Intramolecular Charge-Transfer Interaction in 7,12-Epoxy-7,12-dihydrobenz[*a*]anthracene-8,11-dione and 5,12-Epoxy-5,12-dihydronaphthacene-1,4-dione

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Synopsis. 7,12-Epoxy-7,12-dihydrobenz[*a*]anthracene-8,11-dione and 5,12-epoxy-5,12-dihydronaphthacene-1,4-dione have been synthesized. Both of them had pronounced intramolecular charge-transfer bands, although the donor and the acceptor were in unfavorable spatial position and furthermore in one of them its HOMO–LUMO interaction is forbidden.

During the course of our studies on intramolecular charge transfer complexes with no direct conjugation in a rigid framework, we proposed and substantiated a novel notion, *the charge-transfer transition for the symmetry-forbidden charge-transfer interaction*, by using compounds **1**,[1] **2**,[2] and **3**.[3] All of these compounds contain benzene rings as an electron donor (Chart 1). The electron donor ability of a naphthalene ring is superior to benzene ring, because the ionization potential of naphthalene is smaller than that of benzene. In this paper, we wish to report the intramolecular charge-transfer phenomena in 7,12-epoxy-7,12-dihydrobenz[*a*]-anthracene-8,11-dione (**4**) and 5,12-epoxy-5,12-dihydronaphthacene-1,4-dione (**5**), in which the naphthalene ring is rigidly fixed to be nonparallel with respect to the electron-accepting *p*-benzoquinone ring across a saturated bridge. Compound **4** was prepared by the oxidation of 7,12-epoxy-7,12-dihydrobenz[*a*]anthracene-8,11-diol[4] with freshly prepared silver oxide. Similarly **5** was prepared by the oxidation of 5,12-epoxy-5,12-dihydronaphthacene-1,4-diol, which was obtained by enolation of 5,12-epoxy-4a,5,12,12a-tetrahydro-1,4-naphthacenedione.[4] Although **5** is stable in dichloromethane solution, it turned immediately into insoluble materials when the solvent was evaporated.

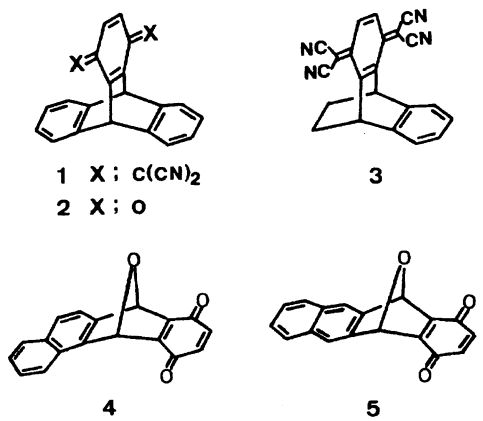

Chart 1.

Due to the high electron affinity of *p*-benzoquinone relative to naphthalene, the HOMO and the LUMO of **4** and **5** localize on the electron-donating naphthalene and the electron-accepting *p*-benzoquinone moieties, respectively. The coefficients of the $HOMO_n$ and the $LUMO_n$ of naphthalene and the $LUMO_q$ of *p*-benzoquinone are schematically depicted in Fig. 1. Obviously the $HOMO_n$–$LUMO_q$ interaction in **4** is forbidden, but that in **5** is symmetry-allowed. On the other hand, the $LUMO_n$–$LUMO_q$ interaction is allowed in **4** and is symmetry-forbidden in **5**. The LUMO is lowered by the $LUMO_n$–$LUMO_q$ interaction and is raised by the $HOMO_n$–$LUMO_q$ interaction. So it can be considered that the LUMO energy of **4** is lower than that of **5**. Consequently, it can be predicted that the half-wave reduction potential of **4** is more positive than that of **5**, because the LUMO is a key orbital when the molecule undergoes reduction. However, the observed results are in conflict with the prediction. Thus, there is not great difference in the $E_{1/2}$'s of **4** (−0.338 V vs. SCE) and **5** (−0.329 V vs. SCE).[5] This may be attributed to the fact that the orbital interaction are rather small in both **4** and **5** due to minimized overlap of both donor and acceptor orbitals. However, the electronic spectra of **4** and **5** have long-wavelength absorptions extending to the visible range (Fig. 2).[6] These absorptions, which are absent in the spectra of the component chromophores, undergo the blue shifts upon changing the solvent to the more polar acetonitrile (about 15 nm blue shifts from dichloromethane to acetonitrile).[7] From these facts, these absorptions are assigned to the intramolecular charge-transfer bands, although the donor and the acceptor are in an unfavorable spatial position and furthermore in **4** HOMO–LUMO interaction is forbidden in the ground

