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Substituent Effects in 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-diones on the Half-wave Potentials

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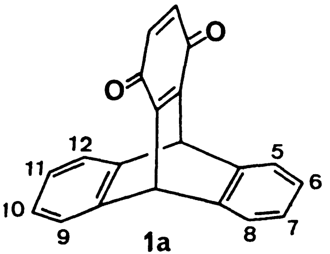
Polarographic half-wave reduction potentials of some 9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diones showed that methoxy group is less electron donating than methyl group. Observed substituent effects are successfully discussed in terms of the inductive effect, the intramolecular LUMO-LUMO interaction, the LUMO amplitudes, and so on.

In the course of our studies on intramolecular charge-transfer (CT) absorption between the nonparallel electron-donor and acceptor components incorporated in a rigid framework,[1] we have proposed a novel notion —— the CT transition for the symmetry-forbidden CT interaction, by employing the title compounds (**1**)[2] and



1a

1b; 5,8-di-OMe
1c; 5,8-di-Me
1d; 6,7-di-OMe
1e; 6,7-di-Me
1f; 5,8,9,12-tetra-Me
1g; 6-COOMe

the related molecules.[3)] This argument was supported by the unequivocal experimental observation that the substituents on the benzene ring strongly affected the CT band shifts. On the other hand, it can be expected that the substituents on the benzene rings in 1 will also affect the half-wave potentials. Herein we will briefly describe the polarography of 1. A numerous polarographic studies on substituent effects of *p*-benzoquinones have so far been carried out.[4)] Furthermore, the half-wave potential of 1a has been reported by Iwamura and Makino,[5)] however, present study of such *indirect* substituent effects is to our knowledge the first example.

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. The half-wave potentials ($E_{1/2}$) of the first waves obtained by the logarithmic analyses are shown graphically in Fig. 1.

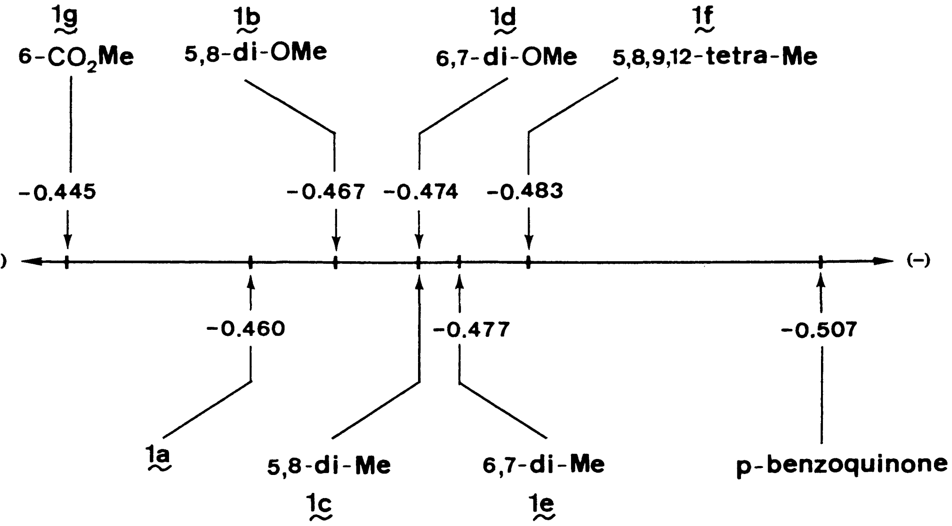


Fig. 1. Graphic illustration of the half-wave potentials ($E_{1/2}$ V vs. SCE) for 1a—1g and *p*-benzoquinone.

Solvent effects are considered reasonably constant since the substituents are not located on the *p*-benzoquinone skeleton of the electron transfer center. Therefore, although the differences of $E_{1/2}$ among a series of 1 are fairly small, these can be regarded as significant values reflecting the electronic features of each molecule.

Several points were obvious: 1) all of the $E_{1/2}$'s of 1 are more positive than the $E_{1/2}$ of *p*-benzoquinone itself; 2) introduction of an electron donating group such as methyl or methoxy into the benzene rings causes the $E_{1/2}$'s to shift in the negative direction and introduction of an electron withdrawing group such as methoxycarbonyl causes the $E_{1/2}$ to shift in the positive direction; 3) the effect of 6,7-substituents is larger than that of 5,8-substituents; 4) interestingly, the methoxy group causes $E_{1/2}$'s to shift in the negative direction less effectively than the methyl group.

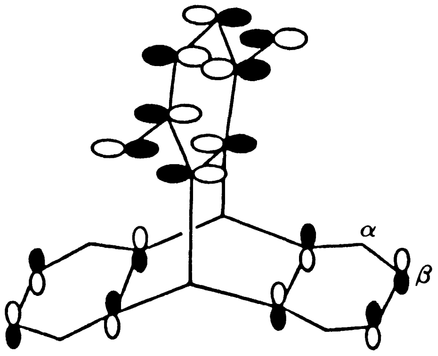


Fig. 2. Schematic representation of the LUMO of 1.

The LUMO is a key orbital when a molecule undergoes reduction. Due to the high electron affinity of *p*-benzoquinone relative to benzene, the major component of the LUMO of 1 is undoubtedly the LUMO of *p*-benzoquinone. The mixing-in of the benzene LUMO's of suitable symmetry (Fig. 2) also lowers the LUMO energy. In addition, the inductive effect of the dihydroanthracene moiety lowers the LUMO of 1 relative to *p*-benzoquinone itself.$^{6)}$ Such effects cause the $E_{1/2}$'s of 1 to shift in the positive direction from the $E_{1/2}$ of *p*-benzoquinone. This is confirmed by experimental observation. The site-dependent substituent effects can be understood in view of the LUMO amplitudes which are greater on the β-positions of the benzene rings. Thus, the substituents on the β-positions are predicted to exhibit more appreciable effects. This is also in agreement with observation.

It is well established that the methoxy group, located on an unsaturated carbon atom, is usually more electron donating than the methyl group in a resonance effect. However, the reverse is true when resonance effects are small compared to inductive effects. Our present results (4) that the methoxy group is a weaker donor than the methyl group might be attributed to the inductive effect. However, a possibilities cannot be ruled out that the methoxy group can adapt the conformation to accept electron as much as possible from the adjacent negatively charged part. At the anion radical states the C-O bond of methoxy group is parallel with the neighboring *p*-orbital. *Ab initio* MO calculations about the model compounds, propene and methyl vinyl ether, seem to support the idea of "*conformational adaptation*" and will be published elsewhere.

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