Color Change of (*E*)-2,3-Bis(2,3,4,5,6-Pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile by the Addition of Amines

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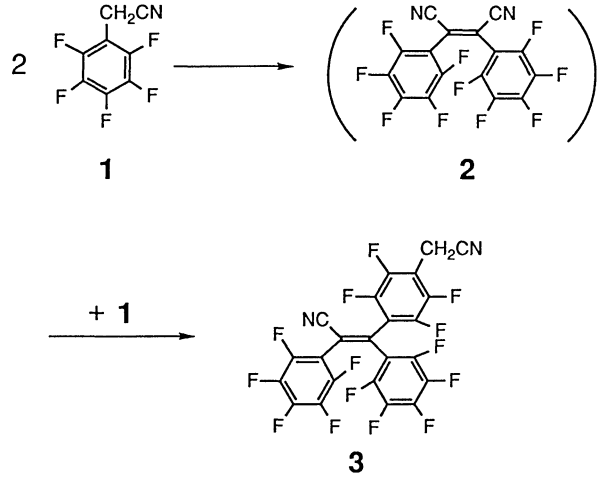
(*E*)-2,3-Bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**3E**) was synthesized. A benzene solution of **3E** turns into a brilliant red color by the addition of aliphatic amines. The coloration mechanism is studied by optical absorption, conductivity and product analyses. It has become apparent that ion-pair formations between **3E** and the amines by proton transfer reactions are responsible for the coloration. Structural requirements of the amines for the ion-pair formation are discussed.

Molecular complexes of macrocyclic polyethers have been utilized in various directions, such as selective extraction, separation and transport of guest molecules, phase transfer catalyses or models of vital systems.[1–6] In spite of such explosive development of host-guest complexes, much less attention has been paid to ion-pair complexes.[7,8]

The ion-pair formation in less polar solvents via an intermolecular proton transfer is also expected to be useful for recognition of ionizable molecules, such as amines. In the present study, we studied structural requirements for the ion-pair formation by using (*E*)-2,3-bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**3E**) as a proton donating molecule. The compound **3E** formed ion-pair complexes with various amines in organic solvents along with a brilliant red coloration. The ion-pair formation depends on the structure of the amines and the nature of the solvents. The association constants (K_a) for the formation of ion-pair complexes between **3E** and various amines have been determined to reveal what factors control the complex formation.

Results and Discussion

Synthesis. (*E*)-2,3-Bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile **3E** was prepared by a self-coupling reaction of two 2,3,4,5,6-pentafluoro-1-(cyanomethyl)benzenes (**1**) followed by replacement of a cyano group by another molecule of **1**. The reaction process is presumed as follows.[9,10]



Scheme 1.

Isolation of the intermediate **2** was failed. The self coupling product **2** and the active fluorine atom at 4 position of **1** is considered to react easily each other to produce **3**.[11,12] Compound **3** was a chief product and a very small amount of by-product was prepared by further replacement of a cyano group of **3** by another molecule of **1**.[22] Compound **3** was obtained as a mixture of *E*/*Z* isomer whose assignment was performed based on ^{19}F NMR spectra. The mixture was dissolved in benzene and exposed to ultraviolet light (280 nm). The *Z* form was efficiently converted to *E* form by the irradiation. The *E* form was isolated by high-performance liquid chromatography and purified by recrystallization from a benzene-hexane mixture. The structure of the product was determined on the basis of mass spectra, NMR spectra, and material analysis whose data are presented in the experimental section. This material was used for further experiments.

Formation of Ion-Pair Complexes and Absorption Spectral Changes. The absorption spectra of (*E*)-2,3-bis(2,3,4,5-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**3E**) in 300—650 nm region were measured at 20 °C in benzene solution in the absence and presence of various amines.

Figure 1 shows a typical absorption spectral change of a dilute benzene solution of **3E** ($[\mathbf{3E}]_0=3.4\times10^{-5}$ mol dm^{-3}) by the addition of Et$_2$NH. The benzene solution turns red in the presence of small amount of Et$_2$NH. An absorption maxima is observed at about 500 nm. The maximum gradually shifts to 503 nm with increasing the amount of Et$_2$NH.[13,14] An isosbestic point is observed at 305 nm in the absorption spectrum.

