Study of Across-Space Intramolecular Charge-Transfer Interaction by Absorption and Fluorescence Spectroscopy

Kiyoshi MUTAI

Department of Chemistry, College of General Education, University of Tokyo, Komaba, Meguro, Tokyo

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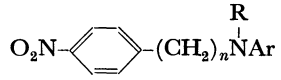
Across-space (through-space) intramolecular charge-transfer (CT) interaction has been observed in homologous series of p-$O_2NC_6H_4(CH_2)_nNHAr$ (I) and p-$O_2NC_6H_4(CH_2)_nNRAr$ (II). Introduction of an alkyl group to the amino nitrogen of I, thus producing II, generally increases the intensity of the CT absorption band. It also induces the red-shift of the band position in most cases owing to the increase of the basicity of the donor, while the blue-shift is observed in *ortho* substituted derivatives. The latter effect is explained by the steric inhibition of the delocalization of nitrogen lone-pair electrons. The CT fluorescence has been observed at room temperature in the lower homologs ($n=1$, 2, and rarely 3) of I and II. Higher intensity of the fluorescence is generally observed in $n=1$. The increase of intensity is observed when a small amount of benzene is added to a cyclohexane solution. The excitation spectrum shows two peaks; one at the ^1L_b transition wavelength of the amine moiety and the other at the CT absorption. The former suggests the possibility that an excited donor collides intramolecularly with a ground state acceptor part (p-nitrophenyl group) to form an excited CT state, and the latter presents a strong evidence for the origin of the fluorescence being the excited CT state.

Of the modes of intermolecular and intramolecular interactions arousing the interest of chemists, hydrogen bonding seems to have been studied most extensively in the past. However, during the last few years interest has grown in the study of intramolecular charge-transfer (CT) interaction.[1,2] This paper deals with the across-space[3] intramolecular CT effect, studied hitherto mainly by absorption spectroscopy with particular attention paid to the CT ground state. The present study is intended to provide information on the excited state of the intramolecular CT interaction with the aid of fluorescence spectroscopy as well as on the ground state.

Since the *intramolecular* CT interaction is subject to conformational restrictions, one can expect to observe spectral features differing from those of the *intermolecular* interaction in which the energetically most favorable conformation is exclusively assumed. Thus the characteristic aspects in the *intramolecular* interaction may provide valuable data for grasping the CT phenomenon. In *intramolecular* interaction the equilibrium constant between interacting and non-interacting molecules is independent of concentration so far as intermolecular interaction is negligible, and enables one to observe purely 1 : 1 interaction at low concentration even if the interaction is hardly detectable in an *intermolecular* case. This condition, of course, simplifies the interpretation of the spectral features.



I, R=H
II, R=Me or Et

a, Ar=C_6H_5
b, Ar=4-MeC_6H_4
c, Ar=2,4-$Me_2C_6H_3$
d, Ar=2,4,6-$Me_3C_6H_2$
e, Ar=4-$MeOC_6H_4$
f, Ar=2,5-$(MeO)_2C_6H_3$
g, Ar=1-$C_{10}H_7$
h, Ar=2-$C_{10}H_7$

The compounds used for the present study are the homologous series of the type, p-$O_2NC_6H_4(CH_2)_nNHAr$ (I) and p-$O_2NC_6H_4(CH_2)_nNRAr$ (II), where R denotes methyl or ethyl groups, and Ar phenyl, p-tolyl, 2,4-dimethylphenyl, mesityl, p-anisyl, 2,5-dimethoxyphenyl or naphthyls. The CT interaction is expected between p-nitrophenyl (acceptor) and arylamino (donor) groups.

Results and Discussion

Absorption Spectra. Absorption spectra of the compounds of type I in carbon tetrachloride solution have been reported.[2] In the present study, a mixture of benzene–cyclohexane (1:4) was used as a common solvent for the measurement of absorption and fluorescence spectra. Addition of benzene to cyclohexane increases both the dissolving power of the solvent system and the intensity of the CT fluorescence. In order to show the effect of the number of methylene groups (n) and the difference between I and II series, some absorption curves are reproduced in Figs. 1 through 3. The data of the CT bands are summarized in Table 1. The CT band is obtained by subtracting a reference or standard spectrum from the spectrum of I or II. There are two ways for setting up the reference spectrum;[2] one is to adopt the spectrum of a sufficiently higher homolog (generally, a homolog with $n\geqq5$), and the other to adopt the sum of the spectra of the compounds having similar chromophores and simple struc-

1) a) W. N. White, *J. Amer. Chem. Soc.*, **81**, 2912 (1959); b) S. Shifrin, *Biochim. Biophys. Acta*, **96**, 173 (1966); c) J. W. Verhoeven, I. P. Dirks, and Th. J. de Boer, *Tetrahedron Lett.*, **1966**, 4399; d) A. J. de Gee, J. W. Verhoeven, I. P. Dirks, and Th. J. de Boer, *Tetrahedron*, **25**, 3407 (1969); e) J. W. Verhoeven, I. P. Dirks, and Th. J. de Boer, *ibid.*, **25**, 4037 (1969); f) H. A. H. Craenen, J. W. Verhoeven, and Th. J. de Boer, *Tetrahedron Lett.*, **1970**, 1167; g) R. Carruthers, F. M. Dean, L. E. Houghton, and A. Ledwith, *Chem. Commun.*, **1967**, 1206; h) M. Ōki and K. Mutai, *Tetrahedron Lett.*, **1968**, 2019; i) M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 1843 (1968); j) J. P. Carrión, D. A. Deranleau, B. Donzel, K. Esko, P. Moser, and R. Schwyzer, *Helv. Chim. Acta*, **51**, 459 (1968); k) P. Moser, *ibid.*, **51**, 1831 (1968); l) K. Mutai, *Tetrahedron Lett.*, **1971**, 1125.

