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PHOTOINDUCED CROSS-COUPLING REACTION OF 5-BROMO-1,3-DIMETHYLURACIL TO ELECTRON-RICH AROMATICS[1]

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Abstract On irradiation with Pyrex-filtered light, 5-bromo-1,3-dimethyluracil **1** coupled with methyl- and methoxynaphthalenes **2–7** to give 5-naphthyl-1,3-dimethyluracils **8–13**. No coupling product was formed by triplet sensitization except in the cases of 2,3-dimethoxynaphthalene **3** and 2-methoxynaphthalene **5**, indicating that the singlet excited states of the naphthalenes are involved in the unsensitized coupling reaction. The $k_q\tau$ values of the fluorescence quenching of 1,4-dimethoxynaphthalene **2** and 1-methoxynaphthalene **4** by **1** in acetonitrile were comparable with those obtained from the kinetics of the coupling reactions. On the basis of this fact and the fluorescence-quenching rate constants k_q in acetonitrile ranging from 10^8 to 10^9 M^{-1} sec^{-1}, involvement of an electron-transfer process possibly via a singlet exciplex is proposed for this cross-coupling reaction.

In the last decade it has been well established that on electronic excitation the increase of both electron-donor and acceptor properties gives rise to electron transfer reactions between excited molecules and non-excited ones.[2] Encounter complex, exciplex and radical ion pair are considered as the intermediate species of numerous photoinduced reactions.[2] Photochemical charge-transfer and electron-transfer reactions are controlled by redox potentials, excitation energy, and solvent polarity.[2a,3] Excited complexes and exciplexes are usually formed in nonpolar solvents, being accompanied with a new red-shifted emission in certain cases, whereas the formation of solvated radical ion pair requires irradiation in polar solvents.[2] There is growing evidence that exciplexes are intermediates in photochemical reactions even when no new emitting species are observed.[2c,4]

We have recently reported the acetone-sensitized photo-cross-coupling of 5-bromouracil derivatives to 3-substituted indoles to give 5-(2-indolyl)uracils.[5–7] This coupling reaction occurs either in the absence[5,6] or presence[6,7] of an electron carrier such as naphthalene derivatives. In the latter case, cross-coupling between the 5-bromouracil and the electron carrier also occurs under certain circumstances. Electron-transfer mechanisms involving the triplet state of the bromouracil were proposed for these two types of coupling as shown in eqns (1) and (2), where

$$ {}^3BrU^* + InH \rightarrow (BrU^{\dot{-}} + InH^{\dot{+}}) \xrightarrow{-HBr} U{-}In \qquad (1)$$

$$\begin{tikzcd} {}^3BrU^* + NH \arrow[r] & (BrU^{\dot{-}} + NH^{\dot{+}}) \arrow[r, "-HBr"] \arrow[d, "InH"', "NH"] & U{-}N \\ & (BrU^{\dot{-}} + InH^{\dot{+}}) \arrow[r, "-HBr"] & U{-}In \end{tikzcd} \qquad (2)$$

BrU, InH and NH denote 5-bromouracil, indole and naphthalene derivatives, respectively.[7]

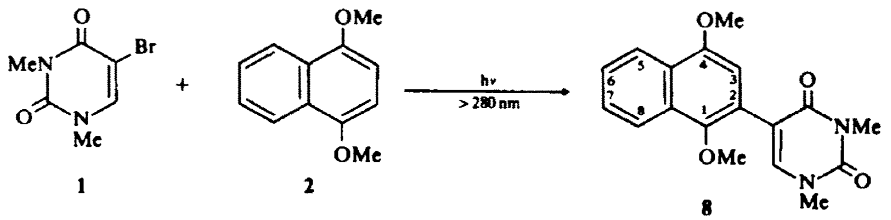
We find that in the absence of triplet sensitizer 5-bromo-1,3-dimethyl-uracil **1** undergoes the third type of photocoupling (eqn 3) to methyl- and methoxy-naphthalenes via an electron-transfer process from the singlet excited state of the naphthalenes, although a few cases may involve partly the naphthalene triplet. Thus, the result provides an unique example in which a similar electron-transfer reaction can occur at singlet as well as triplet excitations by changing electron-donor molecules.

