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# INTRAMOLECULAR CHARGE-TRANSFER INTERACTION BETWEEN LONE PAIR ELECTRONS AND π-ELECTRON SYSTEM

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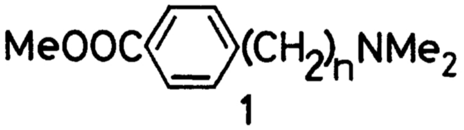
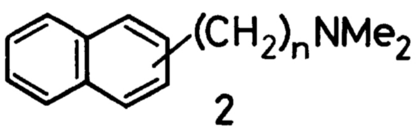
As a model for detecting the intramolecular n-π type charge-transfer interaction, a homologous series of the compounds **3** was chosen and subjected to ultraviolet, fluorescence, and photoelectron spectroscopic study. The interaction was confirmed in the lower homologs of n=1, 2, and 3.

In 1969 Smith and Menger tried to detect the intramolecular charge-transfer (CT) interaction between p-methoxycarbonylphenyl and dimethylamino groups in **1**, but found no feature of the interaction.$^{1)}$ On the other hand, the ionization potentials of aliphatic amines are mostly less than 9 eV small enough for an electron donor in CT interaction. Recent findings of intramolecular exciplex formation in the type **2** series of amines reported by Chandross and Thomas,$^{2)}$ of excimer formation of tertiary aliphatic amines by Halpern et al.,$^{3)}$ and of n-π interaction by Morishima et al.,$^{4)}$ suggest the availability of the nitrogen n-electrons for CT type interaction if appropriate conditions are provided. Strong n-π type CT interaction observed in biphenyl$^{5)}$ and indenone$^{6)}$ derivatives underlines this supposition. These facts prompted us to study the possibility of n-π type intramolecular CT interaction.

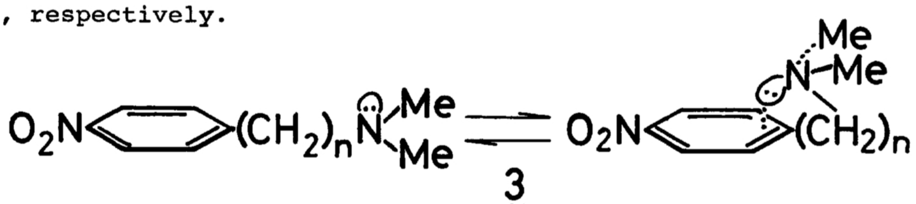


**1**



**2**

The type of the compounds chosen for the present study was 1-(p-nitrophenyl)-alkane bearing a dimethylamino group on the ω-carbon (**3**). Here, p-nitrophenyl and dimethylamino groups were supposed to be a π-acceptor and an n-donor in the interaction, respectively.



**3**

Ultraviolet spectroscopy The typical absorption curves of 3 in cyclohexane are shown in Fig. 1. The absorption maximum(ca. 270 nm) and shoulder(ca. 340 nm) observed for each homolog could be assigned to nitrobenzene chromophore, though the position of n=1 is slightly blue-shifted due to the inductive effect of dimethylamino group. A notable point in Fig. 1 is the excess absorption of the lower homologs (n=1, 2, and 3) in longer wavelength region in comparison to n=4. Though the absorption of n=1 shows only a slight difference, if the curve is removed toward longer wavelength side by ca. 10 nm, thus cancelling the inductive effect of the substituent, fairly strong absorption exceeding that of n=4 could be observed. Subtraction of the curve of n=4, assumed as a standard for non-interacting chromophores, from the others gave peaks with absorption coefficients amounting to more than 10 through 50% of the original curves. The data observed in four solvents are summarized in Table I. The red shift of the peak positions as the solvent changes from cyclohexane(less polar) to acetonitrile(more polar)$^{7)}$ and concomitant intensity decrease suggests that the origin of these excess absorptions are attributable to intramolecular CT interaction.$^{8)}$ The extraordinary long-wavelength CT $\lambda_{max}$ and small intensity of n=1 could be attributed mostly to the blue-shift of its whole absorption curve, and hence the data for n=1 should be regarded as only qualitatively indicating the presence of the interaction. A supporting evidence for this assingment was provided by the data obtained in 95% ethanol. The polarity of this

