenylbenzoyl) peroxide

Condition	Additive	$\frac{\text{Concn}}{\text{mol dm}^{-3}}$	$\frac{\text{Concn of 2-PhBPO}}{\text{mol dm}^{-3}}$	Solvent	Light (nm)	Quantum yield measurement			Emission quenching
						Φ_{lim}	k_d/k_r	$\frac{k_q\tau}{\text{dm}^3\text{ mol}^{-1}}$	$\frac{k_q\tau}{\text{dm}^3\text{ mol}^{-1}}$
Direct irradiation	—	—	1.2×10^{-3} -7.8×10^{-3}	C_6H_6	313	0.48 ± 0.07	—	—	—
	Naphthalene	3×10^{-4} -2.4×10^{-3}	8×10^{-3}	C_6H_6	313	0.48 ± 0.09	—	—	—
Singlet sensitization	Chrysene	0.002	1.9×10^{-3} -1.1×10^{-2}	C_6H_6	366	0.43 ± 0.02	1.3	3.0×10^2	3.3×10^2
Triplet sensitization	Benzophenone	0.02	3.2×10^{-3} -1.1×10^{-2}	CCl_4	366	0.62 ± 0.03	0.61	6.9×10^3	1.3×10^4
	3′-Methoxyacetophenone	0.06	1.6×10^{-3} -5.2×10^{-3}	CCl_4	313	0.60 ± 0.03	0.66	4.2×10^4	—
	2-Benzoylnaphthalene	0.02	8×10^{-3}	C_6H_6	366	0	—	—	—

light, on singlet sensitization by chrysene in benzene with 366-nm light, and on triplet sensitization in carbon tetrachloride by benzophenone with 366-nm light and by 3′-methoxyacetophenone with 313-nm light. An attempted use of 2-benzoylnaphthalene as a triplet sensitizer on 366-nm irradiation did not result in sensitization. For the sensitized decomposition the Stern-Volmer relationship held between the reciprocal of quantum yield and the reciprocal of peroxide concentration. In addition, an attempt was made to examine effects of naphthalene on direct irradiation of 2-PhBPO with 313-nm light in benzene under the conditions in which most incident light was absorbed by the peroxide. The results are depicted in Figs. 1—5. Table 3 summarizes the limiting quantum yields, Φ_{lim}, the quantum yields extrapolated to the infinite concentration of the peroxide or naphthalene, along with the related quantities.

Quenching of the Excited States of Sensitizers by 2-PhBPO. Fluorescence of chrysene was quenched by varying concentrations of 2-PhBPO in benzene under argon to give a linear Stern-Volmer relationship with $k_q\tau_s$ of 330 dm^3/mol, which, combined with the lifetime, τ_s, of singlet chrysene without the peroxide in benzene under argon, 39 ns, affords the quenching rate constant, $k_q=8.5\times10^9$ dm^3 mol^{-1} s^{-1}.

Phosphorescence of benzophenone was quenched by 2-PhBPO, biphenyl, and phenyl 2-phenylbenzoate in carbon tetrachloride under argon at room temperature to show linear Stern-Volmer relationships with $k_q\tau_T$'s of 1.3×10^4, 1.3×10^4, and 3.8×10^3 dm^3/mol, respectively. These values, divided by the lifetime of triplet benzophenone determined in the absence of the quenchers under otherwise similar conditions as above, 6 μs, lead to the quenching rate constants of 2-PhBPO, biphenyl, and phenyl 2-phenylbenzoate, $k_q=2.2\times10^9$, 2.2×10^9, and 6.3×10^8 dm^3 mol^{-1} s^{-1}, respectively.

