

SUBSTITUENT EFFECTS IN POORLY AROMATIC SYSTEMS: DICHLORO-ANTHRAQUINONES AND RELATED SEMI-ANTHRAQUINONE RADICALS

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Quinones are known to belong to the pi-electron systems with strongly localized double bonds /1/-/5/. With aromaticity defined in terms of a set of experimental criteria for degree of delocalization of pi-electrons /6/,/7/, quinones can be readily shown to be very poorly aromatic pi-electron systems.

The aromaticity index values have been calculated by means of the Julg /8/ equation:

$$A = 1 - \frac{225}{n} \sum_{r=1}^m \left(1 - \frac{d}{d_r}\right)^2$$

from the experimental data, listed in Table I. This index is a measure of the degree of averaging of the lengths of peripheral bonds in a given system;  $d$  is the mean bond length,  $d_r$  is the length of the  $r$ -th bond, and  $n$  is the number of pi-electrons in the system. The summation is extended over all peripheral bonds 1,2,...,m.

By analogy, an index defining the degree of averaging of bond orders calculated, e.g. in the Hückel approximation, can be defined as:

$$D = 1 - \frac{2}{m} \sum_{r=1}^m p - p_r$$

where  $p$  is the average bond order,  $p_r$  is the order of an  $r$ -th bond, and  $m$  is the number of peripheral bonds. Owing to the well-known relations between bond length and bond order, the two indices have similar physical meanings.

When applied to cyclic pi-electron systems, they constitute measures of aromaticity, whereas with other pi-electron systems they define only degrees of delocalization of pi-electrons. In Table I and Fig. 1 the two indices are given for a group of compounds varying in pi-electron delocalization. In determining their values both indices were assumed to be unity ( $A=D=1$ ) for benzene in which  $d_r=d$  and  $p_r=p$ , and as zero for Kekulé structure for benzene with alternating single ( $d=1.52\text{\AA}$ ,  $p=0.00$ ) and double bonds ( $d=1.34\text{\AA}$ ,  $p=1.00$ ). As evident from Fig. 1, when treated as the measure of pi-electron delocalization both indices are in good agreement.

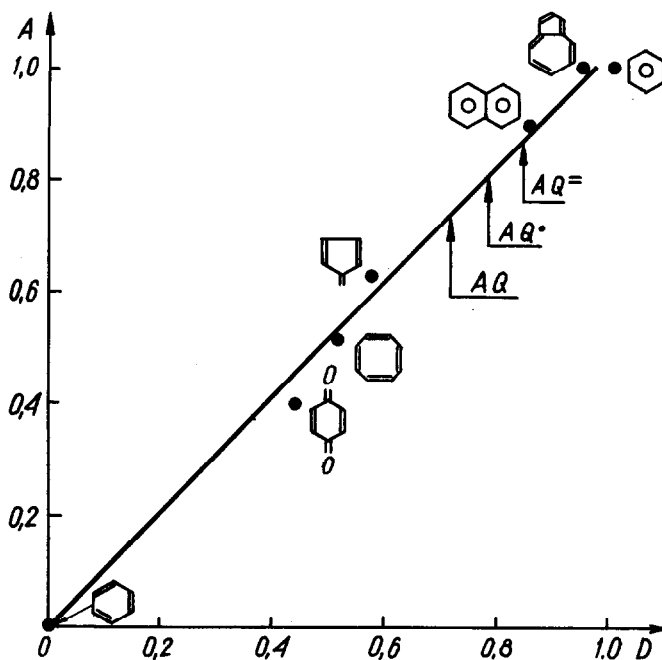


FIG.1. Julg's Aromaticity Index A /8/ vs Delocalization Index D. Arrows denotes Anthraquinene (AQ) its Semiquinone-radical (AQ<sup>·</sup>), and dianion of hydroanthraquinone (AQ<sup>2-</sup>).

TABLE I. Indices of Aromaticity A and of Delocalization D

Compound	A	D
Benzene	1.00 <sup>x</sup>	1.00
Azulene	1.00 <sup>x</sup>	0.94
Naphthalene	0.90 <sup>x</sup>	0.85
Fulvene	0.62 <sup>x</sup>	0.57
Cyclooctatetraene	0.51	0.51
p-Benzoquinone <sup>xx</sup>	0.39	0.44
Kekule structure for benzene	0.00	0.00

<sup>x</sup>) Ref. /8/

<sup>xx</sup>) In calculations for p-benzoquinone the C=O bonds are not allowed for /13/

