Interchromophoric Homoconjugation Effect and Intramolecular Charge-transfer Transition of the Triptycene System Containing a Tetracyanoquinodimethane Chromophore

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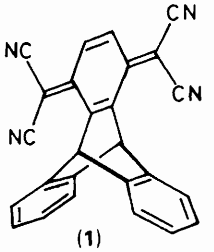
The mechanism of the intramolecular charge-transfer (CT) transition of 2,2′-(9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diylidene)bispropanedinitrile (**1**), a triptycene system containing a tetracyanoquinodimethane (TCNQ) chromophore, has been clarified by the π-electron SCF-CI-dipole velocity (DV) MO calculation. The intramolecular CT transition of (**1**) (λ_{max} 535 nm, log ε 3.40) accepts absorption intensity from the intense π→π* transition of the TCNQ chromophore (λ_{max} 409 nm, log ε 4.66), as follows. The HOMO of the TCNQ group mixes with the HOMO of two benzene groups, by the interchromophoric homoconjugation of a through-space interaction, to build up the new HOMO of the combined system. The CT transition from the new HOMO to the LUMO of TCNQ moiety is partially allowed because the transition includes part of the allowed TCNQ transition. The intensity of the CT transition therefore directly reflects the degree of mixing between the HOMOs of TCNQ and two benzene moieties. The SCF-CI-DV MO calculation corroborates the present mechanism. When the ratio of β(homoconjugation)/β(aromatic) is 35%, the calculated curve is in good agreement with the observed electronic spectrum: Calc., λ_{max} 537 nm (log ε 3.50), λ_{max} 406 nm (log ε 4.59); Found, λ_{max} 535 nm (log ε 3.40), λ_{max} 409 nm (log ε 4.66). As illustrated in Figure 5, the HOMO of the total system obviously contains the HOMO of the TCNQ group. From the results of the calculation the interchromophoric homoconjugation effect β(homo) of the triptycene system was estimated to be *ca*. 30% of the regular aromatic conjugation β(arom).

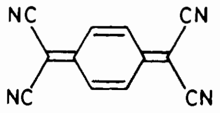
The triptycene system, 9,10-dihydro-9,10-*o*-benzenoanthracene, provides a unique molecular configuration for the investigation of a variety of molecular phenomena because of its very rigid molecular framework and three dimensional disposition of three separate, but still interacting, benzene chromophores. For example, intensive study on the circular dichroism,[1] atrope isomerism,[2] correlated rotation,[3,4] *etc*., has been performed using various kinds of triptycene derivatives. On the nature of the interchromophoric interaction of the triptycene π-electron system, there have been many active discussions[5] since the first synthesis of triptycene by Bartlett.[6] The problem is whether the three benzene chromophores of triptycene interact with one another, and if they do, which interaction of through-space and through-bond is dominant?

One group of authors has reported that the interchromophoric homoconjugation effect of the π-electron system makes a dominant contribution to the c.d. spectra of optically active triptycene compounds.[7,8] In some cases, the shape of the c.d. curve becomes more complex than those of the typical bisignate c.d. Cotton effects expected from the exciton coupling mechanism. Such phenomena were explained well in terms of the interchromophoric homoconjugation effect of the π-electron system, *i.e*., the through-space interaction between three benzenoid chromophores.

A second group of authors[9] has also studied the present problem of the interchromophoric interaction from the viewpoint of the intramolecular charge-transfer (CT) transition observed in the electronic spectra of electron donor–acceptor triptycene systems.[10] Furthermore, Kobayashi and co-workers[11] reported, from studies of the photoelectron spectroscopy of triptycene, that the through-space interaction[12] is predominant for the first six π-MOs, while the through-bond interaction is negligibly small. In this paper, we report clear-cut evidence for the through-space interaction, *i.e*., the interchromophoric homoconjugation effect of the π-electron chromophores of the triptycene system, on the basis of a theoretical calculation of the intramolecular charge-transfer band observed in the system of 2,2′-(9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diylidene)bispropanedinitrile (**1**), and we also describe the mechanism of the intramolecular charge-transfer transition.