The absorption spectrum maintained a constant

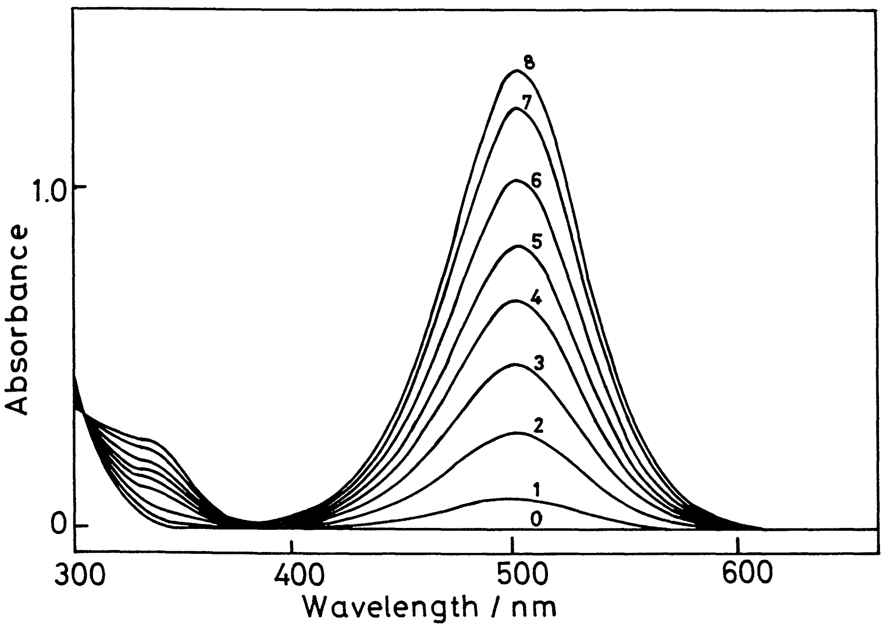


Fig. 1. Absorption spectral change of the benzene solution of **3E** (3.4×10^{-5} mol dm^{-3}) by the addition of Et_2NH.
[Et_2NH]: (0) 0, (1) 3.4×10^{-2}, (2) 6.8×10^{-2}, (3) 1.0×10^{-1}, (4) 1.4×10^{-1}, (5) 1.7×10^{-1}, (6) 2.4×10^{-1}, (7) 3.4×10^{-1}, and (8) 5.1×10^{-1} mol dm^{-3}.

intensity, so far the solution being stored in the dark at room temperature. The addition of H^+ (H_2SO_4, HCl) to the reaction mixture decreased the absorption intensity and the initial colorless solution was obtained. The absorption spectrum of 2,3,4,5,6-pentafluoro-1-(cyanomethyl)benzene (**1**) was not affected by the addition of amines. These results suggest that the absorption observed at around 500 nm is ascribable to the ion-pair complex of **3E** with the amine by proton transfer, as shown right.

Bazavluk et al.[8] reported a similar ion-pair formation for heptafluoro-2-naphthol and aliphatic amines system in undecane.

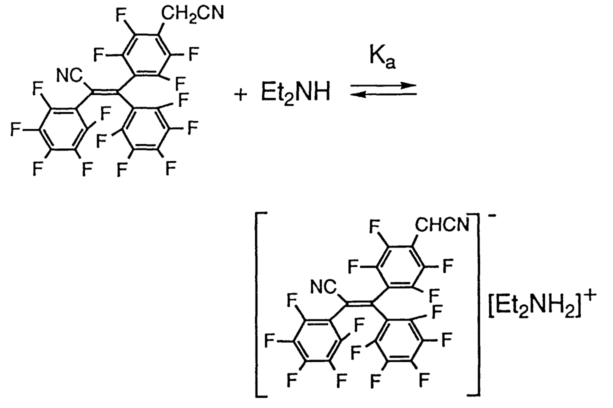


Table 1. Association Constants, Molar Absorption Coefficients and Absorption Maxima of the Complexes of **3E** with Amines in Benzene Solution

