

- (16) Z. Pawlak, *Rocz. Chem.*, **46**, 249 (1972).
 (17) J. C. Synnott and J. N. Butler, *J. Phys. Chem.*, **73**, 1470 (1969).
 (18) R. L. Benoit, D. Lahaie, and G. Boire, *Electrochim. Acta*, in press.
 (19) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N.Y., 1961, pp 108-113.
 (20) W. R. Baird and R. T. Foley, *J. Chem. Eng. Data*, **17**, 356 (1972).
 (21) (a) A. I. Popov, IV International Conference on Non-Aqueous Solutions, Vienna, Austria, July 1974; (b) T. R. Stengle, H. A. Berman, and C. H. Langford, *ibid.*
 (22) T. R. Stengle, Y. C. E. Pan, and C. H. Langford, *J. Amer. Chem. Soc.*, **94**, 9037 (1972).
 (23) R. L. Benoit, A. L. Beauchamp, and M. Deneux, *J. Phys. Chem.*, **73**, 3268 (1969).
 (24) R. L. Benoit, *Inorg. Nucl. Chem. Lett.*, **4**, 723 (1968).
 (25) R. Goitein and T. C. Bruice, *J. Phys. Chem.*, **76**, 432 (1972).
 (26) R. L. Benoit and R. Domain, IV International Conference on Non-Aqueous Solutions, Vienna, Austria, July 1974.
 (27) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963).
 (28) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 2940 (1972).
 (29) The hypothetical enthalpy of solvation of $\text{I}^{\pm}\text{H}_2\text{O}$ into liquid water is calculated according to the method used by Kebarle³⁰ for the hydrated proton.
 (30) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).
 (31) M. K. Chantooni and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **92**, 2236 (1970).
 (32) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).
 (33) E. P. Grimsrud and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 7939 (1973).
 (34) M. Newton and S. Ehrenson, *J. Amer. Chem. Soc.*, **93**, 4971 (1971).
 (35) J. W. Akitt, *J. Chem. Soc., Dalton Trans.*, 175 (1974).

Exciplexes and Electron Donor-Acceptor Complexes in the 9,10-Dicyanoanthracene and Alkyl-naphthalene Systems

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Abstract: The fluorescence and absorption spectra of electron donor-acceptor complexes between 9,10-dicyanoanthracene and alkyl-substituted naphthalenes in a nonpolar solvent were observed below about 125°K, while the exciplex fluorescence was observed from room temperature to about 160°K. The fluorescence maxima and lifetimes of both exciplex (room temperature) and EDA complex (77°K) and the dipole moments in the fluorescent state of the exciplex markedly increase with decreasing ionization potential of the electron donor. The fluorescence and excitation spectra of the EDA complexes at 77°K indicate that CT absorption bands lie in the same wavelength region as the 1L_a band of the electron acceptor. Fluorescent states of the exciplex and the EDA complex previously proposed to be identical are discussed.

Electron donor-acceptor (abbreviated to EDA) systems are classified as EDA complexes (stable in the ground state) and exciplexes (stable only in the excited state).^{1,2} Recent laser photolysis demonstrates that the transient absorption spectra of the exciplex and the EDA complex are essentially identical with the absorption spectra of the anion radical of the electron acceptor molecule in the EDA system.³ Numerous experimental results and theoretical considerations have led to the conclusion that the fluorescent state of the exciplex may be identical with that of the corresponding EDA complex, while their Franck-Condon excited states should be different from each other. However, few cases of exciplex and EDA complex fluorescence in the same EDA system have been reported,⁴ and no direct comparison of the exciplex and the EDA complex has been made.

The previous paper of this series reported the fluorescence and absorption spectra of the EDA complex at low temperature in nonpolar solutions such as 3-methylpentane (MP) of 9,10-dicyanoanthracene (DCA) and 2-methylnaphthalene (2-MN), which showed the exciplex fluorescence at room temperature, and discussed the experimental evidence for an identical fluorescent state of the exciplex and the EDA complex.⁵ On the other hand, two different fluorescent states were suggested for the intramolecular interaction in the (9,10-dicyanoanthracene)-(CH₂)₃-(naphthalene) systems (DCAN) in the nonpolar solvent from temperature dependences of their lifetimes and quantum yields.^{6,7} The electronic interaction producing the difference in the fluorescent states of the exciplex and the EDA complex was ascribed to the forbidden internal or geometrical conversion from the Franck-Condon excited states to an

identical fluorescent state by a steric factor concerned with trimethylene.