$$ {}^1NH^* + BrU \rightarrow (BrU^{\dot{-}} + NH^{\dot{+}}) \xrightarrow{-HBr} U{-}N \qquad (3)$$

RESULTS AND DISCUSSION

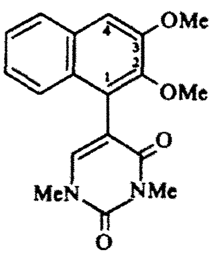
Cross-coupling product

Irradiation of an acetonitrile solution of 5-bromo-1,3-dimethyluracil **1** and 1,4-dimethoxynaphthalene **2** with a high-pressure mercury lamp through Pyrex glass gave the photoproduct **8**. Under the conditions, about 75% of the incident light was absorbed by **2**. The structure of the product was assigned as **8** from its spectral data. The molecular peak at *m/e* 326 indicates that **8** is a 1:1 coupling product formed by intermolecular dehydrobromination. By comparison of the ^1H NMR spectra of the product **8** and the starting material **2** [δ 3.93 (s, 6 H) for 1- and 4-methoxy protons, δ 6.79 (s, 2 H) for H_2 and H_3 on the naphthalene ring, and δ 7.05 and 8.19 (A_2B_2, 4 H) for H_5, H_6, H_7 and H_8], (i) one (δ 3.70) of the methoxy-protons of **8** shifted to up-field due to the deshielding by the uracil ring, (ii) the H_3 proton (δ 6.95) is shifted to down-field, being accompanied with the loss of H_2 proton, and (iii) the A_2B_2 signals became diffused. These spectral changes and other spectral properties agree well with the structure **8**.



1 **2** **8**

Under the same irradiation conditions, 2,3-dimethoxynaphthalene **3** gave a similar type of 1:1 coupling product **9**. In this case, about 80% of the incident light was absorbed by **3**. Comparison of the ^{1}H NMR spectrum of **9** with that of **3** [δ 3.91 (s, 6 H), 7.25 (s, 2 H), and 7.32 and 7.72 (A_2B_2, 4 H)] showed similar spectral changes as in the case of **8**, indicating that the coupling of the uracil ring occurs at the 1-position of **3** as depicted below.



9

In the case of 1-methoxynaphthalene **4**, a similar type of coupling reaction was observed to give a 1:1 mixture of two isomeric products **10** which could not be separated. 2-Methoxynaphthalene **5**, 1-methylnaphthalene **6** and 2-methylnaphthalene **7** also gave an inseparable 1:1 mixture of two isomeric coupling products **11**, **12** and **13**, respectively. The spectral data of these 1:1 mixtures of isomeric products were compatible with the structures depicted below. By analogy with the formation of **8** and **9**, the coupling of the uracil ring is assumed to occur on the methyl- or methoxy-substituted ring of the starting naphthalenes. The yields of the coupling products obtained by the above unsensitized photoreactions are summarized in Table 1.

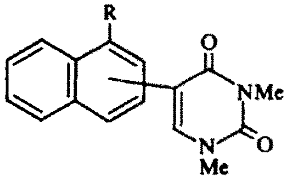
Fluorescence emission maxima of the coupling products are listed in Table 2 together with those and fluorescence quantum yields of the starting naphthalenes. Fluorescence intensities of the coupling products were slightly weaker than those of the starting materials. We have attempted to extend this coupling reaction to a variety of aromatics. However, photoreaction of the anthracenes **14** and **16** with **1** gave no cross-coupling product. In the case of 9-methylanthracene **14**, **1** produced a homo-coupling product, N,N,N′,N′-tetramethyl-5,5′-diuracilyl **15** (47%), which had already been characterized by Ishihara and Wang.[8]

Mechanistic consideration

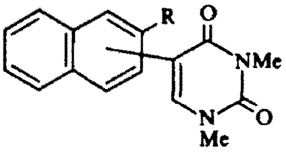
In order to know the multiplicity of the excited state responsible for the coupling reactions, triplet sensitization was carried out with acetone (E_T 78–82 kcal/mol[9]) and benzophenone (69.2 kcal/mol[9]). Under the irradiation conditions, 70–75% of the incident light was absorbed by acetone and 90–95% by benzophenone. The results are summarized in Table 1. Except the 2-methoxy-substituted naphthalenes **3** and **5**, no coupling product was formed and the starting materials were largely recovered. The results suggest that neither triplet naphthalene nor triplet **1** is responsible for the unsensitized coupling reaction (**2**, **4**, **6**, **7**), and that a singlet excited state, most probably naphthalene singlet, is involved in the reaction (eqn 4), since a large part of the incident light was absorbed by the naphthalene, although mechanistic situation is more complicated in the cases of **3** and **5** (*vide infra*).

