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THE CHARGE-TRANSFER TRANSITION FOR THE SYMMETRY-FORBIDDEN CHARGE-TRANSFER INTERACTION IN THE C_s SYSTEM.
9,10-DIHYDRO-9,10-ETHANO-[1,4]-BIS(DICYANOMETHYLENE)ANTHRACENES

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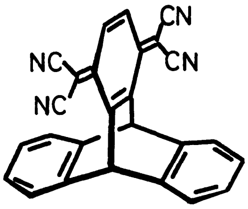
Some 9,10-dihydro-9,10-ethano-[1,4]-bis(dicyanomethylene)-anthracene derivatives have been synthesized. The substituent effects on the charge-transfer band shifts of these compounds strongly supported our previously proposed argument for the charge-transfer transition for the symmetry-forbidden charge-transfer interaction.

In the course of our studies on the intramolecular charge-transfer complexes which contain the nonparallel electron-donor and acceptor components incorporated in a rigid framework,[1] we have recently proposed and substantiated a novel notion —— *the charge-transfer transition for the symmetry-forbidden charge-transfer interaction*, by employing 1,4-dihydro-1,4-bis(dicyanomethylene)triptycenes(1).[2] This notion[3] implies that the orbitals involved in the ground-state CT interaction are not necessarily the same as those involved in photo-exicitation. Furthermore, this argument was confirmed by the substituent effects on the CT band shifts in 9,10-



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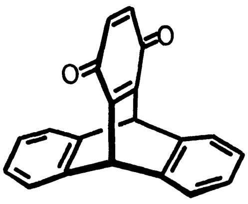

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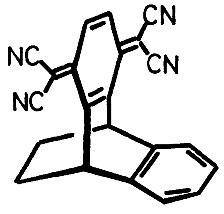

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dihydro-9,10-*o*-benzenoanthracene-1,4-diones(2).[4)] Both 1 and 2 belong to the C_{2v} point group. In principle, this argument should be applicable to the molecules which belong to the C_s point group. We have chosen 9,10-dihydro-9,10-ethano-[1,4]-bis(dicyanomethylene)-anthracene(3) as a model compound to examine the applicability.

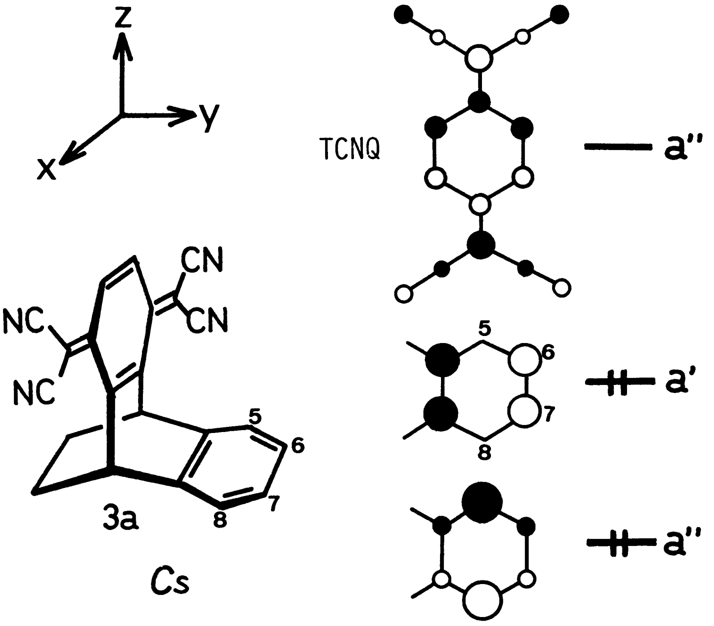
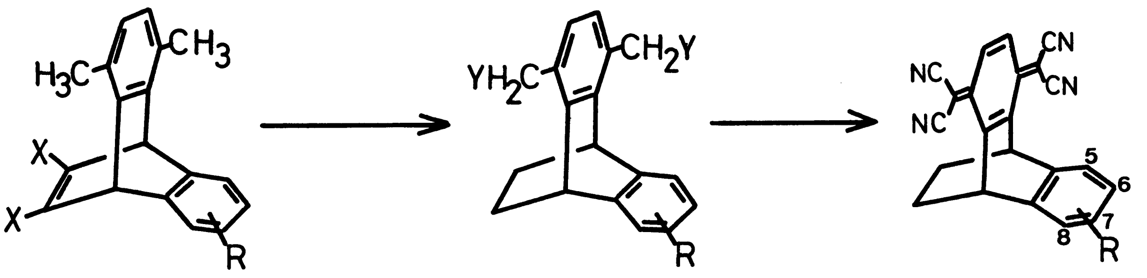


