Intramolecular Exciplex and Charge Transfer Complex Formations in (9,10-Dicyanoanthracene)–$(CH_2)_3$–(Naphthalene) Systems[1]

Michiya Itoh,* Tsutomu Mimura, Hideo Usui, and Toshihiko Okamoto

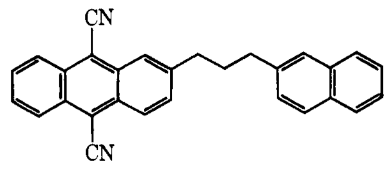
Contribution from the Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan. *Received December 19, 1972*

Abstract: The intramolecular exciplex fluorescence was observed in two (9,10-dicyanoanthracene)–$(CH_2)_3$–(naphthalene) systems in polar and nonpolar solvents, in which activation energies for the exciplex formations were obtained. Only in the nonpolar solvent was another fluorescence observed in the longer wavelength region below ~150°K than the exciplex fluorescence, and it was ascribed to the intramolecular charge-transfer fluorescence between the dicyanoanthracene and naphthalene moieties. Analysis of the temperature dependence of the absorption spectra at low temperature demonstrates considerably great intramolecular interaction in these systems which exhibit exciplex fluorescence at room temperature. Determination of the fluorescence lifetime at various temperatures suggests that these two fluorescences are from the individual excited states.

There have been numerous investigations about exciplex formations between singlet excited aromatic hydrocarbons and various amines or other weak electron donors,[2] where no electronic interaction between the electron donor and acceptor is detected in the ground state. Perylene exhibits excimer and also dimer fluorescences in rigid solution at low temperature.[3] However, few spectroscopic studies of the charge-transfer (CT) interaction between the donor and acceptor in the ground state, which forms the exciplex in the excited state, have been reported.

Efficiency of the trimethylene group for the intramolecular electronic interaction has been demonstrated in the excimer formation,[4,5] in the energy transfer and the fluorescence quenching,[6–9] and in the CT interaction between stable radicals.[10–12] Recently, Chandross and Thomas have examined the geometrical requirement for the exciplex formation in naphthylalkylamines.[13] Okada, *et al.*, suggested an ionic character in the exciplex of (9-anthracene)–$(CH_2)_n$–(*N*,*N*-dimethylaniline) systems by their determination of the solvent effect of the exciplex fluorescence, and $(S_n - S_1)$ absorption spectra.[14]

We have studied the intramolecular electronic interaction between the donor and acceptor moieties in the following compounds[15] both in the ground and excited states, and discussed the excited fluorescent states of both the exciplex and the CT complex.



β,α'- and β,β'-DCAN

Experimental Section

Syntheses of 1-(9,10-Dicyano-2-anthryl)-3-(naphthyl)propanes. Two 1-(9,10-dicyano-2-anthryl)-3-(naphthyl)propanes were synthesized by bromination and cyanation of 1-(2-anthryl)-3-(naphthyl)propanes, which were prepared by the same route as that of the 1,3-dinaphthylpropanes.[5]

1-(9,10-Dicyano-2-anthryl)-3-(2-naphthyl)propane (β,β'-DCAN). An alkaline ethanol solution (1 g of NaOH in 200 ml) of 2-formylanthracene (3 g) and 2-acetylnaphthalene (3 g) was stirred under an argon atmosphere. The unsaturated ketone, 1-(2-anthryl)-2-(2-naphthoyl)ethylene (**1**), precipitated from the reaction mixture and was filtered. The yellow unsaturated ketone **1** was recrystallized from benzene–hexane: mp 268°; ir (KBr) 1655, 1595, 743 cm^{-1}; yield 62%.

Anal. Calcd for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.74; H, 5.09.

A solution of the unsaturated ketone **1** (2.2 g) in tetrahydrofuran (100 ml) was hydrogenated over 5% Pd/C for about 3 hr. The ketone, 1-(2-anthryl)-2-(2-naphthoyl)ethane (**2**), was obtained as colorless crystals: mp 138° (crystallization from hexane); ir (KBr) 1670, 805, 740 cm^{-1}; yield 70.3%.

