

CHARGE TRANSFER TRANSITION FOR SYMMETRY-FORBIDDEN CHARGE TRANSFER INTERACTION. THEORY AND EXPERIMENTAL VERIFICATION

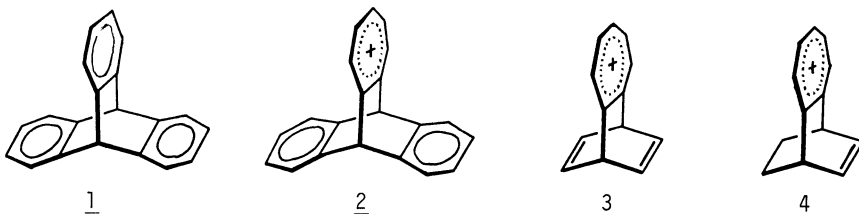
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Abstract - The group theoretical analysis of the electronic structure of 1,4-dihydro-1,4-bis(dicyanomethylene)tritycene leads to an interesting but rarely documented notion, "charge transfer transition for symmetry forbidden charge transfer interaction", which was supported by the substituent effects on the charge transfer band shifts. The substituent effects on the charge transfer band shifts were also observed in a series of 9,10-dihydro-9,10-o-benzoanthracene-1,4-diones. These results provide decisive evidence for the fact that the orbitals involved in the ground state charge transfer interaction need not be the same as those involved in the charge transfer transition. In general, charge transfer phenomena between donor and acceptor components fixed in the rigid frameworks of C_{2v} and C_s point groups are also discussed by means of the symmetry properties of the interacting orbitals.

INTRODUCTION

Mulliken's valence bond treatment of weak intermolecular complexes between electron donors and acceptors provided a main stimulus to the extensive developments in the rich and varied field of chemistry and physics related to the intermolecular charge transfer (CT) interaction and transition (Ref. 1-5). The CT concept has also been extended to a wide range of problems in the intramolecular CT complexes. Since the first synthesis of triptycene (1) by Bartlett and co-workers in 1942 (Ref. 6), transannular electronic interaction between the remote (non-conjugated) benzene rings has been of particular interest and still remains a matter of controversy (Ref. 7). In order to confirm such an interaction, it is important to select the pertinent model system and the proper method of measurements which should be sufficiently sensitive to detect the interaction. In this context, we have recently synthesized 9,10-dihydro-9,10-(o-tropylio)anthracene tetrafluoroborate (2) and shown clear experimental evidence for intramolecular CT transition between the benzene and the tropylium ring (Ref. 8).



Olefins should conceivably be able to replace the aromatic hydrocarbon moiety as the donor for a more fundamental probe. The tropylium analogues of barrelene (3) (Ref. 9) and of bicyclo[2.2.2]octadiene (4) (Ref. 10) were also prepared and found to be simpler models for such CT complexes. Although the tropylium ion was found to be a good electron acceptor (Ref. 11), the doubly degenerate LUMO's of the tropylium ion may complicate the situation being considered. Since tetracyanoquinodimethane (TCNQ) known as a strong electron acceptor has a low-lying single LUMO, the triptycene type compound in which a benzene ring is replaced by TCNQ ring seems to be an attractive model compound for the analysis of the intramolecular CT phenomena.

1,4-DIHYDRO-1,4-BIS(DICYANOMETHYLENE) TRIPTYCENES

Electronic structure

In 1,4-dihydro-1,4-bis(dicyanomethylene)tritycene (5), which is assigned to the C_{2v} point group, there are four high-lying occupied molecular orbitals mainly localized on the electron donating benzene rings. Figure 1 shows in-phase and out-of phase combination of degenerate

HOMO's of benzene rings where the sequence of the orbital energy levels is determined by the through-space (homoconjugative) interaction rather than by the through-bond interaction,