This paper describes the further investigation of the fluorescent states of the exciplex and the EDA complex between DCA and various alkyl-substituted naphthalenes. The fluorescence maxima (λ_{max}) and lifetimes (τ) of both exciplex and EDA complex and the dipole moments in the fluorescent state of the exciplex show parallel increases with decreasing ionization potential (IP) of the electron donor. Continuous changes of λ_{max} and τ from room temperature to 77°K were observed in the exciplex and EDA complex of the DCA and acenaphthene (AcN) system. Furthermore, the determination of the fluorescence and excitation polarizations and the absorption spectra at 77°K demonstrated that the charge-transfer (CT) band in the DCA-AcN system lies at longer wavelengths than that of the 1L_a band of DCA and in the EDA complexes with other alkyl-naphthalenes in almost the same region as that of DCA. On the basis of the observation of these distinct CT absorption bands and the behavior of the fluorescent states of the exciplex and the EDA complex reported here, the fluorescent states of the exciplex and the EDA complex are discussed.

Experimental Section

Purifications of materials and solvents were described in previous papers.⁵⁻⁷ Commercial zone refined samples of naphthalene (Tokyo Kasei) were used after recrystallization (two times) from ethanol. Acenaphthene, 1,5-dimethylnaphthalene, and 2,3,5-trimethylnaphthalene were purified by chromatography (silica: benzene-hexane) and recrystallized six or seven times from ethanol. Determinations of the fluorescence and absorption spectra and fluorescence lifetimes have been described previously. For determination of the fluorescence (excitation) polarization, two polarizers

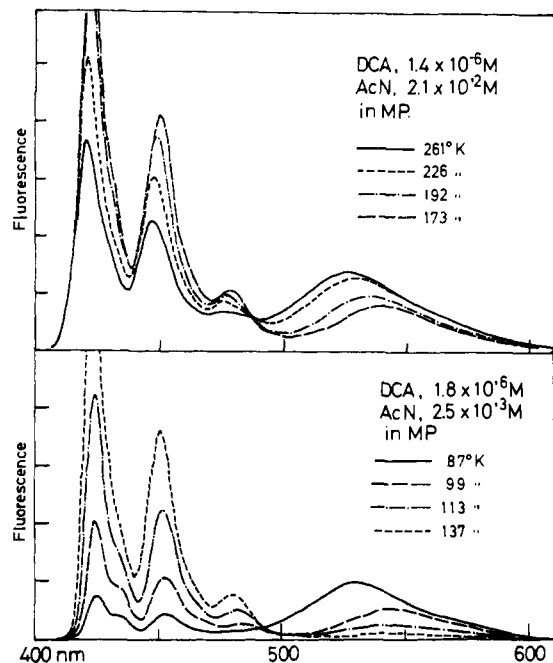


Figure 1. Temperature dependences of fluorescence spectra of MP solutions of DCA and AcN, where the solution is in liquid at room temperature to about 110°K and in viscous liquid below to ~87°K (excited at 375 nm).

(Pentax filters) were used, and the data were corrected as described by Azumi and McGlynn.⁸

Results

The exciplex of 9,10-dicyanoanthracene with various aromatic hydrocarbons was reported first by Chandross and Ferguson.⁹ Figure 1 shows the exciplex fluorescence of an MP solution of DCA and AcN at various temperatures. The exciplex fluorescence as well as temperature dependence were observed with naphthalene and other alkyl naphthalenes in MP solutions by excitation of DCA, for which fluorescence maxima at room temperature are summarized in Table I. Exciplex fluorescence was remarkably

Table I. Fluorescent States of the Exciplex (Room Temperature) and the EDA Complex (77°K) in MP Solutions of DCA and Various Alkyl naphthalenes, and Ionization Potentials of the Electron Donors

Electron donor	Exciplex			EDA complex			IP, ^a eV
	λ , ^b nm	τ , nsec	μ_m , ^c D	λ , ^b nm	τ , nsec		
Naphthalene	490	36	6.1	490	47	8.07	
2-Methylnaphthalene	510	46	5.9	490	49	7.90	
1,5-Dimethylnaphthalene	515	54	7.9	494	56	7.74	
2,3,5-Trimethylnaphthalene	522	72	8.1	497	63	7.66	
Acenaphthene	528	95	8.6	524	106	7.66	

