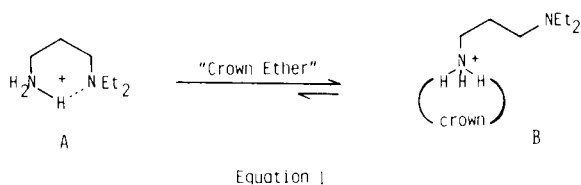




mole/l) to the reaction mixture of II gave the photo-products IVa and IVb (total 50%) after irradiation for 14 hours. As expected irradiation of the crown ether derivative I in the presence of V gave the products IIIa and IIIb as in the presence of triethylamine.



It is noteworthy that 3-diethylamino-1-propanaminium trifluoroacetate (VI,  $n = 3$ ) can cause the photoreaction of II in an idle manner (6%) in contrast to the perchlorate salt V (0%). A trifluoroacetic acid ( $pK_a = 0.2$ ) is weaker acid than perchloric acid ( $pK_a = -10$ ) and therefore trifluoroacetate anion is a much stronger base than the perchlorate anion. Trifluoroacetate anion is expected to associate with the aminium ion more effectively than perchlorate anion and this association may partly destroy the chelated structure A or weaken the chelation to revive the tertiary amino group as an electron donor. Photoreactions of I and II in the presence of  $\omega$ -diethylamino-1-alkanaminium trifluoroacetate (VI) are summarized in Table 1. The product yields in the table are those of the early stage of the reaction (75 minutes irradiation) and most of the starting material was still remained in its intact form. Since absorption and fluorescence spectra of I were essentially not affected by the complex formation, the concentration of the reaction solution ( $1.4 \times 10^{-2}$  mole/l) is high enough to absorb all the quanta from the lamp in 300-400 nm region. The yields of the products under these reaction conditions, therefore, are a reasonable indication of the relative photoreactivity.

The aminium salt VI ( $n = 8$ ) promotes the photoreaction of II (18%) in a more efficient manner than the aminium salt VI ( $n = 3$ ) (6%) due to the absence of chelation (A) in the former. The reactivity of I in the presence of the aminium salt VI ( $n = 8$ ) is highest among the reactions listed in the Table 1, and this result is accounted for by the "Pairing Effect" of the aminium ion to the crown ether moiety. This effect must increase the effective concentration of the diethylamino group in the vicinity of the reaction center, the pyrazinecarbonitrile moiety of I. On the other hand, no acceleration effect was observed in the photoreactivity of I in the presence of the aminium salt VI ( $n = 3$ ). This should be due to the shortage in chain length to deliver the tertiary amino group to the vicinity of the pyrazine ring.

The present results and discussion, together with those of the earlier works [3], indicate the reaction mechanism as shown in Scheme 1. A full detail of this mechanism has

been discussed in the previous paper [3]. In the present case the crown ether derivative I associates appreciably with  $\omega$ -diethylamino-1-alkanaminium ion to form the host-guest complex VII. The electron transfer from the tertiary amino group to the excited pyrazinedicarbonitrile derivative gives the radical ion pair VIII. This electron transfer process should be more efficient than the same process between free I and a tertiary amine.

Scheme 1

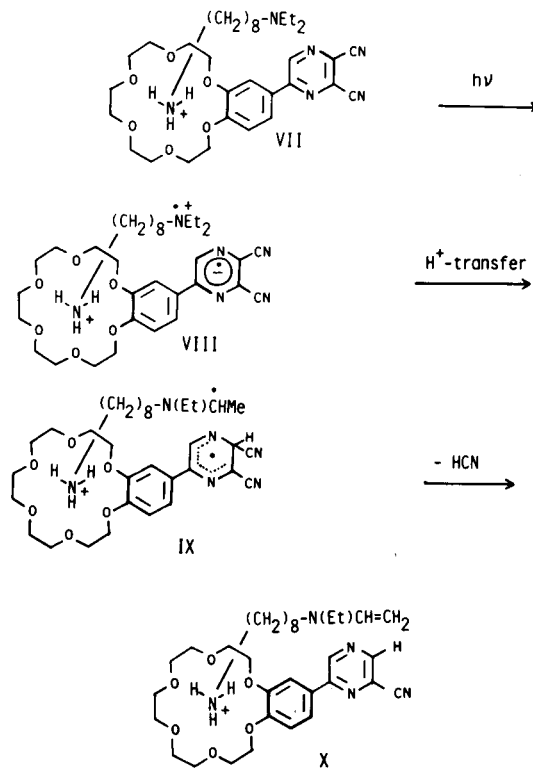


Table 1

Photoreaction of I and II in the Presence of  $\omega$ -Diethylamino-1-alkanaminium Trifluoroacetate (VI)

Starting Material [a]	Aminium Salt (VI)	Product	Yield [b] %
I	$n = 3$	III	15
II	$n = 3$	IV	6
I	$n = 8$	III	34
II	$n = 8$	IV	18

[a]  $1.4 \times 10^{-2}$  mole/l in ethanenitrile. [b] Irradiation, 75 minutes.