The Longuet-Higgins and Salem /9/ and the Coulson and Golzbiewski /10/ relation  $d_{rs} = 1.517 - 0.180p_{rs}$  shows that, in terms of the LCAO MO SC (SC = Self Consistent cf. /9,10,11,12/) method, the two indices become almost equivalent, provided the Julg index

is calculated from the SC data. The error involved is then about  $0.01\text{\AA}$ , i.e. of the same order as the error of measurements /11/, /12/. The deviations visible in Fig. 1 are inherent in the Hückel approximation. The D-index is advantageous in that it is applicable to unstable systems, e.g. radicals, particularly when these systems contain hetero-atoms and are to be compared with their parent systems/14/. Thus the greater value of D for semianthraquinone radical in comparison with D for anthraquinone (0.77 and 0.71 respectively) may account for the stability of such type of radicals. For dianion of hydroanthraquinone, which is rather an aromatic system we find  $D=0.84$ .

The A- and D-indices of polynuclear quinones are greater, because the added benzene rings are carriers of aromaticity. For example, in the series p-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone, the D-index is 0.44, 0.62 and 0.71, respectively. Although the aromaticity increases with increasing number of the benzene rings, the D-index continues to assume the values characteristic for low pi-electron delocalizations.

The poorly aromatic character of quinones is presumably the reason for which the experimental data on either 9,10-anthraquinone or its substituted derivatives are unsusceptible to an interpretation based on the conventional Hückel approximation model as suggested by Pauling and Wheland /15/ for aromatic systems. In this model the effect of substituent is allowed for in terms of parameters introduced into the resonance and Coulomb integrals. These parameters characterize the difference of the substituent atom as compared with the carbon atom and the difference of the carbon-substituent with respect to the  $C_{sp^2} - C_{sp^2}$  bond as well as the change in the electron-donating properties of the substituted carbon atom. This problem has been discussed at length in the literature /16/.

It has been found that with monosubstituted anthraquinone derivatives the purely inductive model of substituent interactions and then an empirically determined parameter for the Coulomb integral of the substituted carbon atom enable a number of physico-chemical substituent-related properties to be interpreted /5/. A constraint is superimposed that the substituent shifts in carbonyl stretching frequency,  $\Delta \nu_{CO}^k(X)$ , are a linear function of the substituent-effected shift in the C=O bond order

$$\Delta \nu_{CO}^k(X) = b \Delta p_{CO}(X) + c$$

The bond order change,  $\Delta p_{CO}(X)$ , is here defined by assuming a purely inductive model of the substituent X in position k, that is, by assuming that the substituent X changes the Coulomb integral for the substituted carbon atom by  $d \alpha_k$ , which in turn affects the bond order

$$dp_{CO}(X) = \prod_{CO,k} d \alpha_k(X)$$

The requirement that the correlation line has the same slope as has the  $\nu_{CO}$

vs  $\rho_{CO}$  correlation line for the quinone series (for details see /5/) allowed the derivation an equation for  $d\alpha_k$  which is hereafter termed the effective inductive parameter or EIP(X). The values of this parameter were calculated by assuming  $d\rho_{CO}$  as the average bond order change for the two carbonyl groups in the quinone:

$$EIP(X) = \Delta \nu_{CO}(X) / b \prod_{CO,k}^{av.}$$

The EIP(X)-values were found to follow a linear relation with respect to the Hammett substituent constant  $\sigma$  taken as the sum of inductive and mesomeric effect constants

$$EIP(X) = -0.03 + 1.70(\sigma_{ind} + \sigma_{mes})$$

In the present work the parameter was assumed /5/ to be  $EIP(Cl) = 0.30$  and the conventional Hückel procedure was used for calculation of quantities which could form the basis for the interpretation of the experimental data.

Let us now consider the effect of substituents on the polarographic half-wave reduction potential of chlorinated 9,10-anthraquinone.