2) M. Ōki and K. Mutai, *Tetrahedron*, **26**, 1181 (1970).

3) The word "across-space" is used in order to distinguish the effect from "through-bond" intramolecular CT interaction.[4,5] "Through-space" may be used instead.

4) a) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); b) S. Nagakura, *ibid.*, **23**, 1441 (1955); c) S. Nagakura, *Pure Appl. Chem.*, **7**, 79 (1963).

5) H. A. Bent, *Chem. Rev.*, **68**, 588 (1968).

Table 1. Charge-transfer bands of p-$O_2NC_6H_4(CH_2)_n$ NHAr (I) and p-$O_2NC_6H_4(CH_2)_n$ NRAr (II) in benzene–cyclohexane (1 : 4)

Ar	R	$n=1$ λ_{max} (nm)	ε	$n=2$ λ_{max} (nm)	ε	$n=3$ λ_{max} (nm)	ε
C_6H_5 (Ia)	H	333	360	325	1030	317	530
(IIa)	Me	356	480	340	1750	329	450
	Et	357	380	347	1430		
4-MeC_6H_4 (Ib)	H	339	380	333	930		
(IIb)	Me	364	455	347	1580		
2,4-$Me_2C_6H_4$ (Ic)	H	350	285	339	785		
(IIc)	Me	321	440	313	1040		
2,4,6-$Me_3C_6H_2$ (Id)	H	326	855	316	1035		
(IId)	Me	323	680	313	1225		
4-$MeOC_6H_4$ (Ie)	H	355	380	347	710		
(IIe)	Et	370	325	361	990		
2,5-$(MeO)_2C_6H_3$ (If)	H	351	260	338	810		
(IIf)	Et	335	565	322	1210		

tures. For practical reasons both methods are adopted. The latter is applied, to some derivatives of I and most of II, since their higher homologs are liquid at room temperature and difficult to be isolated in pure state because of their high boiling points. p-Nitrobutylbenzene and $ArNR-CH_2CH_3$ (R is hydrogen or alkyl) were used as model compounds. Thus the application of the different methods does not yield any significant difference in the CT band characteristics.[2)]

It is generally accepted that alkylation of the nitrogen of aniline or its derivative increases the π-basicity of the compound. Thus when I and II with the same Ar group are compared, II has a stronger electron-donor than I and is expected to have higher population of the CT interacting molecule, the situation leading to a higher intensity of the CT band of II at a longer wavelength than I. Hence, the introduction of an alkyl group to the amine nitrogen of I is a means to confirm the origin of the band as CT interaction.

As regards the band position, however, the prediction does not necessarily hold. We see from Table 1 that there are two groups of derivatives in which one reveals the shift of the band position to the long-wavelength side by the introduction of an alkyl goup to the amino nitrogen, as is observed in the cases of Ia, Ib, and Ie, and the other to the short-wavelength side as is observed in Ic, Id, and If. The effect observed in the latter group is contrary to expectation, but it can be understood if we note that all the Ar's in this group contain *ortho* substituent; that is, the *ortho* substituent hinders the orbital axis of the nitrogen lone-pair electrons from being pararell with p_π orbital axis of benzene, inducing less increase or even decrease of the π-basicity of NRAr group in comparison with the corresponding NHAr group. The group NH-2,4,6-$Me_3C_6H_2$ containing two

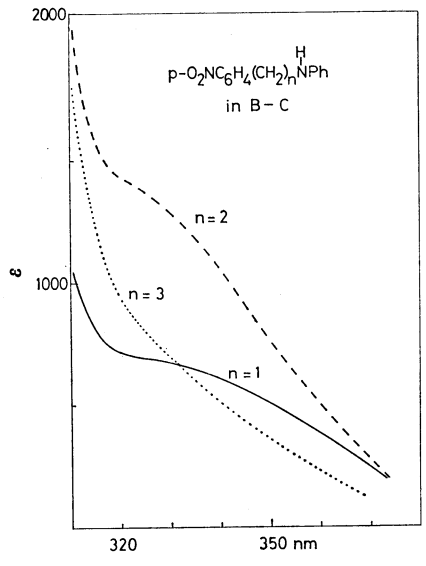


Fig. 1. Absorption spectra of p-$O_2NC_6H_4(CH_2)_n$NHPh (Ia) in long wavelength region in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote the number of methylene group (n).

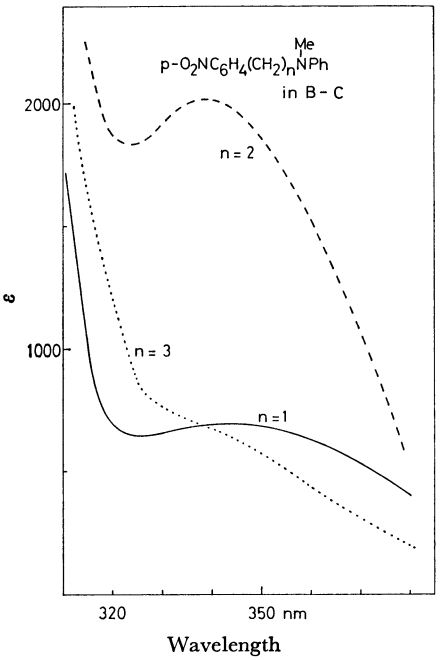


Fig. 2. Absorption spectra of p-$O_2NC_6H_4(CH_2)_n$NMePh (IIa) in long wavelength region in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote the number of methylene group (n).

