constant morphology. This conclusion is derived in part from preliminary investigations of circular dichroic spectra.[14]

On the basis of the results described here, we believe that there is good hope for the design of quite simple synthetic systems that will approach the selectivity of NAD(P)H. Work is continuing in this effort.

(14) CD experiments have thus far been carried out on the more stable bridged pyridines rather than 1,4-dihydropyridines.

Charge-Transfer Transition for Symmetry-Forbidden Charge-Transfer Interaction in 1,4-Dihydro-1,4-bis(dicyanomethylene)triptycenes[1]

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Recently, we have prepared the 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate (1), which consists of the tropylium ion and two benzene rings with rigid spatial arrangement identical with triptycene as a pertinent model for the intramolecular charge transfer.[2] In fact the electronic spectrum of 1 exhibited a clear charge-transfer (CT) band at 300–450-nm region as a broad absorption. The doubly degenerate LUMO's of the tropylium ion may complicate the situation. Since tetracyanoquinodimethane (TCNQ) known as a strong electron acceptor has a single LUMO, the triptycene-type compound in which a benzene ring is replaced by TCNQ moiety appears to be an attractive model. In a recent communication[3] we have already reported the synthesis of 1,4-dihydro-1,4-bis(dicyanomethylene)tripytcene (2a) and its 6-methoxy derivative (2b) which showed distinct CT bands in their electronic spectra. In this communication we describe the theoretical analysis of the electronic structure of 2 leading to an interesting but rarely documented notion—*charge-transfer transition for symmetry-forbidden charge-transfer interaction*—and present unequivocal experimental support by the substituent effects on the CT band shifts.

In 1,4-dihydro-1,4-bis(dicyanomethylene)triptycene (2a), which is assigned to the C_{2v} point group, there are four high-lying occupied molecular orbitals localized on the electron-donating benzene rings. They are in-phase and out-of-phase combinations of degenerate HOMO's of benzene as shown in Figure 1. The sequence of the orbital energy levels is determined by the through–space interaction rather than by the through–bond interaction, because the dihedral angle ($\sim120°$) between benzene rings is small enough.[4] The LUMO of the triptycene 2a localizes on the electron-accepting TCNQ ring. From the group
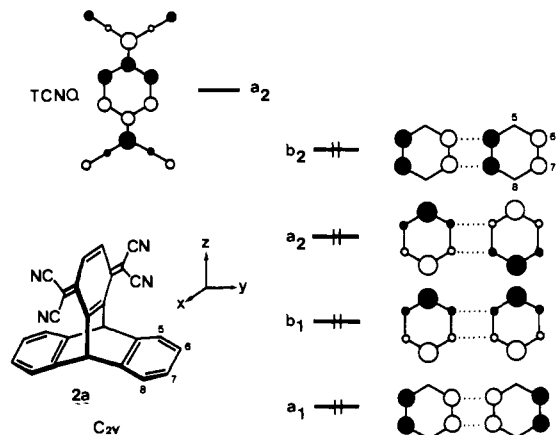

Figure 1. The high-lying MO's of electron-donating benzene rings and the LUMO of TCNQ in 1,4-dihydro-1,4-bis(dicyanomethylene)-triptycene (2a).
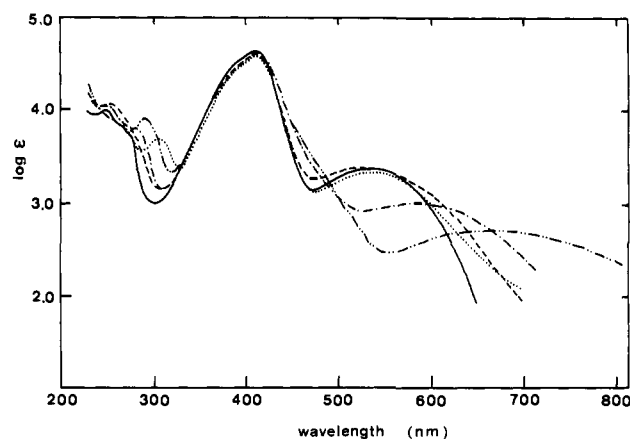

Figure 2. Electronic spectra of 2a (—), 2b (– · – ·), 2c (– –), 2d (– ·· –), and 2e (···) in dichloromethane.