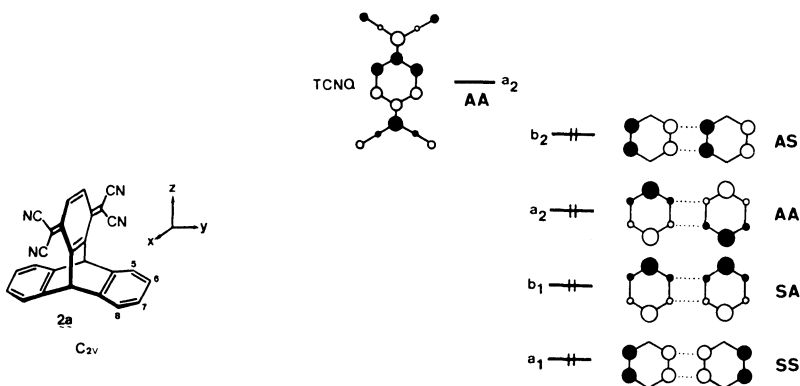


Fig. 1. Symmetry axis of (5) and the high-lying HOMO's of benzene rings and the LUMO of TCNQ in (5).

since the dihedral angle ($\sim 120^\circ$) between the benzene rings is small enough (Ref. 12). The LUMO of the TCNQ-triptycene (5) is considered to be localized on the electron accepting TCNQ moiety (Fig. 1). The conclusions drawn from the group theoretical consideration are summarized in Table 1. Thus, in spite of the symmetry forbiddenness of the HOMO(b_2) - LUMO(a_2) CT interaction, the corresponding lowest energy CT transition ($b_2 \rightarrow a_2$) is symmetry allowed. Furthermore, the charge transfer in the ground state occurs only from the second HOMO(a_2) to the LUMO(a_2).

TABLE 1. Allowedness and forbiddenness of CT-interactions and CT-transitions in (5).

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

In most of usual CT complexes the same electron transferred configuration contributes to the ground and excited state wave functions. In sharp contrast, for the TCNQ-triptycene (5) the main transferred configurations are different between both states and exclusive to each other :

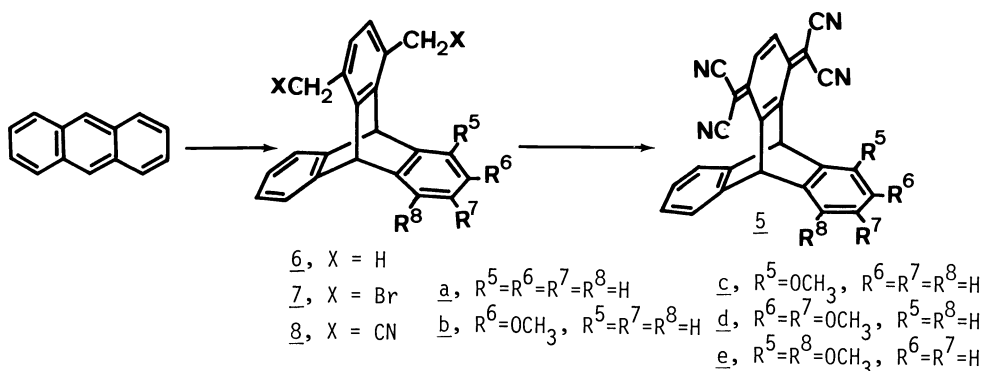
$$\Psi = C_1 \Phi_G + C_2 \Phi_T(b_2 \rightarrow a_2) + C_3 \Phi_T(a_2 \rightarrow a_2) + \dots$$

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 (5) the lowest CT excitation accompanies the electronic transition from the HOMO(b_2) of the benzene rings to the LUMO(a_2) of the TCNQ ring, whereas electrons delocalize from the second HOMO(a_2) of the donor to the LUMO(a_2) of the acceptor in the ground state (Ref. 13).