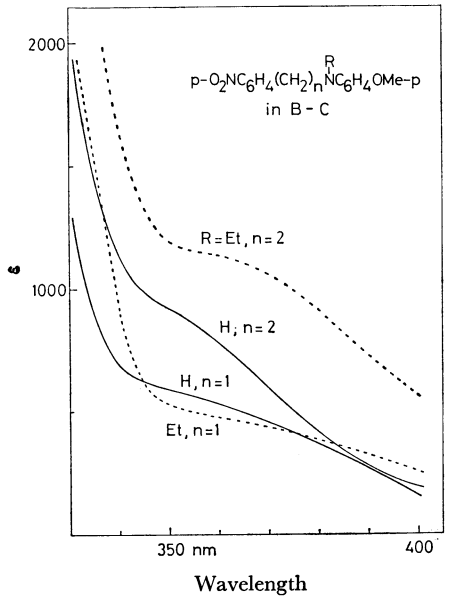


Fig. 3. Absorption spectra of *p*-$O_2NC_6H_4(CH_2)_nNRC_6H_4O$-Me-*p* (Ie and IIe, R=Et) in long wavelength region in benzene–cyclohexane (1:4) mixture.

ortho methyls undergoes this steric effect (λ_{max} of Id at 326 and 316 nm $n=1$ and 2, respectively),[2] which is insignificant for NH-2,4-$Me_2C_6H_3$ group with one *ortho* methyl (λ_{max} of Ic at 350 and 339 nm in $n=1$ and 2, respectively). This steric inhibition of resonance has also been detected by means of the N–H stretching vibration,[2] dipole moment,[6] and ultraviolet absorption spectra of *N,N*-dimethylaniline derivatives.[7] Thus further introduction of a methyl group to the nitrogen of Id causes no further remarkable effect (only 3 nm of blue-shift in both $n=1$ and 2 of IId). On the other hand, we see from band positions of the derivatives of Ic and If that the steric effect makes no appreciable contribution when the nitrogen is a secondary amine type. Consequently it can be said that the introduction of an alkyl group to I increases the π-basicity of the donor only when the Ar group has no *ortho* substituent.

It seems strange that the decrease of the π-basicity of the donor is accompanied by an increase of intensity. However, examination of the CT band data shows a general relationship between the peak position and intensity; the shorter the λ_{max}, the higher the intensity. This phenomenon has also been observed in other solvents[2] and in some intermolecular CT complexes.[8-11] Although no satisfactory explanation has been given to this effect,[12] the abnormal increase of the intensity accompanied by blue-shift is in line with the general rule, and probably not with the increase of the number of interacting molecules.

Fluorescence Spectra. In the fluorescence spectra of I and II at room temperature, a fluorescence peak due to the excited state of the across-space intramolecular CT interaction was observed at 500—550 nm. Some CT fluorescence spectra are shown in Figs. 4 through 9 with excitation spectra. The peak was assigned as above for the following reasons. (1) The concentration of the solution used for measurement was less than 2×10^{-4} mol/*l*, which is dilute enough to exclude intermolecular interacting species. (2) The peak was observed only in the lower homologs and did not appear when the number of the methylenes (n) exceeds three. It should be remembered that the CT absorption band was observed in the lower homologs of $n\leqq4$. (3) Generally, the increase of the π-basicity of the donors owing to the introduction of electron-donating group(s) into the benzene ring or the nitrogen induced red-shift of the fluorescence peak (especially in $n=1$ homolog of I), reflecting the similar feature observed in the CT absorption spectrum. (4) The excitation spectrum showed a maximum at the λ_{max} of the corresponding CT absorption (Figs. 4—9). (1) and (2) provide evidences for intramolecular process. (3) and (4) suggest a close relationship between appearance of peak and CT interaction. The peak positions and their intensities are summarized in Tables 2 and 3.

a) Solvent Effects: The solvents used for the measurement of CT fluorescence are cyclohexane and benzene–cyclohexane (1:4, v/v) mixture. A slight blue-shift of the CT fluorescence is observed (Tables 2 and 3), when the solvent was changed from the latter to the former, and the effect is consistent with the shift of the CT absorption band[2] and also with that observed for intermolecular CT fluorescence.[13] In most cases addition of benzene to cyclohexane increased the intensity. The most significant effect is observed in the spectra of Ia ($n=1$ and 2) and Ib ($n=1$ and 2) which show no peak in cyclohexane. For these derivatives with weak donors the addition of benzene seems to be extraordinarily effective.

It is surprising, however, that the higher homolog of Ia ($n=3$) shows a peak in cyclohexane but not in benzene–cyclohexane system. The peak might be due to impurity, but this can be denied for the following reasons; a similar effect was observed in the series of Ib and IIa ($n=3$ shows the largest peak height), and the presence of an impurity which exhibits fluorescence even at a concentration less than 10^{-6} mol/*l* (since no impurity was detected by any other spectroscopic method, its concentration must be, at most, a few per cent to the sample compound) is incredible.

It is also noteworthy that the addition of benzene does not always result in the increase of intensity.