Table I

symmetry	CT interaction	CT transition
$b_2 \rightarrow a_2$	forbidden	allowed (x)
$a_2 \rightarrow a_2$	allowed	allowed (z)
$b_1 \rightarrow a_2$	forbidden	allowed (y)
$a_1 \rightarrow a_2$	forbidden	forbidden

theory some interesting conclusions are drawn (see Table I): (i) the lowest energy CT transition ($b_2 \rightarrow a_2$) is allowed in spite of the symmetry forbiddenness of the corresponding CT interaction, and (ii) the charge transfer in the ground state occurs only from the second HOMO (a_2). In most of usual CT complexes the same electron-transferred configuration contributes to the ground- and excited-state wave functions.[5] For the triptycene 2a the main transferred configurations are different between both states and exclusive to each other:

$$\Psi = C_1\Phi_G + C_2\Phi_T(b_2 \rightarrow a_2) + C_3\Phi_T(a_2 \rightarrow a_2) + \dots$$

where $|C_1| > |C_3|$, $C_2 = 0$ for the ground state and $C_1 = C_3 = 0$, $C_2 \neq 0$ for the first excited state. As a result, in 2a the first CT excitation accompanies the electronic transition from the HOMO (b_2) of the benzene rings to the LUMO (a_2) of the TCNQ moiety, while electrons delocalize from the second HOMO (a_2) of the donor to the LUMO (a_2) of the acceptor in the ground state.

A series of methoxy-substituted derivatives allows us to examine such a CT transition. The AO coefficient in the b_2 orbital is zero at the 5 and 8 positions and large at the 6 and 7 positions. It is then predicted that 5 and/or 8 substituents exhibit little effect on the wavelength of the CT absorption maximum while elec-

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(2) (a) Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* **1977**, *99*, 1996. (b) Nakazawa, T.; Abe, N.; Kubo, K.; Murata, I. *Tetrahedron Lett.* **1979**, 4995. See also: (c) Komatsu, K.; Takahashi, K.; Okamoto, K. *Ibid.* **1979**, 4747. (d) Nakazawa, T.; Niimoto, Y.; Kubo, K.; Murata, I. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 545. (e) Nakazawa, T.; Kubo, K.; Murata, I. *Ibid.*, in press.

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(5) Foster, R. "Organic Charge Transfer Complexes"; Academic Press: New York, 1969.

Table II. Physical Properties of 2a–e

compd	appearance	mp, °C	visible region λ_{max}, nm (log ϵ) CH$_2$Cl$_2$	CH$_3$CN	^{1}H NMR (CD$_2$Cl$_2$), 100 MHz δ values
2a[a]	red micro needles	>300	409 (4.66) 535 (3.40)	403 (4.61) 505 (3.45)	7.56, 7.13 (AA'BB', 8 H), 7.34 (s, 2 H), 6.84 (s, 2 H)
2b[a]	green powder	>300	411 (4.66) 584 (3.02)	403 (4.64) 544 (3.09)	7.52, 7.12 (AA'BB', 4 H), 7.40 (d, 1 H, J = 8 Hz), 7.34 (s, 2 H), 7.14 (d, 1 H, J = 2.5 Hz), 6.76 (s, 2 H), 6.60 (dd, 1 H, J = 8, 2.5 Hz), 3.75 (s, 3 H)
2c	red powder	>300	409 (4.66) 530 (3.34)	403 (4.60) 500 (3.37)	7.60–6.98 (m, 6 H), 7.31 (s, 2 H), 7.06 (s, 1 H), 6.81 (s, 1 H), 6.68 (dd, 1 H, J = 8, 2 Hz), 3.88 (s, 3 H)
2d	dark green needles	>300	410 (4.64) 662 (2.72)	404 (4.60) 612 (2.66)	7.53, 7.11 (AA'BB', 4 H), 7.33 (s, 2 H), 7.13 (s, 2 H), 6.73 (s, 2 H), 3.80 (s, 6 H)
2e	red needles	>300	408 (4.61) 533 (3.34)	403 (4.59) 506 (3.37)	7.56, 7.10 (AA'BB', 4 H), 7.32 (s, 2 H), 7.27 (s, 2 H), 6.61 (s, 2 H), 3.84 (s, 6 H)

[a] See ref 3.

tron-donating 6 and/or 7 substituents cause the red shift to the extent proportional to the number of substituents. In fact the red shift was observed for 6-methoxy derivative (2b).[3] This result does not rule out the other allowed (a$_2$ → a$_2$) and (b$_1$ → a$_2$) transitions because the electron-donating a$_2$ and b$_1$ orbitals also have a considerable AO coefficient at the 6 position. We now prepared 5-methoxy- (2c), and 6,7-dimethoxy- (2d), and 5,8-dimethoxy derivatives (2e) to confirm the CT transition for the symmetry-forbidden CT interaction.