Discussion

Singlet Sensitization. 2-PhBPO was decomposed by sensitization with singlet excited chrysene. Fluorescence of chrysene was quenched by 2-PhBPO at a rate constant which is close to the diffusion-controlled rate constant, 8.5×10^9 dm^3 mol^{-1} s^{-1}. However, singlet excitation transfer from chrysene to 2-PhBPO cannot take place, since the singlet excitation energy of chrysene, 79 kcal†/mol,[18] would not be sufficient to excite 2-PhBPO possessing the singlet excitation energy of 90—100 kcal/mol as estimated from its absorption spectrum. Therefore, it is probable that 2-PhBPO quenches singlet excited chrysene through formation of an exciplex as previously reported on BPO.[12]

Accordingly, the singlet sensitized decomposition of 2-PhBPO will proceed through the following mechanism as proposed for BPO[12] with rate constants denoted for the corresponding processes, where D and P represent a sensitizer and 2-PhBPO, respectively.

The Stern-Volmer plot (Fig. 1) fits equation 6 derived from Scheme 1.

The $k_q\tau_s$ value, 300 dm^3/mol, obtained from Fig. 1,

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† 1 cal=4.184 J.

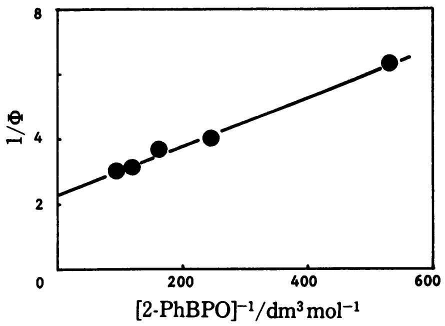

Fig. 1. Stern-Volmer plot for chrysene-sensitized decomposition of bis(2-phenylbenzoyl) peroxide on irradiation with 366-nm light in benzene.

$$\mathrm{D} \xrightarrow{h\nu} {}^1\mathrm{D}^* \qquad (1)$$

$$ {}^1\mathrm{D}^* \xrightarrow{1/\tau_s} \mathrm{D} \qquad (2)$$

$$ {}^1\mathrm{D}^* + \mathrm{P} \xrightarrow{k_q} ({}^1\mathrm{D}^*\mathrm{P}) \qquad (3)$$

$$ ({}^1\mathrm{D}^*\mathrm{P}) \xrightarrow{k_r} \text{Free radicals} + \mathrm{D} \qquad (4)$$

$$ ({}^1\mathrm{D}^*\mathrm{P}) \xrightarrow{k_d} \mathrm{D} + \mathrm{P} \qquad (5)$$

Scheme 1.

$$1/\Phi = (1+k_d/k_r)(1+1/k_q\tau_s[\mathrm{P}]) \qquad (6)$$

agrees well with the $k_q\tau_s$ value, 330 dm³/mol, determined from the fluorescence quenching.

Triplet Sensitization. Among the sensitizers examined, benzophenone and 3′-methoxyacetophenone carrying the triplet excitation energies of 69 and 72 kcal/mol,[18] respectively, effectively sensitized decomposition of the peroxide; however, 2-benzoylnaphthalene with the lower triplet energy, 60 kcal/mol,[18] failed to sensitize. In view of the fact that 2-PhBPO quenched triplet benzophenone at a rate constant which is close to the diffusion-controlled rate constant, 2.2×10^9 dm³ mol⁻¹ s⁻¹, the above result shows that the triplet energy of 2-PhBPO must be much higher than that of 2-benzoylnaphthalene and slightly lower than that of benzophenone. Phosphorescence of 2-PhBPO was not detected in EPA at 77 K; however, it is reasonable to assume that 2-PhBPO has nearly the same triplet energy as biphenyl and 2-phenylbenzoic acid, both of which exhibited in EPA at 77 K phosphorescence corresponding to the triplet energy of 67 kcal/mol.[18] Therefore, the triplet sensitized decomposition of 2-PhBPO will proceed as shown in the following scheme which involves energy transfer from the triplet excited sensitizer to the peroxide resulting in the triplet excited state of the peroxide and its decomposition into free radicals, where Φ_{ST} is the quantum yield for intersystem crossing of the sensitizer.