Experimental Verification of CT Transition for Symmetry-Forbidden CT Interaction

It is apparent from Fig. 1 that 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 band maximum while electron donating 6- and/or 7-substituents cause the bathochromic shift to the extent proportional to the number of substituents. In order to confirm this prediction we have synthesized a series of TCNQ-triptycenes (5a - 5e) substituted with methoxy group(s).

The synthesis of TCNQ-triptycenes (5a - 5e) was accomplished starting from the corresponding triptycenes (6a - 6e), respectively. 1,4-Dimethyltriptycene (6a), 1,4-dimethyl-5-methoxytriptycene (6c), and 1,4-dimethyl-6,7-dimethoxytriptycene (6d) were readily prepared from 1,4-dimethylanthracene with the respective benzyne. On the other hand, 1,4-dimethyl-5,8-dimethoxytriptycene (6e) 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.



Bromination of the triptycene 5a with NBS gave 1,4-bis(bromomethyl)triptycene (7a) which was cyanated with potassium cyanide in acetonitrile in the presence of 18-crown-6 to the bis-(cyanomethyl) derivative 8a (Ref. 14). Conversion of 8a into the TCNQ-triptycene 5a could be accomplished according to the Wheland-Martin procedure for TCNQ synthesis (Ref. 15). Similarly, methoxytriptycenes 6b - 6e readily gave 5b - 5e (Table 2).

TABLE 2. Physical properties of the TCNQ-triptycenes (5a - 5e)

Compd	appearance	mp (°C)	CT bond λ_{\max} nm (log ϵ)	
			in CH ₂ Cl ₂	in CH ₃ CN
<u>5a</u> ^a	red micro needles	>300	535 (3.40)	505 (3.45)
<u>5b</u> ^a	green powder	>300	584 (3.02)	544 (3.09)
<u>5c</u>	red powder	>300	530 (3.34)	500 (3.37)
<u>5d</u>	dark green needles	>300	662 (2.72)	612 (2.66)
<u>5e</u>	red needles	>300	533 (3.34)	506 (3.37)

a, Ref. 14

The electronic spectra of the TCNQ-triptycenes 5a - 5e are shown in Fig. 2. In accord with the above mentioned theoretical prediction, it is quite clear that in spite of the presence of electron donating methoxy group(s) the observed absorption maxima of the CT bands for 5c and 5e are almost the same with that of the unsubstituted compound 5a, whereas the compounds having methoxy group(s) at 6- (5b) and 6,7-positions (5d) display the successive red shift by 49 and 127 nm in dichloromethane, respectively, with increasing number of methoxy substitutions.

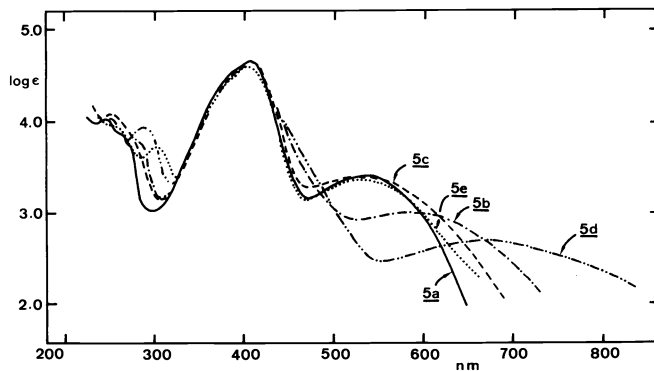


Fig. 2. Electronic spectra of 5a, 5b, 5c, 5d, and 5e in CH₂Cl₂.

A series of TCNQ-triptycenes (5) is the first in which CT transition for symmetry-forbidden CT interaction has been successfully observed, as a well separated band in the longest wavelength region, together with the experimental support of the substituent effects on the CT band shifts.

Molecular Orbital Calculations

Although both through-space and through-bond interactions between the components usually must be invoked to account properly for possible CT interaction and transition in the system, only through-space interaction has been considered in our previous arguments.

