Picosecond Flash Spectroscopy of Solvent-Induced Intramolecular Electron Transfer in the Excited 9,9′-Bianthryl[1)]

Nobuaki NAKASHIMA, Masamichi MURAKAWA, and Noboru MATAGA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received June 21, 1975)

$S_n \leftarrow S_1$ absorption spectra of 9,9′-bianthryl in the visible and near infrared regions have been measured by means of picosecond flash spectroscopy. The $S_n \leftarrow S_1$ spectra in hexane measured at 500 ps after the exciting pulse were similar to those of anthracene while those in acetone were similar to the superposition of spectra of anthracene anion and cation. The results of the $S_n \leftarrow S_1$ spectral measurements together with those of the solvent effects upon the fluorescence yield and lifetime indicate an intramolecular electron transfer induced by the interaction with polar solvents in the excited state of 9,9′-bianthryl.

Solvent-induced changes of electronic structures are observed in the excited state of various systems[1—6)] such as *p*-(*N*,*N*-dimethylamino)-benzonitrile,[2)] 9,9′-bianthryl[3)] and some intramolecular heteroexcimer systems.[4—6)] Of these, 9,9′-bianthryl is one of the most important molecules investigated by various methods.

The fact that the two anthracene chromophores of 9,9′-bianthryl in the ground state as well as Franck-Condon(FC) excited state scarcely interact with each other has been shown by the measurements of polarizability,[7)] dipole moment,[7)] half reduction potential,[8)] molecular refraction,[9)] combustion energy,[10)] absorption, and fluorescence spectra.[3)] Moreover, the absorption spectra show no dependence upon the solvent polarity. The fluorescence spectra in rigid matrices and the absorption spectra in rigid as well as fluid solutions remain well structured as in the case of anthracene. Fluorescence spectra in solvents of low viscosity are diffuse compared with those of anthracene, although a slight vibrational structure can be observed in a nonpolar solvent. In polar solvents, the fluorescence spectra are composed of two bands; one shows a slight vibrational structure and is placed at the same wavelength region as in the nonpolar solvent and the other is structureless and shifted towards red.[3,11)] The results indicate a change of the electronic structure of 9,9′-bianthryl in the relaxation process from the FC excited state to the relaxed fluorescent state.[3)] We call the structured band E band and its emitting state E state, and the structureless band P band and its emitting state P state.

The red shift of the fluorescence in a polar solvent indicates that the relaxed fluorescent state has a dipole moment.[3)] It has been concluded on the basis of this fact as well as some quantum chemical calculations that the intramolecular charge transfer from one anthracene nucleus to another caused by the interaction with polar solvent molecules occurs in the excited state.[3,12)] If this is correct, the above result seems to indicate the phenomenon of solvent-induced "broken symmetry,"[13)] *i.e.* the lowering of the symmetry of the solute molecule due to the interaction with polar solvent molecules, resulting in the charge transfer state even if the molecule is composed of two identical chromophores. One of the most direct experimental methods to confirm this would be the measurement of $S_n \leftarrow S_1$ absorption spectra in various solvents of different polarities.

A method of picosecond flash spectroscopy has recently been developed by use of picosecond continuum (pc) as a monitoring light.[14)] We have also established a method of transient absorption measurement by picosecond flash spectroscopy in the visible, near infrared, and uv regions.[1,15,16)] Our method has a resolution of 50 ps in time and 2 nm in wavelength, and can be used for the transient absorption measurement even in the wavelength region of a strong fluorescence. By means of this method, we have measured the $S_n \leftarrow S_1$ absorption spectra of 9,9′-bianthryl in several solvents and have tried to demonstrate that the solvent-induced change of electronic structure is due to the intramolecular charge transfer from one anthracene nucleus to another.

In addition to the $S_n \leftarrow S_1$ absorption measurements, we have investigated the solvent effects upon the fluorescence yield and lifetime of 9,9′-bianthryl. The results seem to give some evidence for the solvent-induced change of electronic structure. Measurements of $T_n \leftarrow T_1$ spectra have also been carried out.

Experimental

Picosecond Flash Apparatus. The details of the method of picosecond flash photolysis and transient spectral measurements used in the present study have been described elsewhere.[1,15,16)] A summary is given herewith.

