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Formation of Infrared Absorbing Dyes.
Carbazole-Naphthoquinone Intermolecular Charge-Transfer Complexes

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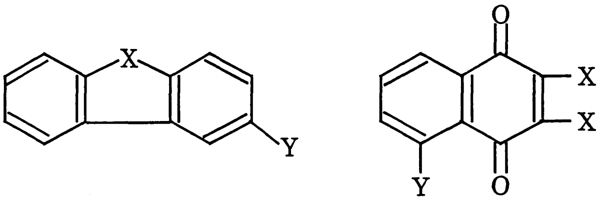
Intermolecular charge-transfer (CT) complexes derived from carbazoles as donors and naphthoquinones as acceptors were evaluated as coloring matters. The PPP MO design, the relation between color and constitution, and the X-ray analysis of the CT complex dye were conducted.

There is a current interest in the development of new dyes for use as functional materials in electronics and optoelectronics devices. There are many dye chromophores which show the intramolecular CT absorption spectra but few are known with respect to the intermolecular CT chromophores which are practically used as coloring matters.

Intermolecular CT complexes have been studied for use as an organic electronic conductor (OEC)$^{1-3)}$ and an organic photoconductor (OPC) for electrophotography.$^{4,5)}$ New types of intermolecular CT complexes are expected not only as OEC or OPC but also as coloring matters. The relation between color and constitution of organic dyes can be evaluated quantitatively by means of the PPP MO calculation method$^{6,7)}$ and the synthetic design from the point of their absorption spectra is now available.$^{8)}$

In this paper, new synthetic design of the intermolecular CT complex dyes by means of the PPP MO method is described. Also the syntheses and the X-ray analysis of infrared absorbing dyes composed of carbazole-naphthoquinone CT complex dyes have been studied.

The donors and acceptors used in this work are summarized in Fig. 1. The carbazoles and their analogues 1 were used as donors. The compounds 1c and 1d are well known as the charge-transfer materials of OPC for electrophotography. The naphthoquinone derivatives 2 were employed as acceptors. The color and structure of the CT dyes can be correlated by the PPP MO method. Figure 2 shows a good linear relationship between the calculated ε_{HOMO} of the donors and the observed ΔE_1 value for the CT dyes obtained from 2a and the various donors. The ε_{HOMO} of donors and the ε_{LUMO} of acceptors can be calculated by the PPP MO method. It was found that the λ_{max} of the CT dyes can be estimated quantitatively from the results in Fig. 2 and the correlation of Eq. 1 is valid.



1

a: X=O, Y=H
b: X=S, Y=H
c: X=NH, Y=H
d: X=NEt, Y=H
e: X=NMe, Y=CH=N-NPh$_2$

2

a: X=CN, Y=NO$_2$
b: X=CN, Y=H
c: X=Cl, Y=NO$_2$

Fig. 1. Donors and acceptors for the CT dyes.

$$\Delta E_1 = -0.66 \times \varepsilon_{HOMO} + 4 \qquad (1)$$

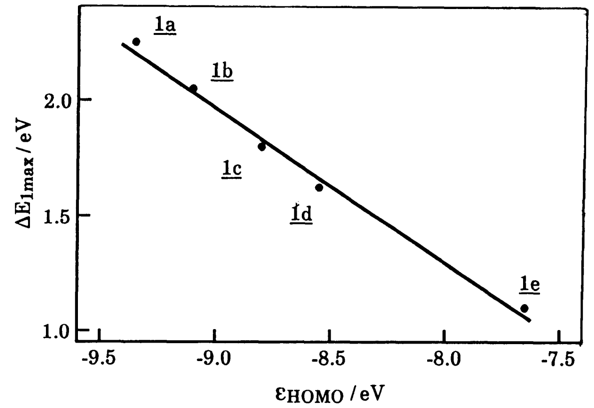


Fig. 2. Linear relationship between ε_{HOMO} of donors and observed ΔE_{1max} (Acceptor : 2a).

Similarly, a good linear relationship can be obtained between the ΔE_1 value and the energy difference between ε_{LUMO} and ε_{HOMO}. Consequently the λ_{max} of the CT dyes in various combinations of the donors and the acceptors can be estimated quantitatively by the PPP MO method.

Table 1 shows the λ_{max} of the CT dyes obtained from 1e and the various acceptors in dichloromethane. The CT dyes were generally formed in the equilibrium mixture, but some of the CT dyes were precipitated from the reaction

Table 1. The absorption maximun of the CT complexes of 1e with various acceptors in dichloromethane

Acceptor	λ_{max1} / nm	λ_{max2} / nm
2a	1100	604
2b	910	546
2c	700	490
TCNE[a)]	950	554
TNF[b)]	660	–
TCNQ[c)]	–	–

a) Tetracyanoethylene.
b) 2,4,7-Trinitro-9-fluorenone.
c) Tetracyanoquinodimethane, no complex formed.

mixture. These CT dyes generally exhibited two absorption maxima at visible and infrared regions. The combination of the strongest donor 1e with the strongest acceptor 2a produced the infrared absorbing dye which absorbs at 650 and 1100 nm, while the CT complex of 1d with 2a absorbed at 580-770 nm. The complex 1e with TCNE showed the absoption peaks at 554 and 950 nm, while that of 1e with TNF did the shoulder at 660 nm. These findings suggest that TCNE is a stronger acceptor than TNF but a weaker one than 2a. No complex was formed between 1e and TCNQ. It was found that a number of CT complex dyes, which absorb the light in the region from visible to infrared wavelengths, can be obtained from the various combinations of the donors 1 and the acceptors 2.