The numerically calculated electronic spectra of 5a by the SCF-CI-dipole velocity molecular orbital method including the through-space (homoconjugative) interaction are illustrated in Fig. 3 (Ref. 16).

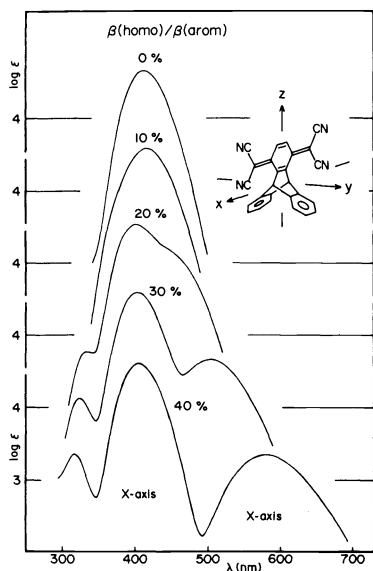


Fig. 3. Calcd. electronic spectra of 5a (SCF-CI-VD MO) in which the value of the $\beta(\text{homo})$ was gradually changed.

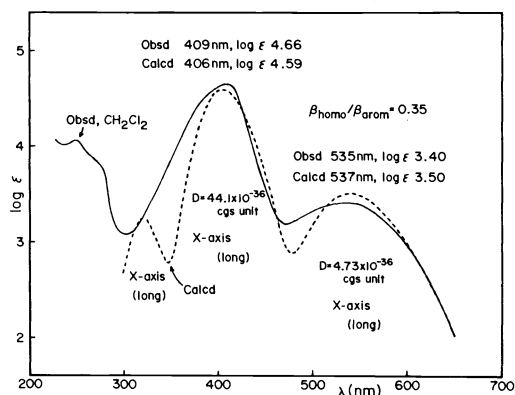


Fig. 4. Comparison of the observed and calcd. electronic spectra of 5a.

When the interchromophoric resonance integral is neglected, i.e., $\beta(\text{homo})=0$, the calculated UV curve exhibits intense absorption at around 400 nm which corresponds to the local excitation of the TCNQ moiety of 5a. As the resonance integral, $\beta(\text{homo})$, gradually increases the UV spectrum of 5a becomes broad and when $\beta(\text{homo})/\beta(\text{arom})=0.3$ ($\beta(\text{arom})=-2.39$ eV), new CT band appears as a separate absorption at longer wavelength region. As shown in Fig. 4, when $\beta(\text{homo})/\beta(\text{arom})=0.35$, good agreement between the observed and calculated spectra was obtained, clarifying the important role of the through-space homoconjugation effect.

In the previous qualitative treatment of the TCNQ-triptycene 5a we have assumed, a priori, that the HOMO and the LUMO of 5a localize on the electron donating benzene rings and the electron accepting TCNQ ring, respectively. In fact the calculations reveal that this is the case for the LUMO as schematically illustrated in Fig. 5. However, the HOMO (b_2) orbital has considerable AO coefficients at the TCNQ moiety, as a result the observed CT transition borrows its intensity from that of the local excitation of the acceptor TCNQ, though the borrowing is, in principle, not necessary (Ref. 17).

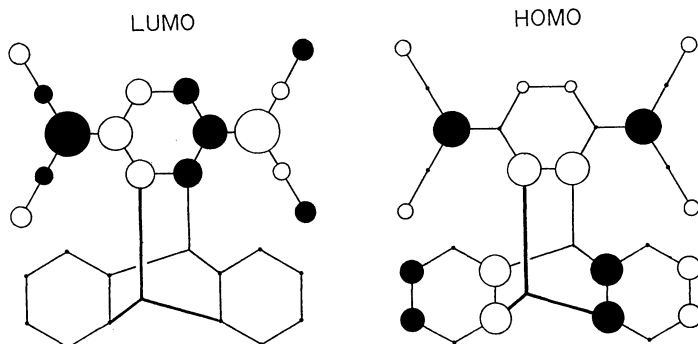
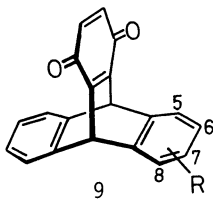


Fig. 5. Frontier orbitals of 5a.