Entry	Amine	K_a / mol dm^{-3}	$10^4\varepsilon$ / dm^3 mol^{-1} cm^{-1}	λ_{max} / nm
1	n-$PrNH_2$	10.0	4.2	509
2	n-$BuNH_2$	7.8	4.3	509
3	Cyclohexylamine	11.1	4.5	507
4	Et_2NH	22.0	4.2	501
5	n-Pr_2NH	4.0	4.5	499
6	i-Pr_2NH	6.8	4.5	501
7	n-Bu_2NH	4.3	4.4	496
8	Et_3N	3.4	3.8	496
9	Aniline	c)	c)	c)
10	Pyridine	c)	c)	c)
11	Et_2NH a)	30.0	4.7	510
12	Et_2NH b)	13.6	4.7	502
13	n-Pr_2NH a)	13.4	4.8	510

a) In CH_2Cl_2. b) In hexane. c) Not observed.

Association Constants Measurements. The association constants and the molar absorption coefficients of the complexes of **3E** with various amines ($[\mathbf{3E}]_0 = 2.2\times10^{-5}$mol dm^{-3}) are shown in Table 1. These values were determined by using the UV-vis spectrophotometric method.15,16)

Table 1 also gives the position of the absorption peaks for the ion-pair complexes of **3E** and various amines.

With some exceptions K_a values increases with increasing λ_{max} and exhibit approximately linear relationships.

Aromatic amines, such as aniline and pyridine do not make ion-pair complexes with **3E**. This is possibly due to the low basicity. The association constant has a tendency to decrease in the order: primary > secondary > tertiary amines. This order agrees with the observation for the charge transfer complex formations.17,18) Primary amines, *n*-PrNH$_2$ and *n*-BuNH$_2$, have large association constants, which are around twice the corresponding secondary amines. Among the secondary amines, Et$_2$NH has an extraordinary large association value, which is 5 times larger than the values of *n*-Pr$_2$NH and *n*-Bu$_2$NH. A simple steric hindrance explanation19,20) that large alkyl groups prohibit the close approach of the amines to **3E** can not be applied to the present system, because the large association constant is observed for cyclohexylamine and the value of Et$_3$N is close to the values of *n*-Pr$_2$NH and *n*-Bu$_2$NH. The large value for Et$_2$NH and cyclohexylamine suggests that **3E** has a site which recognizes the difference in the shape between cyclohexylamine and *n*-Pr$_2$NH, and the site favorably accepts Et$_2$NH. Such a steric requirement to allow close approach is considered to play an important role in the proton transfer process.

The association value is also dependent on the solvent polarity. The value increases with the increases in the solvent polarity. It is worthwhile to note that along with the increases in the association constants the difference in the values between Et$_2$NH and *n*-Pr$_2$NH decreases in polar CH$_2$Cl$_2$. In polar solvents, large stabilization in the ion-pair states possibly diminishes the energy barrier difference in the recognition process.

Coloration Mechanism. In order to confirm the ion-pair mechanism for the coloration, we measured conductivity21) of CH$_2$Cl$_2$ solution containing **3E** and Et$_2$NH.

Figure 2 shows the conductivity change of a dilute CH$_2$Cl$_2$ solution of **3E** by the addition of Et$_2$NH (a) and the change of the optical density at λ_{max} (510 nm) of the same solution (b). Addition of Et$_2$NH increased the absorption intensity along with the increases in the conductivity. Although slight increase in the conductivity is observed even in the absence of **3E**, the value is much smaller than the value in the presence of **3E**. Both the conductivity value and the intensity of the absorbance showed a saturation behavior above 0.3 mol dm^{-3} of amine. The good correlation between the conductivity and the absorption intensity clearly indicates that the coloration is due to the formation of ion-pair between **3E** and the amine.