Figure 1. The high-lying MO's of electron-donating benzene ring and the LUMO of TCNQ in 3a. The coordinate axis are taken for convenience.

The HOMO and the LUMO of 3 localize on the electron-donating benzene and the electron-accepting TCNQ rings, respectively. The degenerate highest occupied orbitals of benzene are split into HOMO(a") and HOMO(a') by ortho cycloalkyl fusion[5)] as shown in Figure 1. In the C_s point group both electronic transition, HOMO(a')→LUMO(a") and HOMO(a")→LUMO(a") are symmetry-allowed. However the CT interaction between HOMO(a') and LUMO(a") is symmetry-forbidden. The AO coefficient in the HOMO(a') is zero at 5- and 8-positions and large at 6- and 7-positions. It is then predicted that 5- and/or 8-substituents on 3 show little effect on the wavelength of the lowest energy absorption band while electron-donating 6- and/or 7-substituents cause a red shift.[6)]

The parent compound(3a), 5,8-dimethoxy(3b) and 6,7-dimethoxy derivatives(3c)



4: X = CO_2CH_3
5: X = H

6: Y = H
7: Y = Br
8: Y = CN

3a: R = H
3b: R = 5,8-di-OCH_3
3c: R = 6,7-di-OCH_3

were synthesized to examine the prediction. Diels-Alder adducts(4) of dimethyl acetylenedicarboxylate with the corresponding 1,4-dimethylanthracenes were converted into 1,4-dimethyl-dibenzobarrelenes(5) by hydrolysis and subsequent decarboxylation in 58∼64% yields based upon 1,4-dimethylanthracenes, this route being reported for the synthesis of 2-substituted dibenzobarrelenes by Figeys and Dralants.7) Hydrogenation of 5 on Pd-C gave 9,10-dihydro-9,10-ethano-1,4-dimethylanthracenes(6) almost quantitatively. Bis(cyanomethyl)derivatives(8) were obtained through the bromination with NBS of the methyl groups on 6, followed by cyanation with KCN in DMSO in 57∼60% yields. Conversion of 8 into 3 was achieved essentially according to the well-known Wheland–Martin procedure for TCNQ synthesis8) as well as our synthesis of 1 reported previuosly,2,9) though in poor yields(ca 6%). The structure of 3a∼3c were confirmed on the basis of their elemental analyses and consistent NMR data.10)

The electronic absorption spectra of 3a∼3c are shown in Figure 2. In contrast to 1,2,9) 3a shows the CT absorption band as a shoulder submerged in the strong absorption band of TCNQ moiety. The absorption maxima of the CT band remains