The sample was pumped with a frequency doubled single picosecond pulse at 347 nm from a mode-locked ruby laser system of JEOL and the transient spectra were monitored by a pc which was generated by collimating a single picosecond pulse at 694 nm into a cell of length 2—20 cm containing polyphosphoric acid (PPA) or water. A single pulse at 694 nm, which was selected from a mode-locked pulse train by a Pockels cell and amplified through a ruby rod, has an energy of *ca.* 100 mJ and a pulse width of 28 ps, and a pulse at 347 nm frequency doubled with KDP an energy of *ca.* 1 mJ. It was first reported by Nakashima and Mataga that the pc from PPA extends from 350 nm to 920 nm and can be used as the most suitable monitoring light in the spectral range 350—650 nm.[16)] The pc probe pulse with *ca.* 50 ps width, determined by an optical Kerr gate, was optically delayed with respect to the exciting pulse (delay time 0—20000 ps).

The 347 nm pump pulse entered the sample cell through one of the two 0.5 mm apertures at the front of the cell. The pc pulse passed through the sample cell from the opposite side was separated into two beams by the apertures. One beam passed through the part of the sample where the molecules were excited. The other passed through the part where the molecules are in the ground state, and was used for correction of shot to shot power variations. The two beams were photographed simultaneously with a Shimadzu GE 100 spectrograph on a Kodak tri-X pan film in the UV~visible wavelength region and on a Kodak high speed infrared 2481 film in the visible near infrared region. We have confirmed that the usual relationship between the photographic density and exposure holds even in the case of the picosecond pulse excitation. Thus, the difference in the photographic densities for the two beams in the spectral range where the ground state absorption is not strong gives transient absorption spectra.

Even in the presence of a strong fluorescence in the same wavelength region as the transient absorption, we can obtain the absorption spectra since the sample cell was set 3 m apart from the spectrograph and the beam divergence of pc is very small (almost the same as that of laser light) in contrast to the fluorescence which becomes very weak after passing the long distance, spreading out in all direction. Our picosecond laser photolysis system was checked by measuring $S_n \leftarrow S_1$ spectra which had been established by the nanosecond laser photolysis method, for example, those of 1,2,4,5-tetracyanobenzene-toluene complex.[17]

Fluorescence Decay Curve Measurements. A 300 kW N_2 gas laser with a half width of 5.5 ns at 337 nm and a Q-switched ruby laser (JEOL, JLR-02A) with an output of *ca.* 100 mJ and a half width of 15 ns at 347 nm were used as the exciting light sources. The fluorescence decay curves were detected through a Nalumi R21 monochrometor with an RCA 1P28 photomultiplier and displayed on a Tektronix 475 oscilloscope. The circuit response time was *ca.* 5 ns. The picosecond pulse at 347 nm from the mode-locked ruby laser was also used for the excitation and the fluorescence was detected with an HTV R617 photodiode and a Tektronix 7912 transient digitizer (0.5 ns time resolution).

Measurements of $T_n \leftarrow T_1$ *Absorption Spectra.* $T_n \leftarrow T_1$ absorption spectra were measured with a conventional μ second flash photolysis apparatus.[18] Both the exciting and monitoring flash lights had a half width of 4 μs. The spectra were photographed with a Shimadzu GE 100 spectrograph.

Measurements of Fluorescence Quantum Spectra. A calibrated Amino-Bowman spectrophotometer was used for the measurements of fluorescence quantum spectra. Fluorescence quantum yields were determined by numerically integrating the areas under the emission curves of both the standard and the sample solutions. Anthracene dissolved in ethanol (2.5×10^{-5} M) was used as a standard, its quantum yield being taken as 0.27.[19]

Synthesis of 9,9'-*Bianthryl.* 9,9'-Bianthryl was prepared by reduction of anthraquinone in glacial acetic acid with zinc powder.[10] The product was recrystallized from chlorobenzene, washed with ethanol, chromatographed on activated alumina using benzene for elution, and recrystallized twice from glacial acetic acid, mp 312 °C. Found: C, 95.07; H, 4.99%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%. The absorption and emission spectra in various solvents were identical with those reported.[3]

Solvents. Hexane (Wako, spectrograde), 2-propanol (Wako, spectrograde), diethyl ether (Wako, analytical grade), acetone (Nakarai, spectrograde), ethanol (Wako, analytical grade), methanol (Wako, analytical grade) and acetonitrile (Merck, spectrograde) were used without further purification. Decalin (Wako, analytical grade) was distilled under reduced pressure before use. All samples were deaerated by repeated freeze-pump-thaw cycles.