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.74; H, 5.60.

The ketone **2** (1.2 g) was reduced in refluxing (4 hr) diethylene glycol (10 ml) containing hydrazine (2 ml, ~95%) and sodium hydroxide (1 g). The mixture was diluted with water and extracted with benzene. The yellow product obtained here was purified through silica gel with benzene–hexane and gave colorless crystals. 1-(2-Anthryl)-3-(2-naphthyl)propane (**3**) was recrystallized from benzene–hexane: mp 171°; ir (KBr) 955, 895, 815, 740 cm^{-1}; yield 61.1%.

Anal. Calcd for $C_{27}H_{22}$: C, 93.64; H, 6.36. Found: C, 93.42; H, 6.34.

The hydrocarbon **3** (0.5 g) and bromine (0.36 g) in carbon tetrachloride (18 ml) were stirred on a water bath (~50°) for 1 hr. After the solvent and bromine were removed by evacuation, the

---

[1] A preliminary report was presented at the Japanese Symposium of Molecular Structure and Spectra, Sendai, Oct 1972.

[2] N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970.

[3] J. Ferguson, *J. Chem. Phys.*, **44**, 2677 (1966).

[4] F. Hirayama, *ibid.*, **42**, 3163 (1965).

[5] E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).

[6] O. Schnepp and M. Levy, *ibid.*, **84**, 172 (1962).

[7] A. A. Lamola, P. A. Leermakers, S. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965).

[8] D. T. Browne, J. Eisinger, and N. J. Leonard, *ibid.*, **90**, 7302 (1968).

[9] T. G. Scott, R. D. Spencer, N. J. Leonard, and G. Weber, *ibid.*, **92**, 687 (1970).

[10] M. Itoh and E. M. Kosower, *ibid.*, **89**, 3955 (1967); **90**, 843 (1968).

[11] M. Itoh, *ibid.*, **93**, 4750 (1971).

[12] M. Itoh, *ibid.*, **94**, 1034 (1972); *Bull. Chem. Soc. Jap.*, **46**, 821 (1973).

[13] E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **6**, 393 (1971).

[14] T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *ibid.*, **14**, 563 (1972).

[15] Chandross and Ferguson reported the exciplex formations between 9,10-dicyanoanthracene (abbreviated to DCA) and several aromatic hydrocarbons at room temperature: E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).

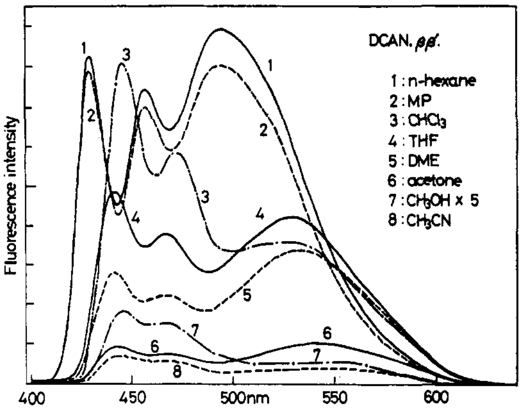


Figure 1. Fluorescence spectra of β,β'-DCAN in the various solvents at room temperature. Concentrations are 2×10^{-5} *M*.

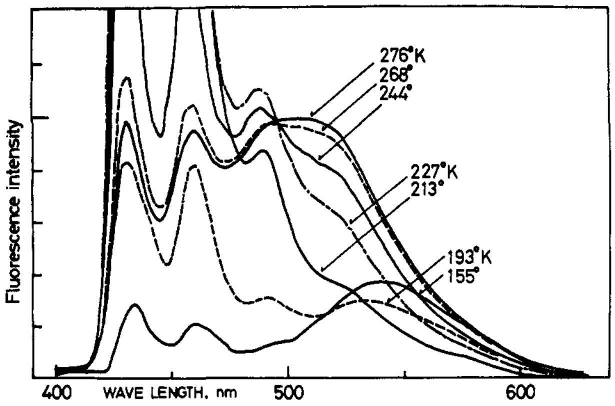


Figure 2. Temperature dependence in the fluorescence spectrum of an MP solution of β,α'-DCAN.