The synthesis of 1,4-dihydro-1,4-bis(dicyanomethylene)-triptycenes substituted with methoxy group(s), 2c–e, was achieved starting from the corresponding triptycenes, 3c–e, respectively.
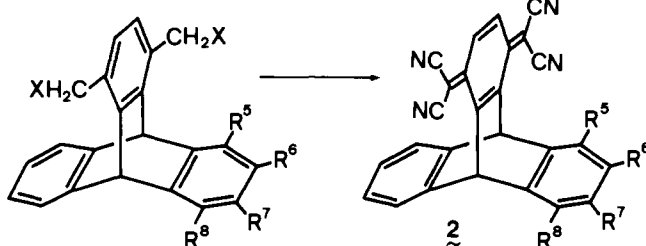
3 : X = H   a : R^5=R^6=R^7=R^8=H ;

4 : X = Br   b : R^6=OCH$_3$, R^5=R^7=R^8= H

5 : X = CN   c : R^5=OCH$_3$, R^6=R^7=R^8= H

                   d : R^6=R^7=OCH$_3$, R^5=R^8= H

                   e : R^5=R^8=OCH$_3$, R^6=R^7= H

1,4-Dimethyl-5-methoxytriptycene (3c),[6] colorless needles, mp 198 °C, 12% yield, and 1,4-dimethyl-6,7-dimethoxytriptycene (3d),[6] colorless prisms, mp 179 °C, 38% yield, were readily prepared from 1,4-dimethylanthracene with 6-methoxybenzene-diazonium-2-carboxylate or 4,5-dimethoxybenzenediaznoium-2-carboxylate, respectively. On the other hand, 1,4-dimethyl-5,8-dimethoxytriptycene (3e)[6] could be obtained through the Diels–Alder reaction of 1,4-dimethylanthracene with p-benzoquinone followed by successive treatment with aqueous potassium hydroxide and dimethyl sulfate in 24% yield.

Bromination of the triptycene 3c with N-bromosuccinimide [(PhCO)$_2$O$_2$ in benzene, reflux, 3h] gave 1,4-bis(bromomethyl)-5-methoxytriptycene (4c),[6] colorless prisms, mp 225–226 °C, 85% yield, which was cyanated with potassium cyanide in acetonitrile in the presence of 18-crown-6 [reflux, 5 h] to the bis(cyanomethyl) derivative (5c),[6] colorless microcrystals, mp 291–292 °C, 45% yield. Conversion of 5c into the TCNQ-type compound 2c[6] could be accomplished according to the Wheland–Martin procedure for TCNQ synthesis[7] as well as our synthesis of 2a and 2b reported previously.[3] The compound 2c

was obtained as dark red needles in 7.6% yield. Similarly, di-methoxytriptycenes, 3d and 3e, readily gave 2d and 2e in 7.1% and 7.3% yields, respectively (Table II).[6,8]

The electronic spectra of 2c–e together with those of 2a and 2b are shown in Figure 2. It is quite clear that in spite of the presence of methoxy group(s) the observed absorption maxima of the CT bands for 2c and 2e are almost the same with that of the parent compound 2a, whereas the compounds having methoxy group(s) at 6 (2b) and 6,7 positions (2d) display the successive red shift by 49 and 127 nm, respectively, with increasing number of methoxy substitutions (see Table II). These observations strongly support the idea of the CT transition for the symmetry-forbidden CT interaction.[9] Further elucidation of this idea by means of the synthesis of 1,4-dihydro-1,4-bis(dicyanomethylene)triptycenes substituted with electron-withdrawing group(s) is the subject of our current attention and is now in progress.

A similar theoretical analysis predicts that the first CT excitation in the triptycene with one benzene ring and two TCNQ groups (6) is another example, but the influencing positions of

6
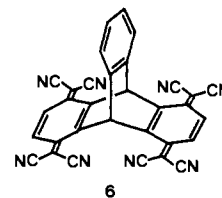
substituents on the benzene ring are opposite to those of 2. The CT band shift is more measurably caused by the substitution on the carbons next to the bridge rather than the distant ones. This will be a target molecule in near future.

(8) 4d, colorless microcrystals, mp 211 °C, 79%; 5d, colorless microcrystals, mp 240–242 °C, 42%; 4e, colorless powder, mp >300 °C, 80%; 5e, colorless microcrystals, mp >300 °C, 40%.

(9) Recently, Iwamura and Makino[10] have reported the synthesis of 5,8-dimethoxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-1,4-dione (i) which

i   ii
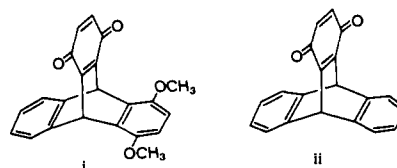
exhibits the CT band at 411 nm (ϵ 450) in acetonitrile. Our treatment described in the text can also be applied to i. In fact, the CT absorption maximum of i was found to be almost the same as that reported for the unsubstituted analogue ii which has a CT band at 415 nm (ϵ 320) in chloroform.[11] It is predicted that the 6,7-dimethoxy derivative of ii should exhibit fairly large red shift of its CT band compared with those of i and ii.

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(11) Birnbaum, H.; Cookson, R. C.; Lewin, N. *J. Chem. Soc.* **1961**, 1224.

(6) All new compounds afforded proper combustion analyses as well as suitable IR and NMR spectra.

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