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The Photochemistry of the Host-Guest Complex. VII. The Photoreaction of Dicyanopyrazine Derivatives Having a Crown Ether Moiety[1]

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The irradiation of 4′-(5,6-dicyano-2-pyrazinyl)benzo-15-crown-5 and 5,6-dicyano-2-(3,4-dimethoxyphenyl)-pyrazine in the presence of a tertiary or secondary amine caused reductive decyanation to give 5-decyano derivatives, which in turn gave bis(decyano) derivatives on further irradiation. Free-energy changes upon single-electron transter from the amine to the excited state of dicyanopyrazine derivatives are exothermic for triethylamine and diethylamine, but endothermic for butylamine. The single-electron transfer was evidenced by the effect of the sodium ion on the quantum yields of the reaction products and the fluorescence quenching.

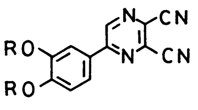
In our studies of crown ether derivatives, we havef previously reported the diverse effects of guest cations on the photoreactivities of the crown ether derivatives. The pairing effect, the variation in the oxidation potential, the change in the intersystem crossing rate, and the destabilization of the transition state are among the effects which we have already discussed.[2] In this paper we would like to report on other effects by a guest cation, a decrease in the reduction potential and an increase in the excitation energy, on the photoreactivity of the pyrazine derivative having a crown ether moiety, 4′-(5,6-dicyano-2-pyrazinyl)benzo-15-crown-5 (**1**).

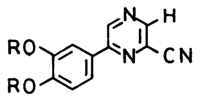
The pyrazine derivative having an electronegative substituent can be a mimicry of an oxidation-reduction coenzyme, such as flavin and biopterin, in which the aromatic system containing nitrogen plays an important role in the redox systems.[3]

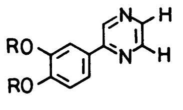
Syntheses of Dicyanopyrazine Derivatives. 4′-(5,6-Dicyano-2-pyrazinyl)benzo-15-crown-5 (**1**) and 5,6-dicyano-2-(3,4-dimethoxyphenyl)pyrazine (**2**) were synthesized by the condensation of diaminomaleonitrile (DAMN) with the corresponding dicarbonyl compounds, which had been prepared from benzo-15-crown-5 or 1,2-dimethoxybenzene by acetylation (acetic acid in polyphosphoric acid), followed by oxidation by selenium dioxide.

The Photoreaction of Dicyanopyrazine Derivatives (1 and 2) in the Presence of Amines. A dry acetonitrile solution of the benzo-15-crown-5 derivative **1** was irradiated in the presence of four equivalents of triethylamine; 4′-(6-cyano-2-pyrazinyl)benzo-15-crown-5 (**3**) was thus obtained in 80% yield. The irradiation of the dimethoxybenzene derivative **2** gave a similar result, affording 6-cyano-2-(3,4-dimethoxyphenyl)pyrazine (**4**) in 80% yield. The structures of both products were deduced from the ^{1}H-NMR spectra, in which a new aromatic hydrogen (C_5–H) at the pyrazine ring (δ 8.95 for **3** and 8.94 for **4**) couples (J=2 Hz) with the meta-hydrogen (δ 9.20 for **3** and 9.18 for **4**).

The irradiations of **1** and **2** in the presence of a large excess of triethylamine (acetonitrile-triethylamine, 3 : 1) gave two bis(decyano) derivatives, 4′-(2-pyrazinyl)-benzo-15-crown-5 (**5**) and 2-(3,4-dimethoxyphenyl)-pyrazine (**6**), in 40 and 46% yields respectively. The same products were also obtained in low yields under the previous reaction conditions (triethylamine; 5.6×10^{-2} mol dm^{-3}) on prolonged irradiation or on the urther irradiation of the isolated **3** or **4**. Therefore, the products **5** and **6** are the secondary products from the primary products, **3** and **4** respectively.