9,10-DIHYDRO-9,10-*o*-BENZENOANTHRACENE-1,4-DIONES

Because of the same symmetry property of the LUMO of TCNQ and *p*-benzoquinone which is also regarded as good electron acceptor, the notion of CT transition for symmetry-forbidden CT interaction found in 5 might also be applicable to the triptycenequinone, 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-dione (9a) (Ref. 18). That is to say, 5- and/or 8-substituents on 9a should exhibit little effect on the wavelength of the CT band while electron donating 6- and/or 7-substituents cause a bathochromic shift proportional to the number of substituents.

a, R=Hb, R=5-CH₃c, R=6-CH₃d, R=5,8-(CH₃)₂e, R=6,7-(CH₃)₂f, R=5,8-(OCH₃)₂g, R=6,7-(OCH₃)₂

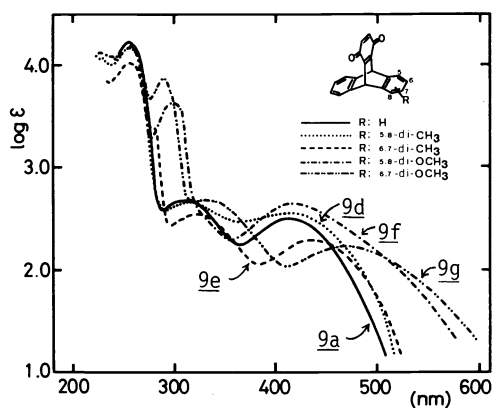
Both unsubstituted and substituted triptycenequinones (9a - 9g) are readily obtained from the corresponding anthracenes through Diels-Alder reaction with *p*-benzoquinone followed by treatment with *p*-toluenesulfonic acid and then oxidation by silver oxide (Table 3).

TABLE 3. Physical properties of a series of triptycenequinones 9a - 9g

Compd	appearance	mp (°C)	CT band in CH ₂ Cl ₂	
			λ _{max} nm	log ε
<u>9a</u>	yellow prisms	>300	414	2.51
<u>9b</u> ^a	yellow crystals		415	2.52
<u>9c</u>	orange prisms	173	423	2.49
<u>9d</u>	yellow prisms	275 (d)	412	2.57
<u>9e</u>	orange prisms	264	437	2.28
<u>9f</u> ^b	yellow crystals	272.5	416	2.64
<u>9g</u>	dark red needles	210	471	2.23

a Ref. 19,

b Ref. 20

Fig. 6. Electronic spectra of (9a), (9d), (9e), (9f), and (9g) in CH₂Cl₂.

The electronic spectra of 9a - 9g are shown in Table 3 and some of them are illustrated in Fig. 6. All exhibit a distinct CT bands in the visible region as well separated absorptions. In spite of the presence of methyl group(s) the observed CT band maxima for 9b and 9d are almost the same as that of the unsubstituted compound 9a, whereas the isomeric derivatives 9c and 9e display a progressive red shift of 9 and 23 nm, respectively, with increasing number of methyl groups. Similar substituent effects were also observed for 9f and 9g in

which two methoxy groups are located at 5,8- and 6,7-positions, respectively. The CT band maximum of 9f was found to be almost the same as that of 9a whereas a pronounced red shift of 57 nm was observed for 9g. Again, these substituent effects on the CT band shifts unambiguously support, in general, the idea of the CT transition for symmetry-forbidden CT interaction.

