Bull. Chem. Soc. Jpn., **69**, 2603—2611 (1996)

Self-Sensitized Photolysis of *N*-(1-Naphthoyl)-*N*-phenyl-*O*-(benzoyl-substituted benzoyl)hydroxylamines

Hiroshi Nagakubo, Gou Kubota, Kanji Kubo, Tsuyoshi Kaneko,
Tadamitsu Sakurai,* and Hiroyasu Inoue

Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Kanagawa-ku, Yokohama 221

(Received April 11, 1996)

The mechanism of intramolecular triplet–triplet (T–T) energy transfer and subsequent reaction in *N*,*O*-diacylhydroxylamines was investigated using the model compounds *N*-(1-naphthoyl)-*N*-phenyl-*O*-(benzoyl-substituted benzoyl)hydroxylamines (NPB) with self-sensitization abilities. An examination of the UV absorption and phosphorescence behavior as well as of energy-minimized conformations of these relatively flexible model compounds established that T–T energy transfer from the benzophenone chromophore to the naphthoyl chromophore occurs in a nearly unit efficiency exhibiting only phosphorescence derived from the latter chromophore in both methanol–ethanol (1 : 1 v/v) and 2-chlorobutane at 77 K and is more likely to proceed by a "through-space" mechanism than by a "through-bond" mechanism. The self-sensitized photolysis of NPB with 366 nm light in methanol at room temperature was found to give the fragmentation products, *N*-phenyl-1-naphthalenecarboxamide (PNA), benzophenone (BP), and benzoyl-substituted benzoic acids (BBA), whereas no BBA was detected in the photolysis in 1,2-dichloroethane and acetonitrile. The finding that the reaction of NPB is efficiently quenched by *trans*-stilbene according to the Stern–Volmer equation in both methanol and 1,2-dichloroethane indicates that all the products come from the first excited triplet state of the naphthoyl chromophore. On the other hand, the enhanced hydrogen bonding ability of the medium resulted in an increase in the quantum yield for the formation of BBA (Φ_{BBA}) accompanied by a decrease in Φ_{BA} holding the magnitude of $\Phi_{\mathrm{BBA}}+\Phi_{\mathrm{BA}}$ nearly constant. But neither Φ_{PNA} nor the quantum yield for the disappearance of NPB was subject to such a hydrogen-bonding effect. This intriguing result was explained in terms of a mechanism in which the N–O bond cleavage in triplet NPB gives a vibrationally excited triplet radical pair whose relaxation is very slow compared to decarboxylation of the caged benzoyl-substituted benzoyloxyl radical in 1,2-dichloroethane. Solvation of this vibrationally hot radical pair through hydrogen bonding substantially promotes its relaxation eventually affording BBA.

Many efforts have been devoted to unravelling the mechanism of photosensitized reactions since an exciplex,[1)] a radical ion pair,[1c,2)] or a radical pair[3)] is involved as a key intermediate in these valuable reactions. Recently, intramolecular triplet–triplet energy transfer that plays a central role as a primary step in a given intramolecular sensitized reaction has received considerable attention as to whether the energy transfer proceeds through "bonds"[4)] or "space".[5)]

We previously showed that *N*-(1-naphthoyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (NT) undergoes benzophenone (triplet)-sensitized photolysis to give the fragmentation products *N*-phenyl-1-naphthalenecarboxamide, *p*-toluic acid, and toluene, whereas the direct photolysis of NT takes place preferentially from the excited singlet state to afford both 1,3- and 1,5-toluoyloxy-migrated products (photoacyloxy rearrangement) along with the fragmentation products.[6)] The absence of the rearranged products in this triplet-sensitized reaction was explained in terms of the much faster diffusional escape of a triplet radical pair as an intermediate, compared with intersystem crossing to the singlet radical pair.[6b)] A kinetic analysis of the substituted benzophenone-sensitized photolysis of NT revealed that either an energy-transfer mechanism or an electron-transfer mechanism operates in the activation process of NT by these triplet sensitizers, depending on the nature of the substituent introduced.[7)] The most remarkable finding was that the participation of an electron-transfer mechanism in the sensitized reaction results in the exclusive formation of *N*-phenyl-1-naphthalenecarboxamide and *p*-toluic acid without leading to toluene, which is obtained in a quantum yield greater than that of the acid in addition to the carboxamide when the reaction proceeds by an energy-transfer pathway. A triplet-exciplex intermediate was proposed to explain the difference in the triplet-state reactivity of NT among the sensitizers studied.

If one could prepare *N*,*O*-diacyl-*N*-phenylhydroxylamines containing a benzophenone moiety, one may explore the mechanism of intramolecular triplet–triplet energy transfer ("through-bond" versus "through-space") as well as the decarboxylation process of aroyloxyl radicals ("out-of-cage" versus "in-cage") in more detail. To these ends, we designed and prepared *N*-(1-naphthoyl)-*N*-phenyl-*O*-(2-benzoylbenzoyl)hydroxylamine (2-NPB), *N*-(1-naphthoyl)-*N*-phenyl-*O*-(3-benzoylbenzoyl)hydroxylamine (3-NPB), and *N*-(1-naphthoyl)-*N*-phenyl-*O*-(4-benzoylbenzoyl)hydroxylamine (4-NPB) having self-sensitization abilities (Chart 1).

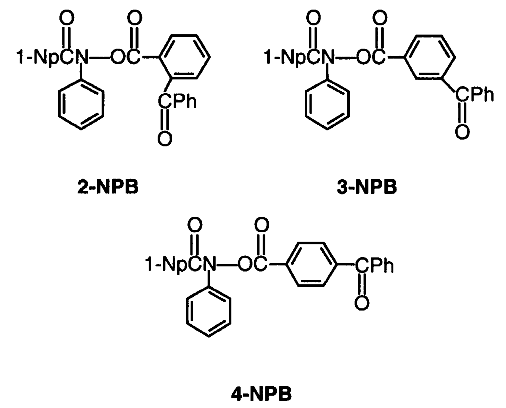


Chart 1. 1-Np= 1-naphthyl

Results and Discussion

Phosphorescence Spectra of NPB Derivatives. As typically shown in Fig. 1, preferential excitation of a benzophenone moiety in 4-NPB resulted in the appearance of phosphorescence, being independent of the NPB concentration (10^{-5}—10^{-2} mol dm^{-3}), with a 0–0 transition at 480 nm at 77 K. This phosphorescence is not consistent with that of 4-benzoylbenzoic acid (4-BBA) but with that of *N*-(1-naphthoyl)-*N*-phenylhydroxylamine (NPH) (Fig. 1), suggesting the occurrence of highly efficient intramolecular excitation transfer. The UV absorption spectrum of 4-NPB is very similar to the sum of the spectra of BBA and NPH (Fig. 2), allowing us to assume that the two chromophores in a 4-NPB molecule, namely the naphthoyl and 4-benzoylbenzoyl groups, have singlet (E_S) and triplet (E_T) excitation energies independent from each other. Since phosphorescence and its excitation spectra of BBA and NPH are virtually compatible with those of benzophenone (BP, $E_S = 310$; $E_T = 290$ kJ mol^{-1})[8] and NT ($E_S = 380$; $E_T = 250$ kJ mol^{-1}),[6a] respectively, excitation energies for these two chromophores can be approximated by those for BP and NT. The interesting finding that the phosphorescence excitation spectrum of 4-NPB having maxima at 304 and 355 nm (Fig. 1) is in good agreement with that of 4-BBA substantiates that the excited singlet state of the benzoylbenzoyl chromophore is responsible for the appearance of the observed phosphorescence as demonstrated in Fig. 3. Exclusive excitation of the benzophenone moiety must form its singlet excited state (S_1) which eventually gives the triplet excited state (T_1) of the naphthoyl chromophore by intersystem crossing followed by triplet–triplet energy transfer. The same phosphorescence behavior was observed also for other NPB derivatives (2-