product was extracted with benzene and purified through silica gel. The product, 1-(9,10-dibromo-2-anthryl)-3-(2-naphthyl)propane (**4**), was obtained by recrystallization from hexane: mp 121°; ir (KBr) 1260, 930, 816, 795, 750 cm^{-1}; yield 37%.

Anal. Calcd for $C_{27}H_{20}Br_2$: C, 64.29; H, 3.97. Found: C, 64.29; H, 4.06.

The dibromide **4** (0.15 g) and cuprous cyanide (0.5 g) in pyridine (1.5 ml) were refluxed (3 hr) and added to ammonia-water (1:1). The product was extracted with benzene and purified through silica gel with benzene-hexane. The dicyanide, 1-(9,10-dicyano-2-anthryl)-3-(2-naphthyl)propane (β,β'-DCAN), was further purified by preparative thin layer chromatography and recrystallized from hexane: mp 172°; ir (KBr) 2220, 820, 760, 750 (sh) cm^{-1}; yield 74.6%.

Anal. Calcd for $C_{29}H_{20}N_2$: C, 87.88; H, 5.05; N, 7.07. Found: C, 87.53; H, 5.15; N, 7.04.

1-(9,10-Dicyano-2-anthryl)-(1-naphthyl)propane (β,α'-DCAN). 1-(2-Anthryl)-3-(1-naphthyl)propane (**5**) was synthesized from 2-formylanthracene and 1-acetylnaphthalene by the same procedures as described above, and recrystallized from benzene-hexane: mp 126°; ir (KBr) 895, 775, 740 cm^{-1}.

Anal. Found: C, 93.37; H, 6.47.

Bromination and cyanation of the hydrocarbon **5** were performed by the same procedures as described above. 1-(9,10-Dibromo-2-anthryl)-3-(1-naphthyl)propane had mp 122°; ir (KBr) 1255, 928, 790, 775, 750 cm^{-1}.

Anal. Found: C, 64.08; H, 4.01.

1-(9,10-Dicyano-2-anthryl)-3-(1-naphthyl)propane (β,α'-DCAN) had mp 182°; ir (KBr) 2220, 802, 780, 764 cm^{-1}.

Anal. Found: C, 87.81; H, 5.16; N, 7.12.

Fluorescence and Absorption Spectra. The synthesized samples of DCAN were used after purification by thin layer chromatography (silica gel) and recrystallization from hexane. 2-Methyltetrahydrofuran (abbreviated MTHF) and 3-methylpentane (MP) were distilled over potassium metal after refluxing with potassium metal for 8–10 hr. These solvents were kept with K mirror in bottles connected to a vacuum system. Good commercial solvents (Dortite spectrosol) of the other solvents were used after distillation.

Solutions of the samples were contained in rectangular quartz cells (1 cm) equipped with graded seals, which were degassed by freeze-thaw cycles (several times) at ~10^{-5} Torr. For determination of the optical absorption spectra of dilute solutions, a 2-cm cell was used. The dewar for the determinations at various temperatures is a flow-through type of cooled nitrogen gas, which is generated from a metal dewar containing a heater and liquid nitrogen. The temperature was determined by means of a thermocouple sealed into the optical cell.

All of the absorption measurements were made on a Cary 11 recording spectrophotometer. Fluorescence and excitation spectra were determined with a Hitachi MPF-2A spectrophotometer.