$$^1NH^* + BrU \rightarrow U{-}N \qquad (4)$$

Acetone-sensitization was effective for the reactions of both **3** and **5**, whereas benzophenone-sensitization was only effective for **5**. In view of the triplet energies of



10 R = OMe
12 R = Me



11 R = OMe
13 R = Me

Table 1. Photoinduced cross-coupling of **1** to naphthalenes and singlet and triplet energies of naphthalenes[a]

Naphthalenes		E_S (kcal/mol)	E_T (kcal/mol)	Yield of coupling product (%)[b]		
				unsensitized	+ acetone	+ benzophenone
1,4-(MeO)$_2$	(2)	90 [c]	60.3[d]	40	0	0
2,3-(MeO)$_2$	(3)	90 [c]	60 [c]	44	10	9
1-MeO	(4)	89.3[e]	59.7[e]	41	0	0
2-MeO	(5)	85.3[f]	62 [d]	12	65	0
1-Me	(6)	90.0[e]	59.6[e]	54	0	g
2-Me	(7)	89.5[e]	60.8[e]	53	0	g

[a] Irradiations in preparative scale runs were done with a 100-W high-pressure mercury lamp through a Pyrex filter for 10 h at ambient temperature. [b] Based on the consumed **1**. [c] Estimated values from other naphthalenes; [d] F. H. Quina, Z. Hamlet and F. A. Carroll, J. Am. Chem. Soc., **99**, 2240 (1977); [e] S. L. Murov in "Handbook of Photochemistry", M. Dekker, New York, 1973; [f] D. Rehm and A. Weller, Isr. J. Chem., **8**, 259 (1970). [g] Not done.

Table 2. Fluorescence spectra of naphthalenes and the coupling products in CH_3CN at 20 C[a]

Naphthalenes		E_{max} (nm)	Φ_f	Coupling Product	E_{max} (nm)
1,4-$(MeO)_2$	(2)	390	0.50[b]	8	457
2,3-$(MeO)_2$	(3)	351	0.47[c]	9	421
1-MeO	(4)	340	0.36[d]	10	426
2-MeO	(5)	349	0.45[b]	11	420
1-Me	(6)	333	0.21[e]	12	409
2-Me	(7)	333	0.27[e]	13	418

[a] Excitation wavelengths were 330 nm (2, 3, 4, 5, 8, 9, 10, and 11) and 320 nm (6, 7, 12 and 13). [b] F. H. Quina, Z. Hamlet and F. A. Carroll, J. Am. Chem. Soc., 99, 2240 (1977); [c] Private communication from Dr. F. Tanaka; [d] J. D. Laposa, E. C. Lim and R. E. Kellogg, J. Chem. Phys., 42, 3025 (1965); [e] I. B. Berlman in "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1965.

the sensitizers, the naphthalenes (~60 kcal/mol; see Table 1) and **1** (estimated to be *ca.* 74 kcal/mol[10]), it seems very likely that the sensitized coupling of **1** to **5** involves a bromouracil triplet formed by energy transfer from acetone triplet (eqn 5) as has been observed in the acetone-sensitized reaction of **1** and tryptophan derivatives.[5,7] Acetone- and benzophenone-sensitized couplings of **1** to **3** may probably involve the triplet state of **3** (NH) formed by energy transfer from the sensitizers (eqn 6).