In the previous paper we discussed the free energy change by the electron transfer from amines to the excited state of pyrazinedicarbonitrile derivative based on the Rehm-Weller's equation (Equation 2) [3,7]. The oxidation potential,  $E(\text{ox})$ , of the diethylamino group of the complexed  $\omega$ -amino-1-octanaminium ion VI ( $n = 8$ ) should be si-

milar to that of triethylamine,  $E(\text{ox}) = +1.35$  volt *vs* S.H.E. The reduction potential of I,  $E(\text{red})$ , is not much affected by the presence of the aminium trifluoroacetate and determined to be  $E(\text{red}) = -0.95$  volt *vs* S.H.E. In contrast to alkali ions, a primary aminium ion does not affect the absorption and fluorescence maxima of the crown ether derivative I, absorption maximum: 373 nm, and fluorescence maximum: 496 nm in ethanenitrile. The energy of

$$\Delta G = E(\text{ox}) - E(\text{red}) - E^* - e^2/r\epsilon \quad (\text{Eq. 2})$$

excited state of I was calculated as in the previous paper [3],  $E^* = 2.85$  eV. These discussions indicate the complex formation between the crown ether derivative I and the aminium ion does not change the first three terms in Equation 2 appreciably. The last Coulomb term, which represents the stabilization energy of the ion pair, can be affected by the reduction of the inter-ion distance due to the formation of host-guest complex. The calculated values of the Coulomb term in ethanenitrile are 0.05 eV (4.8 kJ/mol) for  $r = 70$  nm and 0.09 eV (8.4 kJ/mol) for  $r = 40$  nm. These values afford  $\Delta G = -0.60$  eV ( $r = 70$  nm) or  $\Delta G = -0.64$  eV ( $r = 40$  nm) and the  $\Delta G$ 's show the electron transfer process is an exothermic process. In the paired system, an entropy term should be taken into account in addition to the free energy calculated by the Equation 2. The Equation 3 should be the more accurate expression of the free energy change in the present paired system. This type of acceleration by an entropy term has been recognized in the formation of intramolecular exciplex [8].

$$\Delta G = E(\text{ox}) - E(\text{red}) - E^* - e^2/r\epsilon - T\Delta S \quad (\text{Eq. 3})$$

The "Paired Effect" discussed in this paper, therefore, should be concerned with both Coulomb and entropy terms as considerably important factors.

## EXPERIMENTAL

### Materials.

5-[(Benzo-18-crown-6)-4'-yl]pyrazine-2,3-dicarbonitrile (I) and 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (II) were prepared by the same method described in the previous paper [3]. Compound II was identical in every aspect to that reported in the previous paper [3]; I, mp 131°C;  $\nu$  (ethanenitrile): 237 ( $1.21 \times 10^4$ ), 258 ( $1.17 \times 10^4$ ), 312 ( $1.05 \times 10^4$ ), and 373 nm ( $1.96 \times 10^4$ );  $\nu$  (chloroform): 2247  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  3.64 (s, 4H), 3.71 (diffused s, 8H), 3.95 (m, 4H), 4.25 (m, 4H), 6.97 (d,  $J = 9$  Hz, 1H), 7.70 (m, 2H), and 9.19 (s, 1H).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_6$ : C, 59.99; H, 5.49; N, 12.72. Found: C, 59.76; H, 5.45; N, 12.93.

### The Photoreaction of Pyrazinedicarbonitrile Derivatives I and II.

Irradiations were carried out by a 450 watt high pressure mercury lamp mounted in a rotary irradiation apparatus (Rikosha RH-400). Pyrex reaction tubes are 1 cm in diameter and the distance between the lamp and the reaction tubes is *ca.* 5 cm. In quantitative experiments to obtain

the relative reactivity under varying conditions, the reaction tubes were rotated, and spinned around the lamp so that all the reaction tubes received the same number of quanta.

