A New Observation on the Polarized Absorption Spectra of TCNNQ Molecular Complexes

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A current explanation for the origin of a second charge-transfer (CT) band which appears in some CT molecular complexes is that the second CT band is mainly associated with a charge transfer from the second highest occupied molecular orbital (HOMO) of a donor molecule to the lowest vacant molecular orbital (LVMO) of an acceptor molecule[1]. In this communication, we show a possibility of the charge transfer from the HOMO of donor to the *second* LVMO of acceptor in some TCNNQ (11, 11, 12, 12,-tetracyano-1,4,-naphthaquinodimethane)-polycyclic aromatic hydrocarbon complexes. A similar interpretation was first given by Iwata, Tanaka and Nagakura for the 1,2,4,5- tetracyanobenzene complexes[2].

We measured the polarized absorption spectra in the visible and ultraviolet regions at room temperature and 80°K for the molecular complexes which involve TCNNQ as an acceptor and anthracene (An), pyrene (Py), phenanthrene (Ph), 1,2-benzanthracene (Ba), chrysene (Ch), and triphenylene (Tp) as donors. The mole ratio of donor and acceptor was found to be 2: 1 for TCNNQ-An, -Py, -Ph complexes (Group 1), while that for TCNNQ-Ba, -Ch, and -Tp complexes (Group 2) was 1:1. Two broad bands were observed in each polarized absorption spectrum of these complexes. In Group 1 complexes, the longer wavelength bands (14-19kK) are clearly polarized along the crystal elongated axes, and the shorter wavelength bands (19-23kK) are perpendicular to them. The two bands of Group 2 complexses, however, both have polarization components, though the dichroic ratios of the longer wavelength bands are two to five times larger than those of the shorter wavelength bands. These two bands are not local excitation bands but can be assigned to be the first and second CT bands, since the lowest transition of TCNNQ has an absorption maximum at 25kK and those of the donors appear at much shorter wavelength regions.

The wave numbers of the absorption maxima ($h\nu_{\mathrm{CT1}}$ and $h\nu_{\mathrm{CT2}}$) are plotted in Fig. 1 against the HOMO energy of donor. For the first CT bands, a straight line is obtained (Line I) as usual, so that these bands are undoubtedly associated with the charge transfer from the HOMO of donor to the LVMO of acceptor.

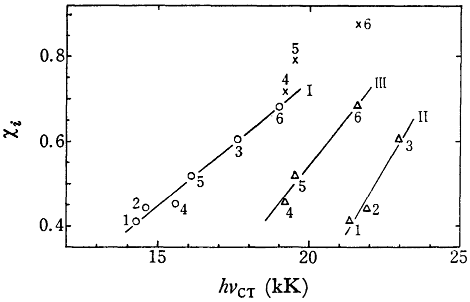

Fig. 1. Charge-transfer transition energies *vs* the Hueckel molecular orbital coefficients, χ_i, of the polycyclic aromatic donors. ○: 1st CT band, △: 2nd CT band; 1:An, 2:Py, 3:Ph, 4:Ba, 5:Ch, 6:Tp. Values of χ_i are taken from C. A. Coulson and A. Stereitwieser, Jr., Dictionary of π-Electron Calculations, W. H. Freeman and Co., San Francisco (1965).

A plot of $h\nu_{\mathrm{CT2}}$ *versus* the HOMO energy of donor produces two linear relationships, one for Group 1 complexes (Line II) and the other for Group 2 complexes (Line III). The charge transfer mechanism for the second CT bands may, therefore, be divided into two classes depending on the mole ratio of donor and acceptor. If we assume a charge transfer from the second HOMO of donor in Group 1 complexes, the magnitude of $h\nu_{\mathrm{CT2}}$ should be in the order An>Py>Ph, which is inconsistent with the present observation. Thus it should be tentatively concluded, that the second CT bands of Group 1 complexes are associated mainly with the charge transfer from the HOMO of donor to the second LVMO of acceptor.

On the other hand, if we plot $h\nu_{\mathrm{CT2}}$ of Group 2 complexes against the second HOMO energy of donor, we obtain the crosses in Fig. 1. Although the data deviate considerably from linearity, some relationship between $h\nu_{\mathrm{CT2}}$ and the second HOMO energy of donor can be recognized. Therefore, we tentatively conclude that the second CT bands of Group 2 complexes are due to a mixed charge transfer mechanism, one from the HOMO of donor to the second LVMO of acceptor and the other from the second HOMO of donor to the LVMO of acceptor.

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1) H. Kuroda, I. Ikemoto and H. Akamatu, This Bulletin, **39**, 1842 (1966), and the references cited therein.

2) S. Iwata, J. Tanaka and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).