6) J. W. Smith, *J. Chem. Soc.*, **1961**, 81.
7) H. B. Klevens and J. R. Platt, *J. Amer. Chem. Soc.*, **71**, 1714 (1949).
8) A. Bier, *Rec. Trav. Chem. Pays-Bas*, **75**, 866 (1956).
9) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).
10) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).
11) M. Tamres, D. R. Virzi, and S. Searles, *ibid.*, **75**, 4358 (1953).
12) It has not yet been elucidated to what extent the spectra of the original chromophores undergo modifications in their band shapes on interaction. It is therefore difficult to discriminate whether the trend is "artificial" or inherent in CT interaction, as long as the CT band is obtained by subtraction of the reference spectrum, or the apparent peak position and intensity in the absorption curve are regarded as "true" as is often the case for intermolecular interaction.
13) K. Kaneta and M. Koizumi, This Bulletin, **40**, 2254 (1967).

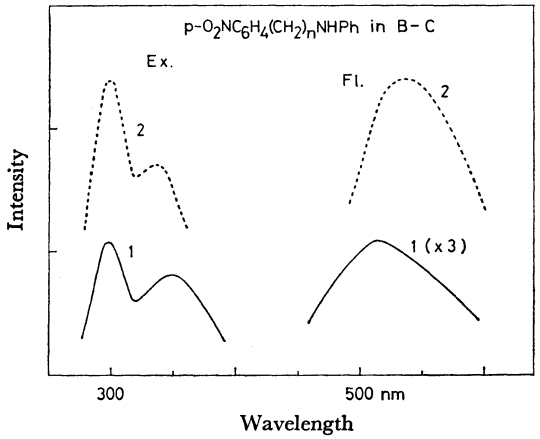


Fig. 4. Fluorescence (Fl.) and excitation (Ex.) spectra of *p*-$O_2NC_6H_4(CH_2)_nNHPh$ (Ia) in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote *n*.

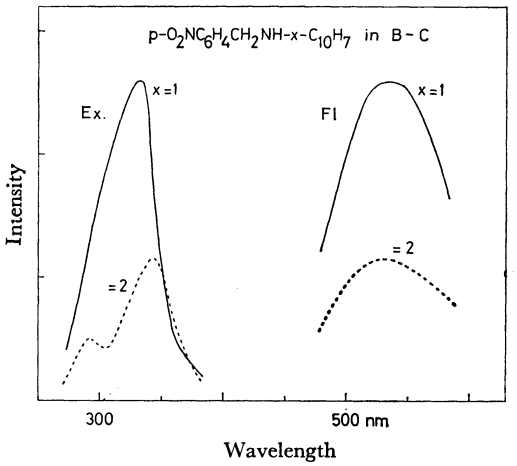


Fig. 7. Fluorescence (Fl.) and excitation (Ex.) spectra of *N*-(*p*-nitrobenzyl)naphthylamines in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote the position of amino group in naphthalene nucleus.

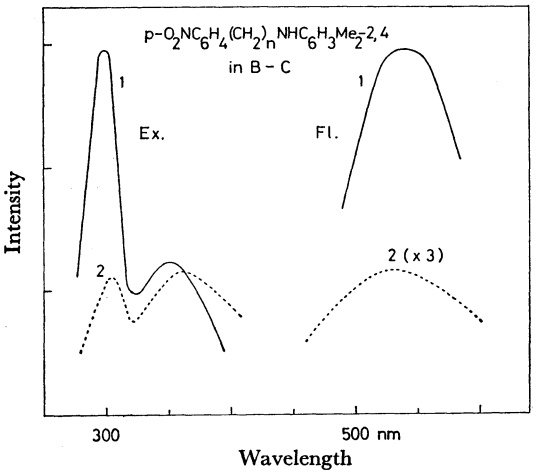


Fig. 5. Fluorescence (Fl.) and excitation (Ex.) spectra of *p*-$O_2NC_6H_4(CH_2)_nNHC_6H_3Me_2$-2,4 (Ic) in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote *n*.

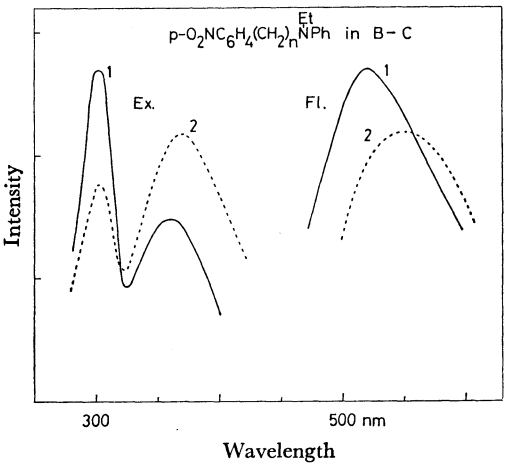


Fig. 8. Fluorescence (Fl.) and excitation (Ex.) spectra of *p*-$O_2NC_6H_4(CH_2)_nNEtPh$ (IIa) in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote *n*.