(**1**)



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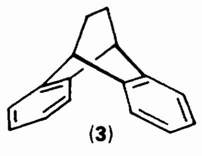

(**3**)

Methods of Calculation

Molecular Structure.—The cartesian co-ordinate system for compound (**1**) is shown in Figure 1, in which the *x*-axis is the

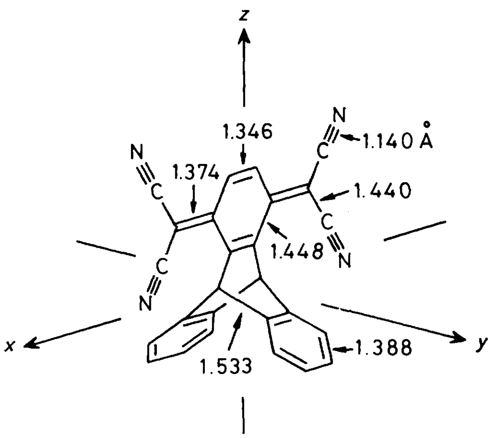

Figure 1. Geometric parameters of compound (**1**) used for the calculation.

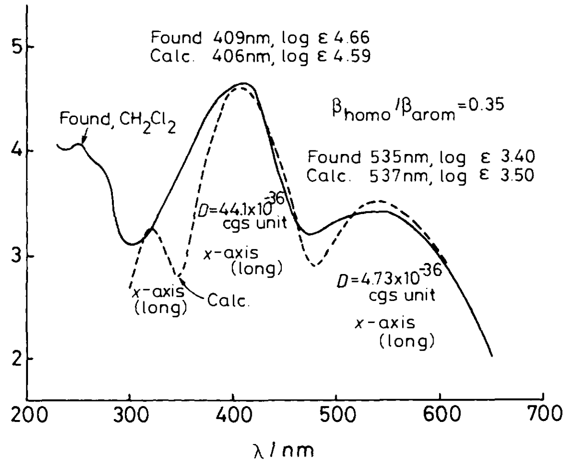

Figure 2. Observed and calculated electronic spectra of the TCNQ–triptycene compound (**1**).

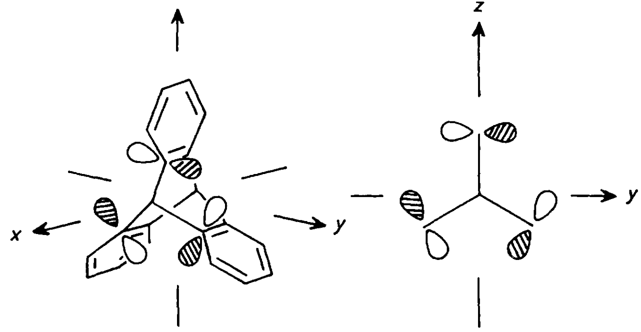

Figure 3. Cyclic interchromophoric homoconjugation effect of the Möbius type in the system of triptycene. The phase of the basic wavefunction of atomic orbitals was taken as shown for the sake of simplicity of calculation.

long axis of the tetracyanoquinodimethane (TCNQ) chromophore. The co-ordinates of atoms were calculated by employing the geometric parameters shown in Figure 1, which were taken from the *X*-ray crystallographic data of TCNQ (**2**)[13] and 6-chloro-1,4-dimethyltriptycene.[14] The bond angles of the sp^2 carbons and the dihedral angles between the two benzene rings and the TCNQ moiety were taken to be *ca.* 120°, respectively.