$$^3BrU^* + NH \rightarrow U{-}N \qquad (5)$$

$$^3NH^* + BrU \rightarrow U{-}N \qquad (6)$$

Electron-transfer processes in photoinduced reactions, such as exciplex and radical ion pair formations, have recently been recognized not only as physical quenching processes of excited species but also as processes yielding products.[2] In several [2 + 2] photocycloaddition reactions, such electron-transfer processes have been suggested and confirmed as essential processes.[2,11] In a fluorescence quenching process, Rehm and Weller proposed a correlation between the quenching rate constants and changes of free energy (ΔG) calculated by eqn (7).[3] Since it is recognized that naphthalenes are able to act as electron-donors[12] and nucleic acid bases, especially pyrimidine bases as electron-acceptors,[13] fluorescence quenching experiments were performed in order to see whether or not such an electron-transfer process is involved in the unsensitized coupling of the naphthalenes to **1**. Table 3 lists the free energy change (ΔG) calculated by eqn (7).

$$\Delta G = 23.06[E(D/D^+)_V - E(A^-/A)_V \; e^2/\varepsilon\alpha] - \Delta E_{0.0} \qquad (7)$$

where 1.3 kcal/mol of the coulomb force ($e^2/\varepsilon\alpha$) estimated by Maroulis *et al.*[14] is employed. The rate constants (k_q) for fluorescence-quenching of the naphthalenes by **1** were obtained experimentally by Stern–Volmer plots. The calculated ΔG values predict that in all cases the electron transfer process of eqn (3) is highly exothermic. With the exception of **3** and **5** (*vide infra*), the observed rate constants of fluorescence-quenching are fairly close to that of diffusion-controlled reaction ($k_{dif} = 2.7 \times 10^{10}\ M^{-1}\ sec^{-1}$ in CH_3CN at 20°C). Another significant finding in the quenching experiments is that the $k_q\tau$ value ($32.7\ M^{-1}$) for the fluorescence-quenching of **2** by **1** was comparable to that ($44.4\ M^{-1}$) obtained from the kinetics of the unsensitized coupling reaction of **1** to **2**. Plotting of $[\text{rel yield of } \mathbf{8}]^{-1}$ vs $[\mathbf{2}]^{-1}$ gave a straight line, and the value of $k_q\tau$ values was calculated from the interapt slope ratio. Similarly, the kg τ values for the fluorescence-quenching of **4** by **1** ($40.5\ M^{-1}$) and that obtained from the unsensitized coupling reaction ($35.0\ M^{-1}$) are also comparable. The results strongly support that complexation of the naphthalene singlet with the uracil **1**, presumably exciplex formation, followed by an electron transfer is a common process in both the fluorescence-quenching and the coupling reaction (eqn 8).

$$NH \xrightarrow{h\nu} {}^1NH^* \xrightarrow{BrU} {}^1(NH{-}BrH)^*$$
$$\rightarrow (NH^- + BrU^-) \xrightarrow{-HBr} N{-}U \qquad (8)$$

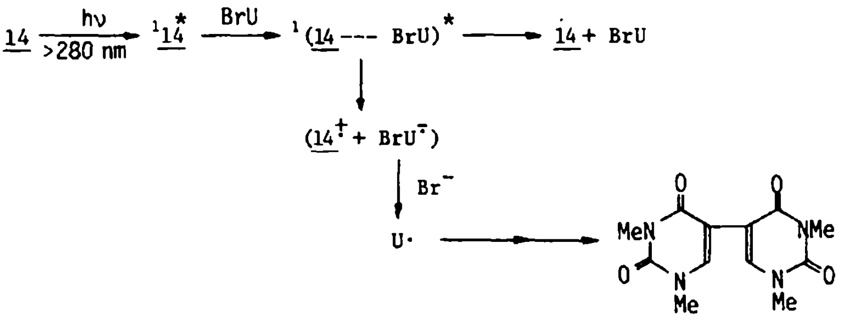
It should be pointed out that the fluorescence quantum yields of the naphthalenes (Table 2) do not account for their different reactivities toward the unsensitized coupling reactions. No evidence for the formation of a ground state complex between **1** and the naphthalenes **2**–**7** was obtained by UV absorption spectroscopy, nor new red-shifted emission being observed in fluorescence-quenching experiments with all of the naphthalenes in any solvents.