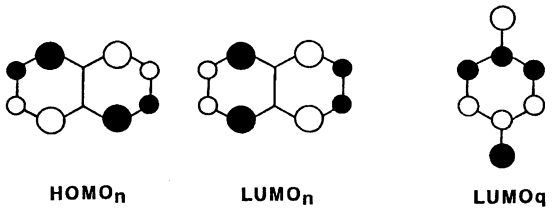

Fig. 1. The coefficients of the $HOMO_n$ and the $LUMO_n$ of naphthalene and the $LUMO_q$ of *p*-benzoquinone.

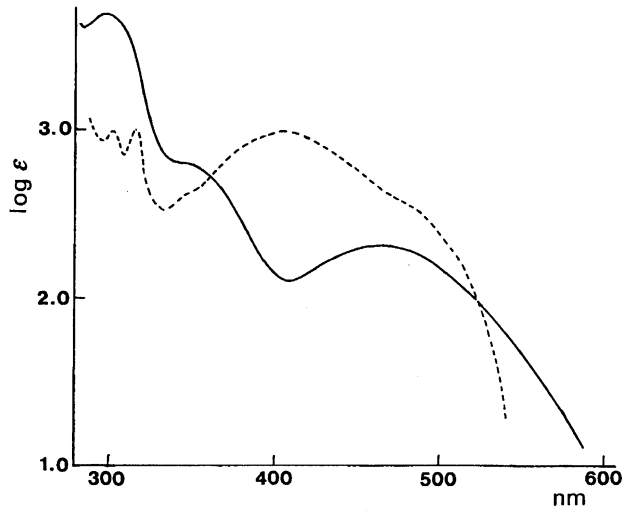

Fig. 2. The UV-vis spectra of **4** (—) and **5** (---) in dichloromethane.

state.

These results support the idea of the charge-transfer transition for symmetry-forbidden charge-transfer interactions, as reported previously.

Experimental

^{1}H NMR spectra were obtained on a Hitachi R-24A spectrometer(60 MHz). UV-vis spectra were taken on a Shimadzu UV-240 spectrophotometer. The electrochemical reduction potentials were measured in acetonitrile by DC polarography using tetraethylammonium perchlorate as the supporting electrolyte.

Preparation of 7,12-Epoxy-7,12-dihydrobenz[*a*]anthracene-8,11-dione (4). A mixture of freshly prepared silver oxide (1.4 g, 6 mmol), anhydrous magnesium sulfate (1 g) and 7,12-epoxy-7,12-dihydrobenz[*a*]anthracene-8,11-diol (0.552 g, 5 mmol) in 20 ml dry acetone was stirred for 2 h at room temperature and filtered. The filtrate was evaporated in vacuo and the residue was chromatographed over silica gel. Elution with benzene–hexane (1 : 1) gave 1.16 g (85.0%) of **4**, reddish-brown needles, mp 153 °C (recrystallized from benzene); Found: C, 78.78; H, 3.65%. Calcd for $C_{18}H_{10}O_3$: C, 78.83; H, 3.67%. ^{1}H NMR ($CDCl_3$) δ=7.85—7.20 (m, 6H), 6.62 (s, 1H), 6.47 (s, 2H), 6.37 (s, 1H).

Preparation of 5,12-Epoxy-5,12-dihydronaphthacene-1,4-dione (5). Compound **5** was prepared as described above. ^{1}H NMR ($CDCl_3$) δ=7.75—7.18 (m, 6H), 6.48 (s, 2H), 6.18 (s, 2H). Elemental analyses could not be done due to its instability.

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References

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5) DC polarograms were taken in acetonitrile with 0.1 M tetraethylammonium perchlorate. Two reduction waves were observed. The limiting currents were diffusion controlled. Plots of E vs. $\log(i_d-i)/i$ for the first wave yielded straight lines with slopes of 58.0—60.0 mV, indicating the reversibility of the first waves with one-electron reduction.

6) The longest wavelength bands of **4** and **5** shifted to longer wavelengths compared with that of [2.2]paracyclophanequinone[8] in which the benzene ring is oriented face-to-face with the *p*-benzoquinone ring. This can be attributed the fact that the ionization potential of naphthalene is smaller than that of benzene.

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