Results and Discussion

Picosecond Flash Photolysis. Photographs of pc are shown in Fig. 1, and the transient absorption spectra of 9,9'-bianthryl in Figs. 2 and 3. Each point in the visible region of the spectra (Fig. 2c and Fig. 3a) was obtained by taking an average of several measurements and contains an error of only ±0.05 in the relative optical density unit. The base line of the spectra has an error of +0.1 since two beams through the apertures do not always have equal intensities.

(1) $S_n \leftarrow S_1$ *Spectra in Hexane Solution*: The $S_n \leftarrow S_1$ absorption spectra of 9,9'-bianthryl in hexane obtained

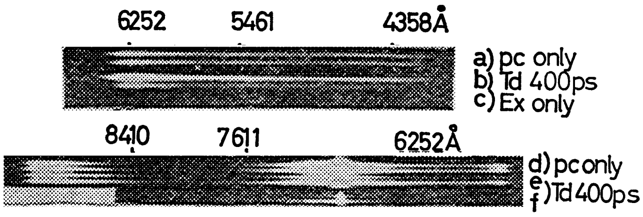


Fig. 1. A photographic display of time-resolved absorption spectra of 9,9'-bianthryl in acetone (5.1×10^{-4} M). a, d; pc without exciting pulse, b; with exciting pulse (lower one) and at 400 ps delay time in the visible region, c; exciting pulse without pc, e; with exciting pulse (upper one) and at 400 ps delay time in the infrared region (over exposure due to exciting Xe flash lamp and ruby fluorescence is observed around 694 nm). f; the same as e except that only the monitoring light intensity was reduced to 1/16. Vertical lines are reference spectra of Hg. The near UV cut off is due to the ground state absorption, and the red or near infrared cut off is due to the low sensitivity of the photographic film.

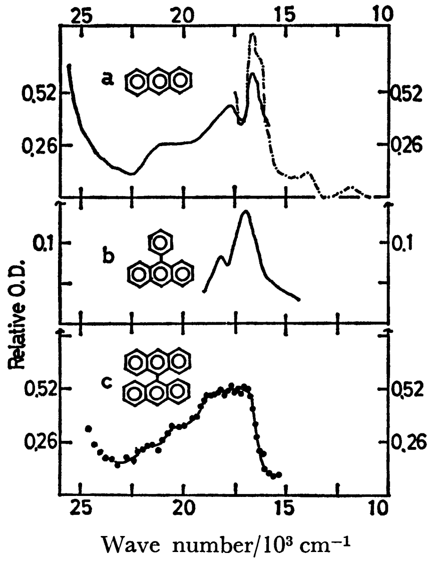
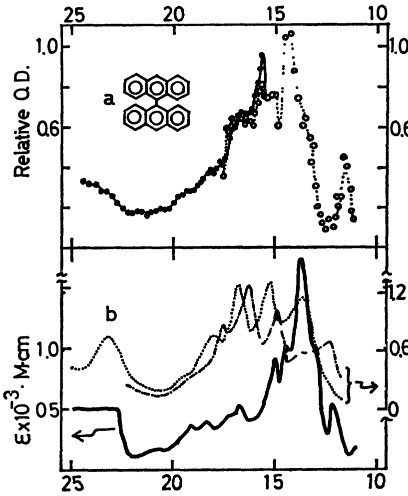


Fig. 2. $S_n \leftarrow S_1$ absorption spectra of anthracene, 9-phenylanthracene and 9,9'-bianthryl. a: Anthracene in hexane, 1.9×10^{-3} M. ——, at 250 ps delay time. —·—, at 300 ps delay time. b: 9-Phenylanthracene in methylcyclohexane. Taken from Ref. 5. c: 9,9'-bianthryl in hexane, 5.1×10^{-4} M. Measured at 500 ps delay time.