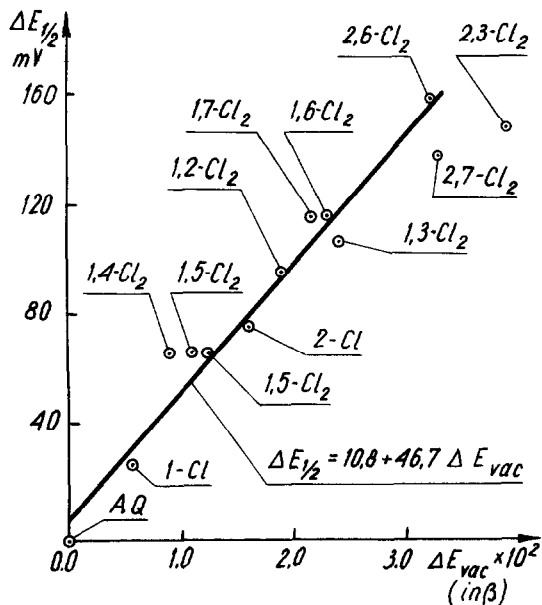


FIG.2.  $E_{1/2}$  vs  $E_{vac}$  for reduction

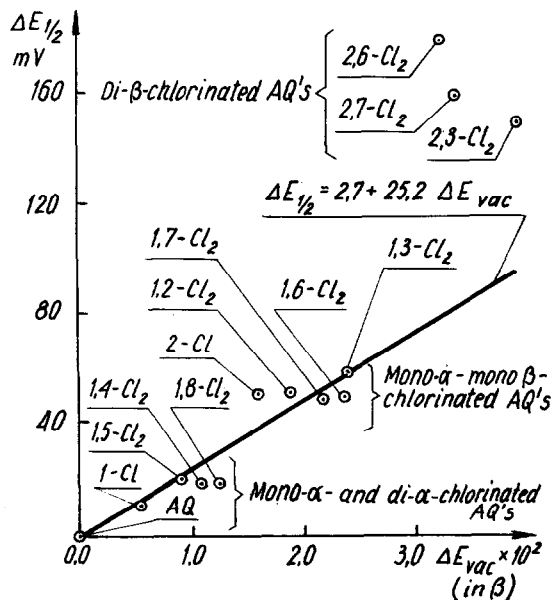
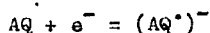
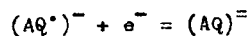


FIG.3.  $E_{1/2}$  vs  $E_{vac}$  for reduction



AQ denotes in both equations the substituted anthraquinones. Positions of substituents are denoted only by numbers, i.e. 1,5-Cl<sub>2</sub> = 1,5-dichloroanthraquinone. Points for 2,6-Cl<sub>2</sub>, 2,7-Cl<sub>2</sub> and 2,3-Cl<sub>2</sub> are not taken into consideration.

In aprotic solvents the reduction is accompanied /17/ usually by a reversible addition of electrons. At first one electron is added



followed by a second



The quinone (I) yields at first an unprotonated semiquinone radical (II) and, upon addition of another electron, it produces the dianion of a hydroquinone (III).

For a single-electron reversible polarographic reduction the half-wave potential  $E_{1/2}$  of the given compound and its substituent-effected shift  $\Delta E_{1/2}$  observed in its derivatives are assumed to be linear functions of the first vacant molecular orbital energy  $E_{vac}$  /18/ or of the substituenteffected change in this energy level as calculated by the Hückel approximation. With  $EIP(Cl) = 0.30$  /5/, substituent shifts were established for mono- and di-chloro-anthraquinones. Plots of  $\Delta E_{1/2}$  vs  $\Delta E_{vac}$  for the half-wave potential measured in *N,N*-dimethylformamide /19/ are given in Fig.2 and 3. They represent substituent effects on the half-wave potentials of the reductions (1) and (2). It is easy to see that for the reduction (1) the slope of the correlation line is greater than that for the reduction (2) (provided the points for 2,6-, 2,7- and 2,3-dichloroanthraquinones are disregarded). This fact means that interactions of the substituents in the semianthraquinone radical (II) with the reducible group are weaker than those in the corresponding quinones. In these cases, the slope of the line has a similar physical significance to that of the Hammett reaction constant; it is a measure of the ability of the system to transfer perturbations from the substituent position to the group which undergoes reduction.

It is evident from Fig.3 that in the radical state the substituent position is of importance: in position of type  $\beta$  the substituent interactions are more strong than those in position of type  $\alpha$ . It appears that in the radical condition  $\alpha$ -chlorine has no essential bearing upon the half-wave potential. For  $\alpha$ -mono and  $\alpha, \alpha'$ -dichloroanthraquinones, the  $\Delta E_{1/2}$ -values are 0 - 20mV, whereas for  $\beta$ -monochloro- and  $\alpha, \beta$ -dichloro-anthraquinones they are 50 - 60mV; at  $\Delta E_{1/2} > 150mV$ ,  $\beta, \beta'$ -dichloro-anthraquinones undergo reduction.

The reason for the correlation in Fig.3 being poor may be also due to the oversimplifications inherent in the Hückel approximation which fails to allow for interaction of electrons and particularly for changes associated with the introduction of the "radical" electron into the pi-electron system. The mechanism of electron transfer accompanying the reduction (2) also may be somewhat different owing to the presence of substituents /14/.

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