Numerical Calculations of Electronic Spectra.—The u.v. and visible spectrum of compound (**1**) was calculated by the π-electron SCF-CI-dipole velocity (DV) MO method.[8,15,16] In the calculation, configuration interactions between all singly excited states were included, and the following standard values of atomic orbital parameters[17,18] were used: $W(\mathrm{C}) = -11.16$ eV, $(rr|rr)(\mathrm{C}) = 11.13$ eV, $\beta(\mathrm{C–C}$: 1.388 Å$) = -2.32$ eV, $\langle\nabla\rangle(\mathrm{C–C}$: 1.388 Å$) = 4.70 \times 10^7\ \mathrm{cm^{-1}}$; $W(\mathrm{N}) = -16.18$ eV, $(rr|rr)(\mathrm{N}) = 11.52$ eV, $\beta(\mathrm{C–N}) = -3.95$ eV, $\langle\nabla\rangle(\mathrm{C–N}) = 5.98 \times 10^7\ \mathrm{cm^{-1}}$. The electric repulsion integral $(rr|ss)$ was estimated by the Nishimoto–Mataga equation. The resonance integral β and $\langle\nabla\rangle$ values were calculated by employing the following equations, respectively:

$$\beta = [S/S(\mathrm{C–C}\text{: 1.388 Å})]\beta(\mathrm{C–C}\text{: 1.388 Å}) \quad (1)$$

$$\langle\nabla\rangle = [\langle\nabla\rangle(\text{empir.: 1.388 Å})/\langle\nabla\rangle(\text{theor.: 1.388 Å})]\langle\nabla\rangle(\text{theor.}) \quad (2)$$

The shape of the component u.v. bands was approximated by the Gaussian distribution [equation (3)] where $2\Delta\sigma$ is the

$$\varepsilon(\sigma) = \Sigma\varepsilon_k \exp\{-[(\sigma - \sigma_k)/\Delta\sigma]^2\} \quad (3)$$

$1/e$-width of the bands. The $\Delta\sigma$ value of 1 715.9 $\mathrm{cm^{-1}}$ was taken from the observed electronic spectrum of TCNQ (**2**).

The numerical calculations were carried out on a HITAC M200H computer at the Computer Centre of the Institute for Molecular Science.

Results and Discussion

Interchromophoric Homoconjugation and Intramolecular Charge-transfer Transition of TCNQ–Triptycene Compound (**1**).—The u.v. and visible spectra of compound (**1**), an electron donor–acceptor system, exhibits a typical charge transfer (CT) band of λ_{max} 535 nm, log ε 3.40, in addition to the intense π→π* TCNQ band of λ_{max} 409 nm, log ε 4.66, as shown in Figure 2. This CT absorption band is usually assigned to the transition of the electron migration from the electron donor of benzene to the electron acceptor of TCNQ, *i.e.*, the CT transition of the HOMO of 9,10-dihydro-9,10-ethanoanthracene (**3**) to the LUMO of TCNQ (**2**): $\varphi(\text{HOMO:benzene}) \longrightarrow \varphi(\text{LUMO: TCNQ})$. However, if this is simply so, the observed medium intensity of the CT band can not be explained, because the theoretical value of the electric transition moment between the LUMO of TCNQ and HOMO of benzene moieties is *ca.* 0. Namely, since the MOs of TCNQ and benzene moieties contain no common atomic orbitals, the integral of the electric transition moment which governs the absorption intensity becomes zero to the first approximation:

$$\mu = \langle\varphi(\text{LUMO:TCNQ})|er|\varphi(\text{HOMO:benzene})\rangle \approx 0 \quad (4)$$

In the triptycene system, although the π-atomic orbitals of the bridge carbons of the three benzene moieties are separated from one another, they can partially conjugate to one another because of the proximity and mutual overlap of the atomic orbitals, as in the case of the spiroconjugation of spirocyclic systems.[19] Namely, these atomic orbitals of triptycene make a cyclic homoconjugation system of Möbius type (Figure 3). The present interchromophoric homoconjugation effect makes a dominant contribution to the intensity of the CT transition, as described below.