Wave number/10^3 cm^{-1}

Fig. 3. $S_n \leftarrow S_1$ absorption spectra of 9,9′-bianthryl. a: -●-●-, Transient spectra at 500 ps delay time. An average of several measurements. -○-○-, Spectra at 400 ps delay time obtained by scanning the photographs of Fig. 1 e and f. b: ——, The superposition of the absorption bands of anthracene anion and cation. Each spectra are quoted from Ref. 23 and the extinction coefficients at 13.8 kcm^{-1} are taken from Ref. 24. —·—·, The spectra of 9.10-diphenylanthracene anion.25) ----, The spectra of 9,10-diphenylanthracene cation.25)

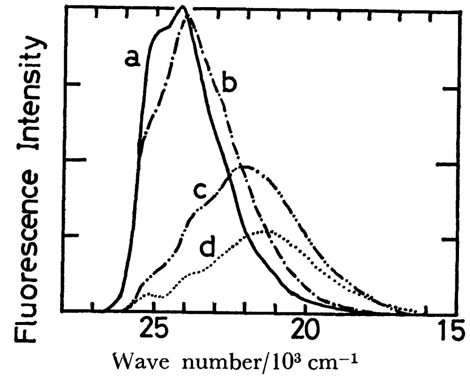


Fig. 4. Fluorescence quantum spectra of 9,9′-bianthryl (2.5×10^{-5} M) in several different solvents. a: ——, hexane. b: —·—·—, diethyl ether. c: —··—, acetone. d: ----, acetonitrile.

at the delay time of 500 ps are shown in Fig. 2c. Since only the E band is observed in this solvent, the spectra contain no contribution from the P state. At a delay time of 500 ps, the formation of the triplet state of 9,9′-bianthryl may be negligible since the fluorescence lifetime and quantum yield are 8 ns and 0.55, respectively. We have confirmed by means of μs flash photolysis that 9,9′-bianthryl shows T_n—T_1 absorption at approximately the same position as that of anthracene. Thus, the spectra (Fig. 2c) contain no contribution from the T_n—T_1 spectra. No strong absorption band was observed in the near infrared regions of 15—11 kcm^{-1}. The S_n—S_1 spectra of anthracene in hexane at 250—300 ps delay time15) as well as those of 9-phenylanthracene in methylcyclohexane measured by the ns laser photolysis method5) are also given in Fig. 2 for the sake of comparison.

The characteristic band of anthracene at 16.7 kcm^{-1} has been assigned to the $^1A_{1g}^- \leftarrow {}^1B_{2u}^+$ transition and that at 18 kcm^{-1} may be assigned partly to the $^1B_{1g}^- \leftarrow {}^1B_{2u}^+$ transition and partly to the vibrational structure of the $^1A_{1g}^- \leftarrow {}^1B_{2u}^+$ transition.20) We can see these characteristic bands in the spectra of 9-phenylanthracene although they are a little shifted towards blue. The spectra of 9,9′-bianthryl are also similar to those of anthracene and 9-phenylanthracene, though the former spectra are somewhat broad and further shifted towards blue as compared with the latter. The results suggest that the E fluorescence state with a slight vibrational structure is the locally excited state or exciton resonance state.

(2) *Formation of P State and Estimation of the Equilibrium Constant between E and P States*: We see from Fig. 4 that, with increasing solvent polarity, the intensity of the E band decreases and is accompanied by the appearance of the P band. Schneider and Lippert3) has shown that the lower the temperature, the stronger the P fluorescence when the viscosity of the solvent is not so high. The results indicate that the P state is formed from the E state. However, it was possible only to observe the single exponential decay of the P as well as E fluorescence. Their lifetimes were almost the same. The result indicates that the P and E states are in equilibrium within 500 ps after the excitation with a picosecond pulse.

Chuang *et al.*21) showed by the picosecond laser technique that the rise of the intramolecular heteroexcimer formation of *N*,*N*-dimethyl-4-[3-(9-anthryl)-propyl]-aniline in hexane is *ca.* 900 ps. Though there seems to be orientational requirement for the heteroexcimer formation, the rise time becomes much shorter (~60 ps) in the anthracene–DEA(*N*,*N*-diethylaniline) two component system.22)

In the case of the present system, our results suggest that orientational requirement for the formation of the P state, if any, is slight. The electron transfer would occur far more rapidly than the above intramolecular heteroexcimer formation, presumably competing with the solvent reorientational relaxation.