### i) Photoreaction of I and II in the Presence of Triethylamine.

A solution of I and II ( $1.4 \times 10^{-2}$  mole/l) in dry ethanenitrile (16 ml) containing triethylamine ( $5.6 \times 10^{-2}$  mole/l) was irradiated for 10 hours. The reaction mixture from four reaction tubes was collected and condensed under reduced pressure. The concentrate was passed through a silicagel column ( $1.5 \times 10$  cm) using benzene as eluent to give the product IIIa and IIIb (*ca.* 10:1, 70%) or IVa and IVb (*ca.* 6:1, 80%). Only IIIa was isolated in the pure state by chromatography of the mixture of crown ether derivative using chloroform as the eluent. Both IVa and IVb were isolated by the same treatment of the product mixture using benzene-chloroform-ethyl acetate (1:1:1) as the eluent. The minor component IIIb in the mixture of crown ether derivatives has the same  $^1\text{H-nmr}$  signals as those of IVb in the region of the hydrogen on the pyrazine ring.

Compound IIIa had mp 132°C;  $\nu$  (ethanenitrile): 236 ( $1.46 \times 10^4$ ), 268 ( $9.35 \times 10^3$ ), 302 ( $1.26 \times 10^4$ ), and 357 nm ( $2.02 \times 10^4$ );  $\nu$  (chloroform): 2246  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  3.66 (s, 4H), 3.73 (diffused s, 8H), 3.95 (m, 4H), 4.25 (m, 4H), 6.96 (d,  $J = 9$  Hz, 1H), 7.70 (m, 2H), 8.85 (d,  $J = 2$  Hz, 1H), and 9.08 (d,  $J = 2$  Hz, 1H).

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_2$ : C, 60.71; H, 6.09; N, 10.21. Found: C, 60.52; H, 6.17; N, 10.26.

Compound IVa had mp 141-142°C;  $\nu$  (ethanenitrile): 233 ( $1.33 \times 10^4$ ), 265 ( $8.48 \times 10^3$ ), 302 ( $9.47 \times 10^3$ ), and 355 nm ( $1.85 \times 10^4$ );  $\nu$  (chloroform): 2245  $\text{cm}^{-1}$  (strong);  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  3.96 (s, 3H), 3.98 (s, 3H), 7.01 (d,  $J = 9$  Hz, 1H), 7.59-7.75 (m, 2H), 8.87 (d,  $J = 2$  Hz, 1H), and 9.09 (d,  $J = 2$  Hz, 1H).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 64.72; H, 4.60; N, 17.42. Found: C, 65.05; H, 4.64; N, 17.16.

Compound IVb had mp 179-180°C;  $\nu$  (ethanenitrile): 234 ( $1.42 \times 10^4$ ), 265 ( $1.23 \times 10^4$ ), 308 ( $1.17 \times 10^4$ ), and 340 nm (sh,  $8.82 \times 10^3$ );  $\nu$  (chloroform): 2250  $\text{cm}^{-1}$  (weak);  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  3.96 (s, 1H), 4.01 (s, 1H), 7.04 (d,  $J = 9$  Hz, 1H), 7.56-7.70 (m, 2H), 8.75 (s, 1H), and 9.19 (s, 1H).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 64.72; H, 4.60; N, 17.42. Found: C, 64.91; H, 4.67; N, 17.19.

### ii) Photoreaction of I and II in the Presence of 3-Diethylamino-1-propanaminium Perchlorate (V).

Triethylamine in the part (i) was replaced by 3-diethylamino-propanaminium perchlorate ( $5.6 \times 10^{-2}$  mole/l) and the mixture was irradiated for 14 hours in the similar manner. In the case of II no reaction took place under those conditions but the addition of benzo-18-crown-6 ( $5.6 \times 10^{-2}$  mole/l) to the above reaction mixture brought the photoreaction to give the product mixture of IVa and IVb in 50% yield.

### iii) Photoreaction of I and II in the Presence of $\omega$ -Diethylaminoalkanamini-um Trifluoroacetate (VI).

Triethylamine in the part (i) was replaced by 3-diethylamino-1-propanaminium trifluoroacetate (VI,  $n = 3$ ) or 8-diethylamino-1-octanamini-um trifluoroacetate ( $5.6 \times 10^{-2}$  mole/l) and the reaction mixture was irradiated in the similar manner but only for 75 minutes. Most of the starting material remained in its intact form under these conditions. The results are summarized in Table 1.

### Measurement of Redox Potential.

Redox potentials were measured by cyclic voltammetry at 25°C using a platinum disk electrode, tetrabutylamini-um perchlorate ( $1.00 \times 10^{-1}$  mole/l) as electrolyte, and an silver/silver chloride couple as the reference electrode. The measurements were carried out using  $5.0 \times 10^{-3}$  mole/l solutions of the sample in ethanenitrile and at the scan rate of 0.5 volt/s. The redox potentials thus obtained were corrected to the values *vs* S.H.E. by adding 0.23 volt.

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