By interchromophoric homoconjugation of the atomic orbitals of the bridge carbons, the HOMO of the benzene

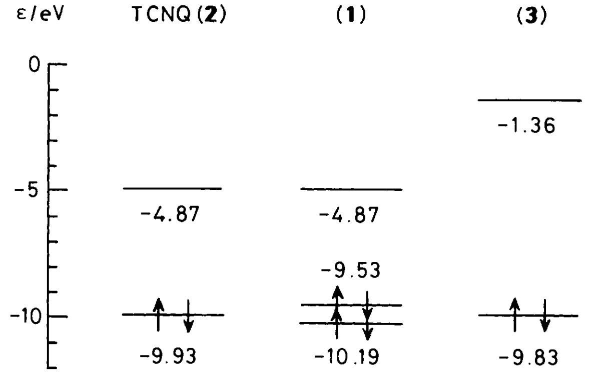

Figure 4. Calculated energy levels of the LUMO and HOMOs of compounds (**1**), (**2**), and (**3**).

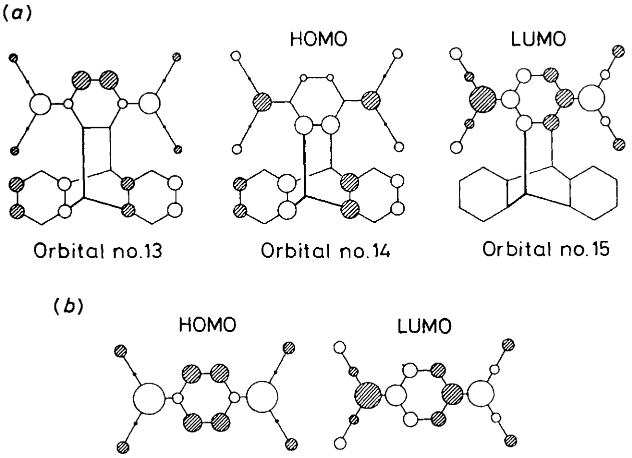

Figure 5. Calculated molecular orbital distribution: (*a*) compound (**1**). The phase of the upper lobe of the orbitals is shown for the benzene moieties, while the phase of the right-side lobe of the orbitals is illustrated for the TCNQ part. (*b*) TCNQ (**2**).

moiety mixes with the HOMO of TCNQ group to build up the new HOMO of the total system of (**1**):

$$\varphi(\text{HOMO:total}) = C_1\varphi(\text{HOMO:TCNQ}) + C_2\varphi(\text{HOMO:benzene}) \quad (5)$$

where C_1 and C_2 are the coefficients of the mixing. In this case, the two MOs coincide with each other in the symmetry of orbitals. On the other hand, the LUMO of the total system is mainly composed of the LUMO of TCNQ:

$$\varphi(\text{LUMO:total}) = \varphi(\text{LUMO:TCNQ}) \quad (6)$$

Since the TCNQ transition from φ(HOMO:TCNQ) to φ(LUMO:TCNQ) is strongly allowed as observed in the intense $\pi \rightarrow \pi^*$ band at 409 nm, the mixing of the two HOMOs of φ(HOMO:benzene) and φ(HOMO:TCNQ) makes the CT transition of compound (**1**) from φ(HOMO:total) to φ(LUMO:total) partially allowed. Therefore, the intensity of the CT transition directly reflects the extent of the mixing *i.e.*, the value of the mixing coefficient C_1. Namely, the CT transition becomes allowed by borrowing absorption intensity from the intense $\pi \rightarrow \pi^*$ TCNQ transition. Therefore, from the observed intensity of the CT transition, one can inversely estimate the extent of the mixing of the two HOMOs of benzene and TCNQ in the system of compound (**1**). The TCNQ–triptycene compound (**1**) is thus an ideal compound for the evaluation of the interchromophoric through-space interaction of the triptycene system.

Numerical Calculation of the U.V. and Visible Spectra of TCNQ–Triptycene Compound (**1**).—In order to establish the above mechanism of the CT transition and interchromophoric homoconjugation effect in a more quantitative sense, we then performed a numerical calculation of the u.v. and visible spectra of compound (**1**). The π-electron SCF-CI-dipole velocity MO method has been accepted to be a powerful and reliable method for the calculation of the u.v. and c.d. spectra of many conjugated π-electron systems;[7,8,20] it was now applied to the calculation of the electronic spectrum of (**1**).