$$\mathrm{D} \xrightarrow{h\nu} {}^1\mathrm{D}^* \xrightarrow{\Phi_{ST}} {}^3\mathrm{D}^* \qquad (7)$$

$$ {}^3\mathrm{D}^* \xrightarrow{1/\tau_T} \mathrm{D} \qquad (8)$$

$$ {}^3\mathrm{D}^* + \mathrm{P} \xrightarrow{k_q} {}^3\mathrm{P}^* + \mathrm{D} \qquad (9)$$

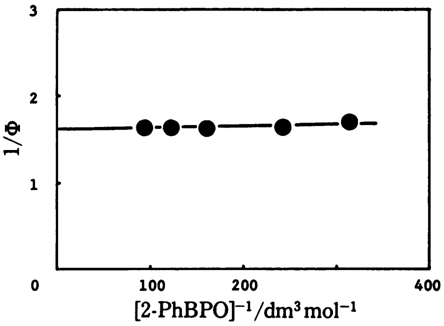

Fig. 2. Stern-Volmer plot for benzophenone-sensitized decomposition of bis(2-phenylbenzoyl) peroxide on irradiation with 366-nm light in carbon tetrachloride.

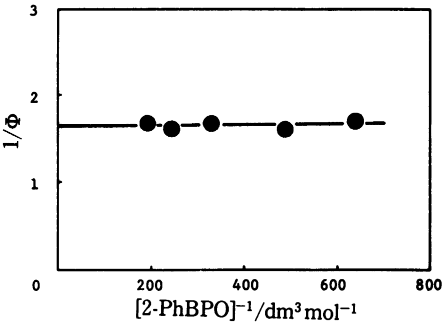

Fig. 3. Stern-Volmer plot for 3′-methoxyacetophenone-sensitized decomposition of bis(2-phenylbenzoyl) peroxide on irradiation with 313-nm light in carbon tetrachloride.

$$ {}^3\mathrm{P}^* \xrightarrow{k_r} \text{Free radicals} \qquad (10)$$

$$ {}^3\mathrm{P}^* \xrightarrow{k_d} \mathrm{P} \qquad (11)$$

Scheme 2.

The above mechanism leads to the following Stern–Volmer relationship.

$$1/\Phi = (1/\Phi_{ST})(1+k_d/k_r)(1+1/k_q\tau_T[\mathrm{P}]) \qquad (12)$$

The Stern-Volmer plots for photolyses sensitized by benzophenone and 3′-methoxyacetophenone (Figs. 2 and 3) exhibited linear relationships to give $k_q\tau_T$ values. The $k_q\tau_T$ value thus obtained for benzophenone, 6.9×10^3 dm³/mol, agrees fairly well with that obtained from phosphorescence quenching, 1.3×10^4 dm³/mol. These results support Scheme 2.

As to the triplet excitation transfer from sensitizers to the peroxide, it is noticeable that phenyl 2-phenylbenzoate and biphenyl quench triplet benzophenone almost as efficiently as 2-PhBPO. Accordingly, triplet excitation of benzophenone must be transferred to the biphenyl moieties of 2-PhBPO and phenyl 2-phenylbenzoate.

The resulting triplet state of 2-PhBPO will dissipate its electronic excitation through cleavage of the peroxide bond with a probability corresponding to the limiting quantum yield, $\Phi_{\mathrm{lim}}=k_r/(k_r+k_d)$, which is nearly 0.6 for both benzophenone and 3′-methoxyacetophenone sensitizations. It is noticeable that this value is in the same magnitude as the quantum yields reported by Leffler and Miley[19] for the decomposition of dibenzoyl peroxides substituted with a benzophenone moiety as an intramolecular sensitizing chromophore. Since the activa-

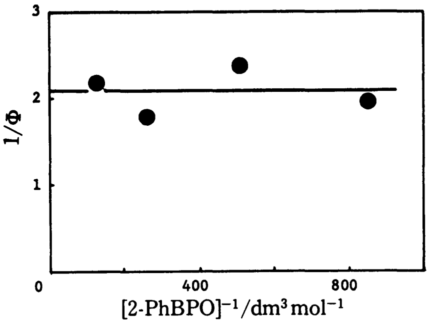

Fig. 4. Reciprocal plot of quantum yield for decomposition of bis(2-phenylbenzoyl) peroxide *vs.* concentration of the peroxide on irradiation with 313-nm light in benzene.