The fluorescence lifetimes were determined by analyzing exponential decay curves measured by an oscilloscope, and by a coaxial N_2 gas laser which has a maximum 20-kW photon peak intensity at 3371 Å, 2-nsec duration, and 15-Hz repetition rate.[16]

Results and Discussion

The fluorescence spectra of the compounds mentioned above (abbreviated β,α'- and β,β'-DCAN) in the various solvents at room temperature are given in Figure 1. The excitation spectra of DCAN are essentially identical with the absorption spectra of the dicyanoanthracene moiety (330–450-nm region) in DCAN, respectively. The absorption spectra of DCAN are quite similar to the sum of the spectra of 9,10-dicyanoanthracene and naphthalene. This fact suggests that there is no appreciable intramolecular electronic interaction between two moieties in the ground state at room temperature. The vibrational progression of the fluorescence at 400–500 nm is a mirror image with that of the absorption spectrum of the dicyanoanthracene moiety. From these results, the longer wavelength fluorescence, as shown in Figure 1, can be ascribed to the exciplex fluorescence in which two moieties in DCAN interact intramolecularly in the excited state

The exciplex fluorescence shows the considerably large solvent shift compared with that of the fluorescence due to the dicyanoanthracene moiety. Okada, *et al.*, reported a large dipole moment (15 D) in the fluorescent state of the (9-anthracene)-$(CH_2)_3$-(*N*,*N*-dimethylaniline) system.[14] From the solvent shift of the fluorescence maxima, the dipole moments in the excited state of DCAN were estimated to be 9.5 D for β,α'- and 8.7 D for β,β'-DCAN by the same procedure as described by Okada, *et al.*, respectively. Figure 1 also shows that the relative fluorescence quantum yield remarkably decreases with increasing the solvent polarity. These behaviors seem to suggest a rather polar structure (DCA^-N^+) in the fluorescent state.[1,14,17]

The fluorescence spectra of DCAN show remarkable temperature dependence with an isoemissive point in the temperature range of 280–220°K. The result in a 3-methylpentane (MP) solution of β,α'-DCAN is shown in Figure 2. There is a steady decrease in exciplex fluorescence accompanied by an increase in monomer (DCA) fluorescence with decreasing temperature.

Now we can consider the following mechanism for

---

[16] The fluorescence lifetimes were determined at the Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan.

[17] H. Leonhart and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

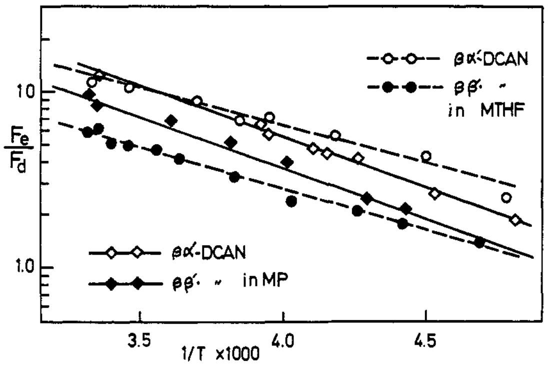


Figure 3. Plots of F_e/F_d against $1/T$ in DCAN.

the exciplex formation and fluorescence

$$\text{DCA-N} \longrightarrow \text{DCA*-N} \xrightarrow{k_f} \text{DCA-N} + h\nu_d$$

$$\text{DCA*-N} \underset{k_b}{\overset{k_a}{\rightleftarrows}} \text{DCAN}_e{}^* \underset{k_q}{\overset{k_{ef}}{\rightleftarrows}} \text{DCA-N} + h\nu_e$$

where DCA and N are the dicyanoanthracene and naphthalene moieties and $\text{DCAN}_e{}^*$ is the exciplex. Using the steady-state approximation, $k_a[\text{DCA*-N}] = (k_b + k_q + k_{ef})[\text{DCAN}_e{}^*]$. F_d and F_e are defined to be the fluorescence intensities of DCA* and the exciplex at the given wavelengths, respectively. They are expressed by the following equations: $F_d = C_d k_f \cdot [\text{DCA*-N}]$ and $F_e = C_e k_{ef}[\text{DCAN}_e{}^*]$, respectively, where C_d and C_e are constants containing various experimental factors.[5]