In the MO calculations, we incorporated the effect of the interchromophoric homoconjugation as the resonance integral, β(homo), between the two atomic orbitals of bridge carbons (Figure 3), and gradually changed the value of β(homo). As will be discussed later, when the value of β(homo) is *ca.* 35% of that of the resonance integral, β(arom), of the regular aromatic C–C bond, the best-fit between the calculated and observed u.v. and visible spectra was obtained (Figure 2). So, in the following discussions, the value of the homoconjugation resonance integral is fixed as $\beta(\text{homo}) = 0.35\ \beta(\text{arom})$.

The calculated energy levels and molecular orbital distributions of the HOMOs and LUMOs of compound (**1**), TCNQ (**2**), and compound (**3**) are illustrated in Figures 4 and 5, respectively. The results of the calculation indicate that the HOMOs of TCNQ (**2**) and compound (**3**) are very close to each other in energy. Therefore, if the two HOMOs coincide with each other in the symmetry of orbitals, they can easily mix with each other to build up the two new HOMOs of the total system. In fact, it was calculated that the HOMO (orbitals No. 14, $E = -9.53$ eV) and second HOMO (orbital No. 13, $E = -10.19$ eV) of compound (**1**) were delocalized over TCNQ and the two benzene moieties, respectively (Figure 5). In the two HOMOs, the pattern of the molecular orbital distribution of the TCNQ part resembles that of the HOMO of the parent TCNQ (**2**). On the other hand, the LUMO of compound (**1**) is composed of the LUMO of TCNQ only.

In the calculation of excited states, configuration interactions between all singly excited states were included to give the following state energies and wavefunctions:

CT transition, $E = 2.297$ eV

$$\psi = 0.910\,(\varphi_{14} \longrightarrow \varphi_{15}) + 0.352\,(\varphi_{13} \longrightarrow \varphi_{15}) + \cdots \quad (7)$$

TCNQ transition, $E = 3.058$ eV

$$\psi = -0.379\,(\varphi_{14} \longrightarrow \varphi_{15}) + 0.887\,(\varphi_{13} \longrightarrow \varphi_{15}) + \cdots \quad (8)$$

These results provide important knowledge on the nature of the CT and TCNQ transitions. The CT transition is mainly composed of the two component transitions, ($\varphi_{14} \longrightarrow \varphi_{15}$) from HOMO to LUMO and ($\varphi_{13} \longrightarrow \varphi_{15}$) from the second HOMO to LUMO; the former component transition makes a more dominant contribution to the CT transition than the latter. Although both of the coefficients have the same positive sign, since the two component transition moments calculated are opposite in phase to each other, the intensity of the CT transition becomes weak.

The TCNQ transition is also composed of the same two component transitions, ($\varphi_{14} \longrightarrow \varphi_{15}$) and ($\varphi_{13} \longrightarrow \varphi_{15}$). In this case, however, the latter component transition is predominant and the two coefficients of the wavefunction are different in sign from each other. Therefore, the TCNQ transition becomes more intense than the CT transition. It should be emphasized that both of the CT and TCNQ transitions of (**1**) consist of the same two component transitions which are polarized along the *x*-axis, *i.e.*, the long axis of the TCNQ chromophore.