1 , 2


3 , 4


5 , 6

1, 3, 5 : R,R = $O(CH_2CH_2OCH_2CH_2)_2$

2, 4, 6 : R = CH_3

The irradiation of **1** or **2** in the presence of diethylamine instead of triethylamine gave essentially the same results. Butylamine, however, did not cause a photoreaction under similar conditions, though the use of a large excess of butylamine caused the thermal substitution of one of the cyano group with a butylamino group in the dark.[4] These photoreactions are accelerated by purging the reaction solution with argon.

Spectroscopic and Electrochemical Studies. The same reaction takes place in benzene, though the reaction is not so clean as in acetonitrile. The fluorescence from **1** and **2** is almost identical, but weaker in acetonitrile than in benzene. The quenching experiment, therefore, was carried out in benzene. Triethylamine ($k_q\tau$=47.0 mol^{-1} dm^3) and diethylamine ($k_q\tau$=28.0 mol^{-1} dm^3) quench the fluorescence efficiently, but butylamine shows no detectable quenching effect. **3** and **4** fluoresce strongly even in acetonitrile, and the emission is quenched by triethylamine ($k_q\tau$=23.0 mol^{-1} dm^3) and diethylamine ($k_q\tau$=18.0 mol^{-1} dm^3), but, again, not with butylamine.

The photoreaction and the fluorescence quenching by animes suggest that a single-electron transfer from the amine to the excited pyrazine derivatives plays an important role. Rehm-Weller's equation,[5] $\Delta G = E_D{}^{ox} - E_A{}^{red} - E_A{}^* - e^2/(r\varepsilon)$, in which $E_D{}^{ox}$, $E_A{}^{red}$, $E_A{}^*$, and $e^2/(r\varepsilon)$ represent the oxidation potential of the amines, the reduction potential of the pyrazine derivatives, the excitation energy of the pyrazine derivative, and the Coulomb stabilization of the radical ion pairs respectively, shows the numerical value for the free-energy change on the electron transfer. The inter-ion

TABLE 1. FREE ENERGY CHANGE IN THE ELECTRON TRANSFER FROM AMINES TO THE EXCITED STATE OF **1** AND **2**, AND QUANTUM YIELD OF THE PHOTODECYANATION

Compound Acceptor	 Donor	E_A^{red} / V$^{a)}$	E_D^{ox} / V$^{a)}$	E_A^* / eV$^{b)}$	$\Delta G'$ / eV$^{c)}$	$\Phi\times10^3$
2	Et_3N	−1.01	+1.35	2.78	−0.42	1.3
2	Et_2NH	−1.01	+1.48	2.78	−0.29	—
2	$BuNH_2$	−1.01	+1.94	2.78	+0.17	—
1	Et_3N	−1.01	+1.35	2.78	−0.42	1.3
[**1**-Na$^+$]	Et_3N	−0.60$^{d)}$	+1.35	2.92$^{e)}$	−0.98	3.3

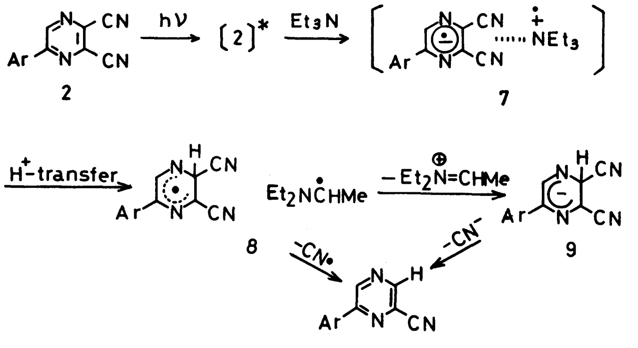
a) Solvent: acetonitrile. V *vs.* S.H.E. (converted from the value *vs.* Ag/AgCl). b) $\lambda_{0\text{-}0}$=445 nm (calculated) in acetonitrile: see text for the calculation. c) $\Delta G'=E_D^{ox}-E_A^{red}-E_A^*$. d) **1**: 5.00 mmol dm^{-3}; $NaClO_4$: 20 mmol dm^{-3}. e) **1**: 1.0×10^{-4} mol dm^{-3}; $NaClO_4$: 5.0 mmol dm^{-3}.

