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Intramolecular Charge-transfer Interaction in Substituted Diphenylmethanes

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In a previous paper,¹⁾ we have reported that aniline and nitrobenzene in cyclohexane form a loose contact pair, are giving rise to the charge-transfer (CT) absorption as the tail of the long wavelength band of nitrobenzene when the concentrations of both are very high. According to White,²⁾ in the case of 4-amino-4'-nitrodiphenylmethane the across-space CT interaction between aniline and nitrobenzene parts causes a new band at 324 nm (30.9 kK), which is hidden under the intense band of nitrobenzene. Therefore, the presence of the CT band was revealed by the subtraction of the absorption spectra of the reference compounds *i.e.*, *p*-toluidine and *p*-nitrotoluene, from that of 4-amino-4'-nitrodiphenylmethane. For many compounds, the intramolecular CT interaction between two moieties separated by a saturated hydrocarbon chain has been established.³⁻⁷⁾

In this paper, we will deal with the absorption and fluorescence spectra of 4-hydroxy-4'-nitrodiphenylmethane (HN) and 4-amino-4'-nitrodiphenylmethane (AN), aiming to give further evidence for the intramolecular CT interaction in these compounds.

Experimental

Materials. The HN was prepared by the diazo-decomposition of AN according to the method of Tsekhanskii and Fedorov⁸⁾ and was purified by repeated recrystallizations from an ethanol-water mixed solvent; mp 118.5 °C (lit,⁸⁾ 119 °C). The AN was prepared by the partial reduction of 4,4'-dinitrodiphenylmethane according to the method of Litvinenko and Levchenko⁹⁾ and was purified by repeated recrystallizations from a methanol-water mixed solvent; mp 98 °C (lit,⁹⁾ 98 °C). Cyclohexane was purified by standard procedures.

Measurements. The ultraviolet absorption spectra were measured with a Shimadzu Spectrophotometer, D-40D, using 1 cm quartz cells. The fluorescence and excitation spectra were recorded on a Hitachi Fluorescence Spectrophotometer, MPF-2A. The concentrations of solutions were of the order of 10⁻⁴ mol/l. No correction for the sensitivity of the instrument was made. The excitation wave number

was 41.7 kK. All the measurements were carried out at room temperature.

Results and Discussion

The ultraviolet absorption spectrum of HN in cyclohexane does not coincide with that of *p*-nitrotoluene in the wave number region lower than 37.0 kK. When the latter is subtracted from the former, a weak broad band appears at 33.3 kK ($\epsilon=1700$). Similarly, in the case of AN, a weak band appears at 32.3 kK ($\epsilon=1950$) as an extra band. Since the shapes of these extra bands are not dependent on the concentrations of the solutions, they can not be attributed to intermolecular interaction. The extra bands are, therefore, considered to be the intramolecular CT bands. In fact, the CT band of HN appears at a higher wave

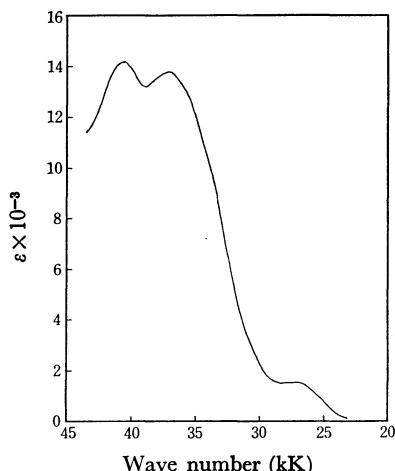


Fig. 1. Absorption spectrum of HN in alkaline aqueous ethanol (pH 13).

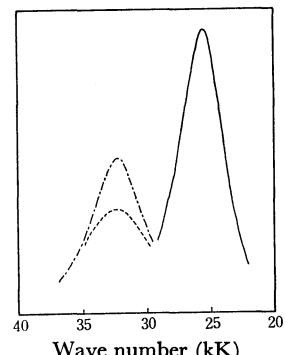


Fig. 2. Absorption (----), fluorescence (—), and excitation (---) spectra of AN in cyclohexane. The absorption band was obtained by subtracting the spectra of the reference compounds.

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number than that of AN, because the ionization potential of HN (8.97 eV) is higher than that of AN (8.14 eV).¹⁰⁾

When the absorption spectrum of HN is measured in alkaline aqueous ethanol (pH 13), the CT band is observed explicitly at 27.0 kK, as is shown in Fig. 1. In this case, the *p*-methylphenolate-ion part acts as the electron donor and its ionization potential seems to be very low compared with those of *p*-cresol and *p*-toluidine.

The presence of the intramolecular CT interaction in HN and AN is confirmed by the fluorescence spectra. That is, new fluorescence bands, which could not be assigned to the reference compounds, appeared at 29.0 and 25.5 kK for HN and AN respectively in

cyclohexane. The fluorescence spectrum of AN, for example, is shown in Fig. 2, in which the excitation spectrum is also presented. As may be seen from this figure, the excitation spectrum agrees well with the extra absorption band. Therefore, this emission is not an excimer fluorescence such as those reported on some diphenyl alkanes,¹¹⁾ but can be attributed to the presence of the intramolecularly-interacting species in the ground electronic state.

It may be expected that the dissociation constant of HN differs from that of *p*-cresol. Accordingly, the pK_a values were determined in a mixed solvent of methanol-water at 25 °C. The pK_a values were 10.8 and 11.1 for HN and *p*-cresol respectively. This can be interpreted in terms of the charge migration from the *p*-cresol part to the *p*-nitrotoluene part in HN.

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