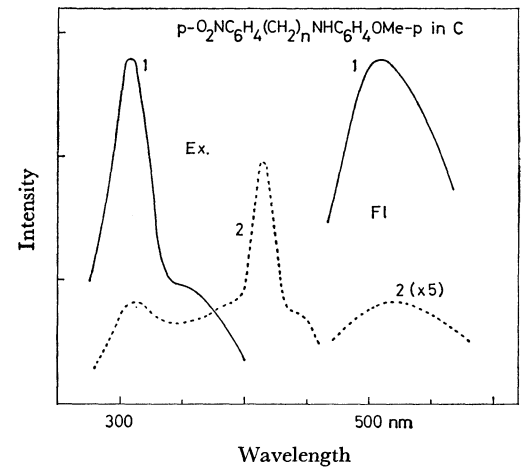


Fig. 6. Fluorescence (Fl.) and excitation (Ex.) spectra of *p*-$O_2NC_6H_4(CH_2)_nNHC_6H_4OMe$-*p* (Ie) in cyclohexane. Numerals attached to the curves denote *n*.

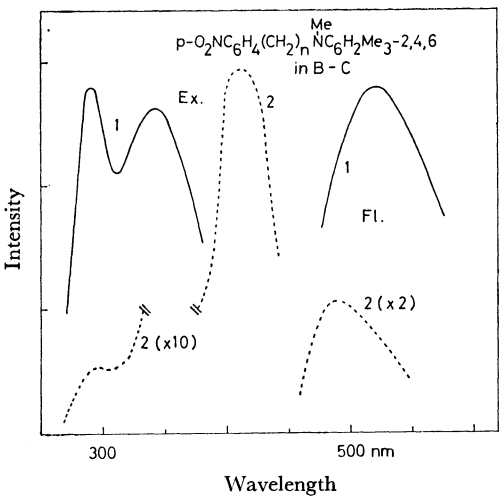


Fig. 9. Fluorescence (Fl.) and excitation (Ex.) spectra of *p*-$O_2NC_6H_4(CH_2)_nNMeC_6H_2Me_3$-2,4,6 (IId) in benzene–cyclohexane (1 : 4) mixture. Numerals attached to the curves denote *n*.

Table 2. Intramolecular charge-transfer fluorescence of p-$O_2NC_6H_4(CH_2)_n$ NHAr (I)

Ar	n	Benzene–cyclohexane (1: 4)		Cyclohexane	
		λ_{max} (nm)	Relative intensity[a]	λ_{max} (nm)	Relative intensity[a]
C_6H_5 (Ia)	1	512	3.3	—	
	2	540	21	—	
	3	±		545	3.1
	4	—		—	
4-MeC_6H_4 (Ib)	1	525	42	—	
	2	535	3.6	500	2.5
	3	—		550±10	
2,4-$Me_2C_6H_3$ (Ic)	1	536	29	492[b]	2.9
	2	530	3.8	510	5.5
	3	—		—	
2,4,6-$Me_3C_6H_2$ (Id)	1	554	31	502	24
	2	525	3.6	523	2.5
	3	—		—	
4-$MeOC_6H_4$ (Ie)	1	>550[c]		510	83
	2	525	5.4	518	4.8
	3	+		—	
2,5-$(MeO)_2C_6H_3$ (If)	1	560±5[c]	3.7	522	10
	2	527	2.5	±	
1-$C_{10}H_7$ (Ig)	1	535	100	493[b]	17
	2	570	15	535	33
	3	—		—	
2-$C_{10}H_7$ (If)	1	527	51	485±10[b]	2.1
	2	570	18	527	13

a) The intensity of p-$O_2NC_6H_4CH_2NH$-1-$C_{10}H_7$(Ig) is taken as 100.
b) Owing to the overlap with stray light in short wavelength region, the exact maximum position is difficult to be determined.
c) Owing to the low sensitivity of the photomultiplier (1P28) in long-wavelength region, the maximum does not appear in the range measured.

Table 3. Intramolecular charge-transfer fluorescence of p-$O_2NC_6H_4(CH_2)_n$ NRAr (II)

Ar	R	n	Benzene–cyclohexane (1: 4)		Cyclohexane	
			λ_{max} (nm)	Realtive intensity[a]	λ_{max} (nm)	Relative intensity[a]
C_6H_5 (IIa)	Me	1	522	51		
		2	545	64	504	2.5
		3	560±10	7.3	560±10	3.0
	Et	1	522	77	496	2.4
		2	550	61	500	3.8
4-MeC_6H_4 (IIb)	Me	1	548	230	490	35
		2	515	7.0	510	4.0
2,4-$Me_2C_6H_3$ (IIc)	Me	1	545	62	490	11
		2	525	6.1	520±5	2.5
2,4,6-$Me_3C_6H_2$ (IId)	Me	1	522	60	492	2.2
		2	490	12	505	3.7
4-$MeOC_6H_4$ (IIe)	Et	1	>550[b]		530	250
		2	525	10	500	12
2,5-$(MeO)_2C_6H_4$ (IIf)	Et	1	>550[b]		525	65
		2	502	6.1	497	4.0
1-$C_{10}H_7$ (IIg)	Et	1	543	160	498	74

a) The intensity of p-$O_2NC_6H_4CH_2NH$-1-$C_{10}H_7$ (Ig) is taken as 100.
b) Owing to the low sensitivity of the photomultiplier (1P28) in long-wavelength region, the maximum does not appear in the range measured.

For instance, $n=1$ homologs of Id, Ie, and Ig exhibited no peak when dissolved in pure benzene as well as in 96% ethanol, while Ia showed the CT peak in benzene.

