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MOLECULAR ORBITAL CALCULATIONS ON THE REACTIVITY OF *o*-BENZOQUINONES TOWARDS DIENES

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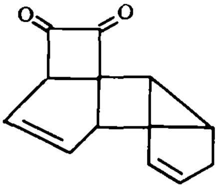
Abstract—The Diels–Alder reactivity of a number of *o*-benzoquinones has been investigated using localization theory. The behaviour of *o*-benzoquinones as philodienes can be satisfactorily explained in terms of paralocalization energy. The bond localization concept is useful in explaining the dienophilic character associated with the double bonds in *o*-benzoquinones.

INTRODUCTION

Unlike *p*-benzoquinones, which can act only as dienophiles[1] in Diels–Alder reactions, *o*-benzoquinones are in principle capable of reacting as dienes and dienophiles.[2] As a rule, however, their capacity for acting as dienes predominates. Recent studies[3-6] on the Diels–Alder reactions of *o*-benzoquinones with cyclopentadiene have shown that depending upon the substitution pattern, products of type I or II are formed.



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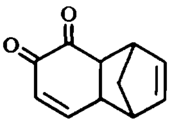

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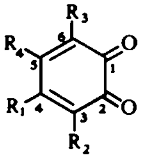
The purpose of the present study is to give a theoretical insight into the dual behaviour of *o*-benzoquinones by means of Hückel MO calculations. Recent attempts to obtain more detailed insight into related problens such as the mechanism of cycloadditions and valence isomerization with the aid of MO calculations and symmetry considerations appear promising.[7-15]

METHOD OF CALCULATION

In the present calculations we have taken all the C atoms as equivalent. Overlap between different orbitals was neglected and the coloumb and resonance integrals were taken a α and β respectively. A different set of parameters for *o*- and *p*-benzoquinone has been suggested by Vincow and Fraenkel[16,17] from ESR measurements. Thus, for *o*-benzoquinones we used $\alpha_o = \alpha + 2\cdot 1\beta$, $\beta_{co} = \beta$. Hetero atom model[18] of Me group was used with $\alpha_x = \alpha + 2\beta$, $\beta_{cx} = 0{\cdot}7\beta$ and for chlorine[18] $\alpha_{cl} = \alpha + 2\beta$, $\beta_{c-cl} = 0{\cdot}4\beta$.



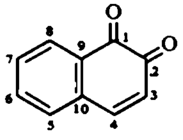


TABLE 1. PARALOCALIZATION ENERGIES AND PARA'ATOM BOND ORDERS OF III

Compound	R_1	R_2	R_3	R_4	$\lvert L^p_{3,6}\rvert$	$-p_{3,6}$
IIIa*	ϕ	H	H	H	3·7060	0·2833
IIIb	CH_3	H	H	H	3·6482	0·3187
IIIc	H	CH_3	H	CH_3	3·6009	0·2710
IIId	Cl	H	H	H	3·5874	0·3442
IIIe	H	H	H	H	3·5590	0·3531
IIIf	H	Cl	H	H	3·5330	0·3501
IIIg	H	CH_3	H	H	3·5019	0·3279
IIIh	H	CH_3	CH_3	H	3·4218	0·3411
IIIi*	H	ϕ	H	H	3·3026	0·2198

* The phenyl group is assumed to be coplanar with the quinone ring.

The Hückel MO calculations were made using a FORTRAN IV Program on an IBM 7044 computer.

RESULTS AND DISCUSSION

Brown has developed a dynamic reactivity index for the Diels–Alder reactions of polyacenes. He defines a "para-localization energy", L^p_{rs} (in units of β), by assuming a concerted reaction proceeding through a symmetric transition state. Benzene and naphthalene do not add maleic anhydride under normal conditions but although anthracene undergoes facile addition at the 9 : 10 positions it appears[7] that appreciable addition can be detected only when $\lvert L_r{}^p{}_s\rvert$ is less than 3·6 in these hydrocarbons. Brown has extended his study to embrace the effects of substituents[7] and to explain the facile dimerization of cyclopentadienone.[19] We have found that $\lvert L_r{}^p{}_s\rvert$ values for several substituted orthoquinones can serve as a valuable aid in correlating the available experimental data on the Diels–Alder reactions of *o*-benzoquinones with cyclopentadiene. In particular it is possible to classify the various substituted *o*-quinones strictly on the basis of $\lvert L_r{}^p{}_s\rvert$ values in accordance with philodienic behaviour. Table 1 gives the para-localization energies of a number of *o*-benzoquinones at the 3,6 position.