From the values of fluorescence quantum yields and lifetimes given in Table 1, we can estimate approximately the equilibrium constant between E and P. The yield of the E fluorescence, η_E, can be given by

$$\eta_E = \frac{q_E}{1+(\tau_E/\tau_P)K_e} \qquad (1)$$

where q_E is the fluorescence quantum yield when there is only the E state, τ_E ans τ_P are intrinsic lifetimes of the E and P states, respectively, and $K_e=[P]/[E]$. The value of (η_E/q_E) in acetone was estimated from the spectra (Fig. 4) using the η_E value in hexane for q_E. From the observed values in hexane and acetone for τ_E and τ_P, and the estimated (η_E/q_E) value, K_e was evaluated to be approximately 40.

(3) $S_n \leftarrow S_1$ *Spectra in Acetone Solution*: The $S_n \leftarrow S_1$ spectra of 9,9′-bianthryl in acetone obtained at the delay time of 500 ps are given in Fig. 3a. We have

confirmed that the rise time of the P fluorescence in acetone is shorter than 500 ps, and that the P state is populated predominantly in the excited state.

The $T_n \leftarrow T_1$ spectra of 9,9′-bianthryl in acetonitrile are similar to those in hexane. This indicates that T_n—T_1 spectra do not depend on solvent polarity. Thus, the spectra in Fig. 3a contain no contribution from the $T_n \leftarrow T_1$ spectra.

The spectra in acetone differ considerably from those in hexane (Fig. 3). Although the spectra in acetone are a little broad and shifted towards blue as compared with the superposition of those[23,24] of anthracene anion and cation (Fig. 3b), both spectra are rather similar. Considering that the reference spectra were taken for the anthracene ions produced by γ-ray irradiation and measured at 77 K,[23] the observed broadening and blue shift can be ascribed to the effects of counter ions (a charged anthryl group in the present case), substituent, and the temperature of the system. This is supported by the fact that the absorption spectra of 9,9′-bianthryl anion and its dianion are similar to those of Fig. 3a,[25] *i.e.* they are somewhat broad and shifted towards blue as compared with those of anthracene anion and that the spectra of 9,10-diphenylanthracene ions are also broad and shifted towards blue as compared with those of anthracene (Fig. 3b).[26] Similar effects of the spectra of ion radicals of aromatic hydrocarbons being affected by the existence of counterions, *etc.* have been observed in the case of ion radicals of naphthalene[23] and fluorene.[27]

The observed shoulder at $16.7\times10^3\,\text{cm}^{-1}$ (Fig. 3a) might be assigned to the back CT transition to the same S_n state as that for the transition corresponding to the $17.5\times10^3\,\text{cm}^{-1}$ band in hexane. However, considering that the fluorescent state of 9,9′-bianthryl in acetone is stabilized due to the reorientation of solvents, the back CT transition in $S_n \leftarrow S_1$ spectra, if any, should be shifted towards blue as compared with the corresponding transition of 9,9′-bianthryl *in hexane solution. Therefore, the shoulder at* $16.7\times10^3\,\text{cm}^{-1}$ *should be assigned to the ion band at ca.* $17\times10^3\,\text{cm}^{-1}$. Thus, the spectra in acetone can be assigned to the transitions localized in anthryl ions.

The electronic structure of the relaxed S_1 state in acetone as well as in more polar solvents seems to be close to the ion-pair with negligibly small delocalization interaction between the pair. This can be possible if the two anthracene planes are almost perpendicular to each other in the relaxed S_1 state in those polar solvents.

