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ACROSS-SPACE INTRAMOLECULAR CHARGE-TRANSFER INTERACTION BETWEEN p-NITROPHENOXY AND ARYLAMINO GROUPS

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It has been reported that the fluorescence due to the across-space intramolecular charge-transfer(CT) interaction is observable at room temperature in the lower homologues of p-$O_2NC_6H_4(CH_2)_nNHAr$(I).[1] The purpose of the present paper is to show the usefulness of fluorescence spectroscopy for the detection of the CT interaction.

The compounds chosen for the present study are a type, p-$O_2NC_6H_4O(CH_2)_nNHAr$ (II), the lower homologues of which have shown a possibility[2] that the two aromatic groups (p-nitrophenoxy and arylamino) are accessible to each other by some forces other than by intramolecular hydrogen bond.

One of the possible causes for the accessibility is the across-space intramolecular CT interaction between these two groups, but ultraviolet and visible region of the absorption spectrum showed no sign of the phenomenon, even with strong electron-donating Ar group (Fig. 1). Carbon tetrachloride, which has been a standard solvent in the study of the CT interaction of I,[3] was employed here on account of its inertness and excellent dissolving power. The higher homologue with n=5 or 6 is regarded as a reference compound with non-interacting chromophores, and the CT band should be found as an extra absrobance superposed on that of the reference.

On the contrary, the fluorescence spectra of the lower homologues of II in cyclohexane or cyclohexane-benzene mixture(1:4) show a peak at ca. 530 nm when Ar group is phenyl (n=2), p-anisyl (n=2 and 3), and 1-naphthyl (n=2). The peak does not appear when n is above 4. Unfortunately, it is difficult to determine the exact position and intensity of the peak on account of its broad band shape

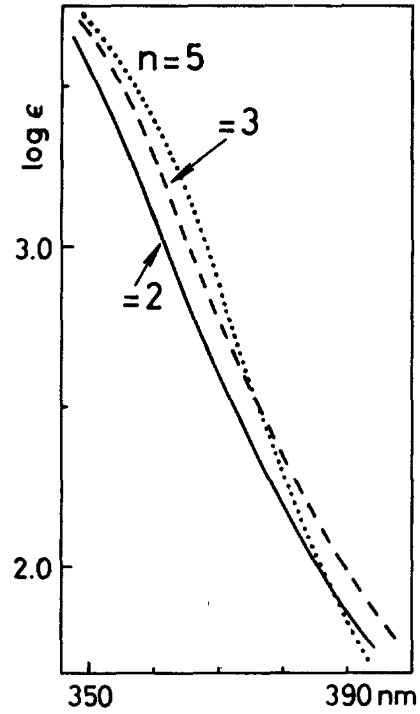

Figure 1. Longer wavelength region of the uv spectra of p-$O_2NC_6H_4O$-$(CH_2)_n$-1-Naphthyl in CCl_4.

and low intensity, and also of the poor solubility of the compounds in these solvents. However, on the basis of the analogy of the peak position and shape with those of I, of its limited appearance to smaller n, and of the concentration of the solution sufficiently low (less than 1.5×10^{-4} M) to exclude intermolecular interaction, it is reasonable to assign the origin of the peak to the excited state of the across-space intramolecular CT interaction.

These inconsistent results obtained from two spectroscopic methods may be explained by the existence of intramolecular N-H···O hydrogen bond in these lower homologues (Fig. 2); the effect is expected to blue-shift the n,π* transition band of the p-nitrophenoxy chromophore, which, in turn, results in the decrease of the absorbance of long wavelength region. The extent of the absorbance loss may counterbalance a gain from the CT interaction or exceed it to produce a spectrum with lower intensity than that of the

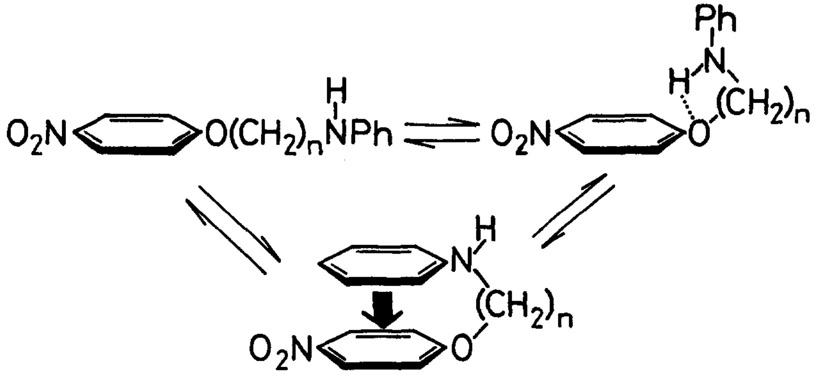

Figure 2. Possible conformations of p-$O_2NC_6H_4O(CH_2)_nNHPh$

reference compound in which neither the hydrogen bond nor the CT interaction is present. If this is the case, the CT absorption band should be observed in protic solvent where the role of the intramolecular hydrogen bonding becomes less important owing to much more predominant intermolecular hydrogen bonding between solute and solvent molecules. As is seen in Table I, the CT band is actually observed in 96% ethanol when n is 2 and 3. Furthermore, this reasoning leads to a supposition that even in aprotic solvent the CT band should be observed if the N-H hydrogen is substituted by an alkyl group. This is also the case as is shown in Table II. All these facts support the explanation above mentioned. This effect of the intramolecular hydrogen bonding on electronic spectrum can probably be used as a model of specific solvent effect.

Table I. The Charge-Transfer Absorption Band of $p\text{-}O_2NC_6H_4O(CH_2)_nNHAr$ in 96% Ethanol

Ar	n = 2		n = 3	
	λ_{max}	ε	λ_{max}	ε
C_6H_5	362 nm	160	365 ± 10 nm	20
$p\text{-}MeOC_6H_4$	365	175	370 ± 10	20
$1\text{-}C_{10}H_7$	385	110	390 ± 10	25

Table II. The Charge-Transfer Absorption Band of $p\text{-}O_2NC_6H_4O(CH_2)_2NRAr$ in CCl_4

Ar	R	λ_{max}	ε
C_6H_5	Me	347 nm	185
$p\text{-}MeOC_6H_4$	Et	372	125

There is no doubt that p-nitrophenoxy group can work as an electron-acceptor, though its accepting ability seems to be fairly weaker than p-nitrophenyl group due to the electron-donating effect of the ether oxygen atom. In this regard, it is also interesting that the longest limit of the chain length for the CT interaction in II is n=3 or when $p\text{-}O_2C_6H_4$ and Ar groups are separated by five atoms, the limit in atom number being the same as found for I. This may indicate that p-nitrophenoxy group is not so weak as expected in electron-accepting ability, at least in across-space interaction, or that some forces other than the CT interaction are predominant in bringing the two groups close together.

Satisfactory analyses were obtained for all new compounds prepared.

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