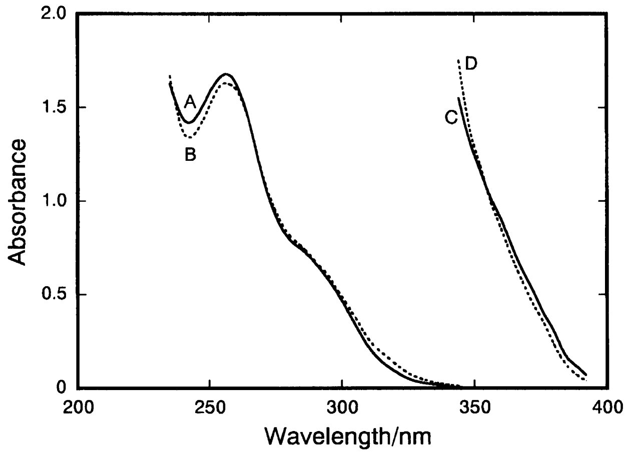


Fig. 2. UV absorption spectra of 4-NPB ([4-NPB]= 5.0×10^{-5} (A); 5.0×10^{-3} (C) mol dm^{-3}) and equimolar mixture of NPH and 4-BBA ([NPH]=[4-BBA]= 5.0×10^{-5} (B); 5.0×10^{-3} (D) mol dm^{-3}) in 1,2-dichloroethane at room temperature.

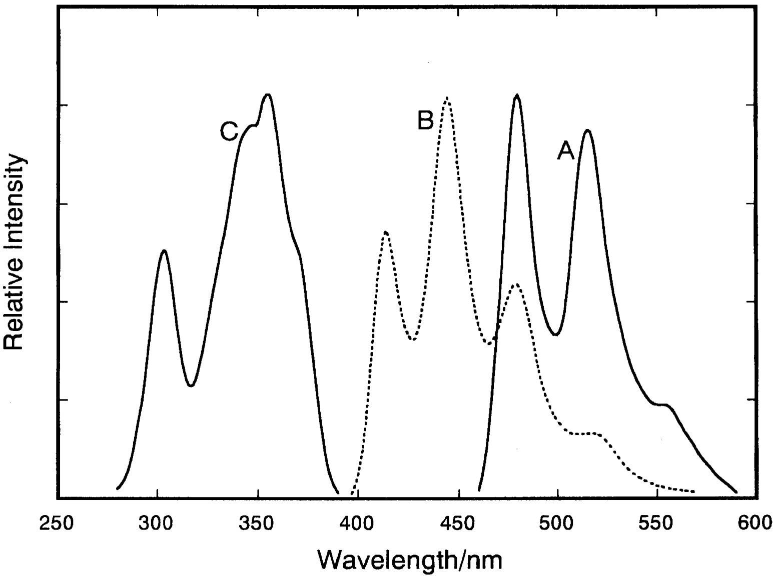


Fig. 1. Phosphorescence (A, B) and phosphorescence excitation (C) spectra of 4-NPB (1.0×10^{-3} mol dm^{-3}; A, C) and 4-BBA (1.0×10^{-3} mol dm^{-3}; B) in 2-chlorobutane at 77 K. Excitation and emission wavelengths monitored are 366 and 480 nm, respectively.

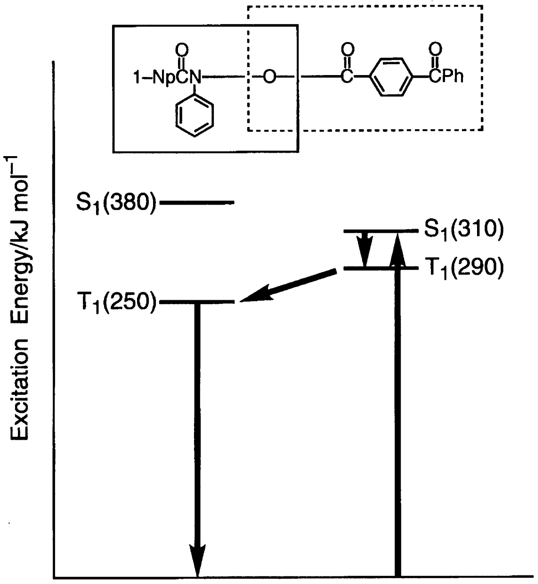


Fig. 3. Electronic states of 4-NPB.

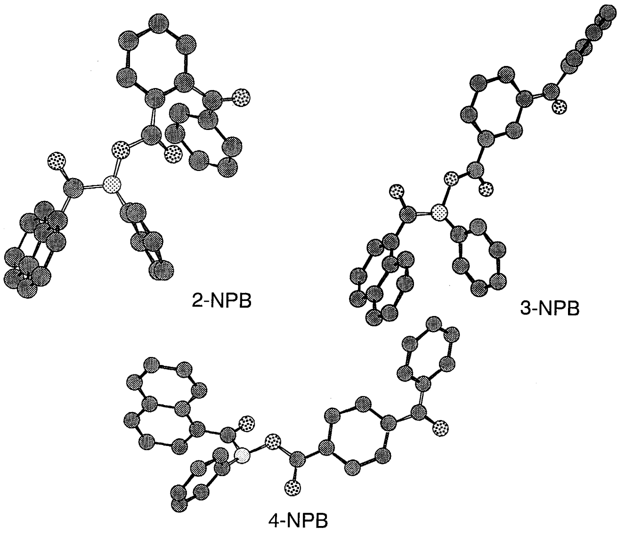
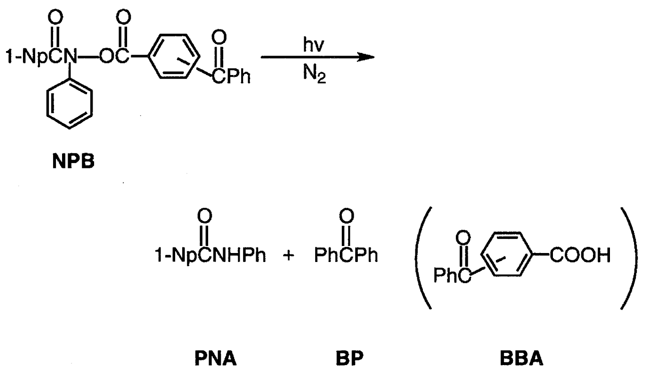


Fig. 4. Energy-minimized conformations of 2-NPB, 3-NPB, and 4-NPB.