^a J. B. Aldokomo and J. B. Birks, *Proc. Roy. Soc., Ser. A*, **248**, 551 (1965). ^b Fluorescence maxima. ^c Dipole moments in the excited state.

quenched and accompanied by a red shift with decreasing temperature, while the fluorescence of DCA increased in intensity as shown in Figure 1. In MP solutions of these DCA and several naphthalene systems, the intensity ratios of the exciplex (λ_{\max}) and DCA (λ_{\max} in the 420–430-nm region) fluorescence exhibit a linear relation vs. $1/T$.¹⁰ An example of these plots in the DCA–AcN system is shown in Figure 2. Activation energies of the inter- and intramolecu-

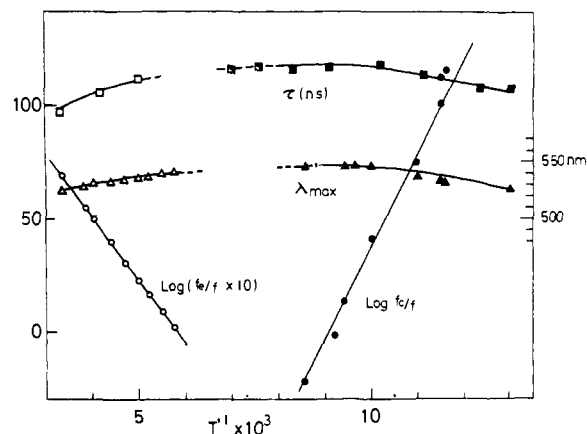


Figure 2. Fluorescence lifetimes and maxima and fluorescence intensity ratios of the exciplex and the EDA complex (f_e and f_c , λ_{\max} in 520–540 nm) to DCA (f , λ_{\max} in 420–430 nm) in the MP solution of DCA and AcN at various temperatures.

lar exciplex formations were obtained from similar plots in the previous papers.^{5,6} In the temperature range of these plots exhibiting a straight line with a negative slope the broad fluorescence in the 490–550-nm region is attributed to the exciplex.

The fluorescence lifetimes monitored at 510 nm of the MP solutions of DCA and various naphthalenes determined at room temperature are listed in Table I, together with IP of the electron donors. An important trend of the data summarized in Table I is the larger τ and the longer wavelength shift of λ_{\max} of the exciplex with the smaller IP of the electron donor. Exciplex fluorescence was observed in various solvents, although the fluorescence was markedly quenched in polar solvents such as acetonitrile. From the fluorescence maxima in various solvents the dipole moments of the fluorescent states were evaluated by the aid of the Lippert–Mataga's equation,¹¹ where alkyl substitution in the naphthalene ring was not assumed to change the radius of the cavity in the theory of reaction field which was assigned a value of 5 Å. The results are also summarized in Table I.

Exciplex fluorescence in solutions of DCA and alkyl naphthalenes was almost completely quenched at temperatures below ~150°K. Although no exciplex fluorescence was observed in the dilute solution of alkyl naphthalene (~10⁻³ M) and DCA in MP at room temperature, an increase of another fluorescence spectrum at almost the same wavelength region as that of the corresponding exciplex and a decrease of the DCA fluorescence were observed with decreasing temperature below about 120°K. An example of this temperature dependence is shown for the DCA–AcN system in Figure 1. In MTHF as a rather polar solvent, no long wavelength fluorescence was observed at low temperature, while an increase of the DCA fluorescence was observed in intensity with decreasing temperature. Here, the fluorescence below about 120°K was tentatively ascribed to the fluorescence of the EDA complex stable in the ground state. Figure 3 shows the concentration dependence of the fluorescence and the 1:1 complex formation between DCA and AcN at 77°K. However, evidence for this stoichiometry could not be obtained by absorption spectroscopy because of the weak absorption band (¹L_a) of DCA (in <5 × 10⁻⁶ M).