distance (r) in the last term should be essentially large and constant with a similar combination of the donor and acceptor in the same solvent.[6] Therefore, we calculated the $\Delta G'$ $(=\Delta G-e^2/(r\varepsilon))$ from the data of cyclic voltammetry (E^{red} and E^{ox}) and the fluorescence spectrum(E_A*). The fluorescence of **2** in acetonitrile has fine structure enabling us to assign the 0-0 band; no therefore, the E_A* was estimated from the ν (0-0) calculated by means of this equation: $\nu\ (0\text{-}0)=(\nu_{max}^{a}+\nu_{max}^{f})/2$, in which ν_{max}^{a} and ν_{max}^{f} represent the frequencies of the maxima of the absorption and the fluorescence respectively. The values of $\Delta G'$ on the electron transfer from amines to the excited state of **2** are negative for triethylamine and diethylamine, but positive for butylamine. These results are perfectly coincident with the photoreactivity and fluorescence quenching.

Reaction Mechanism. The experimental findings described above strongly suggest that the photoreaction proceeds through a single electron-transfer process (Scheme 1). This type of reaction has been reported for the photo-dehalogenation of aromatic halides[7] or a photochemical $S_{R}1$ reaction,[8] and the intervention of aryl radicals has been well documented.[9] Ohashi *et al.* reported that the photoreaction of dicyanobenzenes in the presence of triethylamine or diethylamine gave substitution products, 4-[1-(diethylamino)ethyl]-benzonitrile or 4-[1-(ethylamino)ethyl]benzonitrile, by means of an electron-transfer mechanism.[10]

As in the case of halobenzenes, the hydrogen abstraction of the 3-cyano-2-pyrazinyl radical seems a plausible path to give the photoproducts; the radical can be expected to be formed by the electron transfer from an amine to the excited dicyanopyrazine derivative, generating a radical anion, followed by the rupture of the cyanide ion. In the case of dicyanopyrazines, however, a proton trasfer is proved to be involved after the electron transfer, and the radicals thus formed couple to give a primary product which looses hydrogen cyanide to give a substitution product.

In the present study, the addition of deuterium oxide to the reaction solution of **2** afforded the product **4** in which the C_5–H of the pyrazine ring was replaced by C_5–D. However, the photoreaction of **2** in acetonitrile-d_3 did not give any deuterated product. These results clearly indicate that a proton transfer is involved in the present photoreaction. In the absence of a protic solvent, therefore, the proton must be derived from the α-hydrogen of triethylamine, while in the presence of a protic solvent, the proton comes competitively from the solvent and triethylamine. These results suggest the mechanism shown in Scheme 1. The radical-ion pair **7**, formed by the electron transfer between amine and the excited **2**, collapses into a radical pair **8** by means of a proton transfer. The dicyanohydropyrazinyl radical in **8** gives the product **4** by the direct rupture of a cyano-radical or *via* an additional electron transfer, followed by the loss of a cyanide ion *via* **9**.



Scheme 1.

As has been described earlier, the addition of a deuterated protic solvent induces C_5–D in the product **4**; therefore, the protonation of the radical anion **7** must occur at the *ipso*-position. This selectivity of protonation at the *ipso*-position can be understood in terms of the increased electron density and, consequently, the basicity at the C_5-position of the pyrazine ring.[11] On the other hand, the protonation to the excited state of **2** may occur at one of the nitrogen atoms to afford the pyrazinium ion in its ground state or excited state. This can be expected because of the increased basicity of nitrogen heterocycles in those excited states.[12] The addition of water to the reaction mixture, indeed, quenched the fluorescence and the photoreaction of **2**; this quenching indicates the presence of another relaxation path of the excited state which participates in the photoreaction. In the case of dicyanobenzenes, the radical pair corresponding to **8** couples to give the substitution product,[10] but the radical pair **8** does not coupled, probably because of the stability of the hydropyrazinyl radical resulting from the conjugation with the aryl group at the C_2-position of the dicyanopyrazine ring.