NPB and 3-NPB) and also in methanol–ethanol (1 : 1 v/v) at 77 K, where phosphorescence with a 0–0 transition at 482 nm was detected for any NPB derivative. Further evidence that the emissive state of NPB phosphorescence is the triplet state of the 1-naphthoyl skeleton comes from the observation that almost the same phosphorescence lifetime (0.5±0.1 s) is obtained irrespective of NPB isomers in both aprotic and protic solvents at 77 K.

It has been shown that intramolecular triplet–triplet (T–T) energy transfer in rigid bichromophoric molecules proceeds by a "through-bond" mechanism,[4] and that T–T energy transfer between donor and acceptor groups separated by flexible methylene chains prefers a "through-space" mechanism.[5] If T–T energy transfer in relatively flexible NPB derivatives occurs by a "through-bond" mechanism, the transfer rate should be strongly dependent on the average separation between the benzophenone and naphthalene chromophores[4] as well as on the relative orientation of these two chromophores.[9] The bond distance between the naphthyl α-carbon and the benzoyl phenyl carbonyl carbon in an NPB molecule increases in the following order: 2-NPB (0.98nm) < 3-NPB (1.12nm) < 4-NPB (1.26 nm). Thus, at least 4-NPB may be expected to exhibit dual phosphorescence derived from the naphthoyl and benzoylbenzoyl groups since a 0.1 nm increase in this distance is known to decrease the transfer rate by a factor of about 10.[10] But we could not find such a dual emission behavior for any NPB isomers. On the basis of the reasonable assumption that an NPB molecule frozen in a rigid glassy matrix at 77 K cannot adopt very many conformations in the ground state, MM2 calculations were performed to determine the most probable conformation in each NPB molecule.[11] An inspection of Fig. 4 reveals that not a folded but a fairly stretched conformation is the most stable and the relative orientation of the naphthoyl and benzoylbenzoyl skeletons is not very different among NPB isomers. In addition, the average distance between the carbonyl carbon in a benzophenone moiety and the center of a naphthalene ring is estimated to be 0.74 (2-NPB), 0.95 (3-NPB), and 0.97 nm (4-NPB). Exothermic T–T energy transfer in flexible systems at 77 K has been demonstrated to prefer a "through-space" mechanism and to proceed at a rate constant on the order of 10^5—10^6 s^{-1} even in a glassy matrix when the average interchromophore distance is in the range of 0.74 to 0.97 nm.[5a,5b] If the transfer rate constant (k_{T-T}) in our system is of the same magnitude, phosphorescence attributable to the benzophenone chromophore with a lifetime of 5 ms[5a] is predicted to be no longer observed because k_{T-T} is greater than the rate constant for deactivation of the triplet-state benzophenone ($k_d = 2\times10^2$ s^{-1}) by a factor of 5— 50×10^2. The result obtained is consistent with this prediction. Although direct evidence for a "through-space" mechanism is not available, the flexibility and interchromophore distance of an NPB molecule make this mechanism more likely.

Self-Sensitized Photolysis of NPB Derivatives in 1,2-Dichloroethane. Based on the very efficient intramolecular T–T energy transfer of the NPB derivatives, it was speculated that selective excitation of the benzophenone chromophore with 366 nm light would bring about an extremely effective decomposition of these derivatives (self-sensitized photolysis) affording the fragmentation products corresponding to those observed in the benzophenone-sensitized photolysis of NT. In a previous study, we found that triplet NT has a higher reactivity in 1,2-dichloroethane than in acetonitrile, and that undesired side reactions of the amidyl radical occur in a solvent of low reactivity toward hydrogen abstraction by this radical.[6b] Thus, we selected 1,2-dichloroethane as a solvent and examined the product distribution as well as quantum yields for the disappearance of NPB and for the appearance of each product. A high-performance liquid chromatography (HPLC) analysis of the photodecomposition products of NPB derivatives obtained by irradiation at 366 nm revealed that *N*-phenyl-1-naphthalenecarboxamide (PNA) and benzophenone (BP) are generated as main products along with the amidyl radical-derived by-products (Eq. 1).



1-Np = 1-naphthyl (1)

Not even a trace amount of BBA was detected on the HPLC chromatograms, showing the occurrence of highly efficient decarboxylation of the benzoylbenzoyloxyl radical in 1,2-dichloroethane. In order to estimate to what extent the intermolecular sensitization process contributes to the overall reaction efficiency, quantum yields (Φ) for the self-sensitized photolysis of each NPB isomer were determined at low conversions of 6—12% and the dependence of the Φ values on the NPB concentration was investigated in the range of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}. As typically shown in Fig. 5, the observation of negligible concentration dependence for any quantum yields establishes that intermolecular T–T energy transfer takes place to only a very small extent, if at all, at least in the concentration range studied. The rate of intramolecular energy transfer must be very fast compared to that of intermolecular transfer, as suggested from an analysis of the phosphorescence behavior of these NPB derivatives at low temperature.

It was then necessary to determine the reactive excited state from which the N–O bond cleavage in NPB molecules proceeds, although the triplet excited state of the naphthoyl moiety was the most likely candidate. Since the excitation energies of this moiety can be approximated by those of NT (E_S=380; E_T=250 kJ mol^{-1}), we chose *trans*-stilbene (E_S=390; E_T<210 kJ mol^{-1})[8] and 4-NPB and inspected whether stilbene acts as a triplet quencher through phosphorescence quenching. The finding that the NPB phosphorescence was quenched by stilbene to a small but perceivable extent in a 2-chlorobutane glassy matrix indicates that this molecule is a triplet quencher for the self-sensitized reaction (Fig. 6A). Inspection of the Stern–Volmer plots for the reaction quenching shown in Fig. 7A reveals that the quantum yields for the disappearance of 4-NPB ($\Phi_{\text{–NPB}}$) and for the appearance of BP (Φ_{BP}) and PNA (Φ_{PNA}) decrease with an increase in the quencher concentration according to the Stern–Volmer equation: $\Phi_0/\Phi=1+k_t\tau_T$[Quencher], where

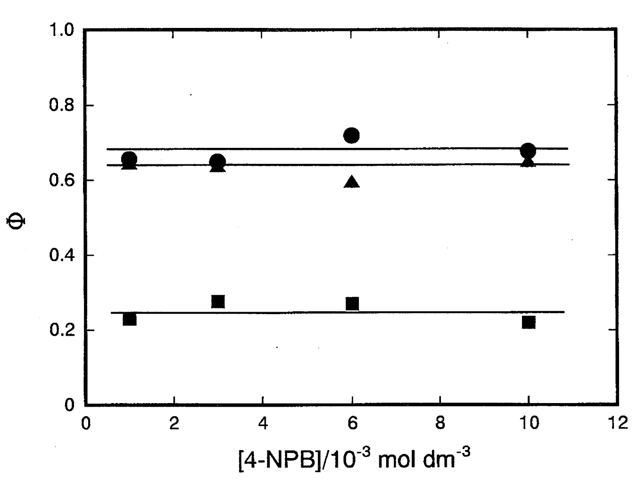


Fig. 5. Quantum Yields (Φ) for the disappearance of 4-NPB (●) and for the appearance of BP (▲) and PNA (■) as a function of the 4-NPB concentration in 1,2-dichloroethane at room temperature.

