Substituent Effects on the Charge-transfer Band Shifts in 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-diones: Further Confirmation of the Charge-transfer Transition for a Symmetry-forbidden Charge-transfer Interaction†

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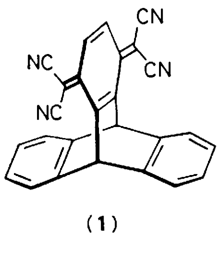
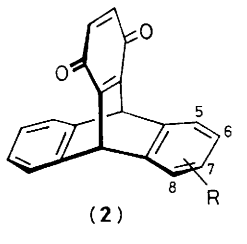
A series of 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diones has been prepared; the substituent effects on the charge-transfer band shifts of these compounds strongly support our argument for a 'charge-transfer transition for a symmetry-forbidden charge-transfer interaction'.

In connection with our study on intramolecular charge-transfer (CT) absorption between a non-parallel electron donor and acceptor incorporated in a rigid skeleton,[1] we have recently reported[2] a charge-transfer transition for a symmetry-forbidden charge-transfer interaction found in a series of 1,4-dihydro-1,4-bis(dicyanomethylene)triptycenes (**1**).[3] Such a transition signifies that the orbitals involved in the ground state CT-interaction need not be the same as those involved in photo-excitation. Iwamura and Makino[4] have recently reported an intramolecular CT band in the electronic spectrum of 5,8-dimethoxy-9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-dione (**2f**) in which the tetracyanoquinodimethane (TCNQ) moiety of (**1**) has been replaced by *p*-benzoquinone as an electron acceptor. Because the symmetry of the LUMO of *p*-benzoquinone is the same as that of TCNQ our previously proposed transition found in (**1**) might also be applicable to a series of triptycenequinones (**2**). Therefore, 5- and/or 8-substituents on (**2**) should exhibit little effect on the wavelength of the CT absorption maximum while electron-donating 6- and/or 7-substituents cause a red shift proportional to the number of substituents. In this publication evidence is presented for the above generalization.



(1)



(2)

Substituted triptycenequinones (**2**) are readily available from the corresponding anthracenes through Diels–Alder reaction with *p*-benzoquinone followed by treatment with toluene-*p*-sulphonic acid and then oxidation by silver oxide; this route has been previously used for the synthesis of (**2f**).[4] In all cases, the yields were *ca.* 70%.‡ (**2a**): yellow prisms, m.p. >300 °C; (**2c**): orange prisms, m.p. 173 °C; (**2d**): yellow prisms, m.p. 275 °C (decomp.); (**2e**): orange prisms, m.p. 264 °C; (**2g**): dark red needles, m.p. 210 °C.

The electronic spectra of (**2**) are shown in Table 1 and some are illustrated in Figure 1. All exhibit a distinct CT-absorption in the visible region. From these findings it has become apparent that in spite of the presence of methyl group(s) the observed CT-absorption maxima for (**2b**) and (**2d**) are almost the same as that of the unsubstituted compound (**2a**), whereas the isomeric derivatives, (**2c**) and (**2e**), display a progressive red shift of 9 and 23 nm, respectively, with increasing number of methyl substituents. Moreover, similar substituent effects were also observed for (**2f**) and (**2g**) in which two methoxy-groups are situated in the 5,8- and 6,7-positions, respectively.

Table 1. CT-absorption maxima of (**2**) in CH_2Cl_2.

(2)	R	λ_{max}/nm	log ϵ
a	H	414	2.51
b[a]	5-Me	415	2.52
c	6-Me	423	2.49
d	5,8-Me_2	412	2.57
e	6,7-Me_2	437	2.28
f[b]	5,8-$(OMe)_2$	416	2.64
g	6,7-$(OMe)_2$	471	2.23

[a] F. Ogura, unpublished. [b] Ref. 4.

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† Presented at the 14th Symposium on Structural Organic Chemistry, Okayama, October 14, 1981.

‡ All new compounds gave satisfactory microanalytical and spectral data in agreement with the assigned structures.

The CT-absorption maximum of **(2f)** was found to be almost the same as that of **(2a)** while a pronounced red shift of 57 nm was observed for **(2g)**. These substituent effects on the CT-absorption band shifts strongly support, in general, the idea of the CT transition for symmetry-forbidden CT-interaction.

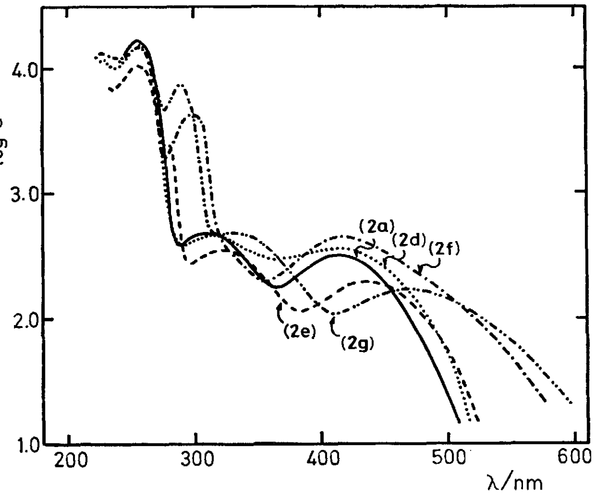

Figure 1. Electronic spectra of **(2a)**, **(2d)**, **(2e)**, **(2f)**, and **(2g)** in dichloromethane.

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