In the previous paper, significant broadening and red shift of the ¹L_a band of DCA below about 120°K were reported for the DCA–2-MN system in an MP solution.⁵ Similar broadening of the ¹L_a band of DCA (and a weak absorption at 440–500 nm in the DCA–AcN system) was observed in MP solutions of DCA and several naphthalenes below 120–100°K, while no significant change in the ab-

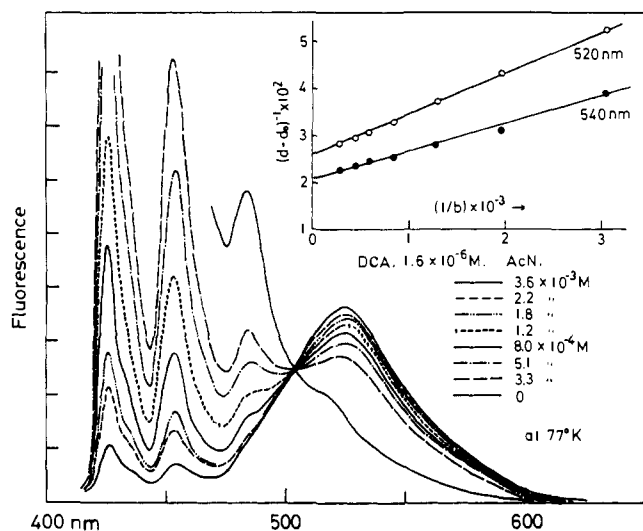


Figure 3. Concentration dependence of the fluorescence spectrum of an MP solution of DCA and AcN at 77°K and Ketterlaar plots for this system at 520 and 540 nm. Here, d and d_0 are fluorescence intensities observed for the ternary solution containing DCA and AcN in MP and for an MP solution of DCA, and b is the concentration of AcN.

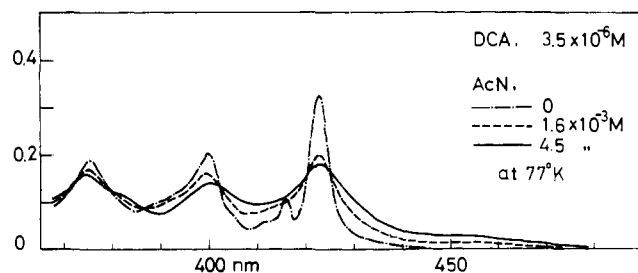


Figure 4. The electronic absorption spectra of MP solutions of DCA and AcN at 77°K (light path length, 3 cm).

sorption spectrum was detected in the MTHF solution at low temperature to 77°K. Figure 4 shows the absorption spectra of MP solutions at 77°K. Similar behavior of the fluorescence and absorption spectra was reported for the intramolecular interaction in DCAN in a previous paper.⁶ These results demonstrate a distinct EDA complex formation in the nonpolar solution of DCA and several naphthalenes in the ground state.¹²

The EDA complex in the ground state, $(DA)_c$, should be in equilibrium with D and A (with an equilibrium constant K). The fluorescence intensity ratios of the EDA complex (f_c , λ_{\max} in 520–540 nm) to DCA (f , λ_{\max} in 420–430 nm) are approximately expressed as follow: $f_c/f = CK\phi_c/\phi$, where ϕ_c and ϕ are fluorescence quantum yields of the EDA complex and DCA, respectively, and C is a constant containing various experimental factors. Since ϕ_c/ϕ cannot depend very much on the temperature, the temperature dependence of f_c/f is mainly attributable to the equilibrium of the EDA complex formation in the ground state. The linear relationship of f_c/f vs. $1/T$ with a positive slope, as shown in Figure 2, demonstrates a completely different mechanism of the fluorescence of the EDA complex from that of the exciplex. On the basis of these arguments, the fluorescence λ_{\max} and τ at various temperatures in the DCA–AcN system are plotted in Figure 2 showing continuous changes from room temperature to 77°K.