Then, the ratio of two fluorescence intensities is as follows

$$\frac{F_e}{F_d} = C\frac{k_a k_{ef}}{(k_b + k_q + k_{ef})k_f}$$

Since the fluorescence was determined with a solution of $\sim 10^{-5}$ M, and in the temperature range as mentioned above, the following assumptions are made: $k_q \ll k_{ef}$ and $k_b \ll k_{ef}$. Under these conditions, the equation simplifies to $F_e/F_d = Ck_a/k_f$. If k_f is independent of temperature in the temperature range mentioned above, only k_a depends on the temperature. An activation energy (E_a) for the exciplex formation is obtained by the following equation: $\partial \ln (F_e/F_d)/\partial(1/T) = -E_a/R$.

Plots of F_e/F_d against $1/T$ are shown in Figure 3. The activation energies required for the intramolecular exciplex formation in DCAN are summarized in Table I. Chandross and Dempster calculated E_a of the intramolecular excimer formation to be 3.3 kcal in 1,3-(α,α'-dinaphthyl)propane in the methylcyclohexane–isopentane (9:1) solvent and 4.0 kcal in 1,3-(β,β'-dinaphthyl)propane.[5] They suggested that these energies were mostly ascribed to the rotational barrier in trimethylene. They reported little excimer formation in the mixed type of dinaphthylpropane (α,β' and β,α'). However, it is noteworthy that no significant change of E_a in β,α'- and β,β'-DCAN was observed, and that E_a is considerably smaller for the exciplex of DCAN than for the excimer of dinaphthylpropane. The conformational requirement may be considered to be the most favorable structure for the electronic interaction between the excited DCA and the ground state naphthalene moieties. It seems that the charge-transfer character in the fluorescent state is much greater in the exciplex than in the excimer, and that the greater CT character in the fluorescent state results in smaller activation energy for the exciplex formation. These arguments are consistent with the result that E_a is smaller in MTHF than in MP, as summarized in Table I.

Table I. Fluorescence Maxima (nm) and Activation Energies (kcal) in the Intramolecular Exciplexes of DCAN's, and Fluorescence Maxima, Enthalpy Change (kcal), and Entropy Change (eu) in the Intramolecular CT Complex

Solvent	Exciplex				CT complex		
	MP		MTHF		MP		
DCAN	λ_{max}	E_a	λ_{max}	E_a	λ_{max}	$-\Delta H$	ΔS
β,α'-	510	2.8	534	2.0	540	2.6	−7.4
β,β'-	500	2.7	527	2.2	540	3.8	−10.8

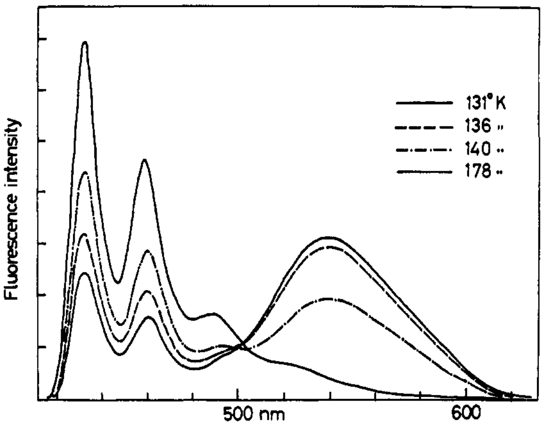


Figure 4. Temperature dependence (below 178°K) in the fluorescence of an MP solution of β,β'-DCAN. Approximate concentration is 2×10^{-5} M.