GENERALIZATION OF THE PROPERTIES OF CT INTERACTION AND TRANSITION IN INTRAMOLECULAR REMOTE CT SYSTEMS

The present discussion described in this section is concerned with the selection rules of CT interaction (CTI) and CT transition (CTT) in the model which belongs to C_{2v} or C_s point group, as do 2, 3, or 4, respectively. Although this model suffers at least one disadvantage in that the extent of the overlap between the components will be considerably diminished, it possesses the advantage that the geometrical arrangement of the components might be adjusted unequivocally and rigidly without adding serious strain to the components.

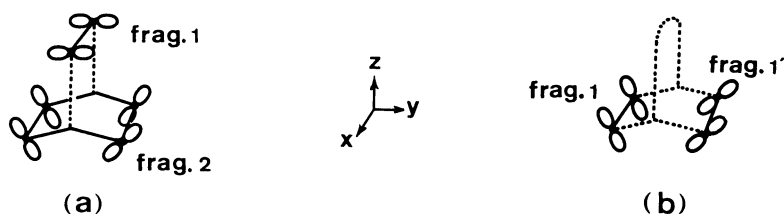


Fig. 7. Schematic illustration of the interacting orbital fragments in C_{2v} (a) and C_s systems (b).

The interacting orbitals in C_{2v} system are divided into fragment-1 (donor) and -2 (acceptor) as illustrated in Fig. 7a. The symmetry properties of the fragment orbitals are classified with respect to the reflection in the xz - and yz -planes, in order. In fragment-1 there are two symmetry properties, AS and AA as shown in Fig. 8a. In fragment-2 there are two sets of symmetry properties (Fig. 8b). One of them, SS and AS, is in-phase and out-of-phase combinations of the interacting orbitals which are symmetric with respect to the yz -plane. The other set, SA and AA, is similar combinations of the orbitals which are antisymmetric with respect to the yz -plane.

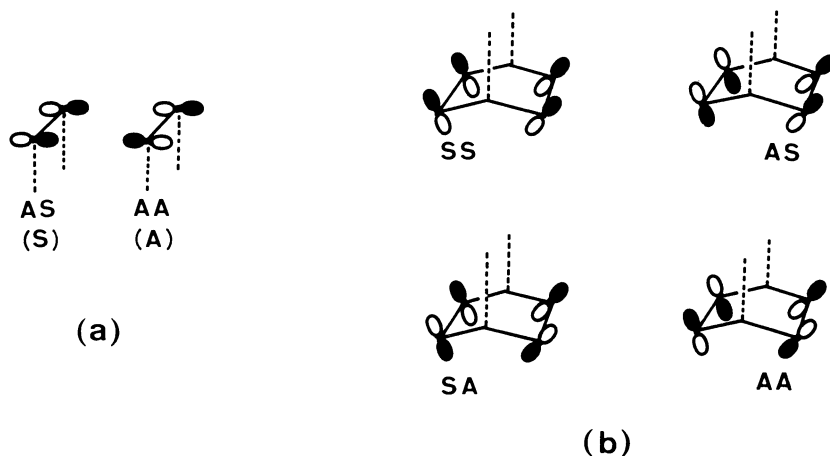


Fig. 8. Symmetry properties of fragment-1 (a) and fragment-2 (b) in C_{2v} system.

One may connect each symmetry property of the fragments in four possible modes, 1 to 4, as depicted in the first to third columns of Table 4. The selection rule for CTI is simply derived from the products of symmetry properties in each fragment. CTI is allowed only in the case of product SS. The selection rule for CTT is derived from both the products and the symmetry properties of each component of the three Cartesian coordinate axes of dipole moment vector (Ref. 21). Thus the products SA, AS, and SS correspond to symmetry allowed transitions with polarization along x -, y -, and z -axis, respectively.