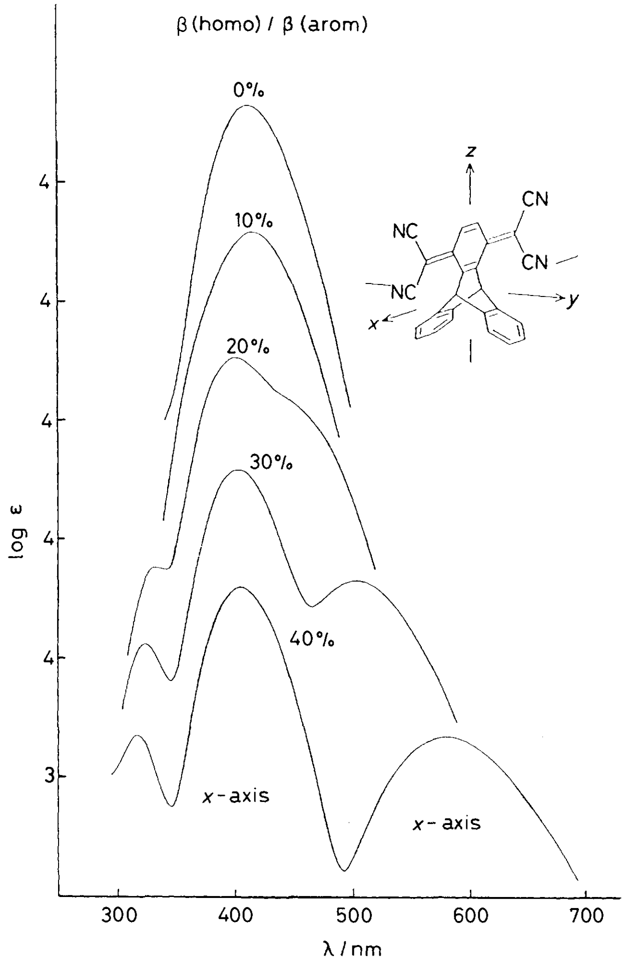

Figure 6. Electronic spectrum curve of compound (**1**) obtained by the π-electron SCF-CI-DV MO calculation, in which the value of the resonance integral for the interchromophoric homoconjugation effect was changed.

In order to evaluate the value of the homoconjugation resonance integral between the atomic orbitals of the bridge carbons of the triptycene system, the electronic spectrum of (**1**) was calculated by changing the ratio of β(homo)/β(arom) where β(arom) = −2.32 eV. When the ratio is 0 and 10%, only the TCNQ absorption band is obtained (Figure 6). At 20%, the CT transition appears as a shoulder of the main band. At 30 and 40%, the CT band obviously separates from the TCNQ band. As the ratio increases, the spectrum curve shows a red shift of the CT absorption band, while the TCNQ band remains at the same position.

As shown in Figure 2, when the ratio is 35%, the best-fit between the calculated and observed electronic spectra was obtained: Calc., λ_{max} 537 nm, log ε 3.50, and λ_{max} 406 nm, log ε 4.59; Found, λ_{max} 535 nm, log ε 3.40, and λ_{max} 409 nm, log ε 4.66. The calculated dipole strength of the CT transition is *ca.* one tenth of that of the TCNQ transition. The u.v. and visible spectra of (**1**) have been thus reproduced well by the molecular orbital calculation including the effect of the interchromophoric homoconjugation. The theoretical value of the ratio β(homo)/β(arom) of the triptycene system has been reported to be *ca.* 25% on the basis of the through-space interaction. Therefore, the present experimental value of 35% is reasonable by comparison with the theoretical value and the previously reported value of 20–30% obtained from the c.d. spectra of chiral triptycene compounds.[7,8] The results of the calculation thus clearly indicate that the interchromophoric homoconjugation effect due to the through-space interaction between the atomic orbitals of the bridge carbons is crucial to the electronic spectra of triptycene compounds.

Conclusions

The present studies revealed that the charge transfer band of the electronic spectrum of the TCNQ–triptycene compound (**1**) can be accurately reproduced by a molecular orbital calculation based on the π-electron SCF-CI-DV MO method, and we have clarified the mechanism proposed, *i.e.*, that the CT transition accepts absorption intensity from the allowed TCNQ transition on the basis of the mixing of HOMOs due to the interchromophoric homoconjugation between the three chromophores of triptycene. The calculation results also elucidated that the through-space interaction between the atomic orbitals of bridge carbons make a dominant contribution to the interchromophoric interaction of the triptycene system.

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