The Effect of the Sodium Ion on the Photochemical Behavior of the Crown Ether Derivative. The formation of a host-guest complex between the crown ether moiety of **1** and the sodium ion must affect the reduction potential ($E_A{}^{red}$) and the excitation energy (E_A*) and, therefore, the photoreactivity of **1**. The absorption spectrum of **1** changes upon the addition of sodium perchlorate (Fig. 1); the analysis of the change by the Benesi-Hildebrand method[13] gave the association constant (K_{ass}=2900 mol^{-1} dm^3, 25 °C). This value indicates that the complex formation is almost complete upon the addition of two equivalents of sodium perchlorate under the present reaction conditions (**1**: 1.4×10^{-2} mol dm^{-3}). On the other hand, the absorption of the dimethoxybenzene derivative **2** does not show any change upon the addition of the sodium ion. The quantum yields of the decyanation products **3** and **4** in the presence of sodium perchlorate are shown in Fig. 2. The pyrazine derivative **1** has a strong absorption between 300—400 nm both in the free form, $\lambda_{\max}^{\mathrm{CH_3CN}}$ (ε) 370 nm (18600), and in its sodium complex, 356 nm (18400). The concentration of **1** for the reaction (1.4×10^{-2} mol dm^{-3}) is enough to absorb essentially all the photons from a high-pressure mercury lamp (313, 334, and 366 nm) in these regions. The yield of the product, therefore, safely gives the quantum yield at the early stage of the reaction, less than 10% conversion. No effect was observed upon the addition of tetrabutylammonium perchlorate to the reaction systems of **1** and **2**. The photoreaction of **2** was, again, not affected by sodium perchlorate (Fig. 2). These findings show that the effect of the sodium salt is due to the sodium ion, not the perchlorate anion, and that the crown ether moiety is essential to show the salt effect. This conclusion clearly indicates that the effect is closely associated with the formation of the host-guest complex.

The fluorescence quenching of the monocyanopyrazine derivative **3** by triethylamine in acetonitrile is stimulated by the addition of sodium perchlorate (Table 2). The variation in the quenching efficiency ($k_q\tau$) is possibly due to the change in the k_q value by the complex formation, since the rather small spectral change indicates only a small variation in the τ-value. In contrast, sodium perchlorate does not affect the fluorescence quenching of the dimethoxybenzene derivative **4** by triethylamine. The fluorescence of some sorts of aromatic compounds can be quenched by sodium salts consisting of a counter ion with a low oxidation potential, such as iodide, but the quenching is negligible by the salts consisting of an anion with a high oxidation potential, such as perchlorate.[14)]

The salt effect discussed in this section is in good accordance with the single-electron transfer in the photochemical behavior of pyrazine derivatives, **1**, **2**, **3**, and **4**. The variation in the quantum yields of the photo-product and the fluorescence quenching are closely related to the changes in the reduction potential (E_A^{red}) and the energy of the singlet excited state ($E_A{}^*$) of the pyrazine derivatives. The quantum yield of the photo-decyanation and the free-energy changes by the electron transfer from triethylamine to the crown ether derivative **1** or its sodium complex are included in Table 1.

Table 2. FLUORESCENCE QUENCHING OF **3**[a)] BY TRIETHYLAMINE IN THE PSESENCE OF SODIUM PERCHLORATE

NaClO$_4$ (10^{-4} mol dm^{-3})	$\lambda_{\max}^{\mathrm{fluo}}$ / nm	$k_q\tau$ / mol^{-1} dm^3
0.0	500	23
2.0	492	30
5.0	485	40

a) Compound **3**: 1.00×10^{-4} mol dm^{-3} in acetonitrile.

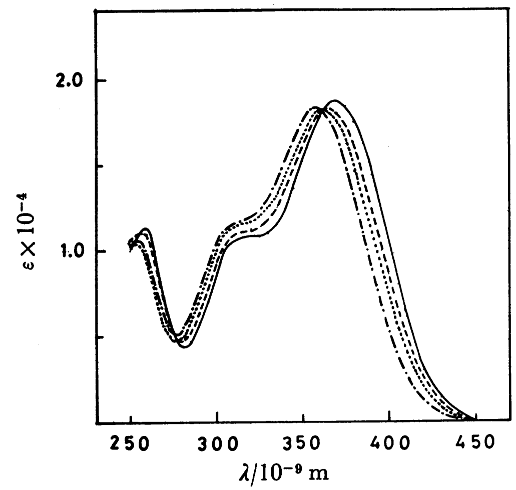


Fig. 1. Absorption spectra of **1** (1.00×10^{-4} mol dm^{-3}) in the presence of NaClO$_4$; —— (none), ––– (1.00×10^{-4} mol dm^{-3}), ------ (2.00×10^{-4} mol dm^{-3}), ·–·–· (5.00×10^{-4} mol dm^{-3}).