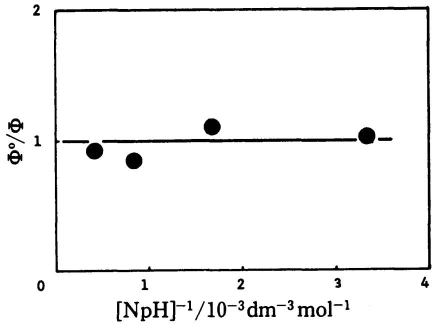

Fig. 5. Plot of relative quantum yield for decomposition of bis(2-phenylbenzoyl) peroxide *vs.* reciprocal concentration of naphthalene on irradiation with 313-nm light in benzene.

tion energy for homolytic cleavage of the peroxide bond is estimated to be around 30 kcal/mol[15,16] the excitation energy of the biphenyl moiety, 67 kcal/mol, must be sufficient to induce cleavage of the peroxide bond in view of the results on triplet sensitized decomposition of aromatic oxime esters, RR′C=NOCOR″, in which only the aromatic moieties, RR′C=, with sufficient triplet energies can induce cleavage of the N–O bond.[20,21]

Direct Irradiation. Direct irradiation of 2-PhBPO in benzene leads to decomposition of the peroxide with a quantum yield of nearly 0.5. As Fig. 4 indicates, the quantum yield was almost unchanged with nearly six fold increase in peroxide concentration. On addition of naphthalene in concentrations varying more than eight times, the quantum yield was essentially unchanged (Fig. 5). This result shows that direct irradiation leads to decomposition of the peroxide either from the singlet excited state or from a triplet state with a lifetime shorter than 10^{-6} s; the triplet state of 2-PhBPO, if its lifetime were longer than 10^{-6} s, should be efficiently quenched by naphthalene, since the quenching must be exothermic.

Mechanism of the Photolyses. As Table 1 indicates, photolyses of 2-PhBPO gave similar products as those resulting from thermolysis in the same solvent. Formation of most products from the photolyses can be understood by the mechanism as reported for the thermolysis, in which the peroxide undergoes homolytic cleavage of the peroxide linkage to give 2-phenylbenzoyloxyl radicals followed by their reactions.[17] However, careful inspection of Table 1 shows that the triplet sensitized photolysis gave lower yields of both carbon dioxide and the products derived from 2-biphenylyl radicals like biphenyl, *o*-terphenyl, and 2-chlorobiphenyl, and on the other hand, a higher yield of biphenyl-2,2′-carbolactone than the direct irradiation and singlet sensitization.

In view of the fact that the direct irradiation and singlet sensitization of BPO induce cleavage of its two bonds, the peroxide bond and the linkage between the carbonyl carbon and aromatic carbon, to give benzoyloxyl and phenyl radicals along with carbon dioxide,[14] it is reasonable to assume that 2-PhBPO, on direct irradiation and singlet sensitization, tends to undergo the two-bond cleavage, whereas, on triplet sensitization as well as on thermolysis, the peroxide undergoes only the usual cleavage of the peroxide bond.[15,16] Thus, direct irradiation and singlet sensitization accelerates production of carbon dioxide and 2-biphenylyl radicals more efficiently than triplet sensitization, ultimately giving higher yields of the products arising from 2-biphenylyl radicals, and, on the contrary, affording lower yields of the products derived from 2-phenylbenzoyloxyl radicals such as biphenyl-2,2′-carbolactone and 2-phenylbenzoic acid.