It is noteworthy that the fluorescence excitation spectra (monitored at 550 nm) below 120°K were different from that of the exciplex, eliminating any confusion between fluorescence spectrum of the EDA complex and that of the ex-

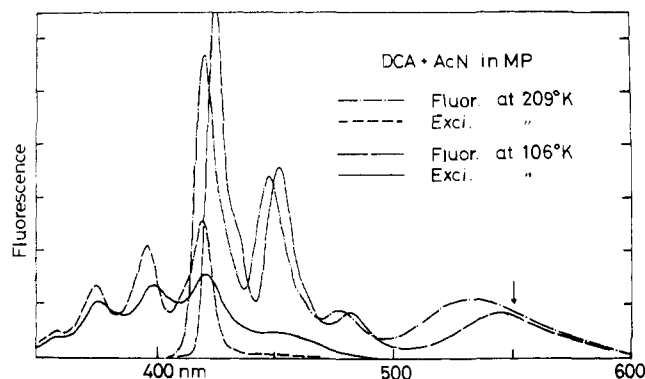


Figure 5. Fluorescence and excitation (monitored at 550 nm) spectra of MP solutions of DCA and AcN. Approximate concentrations of DCA and AcN for spectra at 209°K are $1.8 \times 10^{-6} M$ and $4.3 \times 10^{-2} M$, respectively, and those at 106°K are $1.8 \times 10^{-6} M$ and $2.5 \times 10^{-3} M$.

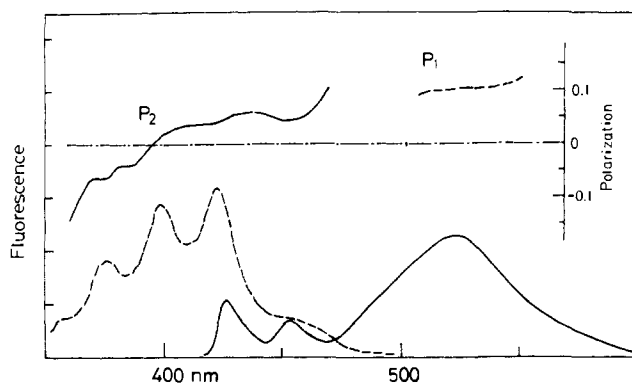


Figure 6. Fluorescence (—, excited at 375 nm) and excitation (---, monitored at 530 nm) spectra at 77°K, and P_1 and P_2 are fluorescence (excited at 470 nm) and excitation (monitored at 530 nm) polarizations of an MP solution of DCA and AcN at 77°K (concentration: DCA, $3 \times 10^{-6} M$; AcN, $2.5 \times 10^{-3} M$).

ciplex. Excitation and fluorescence spectra of the EDA complex (at 106°K, viscous liquid) and of the exciplex (at 209°K, liquid) in the DCA–AcN system in MP are compared in Figure 5. The fluorescence excitation spectrum monitored at 550 nm of an MP solution of DCA and AcN at the low temperature seems to be identical with the absorption spectrum of this solution at 77°K, as shown in Figure 4. A remarkable feature in the excitation and absorption spectra is the absorption band in the 440–500-nm region which was ascribed to the CT absorption band by the subsequent determination of the fluorescence and excitation polarizations at 77°K.⁸

Figure 6 shows the fluorescence and excitation polarizations of the MP solution of DCA–AcN at 77°K. The fluorescence polarization was observed to be negative in excitation at 375 nm and positive in excitation at 470 nm. Since the absorption spectrum with a vibrational progression in the 350–440-nm region may be due to a local excitation of DCA (1L_a) in the EDA complex, the negative polarization by the excitation at 375 nm and positive at 470 nm lead to the conclusion that the absorption band in the wavelength region longer than that of the 1L_a band of DCA is due to the CT absorption band between DCA and AcN,^{13,14} which may be considerably mixed with local excitations.

The fluorescence excitation spectra and their polarizations in MP solutions of DCA and several alkyl-naphthalenes at 77°K are shown in Figure 7, where intensities of the excitation spectra are normalized at 380 nm. These polarizations monitored at 510 nm exhibit similar behavior to that of the DCA–AcN system except that the

wavelength is longer than ~ 430 nm. These results suggest that the CT absorption bands in these EDA complexes lie in the 360–440-nm region and are overlapped by the absorption band of the local excitation in the respective EDA complex. Ishida and Tsubomura¹⁵ suggested the CT absorption bands in the 250–300-nm region between anthracene and various aliphatic amines by the technique of adsorption, though no fluorescence of the corresponding EDA complex was observed. These EDA systems are known to exhibit exciplex fluorescence in liquid media. However, no CT absorption band corresponding to the fluorescence of an EDA complex which also exhibits exciplex fluorescence has been reported. The distinct CT absorption band in DCA–AcN, if it may be considerably mixed with local excitations, is possibly the first observation of a CT absorption band in this kind of EDA system.