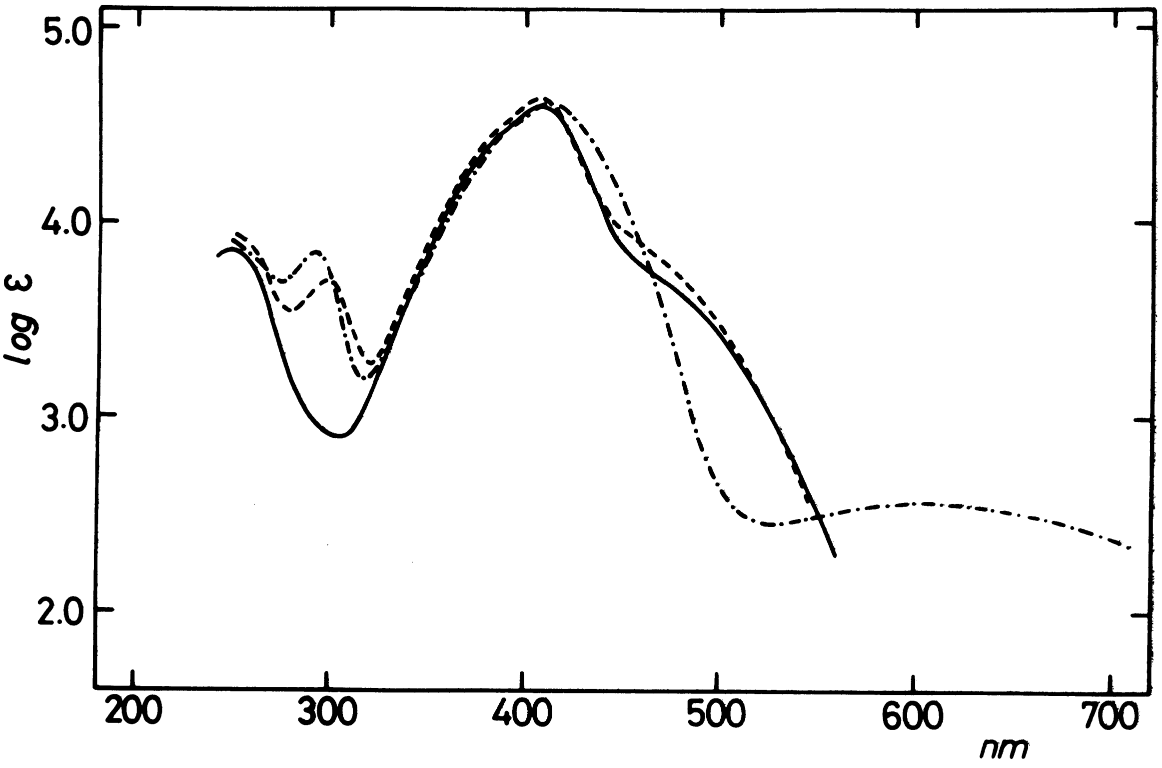


Figure 2. Electronic spectra of 3a(————), 3b(------), and 3c(-·-·-·) in dichloromethane.

almost unchanged on the methoxy substitution at the 5- and 8-positions(3b) whereas the methoxy groups at 6- and 7-positions in 3c cause the substantial red shift. These results confirm the CT transition for the symmetry-forbidden CT interaction in the C_s system.

Since such a CT transition for the symmetry-forbidden CT interaction should be polarized perpendicular (*x*)(see Figure 1.) to the donor-acceptor axis,$^{3)}$ experimental determination of the transition moment for 1 and 3 is of interest and the subject of our current attention.

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6) In view of distribution of HOMO(a") coefficients, the magnitude of the substituent effects at 5- and/or 8-positions on the wavelength of the second CT transition band should be greater than that of 6- and/or 7-positions.
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10) 3a: orange prisms, mp >300°C, ^{1}H-NMR(100 MHz, CD_2Cl_2) δ 7.46∼7.16(AA'BB', 4H), 7.41(s, 2H), 5.67(bs, 2H), 1.80(m, 4H).
3b: green powder (red in a CH_2Cl_2 solution), mp 278∼280°C(dec.), ^{1}H-NMR(100 MHz, $CDCl_3$) δ 7.40(bs, 2H), 6.67(s, 2H), 6.11(bs, 2H), 3.82(s, 6H), 1.77(bs, 4H).
3c: green powder, mp >300°C, ^{1}H-NMR(100 MHz. CD_2Cl_2) δ 7.40(s, 2H), 6.95(s, 2H), 5.57(bs, 2H), 3.81(s, 6H), 1.79(m, 4H).

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