The exciplex fluorescence in DCAN exhibits remarkable quenching at the temperature 200–170°K both in the polar and nonpolar solvents. However, the MP solution of DCAN shows fluorescence (λ_{max} 540 nm) below ~170°K. Figure 4 shows the fluorescence spectra of an MP solution of β,β'-DCAN at several temperatures. The fluorescence intensity increases remarkably, while the maximum is constant with decreasing temperature. The excitation spectra of these new fluorescences monitored at 560 nm are appreciably different from those of the exciplex fluorescences which are shown in Figure 5, and essentially identical with the absorption spectrum of the corresponding solution of DCAN below 120°K, as shown in Figure 6. These results indicate that the fluorescence below 170°K is not ascribed to the exciplex, but to the fluorescence from the excited state of the ground-state complex. Since the MP solution of DCAN exhibits complex fluorescence below ~170°K even in very dilute solutions (10^{-6}–10^{-7} M), the fluorescence (540 nm) and excitation spectra at low temperature may be ascribed to the intramolecular CT complex in the ground state.

Chandross and Ferguson reported the dimer fluorescence and absorption spectra of 9,10-disubstituted anthracenes in cyclohexane solution at 77°K.[18] Figure

---

[18] E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 3554 (1966).

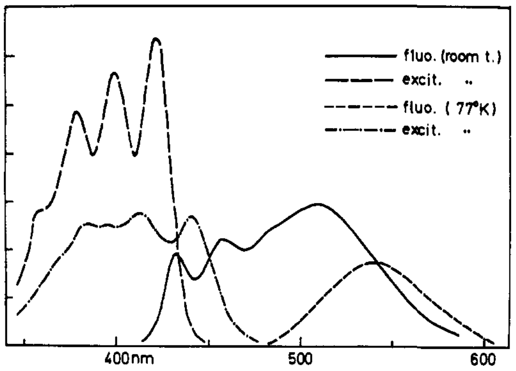


Figure 5. Comparison of the fluorescence and excitation spectra (at room temperature) with those of the CT complex (at 77°K) in an MP solution of β,α'-DCAN. Approximate concentration is 5×10^{-6} *M*. Intensities are arbitrary units.

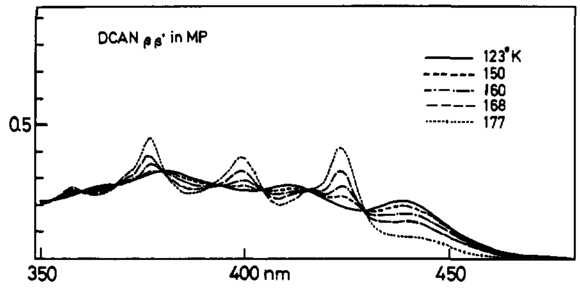


Figure 6. Absorption spectra of an MP solution of β,β'-DCAN at the various temperatures. The temperature was increased from 77°K.

7 shows the fluorescence and absorption spectra of an MP solution of 9,10-dicyanoanthracene at 77°K, which may be attributable to the dimer of this compound. Comparison of these spectra with the results of DCAN shown in Figures 5 and 6 excludes the possibility that the fluorescence and absorption spectra of DCAN at low temperature might be attributed to the intermolecular interaction between two 9,10-dicyanoanthracene moieties.

While the absorption spectra of an MTHF solution of DCAN show no significant temperature dependence, except narrowing the vibrational structure at low temperature (to 77°K), an MP solution of DCAN exhibits appreciably different behavior below ~180°K. Figure 6 shows the absorption spectra (330–460 nm) of an MP solution of β,β'-DCAN at several temperatures below 177°K. The absorption spectrum below ~180°K corresponds to the fluorescence of the intramolecular complex between the DCA and naphthalene moieties which was mentioned above. However, the significant CT absorption band was detected neither in β,β'-DCAN nor β,α'-DCAN. It is likely because the CT absorption might be in the shorter wavelength region than the first absorption band of the DCA moiety.[19] Kobayashi, *et al.*, reported unusually large Stork's shifts in the weak CT complexes which were due to the differences in the electronic and geometrical structures between the CT Franck–Condon state and the fluorescent state.[20] From these arguments, the fluorescence (~540 nm) in an MP solution of DCAN seems to be the CT fluorescence.