Discussion

The wave functions for an EDA system in the excited state (Ψ_e) and in the ground state (Ψ_g) may be written approximately as follows

$$\Psi_e = \sum_1 a_1 \Phi_1(D^* \cdot A) + \sum_2 a_2 \Phi_2(D \cdot A^*) + \sum_{CT} a_{CT} \Phi_{CT}(D^+ \cdot A^-) + a_g \Phi_g(D \cdot A)$$

$$\Psi_g = \sum_1 b_1 \Phi_1(D^* \cdot A) + \sum_2 b_2 \Phi_2(D \cdot A^*) + \sum_{CT} b_{CT} \Phi_{CT}(D^+ \cdot A^-) + b_g \Phi_g(D \cdot A)$$

where the wave functions (Φ 's) and their coefficients (a 's and b 's) are functions of nuclear configurations including solvent molecules. For a weak EDA interaction $|b_g| \gg \sum_1 |b_1|$, $\sum_2 |b_2|$, and $\sum_{CT} |b_{CT}|$, while $\sum_1 |a_1|$ or $\sum_2 |a_2| \gg |a_g|$, and $\sum_{CT} |a_{CT}| \gg |a_g|$.

The fluorescence λ_{max} and τ of both exciplex and EDA complex as summarized in Table I exhibit parallel increases with decreasing IP of the electron donor, and the dipole moments of the fluorescent state of the exciplex also increase. This behavior is usual for EDA interactions¹ and is understood from the following arguments. Since the fluorescent states of both exciplex and EDA complex were proposed to be identical, we discuss them together. If the ionization potential of the electron donor decreases, the energy of the CT configuration, Φ_{CT} , decreases; the weight of Φ_{CT} in the excited state, Ψ_e , increases and the contributions of Φ_1 and Φ_2 decrease with decreasing IP. The transition probability may be reduced for a lower IP of substituted naphthalenes, because the matrix element $\langle \Phi_g \sum |r| \Phi_{CT} \rangle$ in the transition moment is rather small compared with the matrix elements $\langle \Phi_g \sum |r| \Phi_1 \rangle$ and $\langle \Phi_g \sum |r| \Phi_2 \rangle$. The gradual red shift of the exciplex fluorescence and the small increase in lifetimes with lowering the temperature seem to be attributable to the small increase of the solvent polarity at low temperature.¹⁶ Since the D–A distance in the exciplex seems to increase in polar solvents, the matrix element $\langle \Phi_g \sum |r| \Phi_{CT} \rangle$ is reduced and λ_{max} and τ are increased.¹⁶ The shifts of λ_{max} and τ in the temperature region of 140–77°K are ascribed to an emission before the solvent reorientation.¹⁷ From these arguments, it is suggested that the fluorescent state of these EDA systems reported here has a considerable CT character, though there are some exciplexes and EDA complexes of which fluorescences are not from the CT state.^{1,3}

In the intramolecular interaction in the DCAN system, two different fluorescent states of the exciplex and the EDA complex were proposed in the previous papers.^{6,7} The electronic interaction and geometrical arrangement between the excited electron acceptor and the donor in the ground state in the primary process of the exciplex formation seem to be different from those of both ground state donor and acceptor in the EDA complex formation, where EDA complex formation is followed by photoexcitation. The former

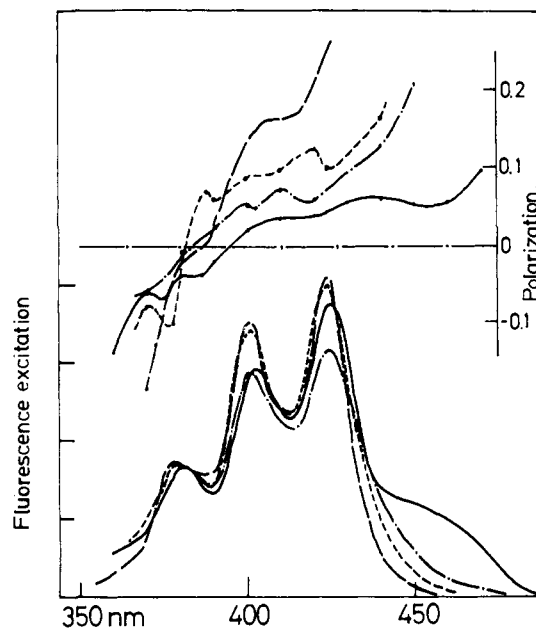


Figure 7. Fluorescence excitation spectra (monitored at 510 nm) and their polarizations of MP solutions of DCA and several alkyl-naphthalenes at 77°K, where intensities of the excitation spectra are normalized at 380 nm: (---) naphthalene; (- · - ·) 2-methylnaphthalene; (— · — ·) 2,3,5-trimethylnaphthalene; (—) acenaphthene.