TABLE 4. Symmetry properties and selection rules for possible modes in C_{2v} system

mode	symmetry properties			selection rules	
	frag-1	frag-2	product	CTI	CTT
1	AS	AS	SS	a	a (z)
	AS	SS	AS	f	a (y)
2	AS	AA	SA	f	a (x)
	AS	SA	AA	f	f
3	AA	AS	SA	f	a (x)
	AA	SS	AA	f	f
4	AA	AA	SS	a	a (z)
	AA	SA	AS	f	a (y)

TABLE 5. Symmetry properties and selection rules for possible modes in C_s system

mode	symmetry properties			selection rules	
	frag-1	frag-2	product	CTI	CTT
5	S	S	S	a	a (y,z)
6	S	A	A	f	a (x)
7	A	S	A	f	a (x)
8	A	A	S	a	a (y,z)

a : allowed f: forbidden

Product AA corresponds to symmetry forbidden transition. The selection rules for the C_{2v} system are summarized in the last two columns of Table 4. Each mode contains two types of the selection rules for the CT phenomena because each set of symmetry properties in fragment-2 is composed of two symmetry properties. Therefore, a total of eight different combinations of symmetry properties of the fragments are obtained. Among them only the case in which both CTI and CTT are allowed is found in one of the combinations of mode 1 or 4. In the remaining six cases, CTI is symmetry forbidden. It should be emphasized that the allowed CTT in the mode 2 or 3 is restricted only to the symmetry forbidden CTI.

In the C_s system, there are four possible modes, 5 - 8 (Fig. 7 and 8). Table 5 represents the generalization of the properties of each mode. The product S corresponds to symmetry allowed CTI and CTT whereas the product A corresponds to forbidden CTI and allowed CTT. CTT's in the modes 5 and 8 correspond to CTT for symmetry allowed CTI whereas the CTT in the modes 6 and 7 correspond to symmetry forbidden CTI. These results can also be confirmed by explicit group theoretical treatments.

Our arguments unambiguously indicate that the analysis of CTI and CTT has to be done independently and contribute to the elimination of a misunderstanding among some that a CTT is an indication of a significant CTI between donor and acceptor in the ground state. In 1966, Dewar correctly pointed out that "the appearance of a CTT provides no evidence that CT plays a dominant, or even a significant, role in the binding" (Ref. 22). Unfortunately, there has never been such convincing experimental evidence as the substituent effects on the CT band shifts of 5. More compelling information is expected from the experimental determination of the direction of the transition moment of CTT for symmetry forbidden CTI. CTT in most of the intermolecular CT complexes reported so far is polarized along the donor-acceptor axis. Actually, in our intramolecular cases, modes 1 and 4 in the C_{2v} system contain such a transition polarized along the donor-acceptor axis(z). All these transitions, however, correspond to CTT for symmetry allowed CTI. Mulliken, 17 years after his first paper on CT complexes, noted the possibility that the CTT of a benzene-halogen complex is polarized perpendicular to the donor-acceptor axis (Ref. 23). Such a transition may be characterized with CTT for symmetry forbidden CTI, and it has never before, to our knowledge, been reported for intra-

molecular CT complexes.

Cookson et al. have ingeniously pointed out at first that the UV spectra of the Diels-Alder adducts of dicyanoacetylene with a wide variety of dienes include bands attributed to CTT in 1968 (Ref. 24). Some of these compounds fall in our category of CTT for symmetry forbidden CTI, however, there was no experimental evidence support our notion at that time.

To conclude, this paper is first to describe "the CT transition for symmetry forbidden CT interaction". The idea may contribute to excluding likely misunderstanding that intense CT bands necessarily mean strong CT interaction, and is general enough to serve to all spectroscopists. Furthermore, the interest in intramolecular CT bands of rigidly constrained π -systems is growing these several years as is described in the text. The notion is indispensable especially for understanding the CT bands in these molecules. The rigid systems are prohibited from choosing the geometry to favor the CT interaction whereas donors and acceptors in usual CT complexes can and must be oriented to do so. Further verification of this idea by the polarized spectrum of a pertinent model compound is now under way.