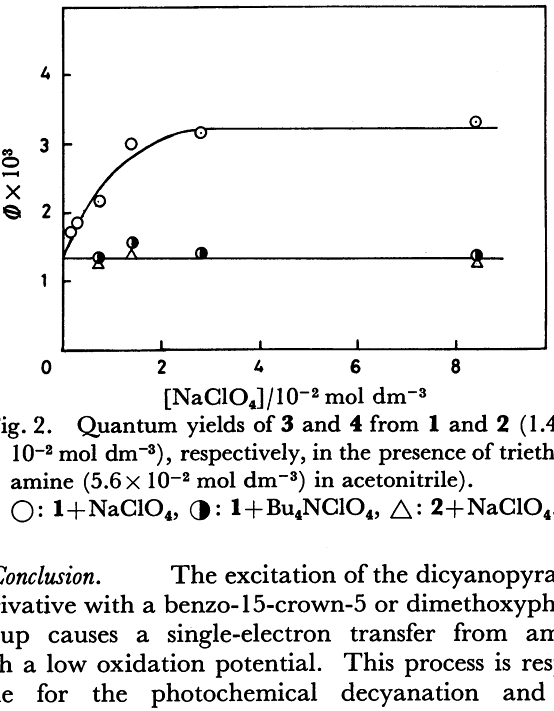


Fig. 2. Quantum yields of **3** and **4** from **1** and **2** (1.4×10^{-2} mol dm^{-3}), respectively, in the presence of triethylamine (5.6×10^{-2} mol dm^{-3}) in acetonitrile).
○: **1**+NaClO$_4$, ◑: **1**+Bu$_4$NClO$_4$, △: **2**+NaClO$_4$.

Conclusion. The excitation of the dicyanopyrazine derivative with a benzo-15-crown-5 or dimethoxyphenyl group causes a single-electron transfer from amines with a low oxidation potential. This process is responsible for the photochemical decyanation and the fluorescence quenching. The formation of the host-guest complex from the benzo-15-crown-5 moiety with the sodium ion enhances the electron-transfer process and, hence, the photoreactivity.

Experimental

Syntheses of Dicyanopyrazine Derivatives (1 and 2). Benzo-15-crown-5 (31.0 g, 115 mmol) was dissolved in 80 cm^3 of polyphosphoric acid, and the mixture was treated with acetic acid (10.5 g, 173 mmol) for 1.0 h at 40—50 °C under stirring. After cooling, 60 cm^3 of water was added to decompose the polyphosphoric acid and the product was extracted with chloroform. The subsequent evaporation of the extract after drying over magnesium sulfate gave a crude product, which was purified by passing it through an alumina column (5.0 $\phi \times$ 18.0 cm) with chloroform to give 4′-acetylbenzo-15-crown-5