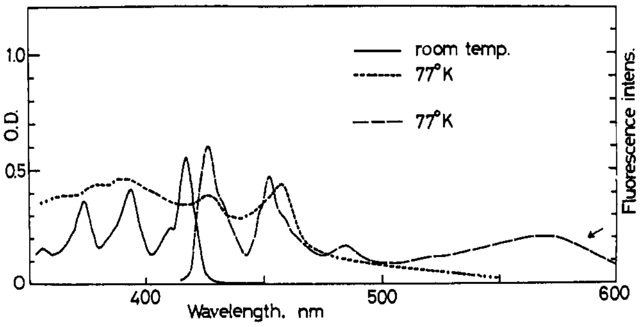


Figure 7. Fluorescence and absorption spectra of an MP solution of 9,10-dicyanoanthracene. The concentration is approximately 2×10^{-4} *M*: (——) and (- - - - - - - -) are the absorption spectra, and (— — — —) is the fluorescence spectrum.

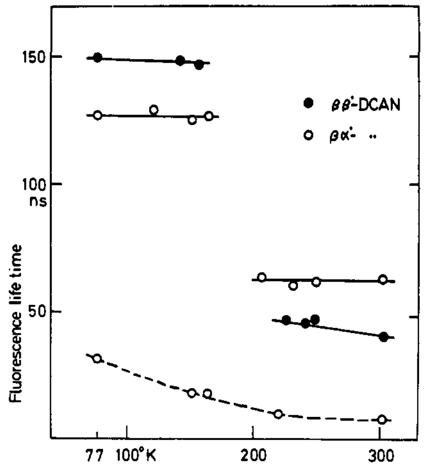


Figure 8. Temperature dependence of the fluorescence lifetime; (——) is determined at 560 nm and (- - - - -) is at 430 nm, which is owing to the 9,10-dicyanoanthracene moiety in the open form of DCAN. At the temperature range 150–200°K, no fluorescence was observed at 560 nm. Concentrations are approximately 10^{-6} *M*.

We assume an equilibrium between the intramolecularly interacted conformation and the noninteracted one,[10–12] though the actual structures are not obvious in this stage. Since the absorption intensity in the region of 330–460 nm of the MP solution shows little change from 77 to 120°K, DCAN is predominantly in the closed form at 77°K. If ϵ_c is assumed to be a molar absorption coefficient of the closed form at 440 nm, plots of log $\epsilon/(\epsilon_c - \epsilon)$ against $1/T$ show a straight line in the dilute solution (~3×10^{-5} *M*), where ϵ is the molar absorption (440 nm) at a certain temperature.[12] The slope of the straight line gives the enthalpy ($-\Delta H$) and entropy (ΔS) changes for the intramolecular complex formation, as summarized in Table I.

The strength of the intramolecular CT interaction, as measured by $-\Delta H$ obtained here, is unexpectedly great in the ground state. While the activation energies for the exciplex formation in two DCAN's have no appreciable difference from each other as mentioned above, the enthalpy change of the CT complex formation is larger in β,β'-DCAN than in β,α'-DCAN. It seems reasonable to say that the enthalpy and entropy changes mean more rigid and more stable complex formation in the former than the latter. On the other hand, no significant difference in the activation energy for the exciplex formation between β,β'-DCAN

---

(19) H. Ishida and H. Tsubomura, *Chem. Phys. Lett.*, **9**, 296 (1971).

(20) T. Kobayashi, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **44**, 2603 (1971).

and β,α'-DCAN seems to demonstrate that the conformational structure of the exciplex fluorescent state is neither rigid nor stable.

Recently, the fluorescent state of the exciplex was proposed to be identical with that of the corresponding CT complex, although the Franck–Condon states are different from each other. According to this argument, two fluorescences may be observed in the same region. However, as summarized in Table I and shown in Figure 5, the two fluorescence spectra seem to have too large an energy difference to be assigned to the fluorescence from the identical excited state. It is likely that the exciplex and CT fluorescences are from the individual excited states. Further evidence was found by determination of the fluorescence lifetime at various temperatures, as shown in Figure 8. The fluorescence lifetimes of the exciplex in β,α'-DCAN and β,β'-DCAN are almost independent of temperature, respectively. The fluorescence lifetime of the CT complex determined at the same wavelength as that of the exciplex is also independent of temperature, and quite different from that of the corresponding exciplex. These results demonstrate that there are two fluorescent states in the potential energy surface in DCAN.