To elucidate the packing mode of the donor and acceptor molecules in the crystals, an X-ray structure analysis has been carried out.

Slow evaporation of a dichloromethane solution of 1:1 mixture of 1d and 2a gave column dark-blue crystals. The crystals belong to the monoclinic space group of $P2_1/n$ with four pairs of 1d and 2a residues in the unit cell of dimensions, a=8.240(1) Å, b=16.576(4) Å, c=15.735(4) Å, and β=97.19(8)°. X-Ray intensities were measured by a four-circle automatic diffractometer with Mo Kα radiation up to 55°. Altogether 4897 reflections were measured, of which 2301 reflections with $|F_o| > 3 (F_o)$ were used for the structure determination.

The structure was solved by the direct method using the program MULTAN 78,[9)] and was refined by the least-square method. All the hydrogen atoms were found and they were included in the least-squares calculations. The final residual index R was 0.078.

The X-ray study verified the 1:1 dye composition in the complex. The molecular arrangements are illustrated in Figs. 3, 4, and 5. In the donor moiety the C-Me bond protrude from the carbazole plane, while in the acceptor moiety the nitro plane is almost perpendicular to the naphthoquinone plane to relieve the steric hindrance between the nitro group and the quinone oxygen atom.

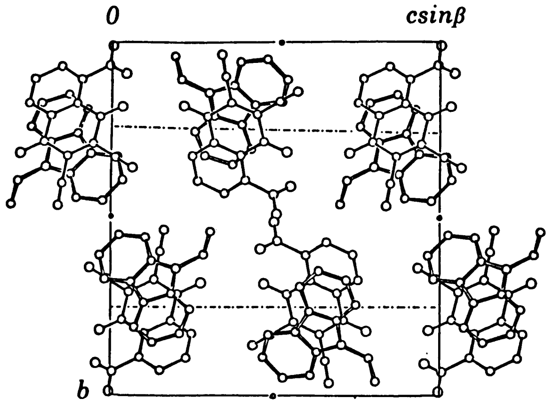


Fig. 3. Crystal structure of the CT complex of 1d and 2a viewed along a axis.

The component molecules are stacked on top of each other to form a column along the a axis. These columns are assembled in a closest packing manner with the usual van der Waals contact between them. In the column the molecular planes are almost parallel to each other(within 1.3). The overlap scheme is illustrated in Fig. 5. The interplanar separations of 3.31 and 3.28 Å are less than the normal van der Waals separations of 3.4 - 3.6 Å between aromatic rings.

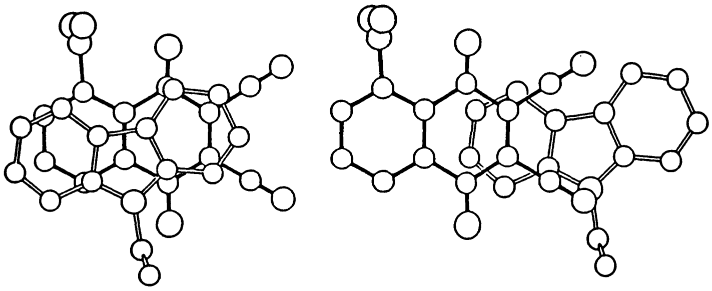


Fig. 4. Two kinds of overlaps between 1d and 2a viewed perpendicular to the molecular plane.

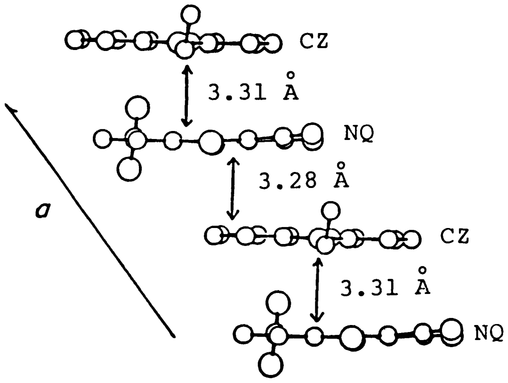


Fig. 5. Alternate stacking mode of 1d and 2a along the a axis, the interplanar separations being given.

In the 2a moiety the bond (bond distance 1.342 Å) between the two carbon atoms to which the CN group is bonded is close to a double bond and resemble the C=C bond of TCNE (tetracyanoethylene). Thus the bond is located on top of the central part of the aromatic ring as in the CT complexes containing aromatic molecule and TCNE (see Fig. 4).[10)]

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