and the latter are both considered to be Franck–Condon excited states. In the intermolecular interaction, the relaxation process from these Franck–Condon excited states to an identical fluorescent state with solvent reorientation may occur.^{16,18} In the intramolecular interaction, however, the geometrical conversion from their Franck–Condon excited states to the fluorescent state is sterically forbidden by trimethylene, which is easily understood with a molecular model. In this case, two different fluorescent states of the exciplex and the EDA complex appeared in DCAN, as proposed in the previous papers.

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References and Notes

- (1) For comprehensive books: (a) R. S. Mulliken and W. B. Person, "Molecular Complexes, A Lecture and Reprint Volume," Wiley-Interscience, New York, N.Y., 1969; (b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N.Y., 1969; (c) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N.Y., 1970.
- (2) (a) H. Leonhart and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); (b) N. Mataga, K. Ezumi, and K. Takahashi, *Z. Phys. Chem.*, **44**, 250 (1965); (c) H. Kribbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968); (d) M. S. Walker, T. W. Bedmor, and R. Lumry, *J. Chem. Phys.*, **45**, 3455 (1966); (e) T. Okada, H. Matsui, H. Oohari, and H. Mastumoto, *ibid.*, **49**, 4717 (1968).
- (3) M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973), and references therein.
- (4) M. Irie, S. Tomimoto, and K. Hayashi, *J. Phys. Chem.*, **76**, 1419 (1972).
- (5) M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974).
- (6) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Amer. Chem. Soc.*, **95**, 4388 (1973).
- (7) M. Itoh, T. Mimura, and T. Okamoto, *Bull. Chem. Soc. Jap.*, **47**, 1078 (1974).
- (8) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).
- (9) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).
- (10) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).
- (11) E. Lippert, *Z. Naturforsch. A*, **10**, 541 (1955); *Z. Elektrochem.*, **61**, 962 (1957); N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **28**, 690 (1955); **29**, 465 (1956).
- (12) Although the fluorescence of these EDA complexes was also detected in isopentane and methylcyclohexane solutions, only MP was used in this paper because of the weak complex formation.

- (13) M. Chaudhury and L. Goodman, *J. Amer. Chem. Soc.*, **86**, 2777 (1964).
 (14) J. Prochorow and A. Tramer, *J. Chem. Phys.*, **47**, 775 (1967).
 (15) H. Ishida and H. Tsubomura, *Chem. Phys. Lett.*, **9**, 296 (1971).
 (16) N. Mataga and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 3144 (1969).

- (17) N. G. Bakshiev, *Opt. Spektrosk.*, **16**, 821 (1964); *Opt. Spectrosc.*, **16**, 446 (1964); **20**, 542 (1966).
 (18) T. Kobayashi, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **44**, 2603 (1971).

The Molecular Zeeman Effect and Magnetic Susceptibility Anisotropies of Oxazole and Isoxazole. A Magnetic Measure of Aromatic Character

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Abstract: The microwave spectra of oxazole- ^{15}N and isoxazole- ^{15}N have been assigned and the molecular Zeeman effect observed and measured. The values of the rotational constants are $A = 10041.00 \pm 0.14$, $B = 9394.06 \pm 0.05$, $C = 4851.80 \pm 0.03$ for oxazole and $A = 9773.54 \pm 0.07$, $B = 9348.04 \pm 0.07$, and $C = 4775.25 \pm 0.04$ for isoxazole. The molecular g values are $g_{aa} = -0.0963 \pm 0.0024$, $g_{bb} = -0.1214 \pm 0.0021$, and $g_{cc} = 0.0394 \pm 0.0016$ for oxazole and $g_{aa} = -0.1044 \pm 0.0006$, $g_{bb} = -0.1220 \pm 0.0009$, and $g_{cc} = 0.0406 \pm 0.0007$ for isoxazole. The values of the magnetic susceptibility anisotropies in units of 10^{-6} erg/(G 2 mol) are $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 39.2 \pm 3.0$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 35.2 \pm 3.4$ for oxazole and $2\chi_{aa} - \chi_{bb} - \chi_{cc} = 35.7 \pm 1.3$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = 45.6 \pm 1.4$ for isoxazole. Subtraction of the local atom contributions to the magnetic susceptibilities indicates both molecules have nonlocal out-of-plane contributions which are within experimental error of one another and of the nonlocal out-of-plane contributions in furan. Neither the replacement of a carbon-carbon double bond by a carbon-nitrogen double bond nor the relative positions of the heteroatoms in the heteroaromatic ring have a major effect on the electron delocalization as measured by the magnetic susceptibility.