75%) (mp 90 °C). 4′-Acetylbenzo-15-crown-5 (27.0 g, 87 mmol) and selenium dioxide (14.5 g, 131 mmol) were heated for 40 h in 500 cm^3 of dioxane-water (3 : 1) under reflux. After the evaporation of most of the solvents under reduced pressure, chloroform was added to the residue and the solid selenium was removed by filtration. The filtrate was dried over magnesium sulfate, condensed, and passed through an alumina column ($5.0\phi \times 15.0$ cm) with chloroform. The crude product thus obtained was 4′-(1-oxo-2,2-dihydroxyethyl)benzo-15-crown-5, which lost water by heating under reduced pressure (100 °C/3066 Pa) to give 4′-(1,2-dioxoethyl)-benzo-15-crown-5 (87%). The dioxo compound (24.0 g, 74 mmol) thus obtained was treated with diaminomaleonitrile (10.4 g, 96 mmol) in 200 cm^3 of THF and stirred at room temperature. Soon after mixing, yellow precipitates appeared and further stirring with gentle heating completed the reaction. The yellow precipitates were collected by filtration and recrysallized from acetonitrile–ethanol (1 : 1) to give the yellow crystal of 4′-(5,6-dicyano-2-pyrazinyl)benzo-15-crown-5 (**1**) (62%); mp 151 °C. Found: C, 60.35; H, 5.19; N, 13.83%. Calcd for $C_{20}H_{20}N_4O_5$: C, 60.60; H, 5.09; N, 14.14%. UV (CH_3CN): λ_{max} (ε) 237 (10200), 258 (11400), 319 (10800), and 370 nm (18600). ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 8H), 3.96 (m, 4H), 4.22 (m, 4H), 6.98 (d, 1H, J=9 Hz), 7.75 (m, 2H), and 9.23 (s, 1H).

5,6-Dicyano-2-(3,4-dimethoxyphenyl)pyrazine (**2**) was obtained in a higher yield by the same procedure, but starting from 1,2-dimethoxybenzene. **2**: Mp 203 °C. Found: C, 63.18; H, 3.73; N, 21.14%. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04%. UV (CH_3CN): λ_{max} (ε) 236 (10600), 257 (11200), 316 (10600), and 369 nm (19300). ^{1}H NMR ($CDCl_3$): δ 4.02 (s, 3H), 4.04 (s, 3H), 7.08 (d, 1H, J=9 Hz), 7.74 (m, 2H), and 9.25 (s, 1H).

*Photoreaction of **1** and **2** in the Presence of Amines.* Irradiations were carried with a 450 w high-pressure mercury lamp mounted in a rotary irradiation apparatus (Rikosha RH-400), unless otherwise mentioned. The reaction tubes were 1.0 cm in diameter, and the distance between the lamp and reaction tubes was 5 cm. In quantitative experiments to obtain the relative quantum yields under varying conditions, the reaction tubes were rotated around the lamp so that all reaction tubes absorbed the same quanta. The quantum yield of the product **3** was determined by benzophenone-benzhydrol actinometry;[15] the reaction samples were irradiated through a solution filter ($CoSO_4 \cdot 7H_2O$, 480 g dm^{-3}; thickness, 1.3 cm) to cut a 404-nm radiation.

(i) Photoreaction in Dry Acetonitrile: A solution of **1** or **2** (14.0 mmol dm^{-3}) and an amine (triethylamine, diethylamine, or butylamine, 0.56 mol dm^{-3}) in dry acetonitrile (16 cm^3) was irradiated for 10 h. The reaction solution from four tubes were collected and condensed under reduced pressure. The condensate was passed through a silica-gel column ($1.5\phi \times 10$ cm), using benzene as the eluent, and the condensate was purified by repeated chromatography on silica gel to give the product as the eluate from chloroform (**3**) or chloroform–benzene (3 : 1) (**4**). The photoreaction was accelerated by the purge of the dissolved oxygen by bubbling a stream of argon into the reaction solution after it had been dipped in an ultrasonic bath. The quantum yields were determined by the measurement of the product yield by means of HPLC (Corasil II, acetonitrile).

3; Mp 137 °C. Found: C, 61.29; H, 5.52; N, 11.40%. Calcd for $C_{19}H_{21}N_3O_5$: C, 61.44; H, 5.70; N, 11.32%. UV (CH_3CN): λ_{max} (ε) 236 (13500), 266 (9000), 305 (10200), and 354 nm (19400). IR (Nujol): 2248 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.75 (s, 8H), 3.93 (m, 4H), 4.20 (m, 4H), 7.03 (d, 1H, J=9 Hz), 7.75 (m, 2H), 8.95 (d, 1H, J=2 Hz), and 9.20 (d, 1H, J=2 Hz).