The intramolecular electronic interaction leading to the differences in the excited fluorescent states of the exciplex and the CT complex can be understood by the following consideration. The electronic interaction and therefore the geometrical arrangement between the DCA and naphthalene moieties are different from each other in the Franck–Condon excited states of the exciplex and the CT complex, because the exciplex formation is the photochemical process but the formation of the latter is really the thermal process followed by the photoexcitation. The internal or geometrical conversion from their Franck–Condon states to the identical fluorescent state, if it is correct, is forbidden in our compounds by the steric factor concerned with the trimethylene chain.

Acknowledgments. The authors are indebted to Dr. Keitaro Yoshihara of the Institute of Physical and Chemical Research for determining the fluorescence lifetime and for valuable discussions.

---

^{13}C and ^{15}N Nuclear Magnetic Resonance Spectroscopy of Nitrile Oxides and Related Reaction Products. Unexpected ^{13}C and ^{15}N Nuclear Magnetic Resonance Parameters of 2,4,6-Trimethylbenzonitrile Oxide[1a]

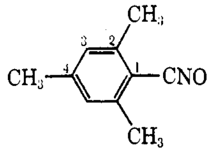
Manfred Christl,[1b] John P. Warren, Bruce L. Hawkins, and John D. Roberts*

Contribution No. 4511 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

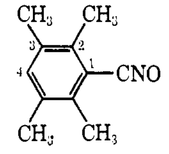
Received July 21, 1972

Abstract: The ^{13}C nmr spectra of several aryl nitrile oxides have been taken. The magnitude of $^1J_{^{13}\mathrm{C}-^{15}\mathrm{N}}$ for 2,4,6-trimethylbenzonitrile-^{15}N oxide has been found to be 77.5 Hz, by far the largest one-bond carbon–nitrogen spin–spin coupling constant yet reported. The ^{13}C resonance of the carbon atom bonded to the nitrogen atom in this nitrile oxide is considerably shifted upfield by comparison with the analogous ^{13}C resonances of nitriles; however, little change is seen in the paramagnetic shielding term for ^{15}N upon conversion of a nitrile to a nitrile oxide. The ^{13}C and ^{15}N spectra are reported for a precursor and some reaction products of 2,4,6-trimethylbenzonitrile-^{15}N oxide. The low-field position of the ^{15}N resonances of isoxazole systems is discussed in relation to nitrogen chemical shifts for other five-membered heterocycles.

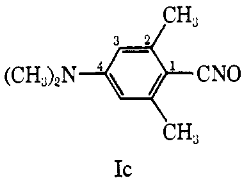
The cmr spectra of 2,4,6-trimethylbenzonitrile oxide (Ia) and three other stable nitrile oxides (Ib-d) have been investigated in an attempt to find a correlation between the chemical shifts of the carbon of the nitrile oxide group and the product ratios observed in the cycloaddition reactions of these nitrile oxides with methyl α,β-unsaturated carboxylates.[2] The cmr spectra were taken of concentrated solutions of the nitrile oxides in methylene chloride, with proton noise decoupling. After a few minutes of spectral accumulation, all the carbon resonances appeared except that of the nitrile oxide carbon atom, and it did not show up even after several hours. There are three factors



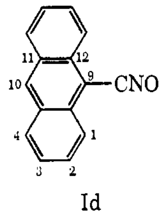
Ia



Ib



Ic



Id

---

(1) (a) Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences; (b) Max Kade Foundation, Inc., Fellow, 1970–1971.

(2) M. Christl and R. Huisgen, *Tetrahedron Lett.*, 5209 (1968); M. Christl and R. Huisgen, to be submitted for publication.