Somewhat different photochemical behaviors are observed in the cases of **3** and **5**, which commonly have a methoxy group at the β-position of the naphthalene ring. (i) The quenching rates of their fluorescence by **1** are relatively slow (Table 3). (ii) Unlike the fluorescence quenching experiment ($k_q\tau = 2.84\ M^{-1}$ for **3**), the cross-coupling reaction between **1** and **3** gave no linear Stern–Volmer type plots. (iii) The same coupling products were obtained from both unsensitized and triplet-sensitized reactions (Table 1). These facts suggest that the unsensitized cross-coupling reaction of **3** or **5** may involve an electron-transfer process from the triplet naphthalene to some extent, presumably via a triplet exciplex (eqn 9), in competition with the electron transfer from the singlet excited naphthalene (eqn 8).

$$\mathrm{NH} \xrightarrow{h\nu} {}^1\mathrm{NH}^* \xrightarrow{isc} {}^3\mathrm{NH}^* \xrightarrow{\mathrm{BrU}} {}^3(\mathrm{NH}{-}\mathrm{BrU})^* \rightarrow (\mathrm{NH}^{+} + \mathrm{BrU}^{\overline{\cdot}}) \xrightarrow{-\mathrm{HBr}} \mathrm{N}{-}\mathrm{U} \qquad (9)$$

Although the reason for the particular behaviors of **3** and **5** different from other naphthalenes is obscure, it is noteworthy to point out that in the triplet-mediated coupling of **1** to N^b-methoxycarbonyltryptamine occurring with the assistance of an electron carrier (eqn 2),[7] **3** and **5** can serve as more efficient electron carriers than any other naphthalene derivatives including 1-methoxy-**4** and 1,4-dimethoxynaphthalene **2**.[6,7,15]

The fluorescence-quenching rate constants for two anthracene derivatives, 9-methyl- and 9,10-dimethoxyanthracenes, were much smaller than those for the naphthalenes (Table 3), suggesting that the nature of their excited state differs from those of the naphthalenes. Although the ΔG values calculated by eqn (7) indicate high exothermicity for an electron-transfer from these anthracenes to **1** (Table 3), they failed to undergo photo-cross-coupling to **1** but gave the homocoupling product of **1** in the case of 9-methylanthracene **14**. For the formation of 5,5'-diuracilyl **15** from 5-bromouracil under irradiation with 254-nm light, Ishihara and Wang proposed a mechanism involving the 5-uracilyl radical (U·) generated from the singlet excited state of 5-bromouracil.[8] In view of the fact that **1** itself was completely inert under our conditions (Pyrex-filtered light) in the absence of 9-methylanthracene, it seems probable that the formation of the homo-coupling product **15** in the presence of 9-methylanthracene **14** may involve an electron-transfer process from the excited state of **14** to **1**. The anion radical of **1** thus formed releases Br$^-$ to give 5-uracilyl radical (U·) (eqn 10).[17]



(10)

(15)

Tab'e 3. Fluorescence-quenching of aromatic by 1 in acetonitrile and calculated free energy change for the electron-transfer process (eqn 3)

Fluorophor	τ (nsec) (Solvent)	k_q ($M^{-1}sec^{-1}$)	E^{ox} (V) vs. SCE	ΔG calcd. (kcal/mol)[a]
1,4-dimethoxynaphthalene (**2**)	5.7[b] (CH$_3$CN)	5.7×10^9	+ 1.10[f]	- 44.7
2,3-dimethoxynaphthalene (**3**)	9.3[c] (CH$_3$CN)	3.1×10^8	+ 1.39[f]	- 38.0
1-methoxynaphthalene (**4**)	13.6[d] (CH$_3$CN)	3.0×10^9	+ 1.38[f]	- 37.5
2-methoxynaphthalene (**5**)	16[b] (CH$_3$CN)	8.0×10^8	+ 1.52[f]	- 30.0
1-methylnaphthalene (**6**)	72.3[d] (CH$_3$CN)	1.1×10^9	+ 1.43[g]	- 37.1
2-methylnaphthalene (**7**)	59[e] (cyclohexane)	1.6×10^9	+ 1.45[g]	- 36.1
9-methylanthracene (**14**)	4.6[e] (cyclohexane)	8.7×10^7	+ 0.96[g]	- 29.9[h]
9,10-dimethoxyanthracene (**16**)	9.2[i] (EtOH)	1.4×10^6	+ 0.98[f]	- 16.6[j]