4; Mp 143 °C. Found: C, 64.88; H, 4.44; N, 17.24%. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42%. UV (CH_3CN): λ_{max} (ε) 234 (13400), 266 (8600), 304 (9800), and 354 nm (19500). IR (Nujol): 2250 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.01 (s, 3H), 4.03 (s, 3H), 7.07 (d, 1H, J=9 Hz), 7.72 (m, 2H), 8.94 (d, 1H, J=2 Hz), and 9.18 (d, 1H, J=2 Hz).

The photoreaction described above gave a small amount of a bis (decyano) derivative **5** or **6**, but the irradiation of **1** or **2** for 16 h in the presence of a large excess of triethylamine (CH_3CN–Et_3N, 3 : 1) and a similar work-up gave the bis (decyano) derivative **5** (40%) or **6** (44%) respectively as the main product. The irradiation of **3** or **4** under similar conditions also gave **5** or **6** respectively.

5; Mp 110 °C. Found: C, 62.71; H, 6.37; N, 7.98%. Calcd for $C_{18}H_{22}N_2O_5$: C, 62.41; H, 6.40; N, 8.08%. UV (CH_3CN): λ_{max} (ε) 223 (18700), 260 (10600), 289 (10400), and 318 nm (11300). ^{1}H NMR ($CDCl_3$): δ 3.77 (s, 8H), 3.92 (m, 4H), 4.18 (m, 4H), 6.95 (d, 1H, J=9 Hz), 7.55 (dd, 1H, J=9 and 2 Hz), 7.62 (d, 1H, J=2 Hz), 8.44 (d, 1H, J=2 Hz), 8.57 (diffused t, 1H), and 8.98 (d, 1H, J=2 Hz).

6; Mp 75 °C. Found: C, 66.66; H, 5.60; N, 13.05%. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96%. UV (CH_3CN): λ_{max} (ε) 225 (18800), 261 (12400), 288 (12300), and 320 nm (13800). ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H), 3.97 (s, 3H), 6.99 (d, 1H, J=9 Hz), 7.58 (dd, 1H, J=9 and 2 Hz), 7.67 (d, 1H, J=2 Hz), 8.48 (d, 1H, J=2 Hz), 8.60 (diffused t, 1H), and 9.02 (d, 1H, J=2 Hz).

(ii) Photoreaction in the Presence of Salts: To the same solutions described in Part *(i)* of this section (amine: triethylamine) were added 0.0—6.0 equivalents of sodium perchlorate monohydrate to the pyrazine derivative **1** or **2**, and the mixtures were irradiated in a similar manner for 1 h. Without the addition of sodium perchlorate, less than 10% of the starting material was converted to the decyano derivatives (**3** or **4**) during 1 h. The reaction mixture was concentrated under reduced pressure, and the product was determined by NMR analyses in DMSO, using 1,1,2,2-tetrachloroethane as the internal reference. The quantum yields obtained in this method are shown in Fig. 2. The reaction of **1** in the presence of tetrabutylammonium perchlorate was carried out in the same manner; the results are shown in Fig. 2.

Absorption Spectra and Fluorescence Spectra. The absorption and fluorescence spectra were measured with a Shimadzu UV-200 spectrophotometer and a Hitachi MPF-4 spectrophotometer in acetonitrile or benzene. The acetonitrile was purified by refluxing and distillation over phosphorus pentaoxide. The benzene was purified by washing with conc sulfuric acid and distillation over metallic sodium. In all the fluorescence measurements, 1.00×10^{-4} mol dm^{-3} solution of the pyrazine derivative (**1**, **2**, **3**, or **4**) were employed; the concentrations of the amine (triethylamine, diethylamine, or butylamine) for the quenching were 0.0, 2.0, 4.0, and 6.0 mmol dm^{-3}. The fluorescence quenching of **3** in acetonitrile in the presence of sodium perchlorate was carried out in the same mammer, with the results shown in Table 2.