In the reaction of cyclopentadiene with *o*-benzoquinone (IIIe), 4-methyl (IIIb), 4-chloro (IIId) and 4-phenyl (IIIa) *o*-benzoquinones adducts of type II have been isolated,[3,5] indicating pronounced dienophilic behaviour of these *o*-benzoquinones. When the substituents occupy 3-position reversal of the behaviour of *o*-benzoquinone (i.e. pronounced diene behaviour) was noticed and adducts of type I were obtained.[3] (Also it is interesting to note that 3,6-dimethyl-*o*-benzoquinone (IIIh) gives a type I adduct with cyclopentadiene whereas 3,5-dimethyl-*o*-benzoquinone (IIIc) behaves as a dienophile towards the latter leading to type II adducts.[3] According to localization

theory[7] the formation of an adduct at a pair of atoms, *m* and *n* (here 3 and 6) of the conjugated system depends only on the energy required to localize two of the Pi electrons upon atoms *m* and *n*, provided *m* and *n* are favourably oriented. Adduct formation at these positions will be more facile if the corresponding localization energy is very small. From Table 1 it is evident that the para localization energies of unsubstituted and 4-substituted *o*-benzoquinones are high compared to the 3-substituted *o*-benzoquinones. Also the low $|L^p_{3,6}|$, 3·4218, associated with the 3,6-dimethyl *o*-benzoquinone (IIIh) shoots up to 3·6009 when one of the methyls occupies 5-position. From these data it is quite evident that if the para localization energy of a substituted *o*-benzoquinone is less than 3·559 which is the paralocalization energy of the parent quinone (IIIe), the diene behaviour predominates and type I adducts are formed. In other cases for which $|L^p_{3,6}|$ values are higher than that of *o*-benzoqiunone pronounced dienophilic behaviour is noticed. The high para localization energy, **4·6786, associated with the pair of atoms 3 and 9 in 1,2-Naphthaquinone (IV)** clearly confirms its dienophilic behaviour. Since *o*-benzoquinone itself gives only a type II adduct the dividing line is between $|L^p_{rs}|$ 3·559 and 3·533.

Recently, Epstein[20] found that para-atom bond orders, p_{rs}, between the pair of nonbonded atoms *r* and *s* of the diene provides a static reactivity index for Diels-Alder reactions. He correlated p_{rs} values with Brown's para localization energy, $L^p_{r,s}$, which is a dynamic index. Following Epstein we calculated the bond orders, p_{rs}, between the 3 and 6 atoms in these *o*-benzoquinones; but we could not get any correlation with L^p_{rs} values in these quinones.

We have also computed the bond localization energies[21] of the *o*-benzoquinones (IIIa to IIIe) with a view to studying whether the dienophilic behaviour is pronounced at the substituted or unsubstituted double bond. Table 2 gives the bond localization energies, $|L^b_{rs}|$, associated with the double bonds in these *o*-benzoquinones. The corresponding bond orders, p_{rs}, are also recorded. As there is a relationship between bond order and the effect of a change in β on π-energy, L^b_{rs} is approximately inversely proportional to the bond order of the bond.

TABLE 2. BOND LOCALIZATION ENERGIES AND BOND ORDERS OF *O*-BENZOQUINONES

Compound	Bond	$\|L^b_{rs}\|$	p_{rs}
IIIa*	3—4	1·0000	0·5780
	5—6	0·8520	0·8017
IIIb	3—4	0·9422	0·6611
	5—6	0·8072	0·8065
IIIc	3—4	0·8152	0·8026
	5—6	0·9502	0·5889
IIId	3—4	0·8814	0·7359
	5—6	0·8350	0·7855
IIIe	3—4	0·8530	0·7719
	5—6	0·8530	0·7719

* The phenyl ring is assumed to be coplanar with the quinone ring.

The diene addition occurs at the unsubstituted double bond in compounds IIIa, IIIb and IIId since the bond localization energy associated with the phenyl, methyl and chloro substituted double bonds are comparatively high. Experimentally it is known that addition occurs at the unsubstituted double bond in these compounds. When 3,5-dimethyl-*o*-benzoquinone (IIIc) acts as a dienophile towards cyclopentadiene, cycloaddition to the 3,4- and not to the 5,6-double bond occurs. The bond localization energy associated with the 3,4- and 5,6-double bonds in IIIc also supports the experimental finding. In 1,2-naphthaquinone (IV) the addition does not occur at the 9,10-double bond conjugated in an aromatic ring, in view of the high bond localization energy (2·4884) associated with this double bond. From Table 2 it is clear that the bond order of the corresponding double bond undergoing cycloaddition is relatively higher than the other double bond in the quinone ring.

CONCLUSION

The concept of para localization energy has been extended to philodienes and is shown to provide a good index of reactivity. The bond localization energy is also found to be a good predictor of the dienophilic character associated with the quinone dienophiles.

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