[a] Calculated free energy change for the electron-transfer process (Eq. 3) using Eq. 7. Reduction potencial of **1** (E^{red}, -0.90 V vs. SCE in CH$_3$CN)[7] measured by cyclic voltammetry and singlet energies in Table 1 were used, unless otherwise stated. [b] F. E. Quina, Z. Hamlet and F. A. Carroll, J. Am. Chem. Soc., **99**, 2240 (1977); [c] Private communication from Dr. F. Tanaka; [d] D. R. Arnold and A. J. Maroulis, J. Am. Chem. Soc., **99**, 7355 (1977); [e] I. B. Berlman in "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1965; [f] A. Zweig, A. H. Maurer and B. G. Roberts, J. Org. Chem., **32**, 1322 (1967); [g] E. S. Pysh and N. C. Yang, J. Am. Chem. Soc., **85**, 2125 (1963); [h] Used E_S value (74 kcal/mol) from ref. 9; [i] A. S. Cherkasov, V. A. Molchanov, T. M. Vember and K. G. Voldaikina, Soviet Phys. Doklady, **1**, 427 (1956); [j] Used E_S value (72 kcal/mol) estimated from other anthracenes.

EXPERIMENTAL

All m.ps are uncorrected. Ultraviolet spectra were recorded with a Shimadzu UV-200 spectrophotometer. Fluorescence spectra were recorded with a Shimadzu RF-500 spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian HA-100 or a T-60 spectrometer using Me_4Si as the internal reference. Mass spectra and high-resolution mass spectra were recorded with a JEOL-JMS-01SG-2 spectrometer. Preparative-scale irradiations were performed with a 100-W high-pressure mercury lamp using a Pyrex reaction vessel fitted with a water-cooling jacket at ambient temperature under nitrogen atmosphere. Preparative TLC was performed on a silica gel plate (Merck 60 PF_{254}) developed with chloroform acetonitrile (9:1). Dimethoxynaphthalenes were prepared by treatment of the commercially available diols with dimethylsulfate and sodium hydroxide and purified by recrystallization from methanol. The melting points of these materials were the same as those described in the literature.[18] The other naphthalene derivatives were commercially available.

Photolysis of 5-bromo-1,3-dimethyluracil **1** *and 1,4-dimethoxynaphthalene* **2**

A soln of **2** (83 mg, 0.45 mmol) and **1** (70 mg, 0.32 mmol) in acetonitrile (150 ml) was irradiated for 10 h. Evaporation of the solvent followed by preparative TLC of the residue yielded **8** (13 mg; 40% based on the consumed **1**), unreacted **1** (48 mg; 69%) and **2** (26 mg; 31%). **8**; m.p. 50–51 (pale yellow fine crystals from MeOH); UV (CH_3CN) 230 nm (log ε 4.53), 244.5 (4.39), 260 (4.20), 295 sh (3.69), 330 sh (3.67); ^1H NMR (acetone-d_6) δ 3.34 (s, 3 H), 3.50 (s, 3 H), 3.70 (s, 3 H), 3.79 (s, 3 H), 6.95 (s, 1 H), 7.56 (A_2 part of diffused A_2B_2 pattern, 2 H), 7.83 (s, 1 H), 8.13 (B_2 part of diffused A_2B_2 pattern, 2 H); MS (rel intensity) *m/e* 326 (M^+, 99), 311 (100), 254 (7), 226 (54), 183 (33). (Exact MS Found: 326.1256. $C_{18}H_{18}O_4N_2$ requires: 326.1265).

Photolysis of **1** *and 2,3-dimethoxynaphthalene* **3**

A soln of **3** (52 mg, 0.28 mmol) and **1** (61 mg, 0.28 mmol) in acetonitrile (150 ml) was irradiated for 10 h under the standard conditions. Evaporation of the solvent followed by preparative TLC of the residue gave **9** (17 mg; 44% based on the consumed **1**), recovered **1** (35 mg) and **3** (28 mg). **9**; m.p. 82–83 (colorless fine crystals from MeOH); UV (CH_3CN) 233 nm (log ε 4.67), 270 (4.02), 281 sh (4.01), 310 sh (3.58), 325 (3.49); ^1H NMR (acetone-d_6) δ 3.22 (s, 3 H), 3.47 (s, 3 H), 3.79 (s, 3 H), 3.93 (s, 3 H), 7.17 (s, 1 H), 7.21–7.45 (m, 3 H), 7.66 (s, 1 H), 7.63 7.86 (m, 1 H); MS (rel. intensity) *m/e* 326 (M^+, 100), 311 (8), 283 (6), 254 (5), 226 (7), 183 (5). (Exact MS Found: 326.1231. $C_{18}H_{18}O_4N_2$ requires: 326.1265).