Measurement of Redox Potential. The redox potential was measured by means of cyclic voltammetry at 25 °C and at the scan rate of 0.5 V s^{-1} using platinum disk electrodes and Ag/AgCl couple as the reference electrode. The oxidation potentials of triethylamine, diethylamine, and butylamine were measured by using 5.0 mmol dm^{-3} solution in acetonitrile containing tetrabutylammonium perchlorate (1.0×10^{-1} mol dm^{-3}) as the electrolyte. The reduction potentials of **1** and **2** were measured in exactly the same method; the results are shown in Table 1. The first oxidation and reduction potentials in cyclic voltammetry are both reversible for the scan to

−2.0 V (**1** and **2**) and +2.0 V (amines).

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References

1) Part VI of this series: M. Tada, H. Hamazaki, and H. Hirano, *Chem. Lett.*, **1980**, 921.

2) M. Tada and H. Hirano, *Tetrahedron Lett.*, **1978**, 5111; M. Tada, A. Suzuki, and H. Hirano, *J. Chem. Soc., Chem. Commun.*, **1979**, 1004; M. Tada, H. Hirano, and A. Suzuki, *Bull. Chem. Soc. Jpn.*, **53**, 2303 (1980); A. Suzuki and M. Tada, *Chem. Lett.*, **1980**, 515; H. Hirano, K. Kurumaya, and M. Tada, *Bull. Chem. Soc. Jpn.*, **53**, 2708 (1981).

3) H. C. S. Wood, "Comprehensive Organic Chemistry," ed by E. Haslam, Pergamon Press, Oxford (1979), Vol. 5, p. 489.

4) H. Hirano, R. Lee, and M. Tada, *J. Heterocycl. Chem.*, in psess (1982).

5) D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).

6) For example, the Coulomb term is only 0.05 eV on $r=7$ nm, and so we can safely neglect the term for the present purpose (see Table 1).

7) J. Nasielsky, A. Kirsch-Demesmae, P. Kirsch, and R. Nasielski-Hinke, *J. Chem. Soc., Chem. Commun.*, **1970**, 302; L. O. Luzo, N. J. Bunce, and S. Safe, *Can. J. Chem.*, **53**, 688 (1975); K. Tsujimoto, T. Tasaka, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, **1975**,758; N. J. Bunce and L. Ravanal, *J. Am. Chem. Soc.*, **99**, 4150(1977); K. A. K. Al-Fakhri, A. C. Mowatt, and A. C. Pratt, *J. Chem. Soc., Chem. Commun.*, **1980**, 566; R. S. Davidson and J. W. Goodin, *Tetrahedron Lett.*, **22**, 163 (1981).

8) K. J. Khimand, and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970); A. P. Komin and J. F. Wolfe, *J. Org. Chem.*, **42**, 2481 (1977); R. A. Rossi and A. B. Dierine, *ibid.*, **45**, 2914 (1980); M. F. Semmelhack and T. Barger, *J. Am. Chem. Soc.*, **102**, 7765 (1980).

9) J. F. Bunnett, *Acc. Chem. Res.*, **11**, 413 (1978); C. P. Andrieux, C. Blocman, J-M. Dumas-Bouchiat, and J-M. Saveant, *J. Am. Chem. Soc.*, **101**, 3431 (1979); C. Galli and J. F. Bunnett, *ibid.*, **101**, 6137 (1979); R. R. Baird, J. F. Bunnett, X, Creary, and M. J. Tremelling, *ibid.*, **102**, 2852 (1980); G. A. Russel and J. Harshberger, *J. Chem. Soc., Chem. Commun.*, **1980**, 216.

10) M. Ohashi, K. Miyake, and K. Tsujimoto, *Bull. Chem. Soc. Jpn.*, **53**, 1683 (1980).

11) Hückel MO calculation by H. Mori and H. Hirano; unpublished results.

12) G. Jackson and G. Porter, *Proc. R. Soc. London, Ser. A*, **260**, 13 (1961); M. Koizumi, S. Kato, N. Mataga, T. Matsuura, and Y. Usui, "Photosensitized Reactions," Kagaku-Dojin, Kyoto (1978), pp. 145—155.

13) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

14) H. Shizuka, T. Saito, and T. Morita, *Chem. Phys. Lett.*, **56**, 516 (1978); H. Shizuka, M. Nakamura, and T. Morita, *J. Phys. Chem.*, **84**, 989 (1980).

15) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).