Solvent Effects upon Fluorescence Yields and Lifetimes

(1) *The Structural Change of E State*: We have measured fluorescence quantum yields and lifetimes. The results are listed in Table 1. From these values we can examine the effect of structural change on the radiative lifetime. The value in hexane was obtained as $\tau_f^0 \simeq$ 14.5 ns from the observed fluorescence quantum yield and lifetime. On the other hand, the radiative lifetime evaluated from the absorption spectra by using Strickler-Berg's equation[28] is $\tau_f^0 \sim 6$ ns. This indicates that, due to the structural change in the relaxation process from the FC excited state to the relaxed fluorescent state, the radiative transition probability is decreased. Namely, two π-electronic systems of 9,9′-bianthryl are oriented perpendicular to each other because of a strong steric hindrance in the relaxed ground state as well as the FC excited state. However, the stable conformation in the excited state may not be the perpendicular one but the oblique one as suggested by Schneider and Lippert.[3] This structural change in the excited state seems to result in the decrease of the radiative transition probability.

TABLE 1. FLUORESCENCE QUANTUM YIELDS AND LIFETIMES OF 9,9′-BIANTHRYL IN VARIOUS SOLVENTS[a]

Solvent	ε[b]	$\tilde{\nu}_{a,max}$[c]/ $10^3\,\text{cm}^{-1}$	$\tilde{\nu}_{f,max}$[d]/ $10^3\,\text{cm}^{-1}$	$\phi_{f,rel}$[e]	τ_f/ns[f]
Hexane	1.88	25.7	24.2	1.00 (0.55±0.05)	8
Decalin	2.15	25.5	24.0	1.07	
Benzene	2.28	25.3	23.7[g]		11.8[g]
Diethyl ether	4.34	25.7	23.9	1.08	15
2-Propanol	17.9	25.7	22.8	0.91	
Acetone	20.7	25.6	22.1	0.71	32
Ethanol	24.6	25.7	22.6	0.71	33
Methanol	32.7	25.8	22.0	0.60	
Acetonitrile	37.5	25.6	21.3	0.41	35

a) All measurements were carried out at room temperature, the concentration of 9,9′-bianthryl being 2.4 10^{-5} M for all the solutions. b) Dielectric constant of the solvent at room temperature. c) Wave numbers of the absorption maxima quoted from Ref. 3. d) Wave numbers of fluorescence maxima measured in the present work. These values are essentially the same as those of Ref. 3. e) The relative fluorescence quantum yield. The value in parentheses is the absolute value determined by using anthracene as a standard. f) Fluorescence lifetimes were measured at $20\times10^3\,\text{cm}^{-1}$ through a monochromator except the value of hexane solution. The latter was obtained with the use of Toshiba color filters VV40 and UV39. g) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N. Y. (1971), p. 366.

(2) *Solvent-Induced Change of Electronic Structure of P State*: The fluorescence spectra observed in highly polar solvents such as acetone, ethanol, and acetonitrile are almost exclusively due to the P state. We see from Table 1 that the fluorescence lifetimes in these polar solvents are considerably longer than those in nonpolar solvents. Moreover, the lifetime in the polar solvent shows a slight increase with an increase in solvent dielectric constant. However, the fluorescence quantum yield decreases considerably in the strongly polar solvents such as methanol and acetonitrile. In alcoholic solutions, in contrast to the case of aprotic polar solution, specific behaviors in the excited solute-solvent interactions are observed. As has been pointed out already by Schneider and Lippert,[3] as well as by Kosower and Tanizawa,[11] the fluorescence wave number in an alcohol solution is large as compared with the value in an aprotic solvent with almost the same dielectric constant. The fluorescence quantum

yield η_P in alcohol is not smaller than that in acetone though the dielectric constant of the former is larger than that of the latter. Similar effects of solvent polarity as well as alcohol on the behavior of excited molecular composite system are found in the case of aromatic hydrocarbon–amine heteroexcimer.[5,29]

The above results concerning the effects of the solvent dielectric constant upon the fluorescence quantum yield and lifetime of 9,9′-bianthryl indicate the decrease of the radiative transition probability with the increase in the solvent polarity, which can be ascribed to the solvent-induced change in the electronic structure of the P state, just as in the case of some intramolecular heteroexcimers.[5,6]

References

1) Preliminary results have been published in: N. Mataga, "The Exciplex" (Proceeding of International Exciplex Conference, held at Western Ontario, Canada, May 28—31, 1974), ed. by M. Gordon and W. R. Ware, Academic Press, New York (1975), p. 57.