Photolysis of **1** *and 1-methoxynaphthalene* **4**

A soln of **4** (94 mg, 0.60 mmol) and **1** (77 mg, 0.35 mmol) in acetonitrile (150 ml) was irradiated for 10 h. Evaporation of the solvent followed by preparative TLC of the residue gave a 1:1 mixture of coupling products **10** (14 mg; 41% based on the consumed **1**), unreacted **1** (52 mg) and **4** (67 mg). **10**; m.p. 56–61 (fine crystals from MeOH); UV (CH_3CN) 216.5 nm (log ε 4.42), 275.5 (3.97), 297 sh (3.84), 323 sh (3.46); ^1H NMR (acetone-d_6) δ 3.32 (s, 3 H), 3.48 (s, 3 H), 3.34 (s, 3 H), 3.50 (s, 3 H), 3.77 (s, 3 H), 4.04 (s, 3 H), 7.80 (s, 1 H), 8.02 (s, 1 H), 6.89 8.30 (m, 6 H × 2); MS (rel. intensity) *m/e* 296 (M^+, 100), 281 (18), 266 (16), 265 (41), 224 (9), 196 (42), 153 (16). (Exact MS Found: 296.1172. $C_{17}H_{16}O_3N_2$ requires: 296.1160).

Photolysis of **1** *and 2-methoxynaphthalene* **5**

A soln of **5** (49 mg, 0.31 mmol) and **1** (61 mg, 0.28 mmol) in acetonitrile (150 ml) was irradiated for 10 h. Evaporation of the solvent followed by preparative TLC of the residue gave a 1:1 mixture of coupling products **11** (5 mg; 12% based on the consumed **1**), unreacted **1** (33 mg) and **5** (36 mg). **11**; m.p. 67 68 (colorless fine crystals from MeOH); UV (CH_3CN) 227 nm (log ε 4.65), 275 (4.04), 287 sh (3.97), 315 (3.52), 330 (3.46); ^1H NMR (acetone-d_6) δ 3.28 (s, 3 H), 3.38 (s, 3 H), 3.29 (s, 3 H), 3.40 (s, 3 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 6.98–8.13 (m, 14 H); MS (rel. intensity) *m/e* 296 (M^+, 100), 295 (25), 281 (12), 266 (40), 265 (40), 168 (21). (Exact MS Found: 296.1187. $C_{17}H_{16}O_3N_2$ requires: 296.1160).

Photolysis of **1** *and 1-methylnaphthalene* **6**

A soln of **6** (55 mg, 0.39 mmol) and **1** (62 mg, 0.28 mmol) in acetonitrile (150 ml) was irradiated for 10 h. Evaporation of the solvent followed by preparative TLC of the residue gave a 1:1 mixture of coupling products **12** (23 mg; 54% based on the consumed **1**), unreacted **1** (29 mg) and **6** (12 mg). **12**; viscous oil; UV (CH_3CN) 223.5 nm (log ε 4.65), 279 (4.04), 299 sh (3.91), 322 sh (3.29); ^1H NMR (acetone-d_6) δ 2.54 (s, 3 H), 2.69 (s, 3 H), 3.30 (s, 3 H), 3.43 (s, 3 H), 3.30 (s, 3 H), 3.44 (s, 3 H), 7.19–8.18 (m, 14 H); MS (rel. intensity) *m/e* 280 (M^+, 100), 265 (9), 263 (39), 223 (13), 195 (19), 153 (23). (Exact MS Found: 280.1241. $C_{17}H_{16}O_2N_2$ requires: 280.1211).