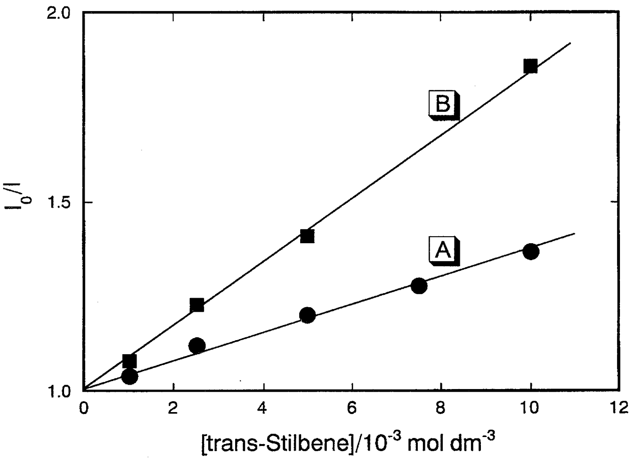


Fig. 6. Stern–Volmer plots for the phosphorescence quenching of 4-NPB (1.0×10^{-3} mol dm^{-3}) by *trans*-stilbene in 2-chlorobutane (A: ●) and methanol–ethanol (1 : 1 v/v, B: ■) at 77 K. I and I_0 refer to the phosphorescence intensities with and without the quencher, respectively and excitation wavelength is 366 nm.

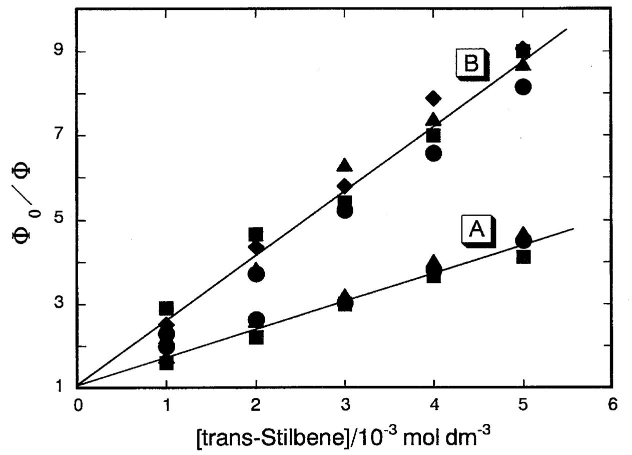
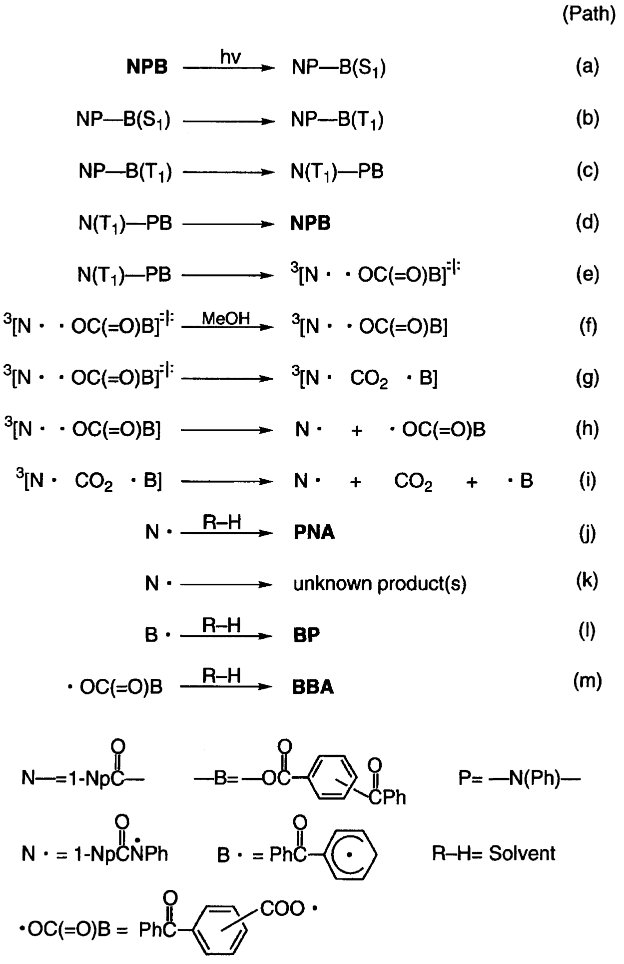


Fig. 7. Stern–Volmer plots for the quenching of self-sensitized reaction of 4-NPB (2.5×10^{-3} mol dm^{-3}) by *trans*-stilbene in nitrogen-purged 1,2-dichloroethane (A) and methanol (B) at room temperature. Φ(●: $\Phi_{\text{–NPB}}$, ▲: Φ_{BP}, ■: Φ_{PNA}, ◆: Φ_{BBA}) and Φ_0 are the quantum yields with and without the quencher, respectively.

Φ and Φ_0 are the quantum yields with and without quencher, k_t is the rate constant for energy transfer from triplet NPB to *trans*-stilbene, and τ_T is the triplet lifetime of NPB in the absence of this quencher. Almost the same quenching constant ($k_t\tau_T$=720±60 dm^3 mol^{-1}) was obtained for all the linear Stern–Volmer plots, providing strong evidence that the products PNA and BP arise from the first triplet excited state of a 4-NPB molecule in which the excitation energy must be localized within the naphthoyl chromophore. Thus, we have proposed Scheme 1 where intersystem crossing (Path b) as well as intramolecular energy transfer (Path c) are assumed to occur in a unit efficiency. The material balance estimated by the magnitude of Φ is good for the formation of BP but not so high for PNA formation, showing that side reactions of the amidyl radical compete with its hydrogen abstraction yielding PNA even in 1,2-dichloroethane. It is interesting to note that $\Phi_{-\mathrm{NPB}}$ (0.65) has a magnitude comparable to the limiting quantum yield for the disappearance of NT ($\Phi_{-\mathrm{NT,lim}}$=0.82)[6b] in the BP-sensitized reaction under the same irradiation conditions. This may reflect the occurrence of intramolecular nonradiative processes in a nearly unit efficiency as assumed above.

Self-Sensitized Photolysis of NPB Derivatives in Methanol. In a previous study of the substituted BP-sensitized photolysis of NT,[7] we speculated on the decarboxylation mechanism of the *p*-toluoyloxyl radical. One possibility is that N–O bond cleavage in the excited triplet state of NT directly generates a vibrationally hot triplet radical pair, relaxation of which competes with decarboxylation of the toluoyloxyl radical in a triplet cage. This possibility was proposed based on the fact that the vibrationally relaxed toluoyloxyl radical produced by way of the NT anion radical gives only toluic acid without leading to toluene. The electronic state of the vibrationally hot toluoyloxyl radical, i.e., a σ- or π-radical within the cage,[12] might play a role in determining the ease with which decarboxylation occurs. On the other hand, hydrogen-bond formation between the amide carbonyl oxygen in NT and the hydroxyl hydrogen in methanol was shown to affect the singlet excited-state reactivity of NT,[13] leading us to expect that the reactivity of triplet NPB is also affected in the presence of methanol.



Scheme 1.