2) E. Lippert, W. Lüder, and H. Boos, "Advances in Molecular Spectroscopy", Pergamon Press, 1962, p. 443; N. Nakashima, E. Inoue, N. Mataga, and C. Yamanaka, *Bull. Chem. Soc. Jpn.*, **46**, 2288 (1973); N. Nakashima and N. Mataga, *ibid.*, **46**, 3016 (1973); W. S. Struve, P. M. Rentzepis, and J. Jortner, *J. Chem. Phys.*, **59**, 5014 (1973); W. S. Struve and P. M. Rentzepis, *ibid.*, **60**, 1533 (1974).

3) F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **72**, 1155 (1968); *ibid.*, **74**, 624 (1970).

4) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393 (1971); E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).

5) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972); T. Okada, T. Fujita, and N. Mataga, *Z. Phys. Chem. N. F.*, to be published. Intramolecular Charge Transfer Interactions and Dynamic Behaviors of Excited *p*-(9′-Anthryl)-*N*,*N*-dimethylaniline.

6) N. Mataga, T. Okada, H. Masuhara, N. Nakashima, Y. Sakata, and S. Misumi, *J. Lumin.*, to be published. Electronic Structures and Dynamical Behaviors of Some Intramolecular Exciplexes.

7) W. Liptay, G. Walz, W. Baumann, H. Schlosser, H. Deckers, and N. Detzer, *Z. Naturforsch.*, **26a**, 2020 (1971).

8) G. J. Hoijtink, *Rec. Trav. Chim. Pays-Bas*, **74**, 1525 (1955).

9) J. A. Bigot and D. W. Van Krevelen, *Trans. Faraday Soc.*, **56**, 322 (1960).

10) A. Magnus, H. Hartmann, and F. Becker, *Z. Phys. Chem.*, **197**, 75 (1951).

11) E. M. Kosower and K. Tanizawa, *Chem. Phys. Lett.*, **16**, 419 (1972); *ibid.*, **26**, 545 (1974).

12) H. Beens and A. Weller, *Chem. Phys. Lett.*, **3**, 666 (1969).

13) See for example, P. W. Anderson, *Science*, **177**, 393 (1972).

14) P. M. Rentzepis, R. P. Jones, and J. Jortner, *J. Chem. Phys.*, **59**, 766 (1973); H. Kuroda and S. Shionoya, *Opt. Commun.*, **10**, 74 (1974); H. Tashiro and T. Yajima, *Chem. Phys. Lett.*, **25**, 582 (1974); D. Magde and M. W. Windsor, *ibid.*, **27**, 31 (1974).

15) N. Mataga and N. Nakashima, *Spectrosc. Lett.*, **8**, 275 (1975).

16) N. Nakashima and N. Mataga, *Chem. Phys. Lett.*, **35**, 487 (1975).

17) H. Masuhara and N. Mataga, *Chem. Phys. Lett.*, **6**, 608 (1970); *Bull. Chem. Soc. Jpn.*, **45**, 43 (1972); R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970).

18) N. Yamamoto, Y. Nakato, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **39**, 2603 (1966).

19) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

20) C. R. Goldschmidt and M. Ottolenghi, *Chem. Phys. Lett.*, **4**, 570 (1970); D. Bebelaar, *Chem. Phys.*, **3**, 205 (1974).

21) T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Am. Chem. Soc.*, **96**, 6828 (1974).

22) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **59**, 2140 (1973).

23) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).

24) P. Balk, G. J. Hoijtink, and J. W. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957); W. Ij. Aalbersberg, G. J. Hoijtink, G. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3055.

25) W. H. Hamill, "Radical Ions", ed. by E. T. Kaiser and L. Kevan, John Wiley & Sons, New York (1968), p. 321.

26) M. Hoshino, K. Kimura, and M. Imamura, *Chem. Phys. Lett.*, **20**, 193 (1973).

27) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

28) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

29) N. Mataga, T. Okada, and N. Yamamoto *Chem. Phys. Lett.*, **1**, 119 (1967); H. Knibbe, K. Rollig, F. P. Schafer, and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967); H. Knibbe, Thesis, Free University, Amsterdam, 1969; N. Orbach and M. Ottolenghi, Private Communication.