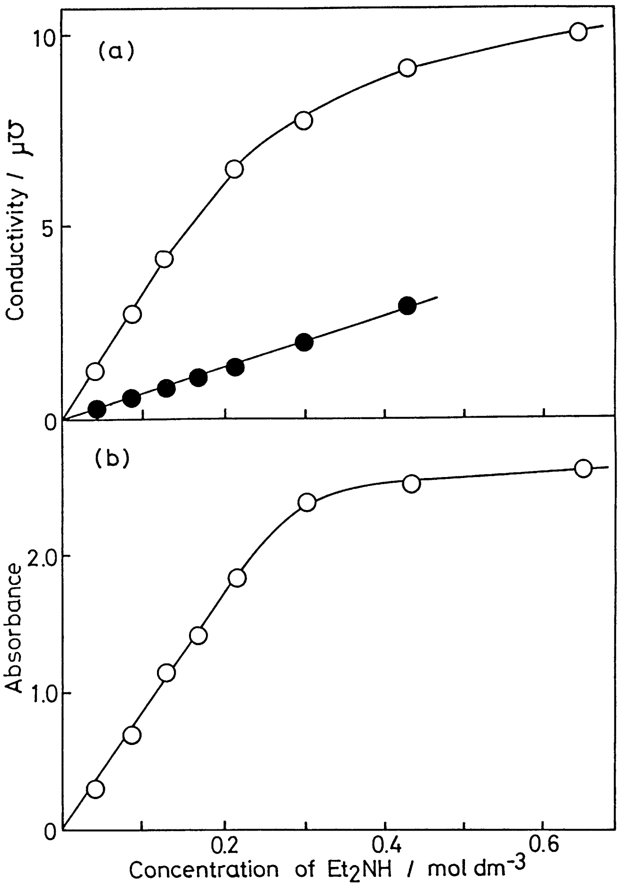


Fig. 2. (a) Conductivity change of **3E**–Et$_2$NH system in CH$_2$Cl$_2$.
(○), with **3E** (4.3×10^{-5} mol dm^{-3}); (●), without **3E**.
(b) Absorption intensity change of **3E**–Et$_2$NH system in CH$_2$Cl$_2$ at 510 nm.

Product analysis also supported the ion-pair formation. The colored form was quenched in CH$_2$Cl$_2$ by deuterium chloride and then **3E** was analyzed. One of the cyano methyl protons of **3E** was found to be replaced by a deuterium atom.22) Addition of deuterium chloride to a colorless benzene solution of **3E** does not led to the exchange reaction of a deuterium and proton atom.22) These are unambiguous evidence that a proton is transferred from CH$_2$CN group of **3E** to the amine in the formation of ion-pair complex.23–25)

The compound **3E** also interacts with many compounds with basic nature to produce red colored solutions, such as ethers, THF, or alcohols. When **3E** in solid state was placed in the THF vapor, the solid turned to red. By evacuating THF from the solid, the solid again returned to colorless state. It was possible to repeat the coloration/decoloration cycles many times.

Experimental

IR spectra were measured with a Shimadzu IR-408 spectrophotometer. ^{1}H NMR spectra (360 MHz) and ^{13}C NMR spectra (91 MHz) were recorded in $CDCl_3$ with a Bruker WN-360 instrument. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. ^{19}F NMR were recorded on a Bruker WN-360 instrument at 339 MHz and are reported in ppm from internal trichlorofluoromethane. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. HPLC analysis was performed on a JASCO 800 system. Absorption spectra were measured with a Shimadzu MPS-200 instrument. Photoisomerization was performed by a mercury lamp (Ushio, 1 kW), associated with a monochrometer (Jobin Yvon H10-UV) and filters (agueous solution of $CuSO_4$ and Toshiba UV-28 glass filter), as a light source. Ion-pair complex formation constants (association constant) (K_a) were determined by using the UV-vis spectrophotometric method.[15,16] K_a and molar absorption coefficients (ε) of the complexes are obtained from the plots of $[\mathbf{3E}]_0$ $[\mathbf{Amine}]_0$/OD values vs $[\mathbf{Amine}]_0$ values.

$$\frac{l[\mathbf{3E}]_0[\mathbf{Amine}]_0}{\mathrm{OD}} = \frac{1}{\varepsilon}[\mathbf{Amine}]_0 + \frac{1}{\varepsilon K_a}$$

In the equation, OD is the optical density of the solution and l is the cell width (1 cm). Conductivities were measured at 20 °C using a autobalance universal bridge (WAYNE KERR B642). The solvent was CH_2Cl_2 which was dried with phosphorus pentoxide and distilled from potassium carbonate.

Reversible coloration of **3E** in solid state with THF was performed as follows. Compound **3E** adsorbed on the surface of a silica-gel plate was placed in the THF vapor until the red color was attained. The coloration time was less than few second. Then, upon the adsorbed THF gas was released by heated weakly, the red color disappeared and initial colorless **3E** was restored. It also took less than few second. The coloration/decoloration cycles was repeated.