Irradiation of an oxygen-free methanol solution of NPB isomers with 366 nm light resulted in the appearance of BBA in addition to BP and PNA. For example, the quantum yields for the disappearance of 4-NPB ([4-NPB]=2.5×10^{-3} mol dm^{-3}) and for the appearance of 4-BBA, BP, and PNA were measured to be 0.58, 0.31, 0.23, and 0.27, respectively. Additionally, all of these quantum yields exhibited negligible NPB-concentration dependence in the range 0.85—4.0×10^{-3} mol dm^{-3} within an experimental error of about 10%. The lack of formation of benzopinacol-type products is consistent with much faster intramolecular T–T energy transfer than hydrogen abstraction by the benzophenone-type carbonyl oxygen in NPB molecules.

In order to confirm that BBA also arises from the excited triplet-state naphthoyl chromophore, we conducted quenching experiments of the phosphorescence and photolysis of 4-NPB by *trans*-stilbene in methanol–ethanol (1 : 1 v/v) and methanol, respectively (Figs. 6B and 7B). Clearly, stilbene quenched not only the NPB emission at 77 K (Fig. 6B) but also the reaction at room temperature (Fig. 7B) to a greater extent than that of the corresponding quenching in aprotic solvents. The observation of very similar magnitudes of the $k_t\tau_T$ values for the linear Stern–Volmer plots provides evidence that BBA originates from the same triplet state as that responsible for the formation of BP and PNA. From a comparison of the plots shown in Figs. 6 and 7, we see that the reaction quenching constant in methanol ($k_t\tau_T$=1600 dm^3 mol^{-1}) is more than twice as large as that ($k_t\tau_T$=720 dm^3 mol^{-1}) in 1,2-dichloroethane. The difference in the extent of reaction quenching between these two solvent systems corresponds nicely to that of phosphorescence quenching at 77 K. It is likely that hydrogen-bond formation between 4-NPB and methanol results in an increase in the energy-transfer efficiency from triplet NPB to stilbene. The fluorescence quenching of pyrene by NT was previously shown to proceed through a non-emissive singlet exciplex, formation of which is more stimulated in methanol than in 1,2-dichloroethane.[13] Based on the similar magnitudes of the pyrene-fluorescence lifetimes in these two solvents, the hydrogen bonding previously mentioned was verified to increase the rate of the exciplex formation by a factor of 2.4. Thus, the more enhanced T–T energy-transfer efficiency in methanol may indicate the participation of a triplet exciplex with a charge-transfer character. Since the E_T value of 4-NPB undergoes the hydrogen-bonding effect to only a very small extent, solvation of the amide carbonyl in an NPB molecule by methanol is considered to make NPB more electrophilic toward stilbene.

We will now explain the reason why BBA is obtained in a rather large quantum yield along with BP and PNA for the photolysis in methanol. As already described, the NT anion radical-derived "out-of-cage" toluoyloxyl radical, which should be vibrationally relaxed, exclusively affords toluic acid by its hydrogen abstraction from a 1,2-dichloroethane molecule,[7] being consistent with the much lower activation energy for hydrogen abstraction of aroyloxyl radicals than that for their decarboxylation.[14] The toluoyloxyl radical formed by the direct photolysis of NT also exhibited a similar reactivity toward hydrogen abstraction from 1,2-dichloroethane and methanol.[6b,13] In addition to these findings, the reasonable assumption that the bond dissociation energy of the C–H bond in a methanol molecule (390 kJ mol^{-1})[8] has almost the same magnitude as that of the C–H bond in a 1,2-dichloroethane molecule (ca. 390 kJ mol^{-1})[15] makes the possibility that the "out-of-cage" benzoylbenzoyloxyl radical abstracts a hydrogen atom from methanol in competition with its decarboxylation unlikely. If the "out-of-cage" benzoyl-substituted benzoyloxyl radicals are subject to stabilization by solvation in the hydrogen bonding solvent, there may be some contribution of the increased stability of these radicals to decreasing the relative rate of decarboxylation to hydrogen abstraction.[12d,16]

Provided that BBA and BP are formed via the "out-of-cage" reaction of the aroyloxyl radical, an increase in solvent viscosity is predicted to affect the relative quantum yield of the "out-of-cage" to "in-cage" reactions[6b,13] but not the quantum-yield ratio Φ_{BBA}/Φ_{BP} because the "out-of-cage" reaction, which does not compete with the "in-cage" one, is thought to undergo viscosity effects to only a very little, if any, extent. Solvent viscosity was changed by using methanol ($\eta_{25^\circ}=0.540$ cP, 1 cP=1 mPa s), methanol–ethylene glycol (60:40 v/v, $\eta_{25^\circ}=1.93$ cP), and methanol–glycerol (60:40 v/v, $\eta_{25^\circ}=5.65$ cP) as solvents. As clearly seen from Fig. 8, Φ_{-NPB} and Φ_{PNA} are regarded as being almost constant irrespective of solvent viscosity,whereas Φ_{BP} decreases as the viscosity is increased and Φ_{BBA} shows a reverse viscosity dependence holding the sum of Φ_{BP} and Φ_{BBA} constant within experimental error. This intriguing result is not compatible with our prediction and, thus, establishes that negligible decarboxylation of the "out-of-cage" 4-benzoylbenzoyloxyl radical takes place in competition with its hydrogen abstraction. The very small viscosity dependence of Φ_{-NPB}, Φ_{PNA}, and $\Phi_{BP}+\Phi_{BBA}$ strongly suggests that intersystem crossing from the triplet pair to the singlet pair is slow enough to allow the exclusive escape of radicals from the triplet cage even in the presence of 40 vol% glycerol. Although both the hydrogen-bonding ability of alcoholic solvents and the reactivity of the solvents toward hydrogen abstraction should increase in the following order: MeOH < MeOH–Ethylene glycol < MeOH–Glycerol,[17] the finding of the minor contribution of the "out-of-cage" decarboxylation makes it more likely that the increased hydrogen-bonding ability of the solvents decreases Φ_{BP} but increases Φ_{BBA}.

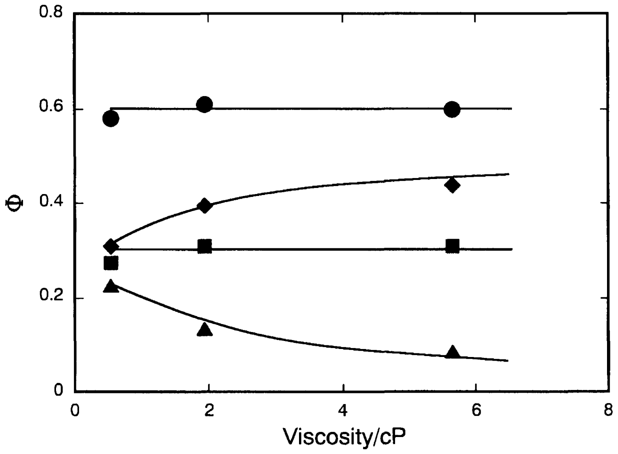


Fig. 8. Solvent viscosity effects on the quantum yields (Φ) for disappearance of 4-NPB (●) and for appearance of BP (▲), PNA (■), and 4-BBA (◆) in the photolysis of 4-NPB (2.5×10^{-3} mol dm^{-3}) with 366 nm light in oxygen-free protic solvents at room temperature.