Photolysis of **1** *and 2-methylnaphthalene* **7**

A soln of **7** (49 mg, 0.35 mmol) and **1** (68 mg, 0.31 mmol) in acetonitrile (150 ml) was irradiated for 10 h. Evaporation of the solvent followed by preparative TLC of the residue gave a 1:1 mixture of coupling products **13** (30 mg; 53% based on **1** consumed), recovered **1** (24 mg) and **7** (22 mg). **13**; m.p. 66 71 (colorless fine crystals from MeOH); UV (CH_3CN) 223.5 nm (log ε 4.79), 280 (3.86), 306 sh (3.65), 320 sh (3.26); ^1H NMR (acetone-d_6) δ 2.31 (s, 3 H), 2.47 (s, 3 H), 3.28 (s, 3 H), 3.30 (s, 3 H), 3.40 (s, 3 H), 3.42 (s, 3 H), 7.17 – 7.93 (m, 14 H); MS (rel intensity) *m/e* 280 (M^+, 100), 265 (6), 263 (23), 223 (10), 195 (20), 194 (21), 166 (22), 153 (14). (Exact MS Found: 280.1239. $C_{17}H_{16}O_6N_2$ requires: 280.1211).

Sensitized irradiation

Acetone-sensitized irradiations were performed under the conditions where 70–75% of the incident light was absorbed by acetone. In a typical run, a soln of **2** (17 mg, 0.09 mmol) and **1** (39 mg, 0.18 mmol) in acetonitrile-acetone (3:1; 150 ml) was irradiated for 10 h under the standard conditions. Evaporation of the solvent followed by preparative TLC of the residue gave the unreacted starting materials (*ca.* 90% recovery). For compounds **3**, **4**, **5**, **6** and **7**, acetone-sensitized reactions were carried out similarly and the results are shown in Table 1.

Benzophenone-sensitized irradiations were performed under the standard conditions where 90–95% of the incident light was absorbed by benzophenone. Evaporation of the solvent followed by silica gel column chromatography (eluted with $CHCl_3$ to separate the recovered benzophenone and naphthalenes from the reaction mixture) and preparative TLC gave the unreacted starting materials and a coupling product. In a typical run, a solution of **3** (68 mg, 0.36 mmol), **1** (84 mg, 0.39 mmol) and benzophenone (3.38 g, 18.6 mmol) in acetonitrile (150 ml) was irradiated for 10 h under the standard conditions. Evaporation of the solvent followed by silica gel column chromatography and preparative TLC of the residue gave **9** (6 mg; 9%) and the unreacted **1** (35 mg). Benzophenone-sensitized reactions of **2**, **4** and **5** were carried out similarly. The results are shown in Table 1.

Fluorescence quenching

Fluorescence-quenching experiments of naphthalene derivatives by **1** were performed at 20 C in acetonitrile. The concentrations of fluorophors were about 2–4 × 10^{-5} mol/l and those of quenchers were 1–4 × 10^{-3} mol/l. The $k_q\tau$ values for relative reactivities of **1** toward naphthalene derivatives (**2**, **3**, **4** and **5**) were measured in acetonitrile in Pyrex tubes using a merry-go-round apparatus. The concentrations of naphthalenes were 5–7 × 10^{-3} mol/l and those of **1** were 1–4 × 10^{-3} mol/l. Under the conditions the incident light was mostly absorbed by naphthalenes. The reaction was monitored by NMR measurements of the reaction mixture.

Photoreaction of **1** *and 9-methylanthracene* **14**

A soln of **14** (65 mg, 0.34 mmol) and **1** (67 mg, 0.31 mmol) in acetonitrile (150 ml) was irradiated for 10 h where 80–85 % of the incident light was absorbed by **14**. Evaporation of the solvent followed by preparative TLC of the residue gave N,N,N′,N′-tetramethyl-5,5′-diuracilyl **15** (21 mg; 47 % based on the consumed **1**), m.p. 284–286° (from MeOH) lit.[9] m.p. 281–282°. The NMR spectrum of **15** was identical with that described in the literature.[9]

Photoreaction of **1** *and 9,10-dimethoxyanthracene* **16**

A soln of 9,10-dimethoxyanthracene (77 mg, 0.32 mmol) and **1** (64 mg, 0.29 mmol) in acetonitrile (150 ml) was irradiated for 10 h where 85 % of the incident light was absorbed by anthracene. Evaporation of the solvent gave a complex mixture of products.

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