So far there is no satisfactory explanation for these phenomena caused by the added benzene and sufficient evidence to assign the effects to electronic origin (*e.g.* energy-transfer process) or to environmental origin (*e.g.* solvation), or both.

b) Peak Position and Intensity: A comparison of Tables 2 and 3 with Table 1 shows that there is no simple relationship between the maximum positions of the CT absorption band and the fluorescence. As regards CT absorption, it has been found that the longer the n ($n \leqq 3$), the shorter the wavelength of its λ_{max}, irrespective of solvent.[2] In benzene–cyclohexane system, most of the homologous series reveal the same tendency in their CT fluorescence bands. However, the tendency is reversed when the solvent was changed to cyclohexane. This might be due to the change of the potential energy curves of the CT ground and excited states caused by different solvation.

It is noteworthy that the peak position and intensity of $n=1$ homolog are generally more affected by solvent than $n=2$. A scale model shows only partial overlap of π-electron clouds of the donor and acceptor is allowed in $n=1$ because of the short methylene chain, but parallel plane conformation of the benzene rings is possible for $n=2$, the situation being the same both in I and II. The latter face-to-face conformation which permits sufficient overlap of the π-electron clouds is expected to be more stable than the conformation of $n=1$ and less susceptible to environmental factors. Probably this is the main reason for the fluorescence characteristics of $n=1$ being more sensitive to solvent.

For the series I ($n=1$) in benzene–cyclohexane, the CT fluorescence λ_{max} is in the order Ia<Ib<Ic<Id<Ie, which reflects the order of the electron-donating ability of Ar group and also nearly that of the λ_{max} of the CT absorption. The exception is Id, the CT absorption band of which is at the shortest wavelength due to the steric inhibition of delocalization of the nitrogen lone-pair electrons by two *ortho* methyls. Thus the fluorescence λ_{max} is expected at a shorter wavelength than Ia. However, since the most stable conformation of the excited state is achieved during much longer life time of fluorescence (about 10^{-9} sec) than conformational readjustment (about 10^{-12} sec) and the CT absorption observed is merely a vertical transi-

Table 4. Excitation spectra of the CT fluorescence of p-$O_2NC_6H_4(CH_2)_n$ NHAr (I)

Ar	n	Benzene–cyclohexane (1:4) λ_I (nm)	λ_{II} (nm)	Intensity ratio λ_I/λ_{II}		Cyclohexane λ_I (nm)	λ_{II} (nm)	Intensity ratio λ_I/λ_{II}	^1L_b[a] (nm)	CT λ_{max} (nm)
C_6H_5 (Ia)	1	298	345	0.75		—	—		295	333
	2	300	335	0.73		—	—			325
4-MeC_6H_4 (Ib)	1	300	350	0.52		—	—		304	339
	2	308	350	0.95	+400	305	350	0.87		333
2,4-$Me_2C_6H_3$ (Ic)	1	298	350	0.42		297	352	0.74	299	350
	2	303	360	1.1	+405	300	350	0.69		339
2,4,6-$Me_3C_6H_2$ (Id)	1	290	340	1.1		290	340	1.1	286	326
	2	300—355	Broad			290	325	0.62		316
4-$MeOC_6H_4$ (Ie)	1	313	355	0.44		310	355sh[c]	0.34	308	355
	2	315	415[b]	0.81		315	415	1		347
2,5-$(MeO)_2C_6H_3$ (If)	1	300	355	0.47		300	355	0.37	298	351
	2	305	350	0.9		±				

a) The ^1L_b transition of ArNHEt in cyclohexane. b) A sharp peak (see Figs. 6 and 9). c) Shoulder.

Table 5. Excitation spectra of the CT fluorescence of p-$O_2NC_6H_4(CH_2)_n$ NRAr (II)

Ar	R	n	Benzene–cyclohexane (1:4) λ_I (nm)	λ_{II} (nm)	Intensity ratio λ_I/λ_{II}	Cyclohexane λ_I (nm)	λ_{II} (nm)	Intentity ratio λ_I/λ_{II}	^1L_b[a] (nm)	CT λ_{max} (nm)
C_6H_5 (IIa)	Me	1	300	360	0.68				300	356
		2	303	358	0.92	303	365	1.2		340
		3	303	350	0.52	305	355	0.52		329
	Et	1	302	362	0.55	302	365	0.72	303	357
		2	303	370	1.3	307	375	1.6		347
4-MeC_6H_4 (IIb)	Me	1	306	365	0.55	305	365	0.62	307	364
		2	312	360	1.4	310	360	0.91		347
2,4-$Me_2C_6H_3$ (IIc)	Me	1	290	340sh[b]	0.52	287	330sh[b]	0.73	285±5	321
		2	300	415[c]	4.2	290	415[c]	1.3		313
2,4,6-$Me_3C_6H_2$ (IId)	Me	1	290	345	1.1	290sh[b]	355	1.9		323
		2	295	412	54	310	405	14		313
4-$MeOC_6H_4$ (IIe)	Et	1	320	Plateau	0.26	315	365	0.33	318	370
		2	330	415[c]	4.0	325	410[c]	1.4		361
2,5-$(MeO)_2C_6H_4$ (IIf)	Et	1	312	355[c]	0.70	302	350	0.41	297	335
		2	307	410[c]	8.1	305	410[c]	2.6		322

a) The ^1L_b transition of ArNREt in cyclohexane. b) Shoulder. c) A sharp peak (see Figs. 6 and 9).