In order to obtain further evidence in support of the hydrogen bonding mentioned above, we examined the effect of added methanol on the quantum yields Φ_{-NPB}, Φ_{BP}, Φ_{BBA}, and Φ_{PNA} in 1,2-dichloroethane (Figs. 9A—C). For any NPB derivative, neither Φ_{-NPB} nor Φ_{PNA} is subject to hydrogen-bonding effects whereas Φ_{BP} and Φ_{BBA} exhibit a reverse dependence on the methanol concentration, maintaining a nearly constant sum of these two quantum yields. Evidently, the increased concentration of methanol results in an increase in Φ_{BBA} accompanied by a decrease in Φ_{BP}. Lack of formation of BBA in the photolysis of NPB in acetonitrile substantiates that not the polarity but the hydrogen-bonding ability of methanol becomes a key factor controlling the relative magnitude of Φ_{BBA} to Φ_{BP}. It was previously indicated that the IR absorption band of the amide carbonyl group of NT in chloroform is red-shifted by 15 cm^{-1} in the presence of 15 vol% methanol while that of the ester carbonyl group undergoes only a very small red shift (1—2 cm^{-1}), and hence that the amide carbonyl oxygen is capable of forming a strong hydrogen bond to the methanol hydroxyl hydrogen.[13] Additionally, examination of the quantum yields for the pyrene-sensitized photolysis of NT in protic and aprotic solvents suggested the possible formation of this type of hydrogen bonding even in the excited singlet state of NT, allowing us to assume it also in the excited triplet state. As already demonstrated, the enhanced rate for quenching of triplet 4-NPB by stilbene in protic solvents supports this assumption. Typically, 4-NPB shows IR absorption bands, corresponding to carbonyl stretching, at 1770 and 1670 cm^{-1} in 1,2-di-

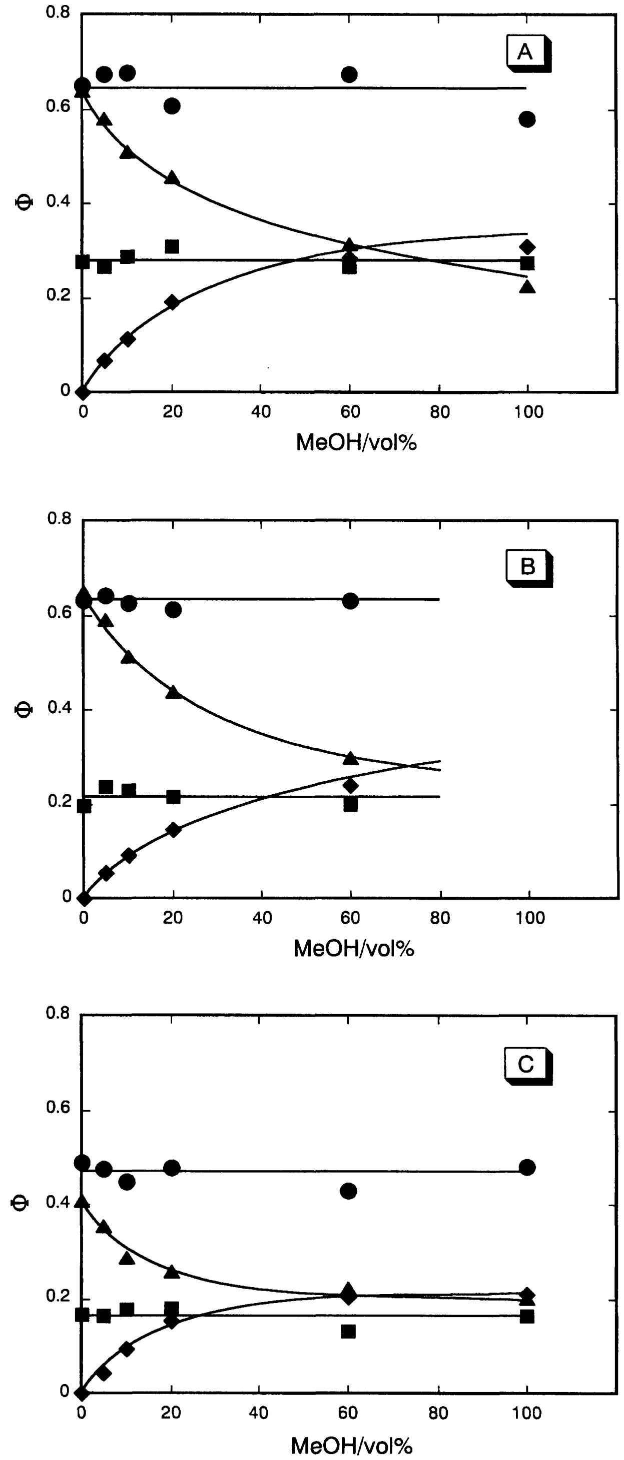


Fig. 9. Effects of added methanol on the quantum yields (Φ) for disappearance of NPB (●) and for appearance of BP (▲), PNA (■), and BBA (◆) in the self-sensitized reactions of 4-NPB (A), 3-NPB (B), and 2-NPB (C) with 366 nm light in nitrogen-saturated 1,2-dichloroethane at room temperature. [NPB]=2.5×10^{-3} mol dm^{-3}. Quantum yields for 3-NPB in 100 vol% methanol could not be determined owing to the poor solubility of a 3-NPB isomer toward this protic solvent.

chloroethane. The former band is safely assigned to the ester carbonyl stretching vibration and the latter one is attributable to the amide and benzoyl carbonyl groups overlapping each other. When 15 vol% methanol was added to a 1,2-dichloroethane solution of 4-NPB (5.0×10^{-3} mol dm^{-3}), the 1670 cm^{-1} band was red-shifted by 10 cm^{-1} whereas the 1770 cm^{-1} band underwent negligible effects. Although this finding does not provide definite evidence for hydrogen bonding between the carbonyl oxygen in a benzophenone moiety of NPB and the hydroxyl hydroegn of methanol, we can say that at least the amide carbonyl forms a strong hydrogen bond to the solvent but this hydrogen bonding affects the triplet excitation energy of the naphthoyl chromophore to a negligible extent as already mentioned. These considerations of hydrogen bonding in the ground and excited states lead us to propose that solvation of each triplet NPB through hydrogen bonding is responsible for the production of benzoyl-substituted benzoic acids. Thus, the hydrogen-bonding effects on $\Phi_{\rm BBA}$ and $\Phi_{\rm BP}$ make Scheme 1 reasonable, in which the N–O bond scission in triplet NPB (Path e) produces a vibrationally excited triplet radical pair whose relaxation (Path f) may compete with decarboxylation of the benzoyl-substituted benzoyloxyl radical within the cage (Path g) to give the secondary triplet cage ^{3}[N$\cdot$ CO$_2$ $\cdot$B] along with the relaxed triplet cage ^{3}[N$\cdot$ $\cdot$OC(=O)B]. The lack of formation of BBA in the self-sensitized photolysis of NPB isomers in aprotic solvents demonstrates that the decarboxylation process (Path g) must be extremely fast as compared to the relaxation process of the caged triplet radical pair (Path f). Since the difference in energy between the vibrationally hot radical pair and the triplet excited state of the 1-naphthoyl group should be not so great, the triplet excitation energy of 250 kJ mol^{-1} for this group is large enough to allow exclusive decarboxylation, whose activation energy may be in the range of 24 to 46 kJ mol^{-1},[16] within the cage. From the observation that BBA is obtained in a quantum yield comparable to that of BP in the reaction of any NPB derivative in protic solvents, solvation of the hot radical pair ^{3}[N$\cdot$ $\cdot$OC(=O)B]‡ by hydrogen bonding is strongly suggested to promote vibrational relaxation of this radical pair to a substantial extent. It is very likely that the amide carbonyl and, possibly, also the benzoyl carbonyl groups in the vibrationally excited radical pair is still hydrogen bonded to protic solvent molecules. These two hydrogen bonds are supposed to exert dramatic effects on the unimolecular relaxation process of the hot radical pair, whereas such a hydrogen-bond formation is less likely to affect the rate of decarboxylation to a substantial extent. Taking into account that decarboxylation of the aroyloxyl radical with a σ-radical character is a symmetry-allowed process while that of the π-type aroyloxyl radical is symmetry-forbidden,[12b] we conclude that the benzoyl-substituted benzoyloxyl radical in the vibrationally hot state must be a σ-radical.[18]