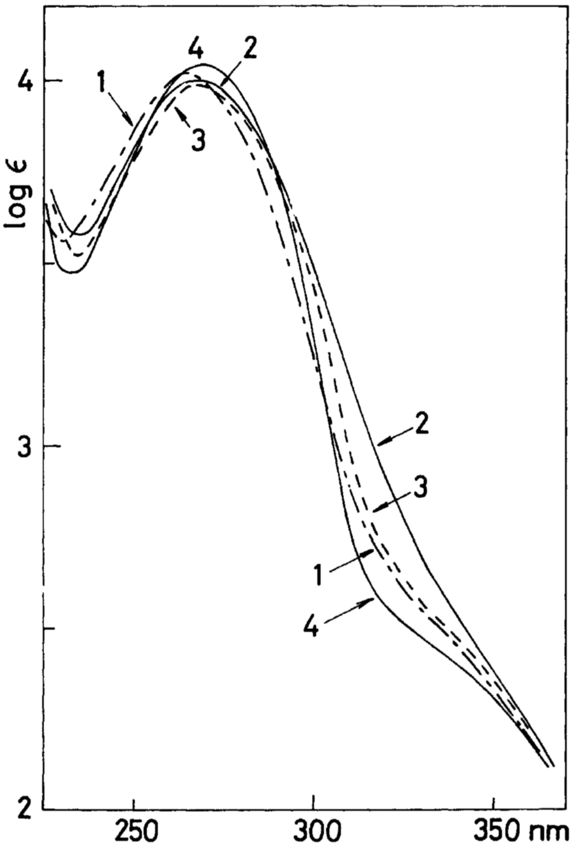


Fig. 1. Ultraviolet spectra of 3 in cyclohexane. The numerals at the curves denote the numbers of methylenes.

TAble I. Intramolecular CT spectra of p-$O_2NC_6H_4(CH_2)_nNMe$ (3)

| Solvent | n=1 | | n=2 | | n=3 | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε |
| Cyclohexane | 308±3nm | 230±10 | 303±2nm | 1100±50 | 303±2nm | 700±30 |
| 1,2-Dichloroethane | 332±5 | 120±10 | 322±2 | 880±20 | 320±2 | 500±10 |
| Acetonitrile | 333±3 | 110±10 | 323±2 | 590±10 | 320±3 | 400±20 |
| 95% Ethanol | * | * | 317±2 | 470±20 | 321±3 | 120±20 |

*Not observed.

solvent is the largest among the four, but the peaks of n=2 and n=3 were blue-shifted, their intensities strongly diminished, and the absorption of n=1 vanished. Assuming the presence of the interaction, the effect could be explained by the decrease of the availability of the lone pair electrons of the amine nitrogen owing to hydrogen bonding with the solvent ethanol.