Temperature effects on product yields are not remarkable, particularly in the direct and chrysene-sensitized photolyses, which seems to be consistent with the mechanism involving the two-bond cleavage. On the other hand, on triplet sensitization and thermolysis, the yields of biphenyl and *o*-terphenyl resulting from 2-biphenylyl radicals increase with increasing temperature. These must be due to enhanced decarboxylation of 2-phenylbenzoyloxyl radicals at higher temperatures. The yields of the lactone and acid decrease in the thermolysis, but increase in the triplet sensitization with increasing temperature. This behavior of 2-phenylbenzoyloxyl radicals indicates that their cyclization and disproportionation proceed with lower activation energies than the decarboxylation.[22]

Experimental

Materials. Bis(2-phenylbenzoyl) peroxide (2-PhBPO) was prepared from 2-phenylbenzoic acid and hydrogen peroxide in the presence of dicyclohexylcarbodiimide,[23] and recrystallized from dichloromethane–methanol. Chrysene and naphthalene were purified by column chromatography and crystallization. Benzophenone and 2-benzoylnaphthalene were recrystallized three times from ethanol. 3′-Methoxyacetophenone was distilled under reduced pressure. Benzene was distilled before use and carbon tetrachloride was purified by the method of Steel and coworkers.[24]

Photolysis. A solution of 2-PhBPO (0.02 mol/dm^3) in benzene or carbon tetrachloride (3 ml) in the absence of any sensitizer or in the presence of chrysene (0.002 mol/dm^3) or benzophenone (0.05 mol/dm^3) in a Uranium glass tube was deaerated by bubbling of argon, and irradiated for five times half-life periods determined by iodometry with a 1 kW high pressure mercury lamp immersed in a Pyrex cooling bath and further surrounded by Toshiba UV-D36A glass filters using a merry-go-round type Riko Rotary photochemical Reactor. Products were determined by GLPC analyses on a Shimadzu GC 4CM gas chromatograph equipped with a flame ionization detector. The following columns were used for quantitative analyses: Diethylene glycol succinate (2%) with H_3PO_4

(0.5%), Thermon 3000 (2%). Carbon dioxide was determined gravimetrically using an Ascarite tube.

Thermolysis. A solution of 2-PhBPO (0.02 mol/dm^3) in benzene or carbon tetrachloride (3 ml) in a Pyrex tube was degassed by the usual freeze-thaw cycles and heated in an air bath constantly maintained at a given temperature (60, 70, 78, and 80 °C) for five times half-life periods. The products were similarly analyzed by GLPC.

Quantum Yields. Quantum yields for photolyses of 2-PhBPO (0.001—0.008 mol/dm^3) were measured in benzene in the absence of any additive or in the presence of naphthalene ($(0.3—2.4)\times10^{-3}$ mol/dm^3) and in carbon tetrachloride in the presence of 3′-methoxyacetophenone (0.06 mol/dm^3) by irradiating with 313 nm light isolated from a 100 W high pressure mercury lamp through a Toshiba UV-D33S glass filter and a K_2CrO_4 solution filter, and in benzene in the presence of chrysene (0.002 mol/dm^3) or 2-benzoylnaphthalene (0.02 mol/dm^3) and in carbon tetrachloride in the presence of benzophenone (0.02 mol/dm^3) by irradiating with 366 nm light isolated through a Toshiba UV-D36A glass filter. Disappearance of the peroxide was determined on a JASCO Trirotar HPLC with a 15 cm ODS column. Conversion of the peroxide was less than 15%. More than 95% of the incident light was absorbed by the sensitizer except the case of chrysene, by which *ca.* 80% of the light was absorbed.

Quenching Rate Constants. Fluorescence of chrysene (3×10^{-4} mol/dm^3) was measured in the presence of 2-PhBPO ($(0—6)\times10^{-3}$ mol/dm^3) in benzene under argon on a Hitachi 650-10S fluorescence spectrophotometer. Phosphorescence of benzophenone (0.01 mol/dm^3) was measured in the presence of 2-PhBPO ($(0—4)\times10^{-5}$ mol/dm^3), biphenyl ($(0—1.6)\times10^{-4}$ mol/dm^3), and phenyl 2-phenylbenzoate ($(0—1.6)\times10^{-4}$ mol/dm^3). Fluorescence lifetime of chrysene and phosphorescence lifetime of benzophenone were measured at room temperature by single photon counting technique on an Applied Photophysic SP-3X.

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