Experimental and theoretical analyses of aromatic character often begin with benzene and progress by consideration of the effects of perturbations on that aromatic system.¹ For example, furan is formally derived from benzene by replacement of two π electrons of a carbon-carbon double bond by two π electrons of an oxygen, an effect which appears to reduce delocalization in the heteroaromatic ring, provided that delocalization is considered to be measured by magnetic susceptibility anisotropy. On the other hand substitution of a carbon-nitrogen double bond for a carbon-carbon double bond appears to reduce delocalization in pyridine relative to that in benzene much less by this criterion.²

In a previous report from these laboratories we have noted that formal insertion of a carbonyl group into benzene, to give tropone, or into furan, to give 2-pyrone or 4-pyrone, results in a suppression of the magnetic characteristics of delocalization.³ In further studies designed to test the effect of atom position on aromatic character as manifest in magnetic properties we have measured the molecular Zeeman



man effects in the formally aromatic molecules oxazole (1) and isoxazole (2). Our data suggest that both molecules have slightly lower nonlocal contributions to the out-of-plane magnetic susceptibility than does furan.

Experimental Section

Purified samples of the nitrogen-15 isotopes of oxazole and isoxazole were obtained by synthesis of **1**⁴ from formamide- ^{15}N and of **2**⁵ from hydroxylamine- ^{15}N hydrochloride. The products were characterized by nmr as well as microwave spectroscopy. The ^{15}N isotopes were used to eliminate nitrogen quadrupole interactions, thus simplifying the spectra considerably.

The zero-field microwave spectra of the normal isotopes of both compounds have been previously assigned.⁶ Reasonable structures were determined from the previous results and these structures were used to predict the microwave spectra of the ^{15}N isotopes. Both a -dipole and b -dipole transitions were observed in oxazole and isoxazole and assignments were readily achieved by standard techniques. The lines that were observed and assigned at Dry Ice temperature are listed in Table I. The resulting least-squares fit produced the rotational constants given in Table II.

The microwave spectrometer and high-field electromagnet used in the Zeeman study reported here have been described previously.⁷ The measurements were made in a C-band waveguide at -60° . The theory of the rotational Zeeman effect in diamagnetic molecules has been given by Hüttner and Flygare.⁸ They have shown that five independent parameters may be obtained from the Zeeman spectra: the three molecular g values, and two magnetic susceptibility anisotropies. In the usual microwave spectrograph employing plane polarized radiation, the absolute sign of the M transitions cannot be determined, thus only the relative signs of the three g values can be obtained. From the g values and magnetic susceptibility anisotropies obtained from the Zeeman spectra and the rotational constants obtained from the zero-field assignments for the molecules, the molecular quadrupole moments may be calculated. For a given choice of relative signs of the g values, a given set of molecular quadrupole moments are obtained. Usually only one choice of relative signs will give reasonable values for the molecular quadrupole moments.⁹ The Zeeman parameters for oxazole and isoxazole are listed in Table III. The values listed are for the choice of signs for the g values which give reasonable values for the quadrupole moments compared to similar molecules in the literature.¹⁰

If other information is known about the molecule it often can be combined with the Zeeman results to obtain other molecular parameters.¹⁰ If the bulk susceptibility is known, one can calculate the diagonal elements of the susceptibility tensor in the principle inertial axis system. The bulk value has been determined for isoxazole by an nmr technique.¹¹ The structure of isoxazole is also known¹² which allows the second moments of the electronic charge distributions and paramagnetic contribution to the magnetic susceptibility elements to be calculated. The total and paramagnetic