Materials. All amines were obtained commercially and were purified by distillation.

2,3,4,5,6-Pentafluoro-1-(Cyanomethyl)benzene (1).[26,27] NaCN (9.2 g, 0 19 mol) and tetrabutylammonium chloride (0.108 g, 0.39 mmol) was dissolved in 32.8 mL of water. To this solution was added 2,3,4,5,6-pentafluoro-1-(bromomethyl)benzene (10.0 g, 38 mmol) in 32.8 mL of THF, and stirred for 10 min. The reaction mixture was poured into water and then the product was extracted with ether. Removal of the ether and distillation of the residual under vacuum gave 5.0 g of 2,3,4,5,6-pentafluoro-1-(cyanomethyl)benzene. 63% yield; bp 101 °C; ^{1}H NMR ($CDCl_3$) δ=3.71 (s); ^{13}C NMR ($CDCl_3$) δ=104.17—104.69, 114.38, 135.70—136.21, 139.50—139.85, 143.03—143.55, 146.83—146.94; ^{19}F NMR ($CDCl_3$) δ=−160.73 (m, 2F), −152.51 (m, 1F), −141.65 (m, 2F); IR (KBr) 2260 cm^{-1} (-CN). MS (EI) m/z (rel intensity) 207 (M$^+$, 100), 188 (M$^+$—F, 35), 181 (M$^+$—CN, 28). Found: C, 46.40; H, 0.97; N, 6.76; F, 45.87%. Calcd for $C_8H_2N_1F_5$: C, 46.64; H, 0.87; N, 6.52; F, 45.75%.

(*E*)-2,3-Bis(2,3,4,5,6-Pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (3E).[9,10] To 2.9 mL of 50% NaOH aqueous solution containing tetrabutylammonium bromide (0.195 g, 0.6 mmol) was added, over a period 0.5 h a mixture of 2,3,4,5,6-pentafluoro-1-(cyanomethyl)benzene (**1**) 3 g (14.5 mmol) and CCl_4 2.25 mL (23.3 mmol) at 40 °C. The solution was stirred for 1.5 h at 45 °C. Then, the reaction mixture was poured into water. The aqueous solution was extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After the solvent was removed, the mixture of *E* and *Z* forms of 2,3-Bis[2,3,4,5,6-pentafluorophenyl]-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile was obtained in 4.7% yield by column chromatography on silica gel using THF/hexane (1 : 1) and then benzene as the eluting solvent. The *Z*/*E* mixture was dissolved in benzene and exposed to ultraviolet light (280 um). The *Z* form converted to *E* form by the irradiation. The *E* form (**3E**) was separated by HPLC[28] and then purified by recrystallization from a benzene–hexane mixture. The compound **3E** was obtained in 4% yield; mp 135 °C; ^{1}H NMR ($CDCl_3$) δ=5.83 (s); ^{19}F NMR ($CDCl_3$)[29] δ=159.60 (m, 2F), −159.28 (m, 2F), −149.84 (m, 1F), −148.90 (m, 1F), −139.75 (m, 2F), −139.46 (m, 2F), −138.80 (m, 2F), −134.18 (m, 2F). MS (EI) m/z (rel intensity) 572 (M$^+$, 100), 405 (M$^+$—C_6F_5, 14); IR (KBr) 2240 cm^{-1} (-CN). Found: C, 48.02; H, 0.52; N, 4.94%, Calcd for $C_{23}H_2N_2F_{14}$: C, 48.27: H, 0.35; N, 4.90; F, 46.48%.

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28) Conditions of HPLC analysis is as follows: Column JASCO Fine SIL (silica gel) 4.6×250 mm for analytical purposes: Elution, benzene: Flow rate, 1 mL: retention time: **3E**, 4.3 min and **3Z**, 5.3 min: Column JASCO Fine SIL (silica gel) 10.0×250 mm for preparative purposes.

29) **3Z**, ^{19}F NMR ($CDCl_3$), $\delta=-159.25$ (m, 2F), -159.10 (m, 2F), -149.60 (m, 1F), -147.96 (m, 1F), -140.05 (m, 2F), -138.37 (m, 2F) -138.12 (m, 2F), -135.78 (m, 2F).