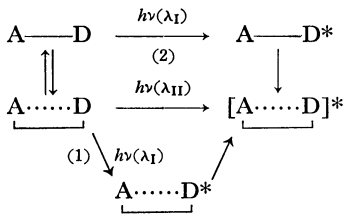
tion from the ground state, the "abnormal" behavior of Id might not be surprising if it is admitted that the most stable conformation of these two states differs.

c) Excitation Spectra of CT Fluorescence: Some typical examples of the excitation spectral curves are shown in Figs. 4 through 9. We see at a glance that a curve consists of two bands. One peak at shorter wavelength approximately agrees with the position of ^1L_b transition of ArNR-group, and the other with the CT absorption (see Tables 4 and 5). Agreement of these values can be said to be satisfactory, if we take into consideration some uncertainties possibly involved in both the excitation and absorption spectra (no correction has been made for the wavelength dependence of the sensitivity of the spectrometer).

The fact that the light having the same wavelength as CT absorption is effective for fluorescence is a strong evidence for the CT fluorescence.

It is interesting but puzzling that the excitation spectra of $n=2$ homologs of IIc—IIf showed a narrow but intense peak at about 410 nm (Fig. 9). The same phenomenon is also observed in some derivatives of I (Fig. 6). Appearance of this extra peak is restricted only to the $n=2$ homologs in both I and II series. No corresponding absorption is found in the absorption spectra of these compounds, and no convincing explanation has been obtained.

It is also interesting that the mere excitation of the amine moiety is effective for CT fluorescence. This suggests at least two processes possible for the appearance of the excited CT state; (1) only an amine moiety in a CT interacting molecule is excited and falls to the lowest excited singlet level of CT interaction releasing the excess energy nonradiatively. (2) An amine moiety free from the interaction absorbs light, and in its excited state during the stay collides with the *p*-nitrophenyl group at the other end of the methylene chain to form a CT interacting molecule in excited state. The processes are described in the following scheme, where A and D are the acceptor (*p*-nitrophenyl) and the donor (NRAr) groups, respectively (for λ_I and λ_{II}, see Tables 4 and 5).



From the viewpoint of energy level, ^1L_a band of *p*-nitrophenyl group at 265 nm (in heptane)[14] is higher than the ^1L_b of the amine moieties and the excitation of the nitrophenyl group should be effective in either process. Contrary to expectation no peak could be detected at the wavelength corresponding to this absorption. In this respect, it is notable that in 1,4-dimethoxybenzene — trinitrobenzene or — chloranil system the excitation of an acceptor results in the formation of donor cation,[15] suggesting that the encounter of the excited acceptor with the donor leads to the transient acceptor anion and donor cation likely to be formed when a CT complex is excited in polar solvent. Although there is no reason why this intermolecular process should not be observed in an intramolecular case, no satisfactory explanation has been found as yet.

Of the two processes, (2) is considered as more probable, since an excimer and an exciplex are formed in a similar process. The same process has been considered possible for the intermolecular CT interaction between anilines and oxygen molecule,[16] and between *N,N*-dimethylnaphthylamine and methyl benzoate.[17] As an evidence, it may be cited that the ratio of the apparent peak heights of the excitation spectrum, λ_{II}/λ_I, is in almost all the cases larger in $n=2$ than $n=1$ (for typical example, see Figs. 5 and 8). The ratio is independent of the quantum yield of the fluorescence and of the intensity distribution of light source, and, therefore, represents the relative effectiveness of two types of excitations. The larger value of $n=2$ homolog shows that the excitation of the CT state is more effective than that of the same band of $n=1$ homolog, or, in other words, the excitation of the amine moiety is less effective in $n=2$. According to process (2), the effect is explained as follows. The excited donor in $n=2$ homolog has a smaller chance to encounter the acceptor before transition to the ground state due to its longer chain length than $n=1$, the situation leading to the relative inefficiency of ^1L_b excitation and the increase of the relative effectiveness of CT band excitation.

Conclusion

It was suggested[2] that the interaction might be "contact charge-transfer",[18] but the occurrence of CT fluorescence indicates the presence of energy minimum in the excited energy level of the CT interaction. It might be said that in the interacting species some stable and unstable complexes are present whose stability depends mostly on conformational factors of the interacting groups.

Intramolecular excimer formation has been studied by several investigators,[19] who showed that strict conditions are required for the occurrence of the phenomenon. As an example, the number of methylene groups in Ar–$(CH_2)_n$–Ar system must be three for the observation of intramolecular excimer fluorescence. When the number is two, insufficient overlap of π-electron clouds in the aromatic rings prevents the radiative

14) W. M. Schubert and J. Robins, *J. Amer. Chem. Soc.*, **80**, 559 (1958).

15) K. Kawai, N. Yamamoto, and H. Tsubomura, This Bulletin, **42**, 369 (1969).

16) M. Hori, H. Itoi, and H. Tsubomura, *ibid.*, **43**, 3765 (1970).

17) T. Miwa and M. Koizumi, *ibid.*, **39**, 2588 (1966).

18) E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **89**, 6056 (1967).

19) a) F. Hirayama, *J. Chem. Phys.*, **42**, 3136 (1965); b) M. T. Vala, Jr., J. Haebig, and S. A. Rice, *ibid.*, **43**, 886 (1965); c) J. W. Longworth and F. A. Bovey, *Biopolymers*, **4**, 115 (1966); d) D. T. Browne, J. Eisinger, and N. J. Leonard, *J. Amer. Chem. Soc.*, **90**, 7302 (1968); e) E. A. Chandross and C. J. Dempster, *ibid.*, **92**, 3586 (1970).