Experimental

General Methods. HPLC analyses of the photoproducts were performed on a Shimadzu Model LC-6A high-performance liquid chromatography system equipped with a 4.6×250-mm ODS

(Zorbax) column and a Shimadzu Model SPD-2A UV detector (detection wavelength=240 nm; mobile phase, MeCN : H_2O= 65 : 35 v/v). UV and IR spectra were taken at room temperature with a Shimadzu Model UV-2200 spectrophotometer and a Hitachi Model 270-30 infrared spectrometer, respectively. ^1H and ^{13}C NMR spectra were recorded using tetramethylsilane as an internal standard on a JEOL Model JNM-500 spectrometer. Phosphorescence spectra and lifetimes at 77 K were measured with a Hitachi Model F-4500 spectrofluorimeter fitted with a phosphorescence attachment which made it possible to trace phosphorescence decays. The viscosities of methanol and methanol containing ethylene glycol or glycerol were determined in triplicate by use of an Ubbelohde viscometer at 25 °C.

Materials and Solvents. *N*-(1-Naphthoyl)-*N*-phenylhydroxylamine was prepared according to the previously described procedures.[6a)] *O*-Aroylation of this hydroxylamine with benzoyl-substituted benzoyl chlorides, which were prepared by treatment of the corresponding benzoyl-substituted benzoic acids with thionyl chloride in the presence of a small amount of pyridine, in dichloromethane containing pyridine gave *N*-(1-naphthoyl)-*N*-phenyl-*O*-(benzoyl-substituted benzoyl) hydroxylamines in good yields. The crude products were purified by column chromatography over silica gel (70—230 mesh, Merck) using chloroform as eluent followed by repeated recrystallization from hexane–ethyl acetate or ethanol to afford analytically pure samples with the following physical properties.

***N*-(1-Naphthoyl)-*N*-phenyl-*O*-(2-benzoylbenzoyl)hydroxylamine (2-NPB):** Mp 125.5—126.5 °C; IR (KBr) 1764 and 1677 cm^{-1}; ^1HNMR ($CDCl_3$) δ=7.10 (br s, 3H), 7.14 (br s, 2H), 7.24 (t, 1H, J=8.3 Hz), 7.35—7.54 (m, 9H), 7.65 (t, 1H, J=8.3 Hz), 7.73 (d, 2H, J=8.3 Hz), 7.76 (t, 2H, J=8.3 Hz), and 8.17 (d, 1H, J=8.3 Hz); ^{13}CNMR ($CDCl_3$) δ=124.46, 125.30, 126.32, 126.39, 126.6 (br), 127.28, 128.20, 128.36, 128.42, 128.47, 128.91 (2C), 129.70, 129.89, 130.13, 130.35, 130.49, 131.58, 133.10, 133.27, 133.31, 136.69, 139.25, 142.02, 163.78, 166.3 (br), and 196.00. Found: C, 78.56; H, 4.91; N, 2.90%. Calcd for $C_{31}H_{21}NO_4$: C, 78.97; H, 4.49; N, 2.97%.

***N*-(1-Naphthoyl)-*N*-phenyl-*O*-(3-benzoylbenzoyl)hydroxylamine (3-NPB):** Mp 161—162 °C; IR (KBr) 1762, 1674, and 1656 cm^{-1}; ^1HNMR ($CDCl_3$) δ=7.16—7.19 (m, 3H), 7.30 (t, 1H, J=8.0 Hz), 7.40 (bd, 2H, $J\approx 8$ Hz), 7.48—7.54 (m, 4H), 7.57—7.64 (m, 3H), 7.77—7.80 (m, 4H), 8.04 (d, 1H, J=8.0 Hz), 8.26 (br s, 1H), 8.38 (d, 1H, J=8.0 Hz), and 8.45 (br s, 1H); ^{13}CNMR ($CDCl_3$) δ=124.50, 125.33, 126.35, 126.50, 126.7 (br), 127.28, 127.40, 128.28, 128.58, 128.70, 128.91, 129.08, 130.06, 130.21, 130.47, 131.43, 131.68, 132.97, 133.36, 133.55, 135.14, 136.82, 138.30, 139.63, 163.55, 166.3 (br), and 195.27. Found: C, 78.55; H, 4.81; N, 2.85%. Calcd for $C_{31}H_{21}NO_4$: C, 78.97; H, 4.49; N, 2.97%.

***N*-(1-Naphthoyl)-*N*-phenyl-*O*-(4-benzoylbenzoyl)hydroxylamine (4-NPB):** Mp 134—135 °C; IR (KBr) 1764, 1683, and 1659 cm^{-1}; ^1HNMR ($CDCl_3$) δ=7.16—7.20 (m, 3H), 7.31 (t, 1H, J=8.2 Hz), 7.42 (br d, 2H, $J\approx 8$ Hz), 7.47—7.53 (m, 3H), 7.56 (d, 1H, J=7.4 Hz), 7.59—7.64 (m, 2H), 7.77—7.83 (m, 6H), 8.15 (br s, 2H), and 8.40 (d, 1H, J=8.2 Hz); ^{13}CNMR ($CDCl_3$) δ=124.52, 125.32, 126.35, 126.51, 126.7 (br), 127.41, 128.32, 128.53, 128.70, 129.11, 129.84, 129.94, 130.06, 130.10, 130.21, 130.50, 131.68, 133.12, 133.38, 136.72, 139.65, 142.39, 163.57, 166.4 (br), and 195.66. Found: C, 79.21; H, 4.92; N, 2.84%. Calcd for $C_{31}H_{21}NO_4$: C, 78.97; H, 4.49; H, 2.97%.

N-Phenyl-1-naphthalenecarboxamide (PNA) was prepared and purified according to the previously described method.[6a)] *trans*-Stilbene, benzophenone (BP), and benzoyl-substituted benzoic acids (BBA) were recrystallized twice from ethanol or aqueous ethanol. 1,2-Dichloroethane, ethylene glycol,and glycerol were of spectroscopic grade and were used as received. Purification of methanol, ethanol, acetonitrile, and 2-chlorobutane was done by standard methods.[22)] Distilled acetonitrile and water were employed as a mobile phase for the HPLC analysis.