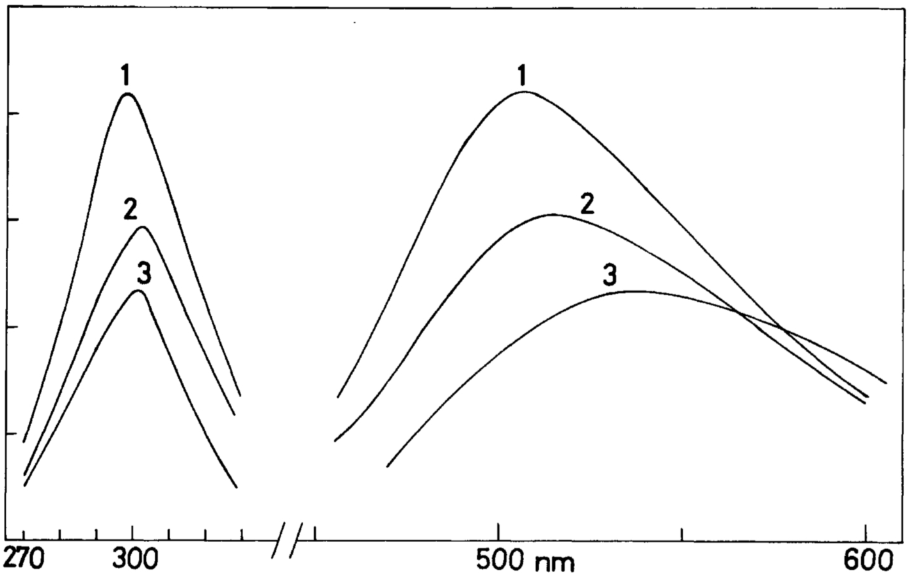


Fig. 2. Fluorescence (right) and their excitation (left) spectra of 3 in cyclohexane-benzene (4:1) mixture at room temperature. The numerals denote the number of methylenes.

<u>Fluorescence spectroscopy</u> In order to further confirm the presence of the CT interaction, the fluorescence spectra of these homologs in cyclohexane-benzene (4:1) mixture were measured at room temperature. No emission was observed in dichloroethane, acetonitrile, and 95% ethanol. The lower three homologs exhibited low intensity fluorescence at ca. 500 nm, which were reproduced in Fig. 2 with their excitation spectra. The highest homolog n=4 showed no fluorescence. Their excitation spectra had maxima at around 300 nm in agreement with the CT absorption peak in cyclohexane. This fact suggests that the fluorescence observed is from the excited state of the intramolecular CT interacting form. The interpretation of the emission in terms of intramolecular exciplex formation could be denied on account of the excitation spectrum and the severe conformational requirements usually observed in this phenomenon; as for the latter, the fact that the n=1 homolog of 2, in contrast to the present case, gave no evidence for the intramolecular formation of exciplex may be cited.

Photoelectron spectroscopy It was expected that the n-$\pi$ type CT interaction should affect the ionization potential (IP) of the n-electrons of dimethylamino group. Thus the photoelectron spectra of these homologs were measured.$^{9)}$ The spectra are shown in Fig. 3. The first band of each compound well separated from the following bands corresponds to the ionization from the n orbital of the amino group: IP(Temp., °C); n=1, 8.67(eV)(93); n=2, 8.61(95); n=3, 8.50(100); n=4, 8.50(103). Concerning the shape and position of these bands, no apparent anomaly which might be ascribed to the intramolecular n-$\pi$ type CT interaction was noticed. This fact suggests that the CT interaction is weak and these compounds are present almost in their open chain forms especially under the experimental conditions employed for the present IP measurement.

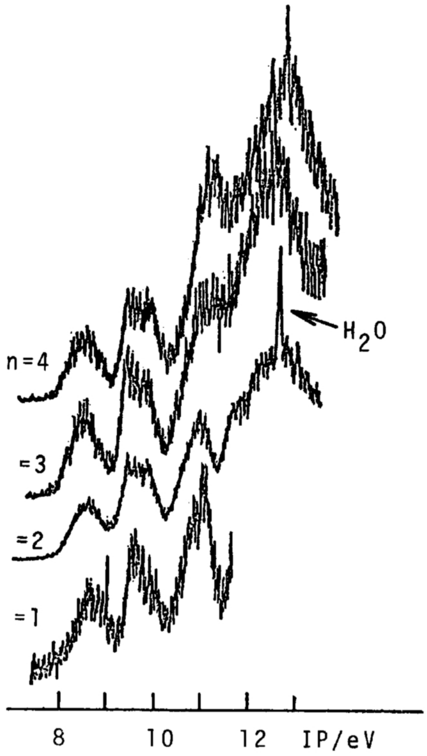


Fig. 3. Photoelectron spectra of p-$O_2NC_6H_4(CH_2)_nNHPh$ (3).

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