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REFERENCES

1. R.S. Mulliken, *J. Am. Chem. Soc.* **74**, 811 (1952).
2. G. Briegleb, *Elektronen-Donor-Acceptor-Komplexe*, Springer, Berlin (1961).
3. L.J. Andrews and R.M. Keefer, *Molecular Complexes in Organic Chemistry*, Holden-Day, San Francisco (1964).
4. W.B. Person and R.S. Mulliken, *Molecular Complexes : A Lecture and Reprint Volume*, Wiley, New York (1969).
5. R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, New York (1969).
6. P.D. Bartlett, M.J. Ryan, and S.G. Cohen, *J. Am. Chem. Soc.* **64**, 2649 (1942).
7. P.D. Bartlett and E.S. Lewis, *J. Am. Chem. Soc.* **72**, 1005 (1950); C.F. Wilcox, Jr., *J. Chem. Phys.* **33**, 1874 (1960); C.F. Wilcox, Jr. and A.C. Craig, *J. Org. Chem.* **26**, 2491 (1961); I. Mori, T. Kadosaka, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.* **44**, 1649 (1971); **45**, 2836 (1972); W. Theilacker, K. Albrecht, and H. Uffmann, *Chem. Ber.* **98**, 428 (1965); H. Birnbaum, R.C. Cookson, and N. Lewin, *J. Chem. Soc.* 1224 (1961); P.H. Heller and D.H. Geske, *J. Org. Chem.* **31**, 4249 (1966); R.M. Dessau, *J. Chem. Phys.* **54**, 5430 (1971); C.M. Stock and J. Suzuki, *J. Am. Chem. Soc.* **87**, 3909 (1965); J. deWit and H. Wynberg, *Tetrahedron*, **28**, 4617 (1972); **29**, 1379 (1973).
8. T. Nakazawa and I. Murata, *J. Am. Chem. Soc.* **99**, 1996 (1977).
9. T. Nakazawa, K. Kubo, and I. Murata, *Angew. Chem., Int. Ed. Engl.* **20**, 189 (1981).
10. T. Nakazawa, Y. Niimoto, K. Kubo, and I. Murata, *Angew. Chem., Int. Ed. Engl.* **19**, 545 (1980).
11. M. Feldman and S. Winstein, *J. Am. Chem. Soc.* **83**, 3338 (1961); Idem, *Theoret. Chim. Acta.* **10**, 86 (1968); H.J. Dauben, Jr. and J.D. Wilson, *Chem. Commun.* 1629 (1968).
12. H. Bock and B.G. Ramsey, *Angew. Chem., Int. Ed. Engl.* **12**, 743 (1973).
13. S. Inagaki, K. Yamamura, K. Nakasuji, T. Nakazawa, and I. Murata, *J. Am. Chem. Soc.* **103**, 2093 (1981).
14. K. Yamamura, T. Nakazawa, and I. Murata, *Angew. Chem., Int. Ed. Engl.* **19**, 543 (1980).
15. R.C. Wheland and E.L. Martin, *J. Org. Chem.* **40**, 3101 (1975).
16. N. Harada, H. Uda, K. Nakasuji, and I. Murata, unpublished results.
17. Ref. 4, Chapters 11 and 13.
18. K. Yamamura, K. Nakasuji, I. Murata, and S. Inagaki, *J. Chem. Soc., Chem. Commun.* 396 (1982).
19. F. Ogura, unpublished result.
20. H. Iwamura and K. Makino, *J. Chem. Soc., Chem. Commun.* 720 (1978).
21. H.H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, Chapter 6 (1962).
22. M.J.S. Dewar and C.C. Thompson, Jr. *Tetrahedron, Suppl.* **7**, 97 (1966).
23. Ref. 4, Chapter 11.
24. R.C. Cookson, J. Dance, and M. Godfrey, *Tetrahedron*, **24**, 1529 (1968).