Quantum Yields. A potassium trioxalatoferrate(III) actinometer was employed to determine the quantum yields for the self-sensitized photolysis of 2-NPB, 3-NPB, and 4-NPB at their low conversions (<12%).[23)] A 450 W high-pressure Hg lamp was used as the light source from which 366 nm light for the photolysis was selected with Corning 0-52, Corning 7-60, and Toshiba IRA-25S glass filters. Linear calibration curves for each compound, made under the same analytical conditions, were utilized to quantify both the disappearance of NPB derivatives and the appearance of PNA, BBA, and BP. Quantum yields for the reaction in the presence of *trans*-stilbene, absorption of which was negligibly weak at 366 nm, were measured similarly. Molar extinction coefficients of 4-NPB and stilbene at 366 nm were evaluated to be 130 and <1 $dm^3\,mol^{-1}\,cm^{-1}$ in 1,2-dichloroethane, respectively. All the quantum yields are an average of more than five determinations.

References

1) a) M. Koizumi, S. Kato, N. Mataga, T. Matsuura, and Y. Usui, "Photosensitized Reactions," Kagaku Dojin, Tokyo (1978), Chap. 9; b) R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980); c) S. L. Mattes and S. Farid, *Acc. Chem. Res.*, **15**, 80 (1982); d) R. S. Davidson, *Adv. Phys. Org. Chem.*, **19**, 1 (1983); e) H. Itoh, Y. Senda, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **66**, 1312 (1993), and references cited therein.

2) G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, **86**, 401 (1986); C. J. Schlesener, C. Amatore, and J. K. Kochi, *J. Phys. Chem.*, **90**, 3747 (1986); J. J. McCullough, *Chem. Rev.*, **87**, 811 (1987); "Photoinduced Electron Transfer. Part C. Photoinduced Electron Transfer Reactions: Organic Substrates," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988).

3) D. Bellus, *Adv. Photochem.*, **8**, 109 (1971); T. Sakurai, K. Inomata, T. Ishikawa, H. Inoue, T. Hoshi, and J. Okubo, *Bull. Chem. Soc. Jpn.*, **60**, 4099 (1987); T. Sakurai, H. Mizuno, T. Kubota, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **64**, 2140 (1991); T. Sakurai, M. Nakamura, T. Hakii, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **65**, 2789 (1992).

4) G. L. Closs, P. Piotrowiak, J. M. MacInnis, and G. R. Fleming, *J. Am. Chem. Soc.*, **110**, 2652 (1988); G. L. Closs, M. D. Johnson, J. R. Miller, and P. Piotrowiak, *J. Am. Chem. Soc.*, **111**, 375 (1989).

5) a) H. Katayama, S. Maruyama, S. Ito, Y. Tsujii, A. Tsuchida, and M. Yamamoto, *J. Phys. Chem.*, **95**, 3480 (1991); b) H. Katayama, S. Ito, and M. Yamamoto, *J. Phys. Chem.*, **96**, 10115 (1992); c) P. J. Wagner and G. M. El-Taliawi, *J. Am. Chem. Soc.*, **114**, 8325 (1992); d) G. W. Haggquist, H. Katayama, A. Tsuchida, S. Ito, and M. Yamamoto, *J. Phys. Chem.*, **97**, 9270 (1993); e) A. Farrán, K. Deshayes, C. Matthews, and I. Balanescu, *J. Am. Chem. Soc.*, **117**, 9614 (1995).

6) a) T. Sakurai, H. Yamamoto, S. Yamada, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **58**, 1174 (1985); b) T. Sakurai, H. Sukegawa, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **58**, 2875 (1985).

7) T. Sakurai, K. Utsumi, A. Ohkita, M. Nakamura, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **65**, 1950 (1992).

8) S. L. Murov, I. Carmichael, and G. L. Hug, "Handbook of

Photochemistry," 2nd ed, Marcel Dekker, New York (1993).

9) S.-T. Levy, M. B. Rubin, and S. Speiser, *J. Photochem. Photobiol. A: Chem.*, **66**, 159 (1992); S.-T. Levy, M. B. Rubin, and S. Speiser, *J. Photochem. Photobiol. A: Chem.*, **69**, 287 (1993).

10) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953); P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 6883 (1972); H. Kobashi, T. Morita, and N. Mataga, *Chem. Phys. Lett.*, **20**, 376 (1973).

11) Computer calculations were accomplished by using the CAChe-MM2 program available from Sony-Tektronix.

12) a) J. M. McBride and R. A. Merrill, *J. Am. Chem. Soc.*, **102**, 1723 (1980); b) M. J. S. Dewar, A. H. Pakiari, and A. B. Pierini, *J. Am. Chem. Soc.*, **104**, 3242 (1982); c) S. Yamauchi, N. Hirota, S. Takahara, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **107**, 5021 (1985); d) J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **110**, 2886 (1988); e) H. G. Korth, J. Chateauneuf, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **110**, 5929 (1988).

13) T. Sakurai, K. Wada, and H. Inoue, *Nippon Kagaku Kaishi*, **1993**, 728.

14) H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1988**, 357.

15) G. A. Russell, "Free Radicals," ed by J. K. Kochi, Wiley-Interscience, New York (1973), Vol. 1, p. 284.

16) J. Wang, H. Itoh, M. Tsuchiya, K. Tokumaru, and H. Sakuragi, *Tetrahedron*, **51**, 11967 (1995); J. Wang, T. Tateno, H. Sakuragi, and K. Tokumaru, *J. Photochem. Photobiol. A: Chem.*, **92**, 53 (1995).

17) T. Sakurai, K. Miyoshi, M. Obitsu, and H. Inoue, *Ber. Bunsenges. Phys. Chem.*, **100**, 46 (1996).

18) Another possibility is that triplet NPB in aprotic solvents is subject to simultaneous two bond fission affording directly the amidyl-benzoylphenyl radical pair ^{3}[N· CO$_2$ ·B] (Scheme 1). This idea has previously been applied to interpreting the formation of phenyl benzoate from the photolysis of benzoyl peroxide.[19] If simultaneous two bond cleavage in the excited triplet state is a reasonable assumption, then hydrogen bonding between triplet NPB and protic solvents may function so as to suppress this type of bond fission and, hence, to enhance the relative contribution of one bond fission giving the amidyl-benzoylbenzoyloxyl radical pair ^{3}[N· ·OC(=O)B]. However, the fact that there is a large difference in bond dissociation energy between the N–O (220 kJ mol^{-1})[20] and C–C (350 kJ mol^{-1})[20a] bonds makes the occurrence of such a two bond scission very unlikely.[21]

19) J. C. Bevington and T. D. Lewis, *Trans. Faraday. Soc.*, **54**, 1340 (1958); A. Kitamura, H. Sakuragi, M. Yoshida, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **53**, 1393 (1980); J. C. Scaiano and L. C. Stewart, *J. Am. Chem. Soc.*, **105**, 3609 (1983).

20) a) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York (1970); b) H. Sakuragi, M. Yoshida, H. Kinoshita, K. Utena, K. Tokumaru, and M. Hoshino, *Tetrahedron Lett.*, **1978**, 1529.

21) S. Yamauchi, N. Hirota, S. Takahara, H. Misawa, K. Sawabe, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **111**, 4402 (1989).

22) J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents," 4th ed, Wiley-Interscience, New York (1986)

23) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).