Table 6. Elemental analyses and yields of new compounds used in this study
p-$O_2NC_6H_4(CH_2)_n$ NRAr

Ar	R	n	Yield, %	Mp or (bp/mmHg), °C	Formula	C %		H %		N %	
						Calcd	Found	Calcd	Found	Calcd	Found
4-MeC_6H_4	H	1	61	67—68	$C_{14}H_{14}N_2O_2$	69.40	69.45	5.83	5.65	11.56	11.71
		2	27	76—77	$C_{15}H_{16}N_2O_2$	70.29	70.10	6.29	6.12	10.93	10.92
2,5-$(MeO)_2C_6H_3$	H	1	66	118—118.5	$C_{15}H_{16}N_2O_4$	62.49	62.67	5.59	5.49	9.72	9.92
		2	26	63—64	$C_{16}H_{18}N_2O_4$	63.56	63.77	6.00	5.87	9.27	9.40
C_6H_5	Me	3	37	(185—190/2)[a]	$C_{16}H_{18}N_2O_2$	71.09	70.81	6.71	6.49	10.36	10.34
	Et	1	53	65—66	$C_{15}H_{16}N_2O_2$	70.29	70.34	6.29	6.19	10.93	10.69
		2	23	(187—190/1)[b]	$C_{16}H_{18}N_2O_2$	71.09	70.93	6.71	6.68	10.36	10.53
4-MeC_6H_4	Me	1	43	48—49	$C_{15}H_{16}N_2O_2$	70.29	70.54	6.29	5.99	10.93	11.20
		2	35	59—60	$C_{16}H_{18}N_2O_2$	71.09	70.99	6.71	6.53	10.36	10.60
2,4-$Me_2C_6H_3$	Me	1	37	72—73	$C_{16}H_{18}N_2O_2$	71.09	70.90	6.71	6.91	10.36	10.22
		2	34	(189—192/3)[c]	$C_{17}H_{20}N_2O_2$	71.88	71.80	7.34	7.09	10.09	9.85
2,4,6-$Me_3C_6H_2$	Me	1	30	61—62	$C_{17}H_{20}N_2O_2$	71.88	71.66	7.34	6.99	10.09	10.08
		2	47	(180—187/2)[d]	$C_{18}H_{22}N_2O_2$	72.45	72.26	7.43	7.30	9.39	9.52
4-$MeOC_6H_4$	Et	1	20	64—65	$C_{16}H_{18}N_2O_3$	67.11	66.84	6.34	6.18	9.78	10.03
		2	11	(197—200/2)	$C_{17}H_{20}N_2O_3$	67.98	68.28	6.71	6.80	9.33	9.58
2,5-$(MeO)_2C_6H_3$	Et	1	34	85—86	$C_{17}H_{20}N_2O_4$	64.54	64.53	6.37	6.46	8.86	8.99
		2	16	(186—190/1.5)[e]	$C_{18}H_{22}N_2O_4$	65.44	65.26	6.71	6.45	8.48	8.37
1-$C_{10}H_7$	Et	1	34	91—92	$C_{19}H_{18}N_2O_2$	74.49	74.61	5.92	5.85	9.15	8.98

a) n_D^{23} 1.6018. b) n_D^{25} 1.6079. c) n_D^{20} 1.5838. d) n_D^{26} 1.5795. e) n_D^{23} 1.5815.

process. If we compare the *number of atoms* separating donor and acceptor allowed for excimer fluorescence (only 3) with that allowed for CT fluorescence (2, 3, and in some cases 4), it is clear that the CT excited state depends to a smaller extent on conformational requirements as expected from its larger stabilizing energy.

Experimental

Electronic Absorption Studies. Spectra were recorded on a Shimadzu MPS-50L automatic recording spectrophotometer. Quartz cells of 1.0 cm in length were used. The concentration of benzene–cyclohexane solution was less than 2×10^{-3} mol/*l*.

Emission Studies. Fluorescence spectra were recorded at room temperature on an Aminco-Bowman spectrophotofluorometer. The concentration of both benzene–cyclohexane and cyclohexane solution was always in the range $1-2\times10^{-4}$ mol/*l*. In every measurement, the peak height of the CT fluorescence band p-$O_2NC_6H_4CH_2NH$-1-naphthyl (Ig, $n=1$) was determined in order to obtain a factor necessary for the adjustment of intensity fluctuation of incident light. The CT fluorescence intensities were given relative to that of this compound (relative intensity=100) in Tables 2 and 3. The fluorescence peak height of *N*-ethyl-1-naphthylamine is 8.5×10^4 (at 390 nm, corrected for the sensitivity of 1P28) in this scale. The excitation wavelength was 313 nm. The data in Tables 2 and 3, and fluorescence curves in Figs. 4—9 are corrected for the sensitivity of photomultiplier (1P28).[20] As a result, in some compounds ($n=1$ of Ie, IIe, and IIf) no peak was found in their corrected spectral curve, on account of large and uncertain correction factors in long wavelength region.

Excitation spectra were determined with the same spectrophotofluorometer equipped with an "off-axis ellipsoidal mirror condensing" system. No correction for the wavelength dependence of the sensitivity of the instrument was made.

Solvents. Spectrograde or guaranteed reagents were used after careful distillation.

Materials. Both types of compounds (I and II) were prepared as described in a previous paper.[2] The physical constants and results of elemental analyses of the new products are given in Table 6.

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20) C. E. White, M. Ho, and E. Q. Weimer, *Anal. Chem.*, **32**, 32, 438 (1960).