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THE ANTIAROMATICITY OF CYCLOBUTADIENE

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Abstract—The antiaromaticity of cyclobutadiene systems is explored by means of theoretical studies on quinone electrochemical oxidation reactions.

The nearest anyone has been able to come to an experimental quantitative determination of the thermodynamic destabilizing power of cyclobutadiene[1] is a series of electrochemical studies on cyclobutadiene-substituted quinoidal systems made by Breslow *et al.*[2] We undertook theoretical investigations of these reactions to determine what additional supportive information might be derived using an SCF-PI-MO method developed by Dewar *et al.*[3] which had proved successful in a number of other applications.[4]

Breslow's results are summarized in Fig. 1 and Table 1. Structures **2a** are drawn as dimethylenecyclobutene derivatives. The reason for doing this is discussed below. It should be noted, however, that these compounds can be drawn in an alternative resonance form, **2c**, which is a cyclobutadiene derivative. The actual contribution of this form will be discussed later.

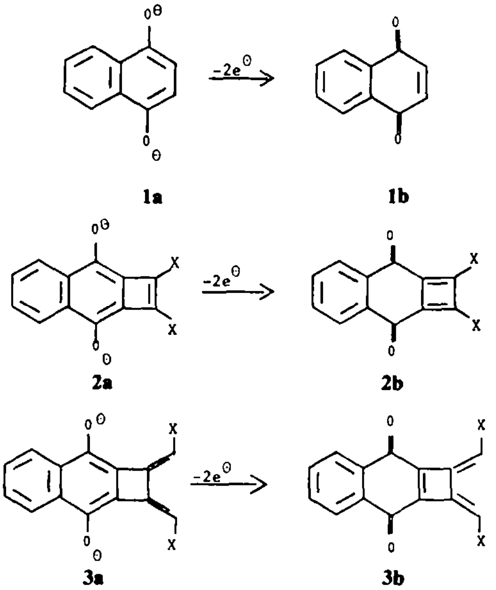
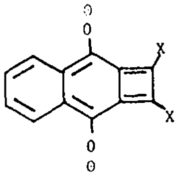


Fig. 1. Electrochemical oxidations of hydroquinone dianions.

Table 1. Oxidation potentials

Compound	Total Oxidation Potential[a]
1	-2.18
2 (X = phenyl)	-1.15
2 (X = anisyl)	-1.38
3 (X = phenyl)	-1.67

[a]Concentration ≤ 0.5 mM in DMF at 20° with 0.5 M tetrabutylammonium perchlorate using a Pt working electrode. Potentials in V vs Ag|AgCl reference electrode.

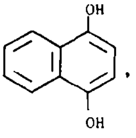


2c

Thus, when compounds **2a** are oxidized, they go from a hydroquinone form having only partial cyclobutadiene character to a quinone form that has full cyclobutadiene character, i.e. the cyclobutadiene character becomes, to some extent, switched on. It is found that compounds **2a** are significantly more difficult to oxidize than is compound **1a** which is regarded as a model compound. It may be argued, however, that the increased difficulty of oxidation is not due to antiaromatic character, but instead is a steric consequence of the fused 4-membered ring. To counter these arguments, a study was made of compound **3a** where the four membered ring is still a factor, but the product of oxidation has no cyclobutadiene character. It was found to be more easily oxidized.

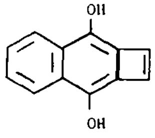
The theoretical method we used[3] is a modification of the Pople pi-electron MO method[5] which has proved to give excellent calculated ground state properties for conjugated pi-systems. In particular, it has been used with reference to quinone redox potentials[4b] and the polarographic reduction potentials of hydrocarbons.[4f] The method incorporates a variable β procedure which, through a bond order—bond length relation, provides very reliable calculated bond lengths. The calculation of resonance energies involves the comparison of the heat of atomization of a compound as experimentally determined or as calculated by the SCF-PI method vs the heat of atomization of a hypothetical model of the compound which has its bonds localized. This method is discussed in several sources.[3a,4c,4e,6]

The heats of atomization and resonance energies resulting from our calculations on these reactions and some reference compounds are shown in Table 2. Note that the calculations are not on the dianions, but are instead on the parent hydroquinones:



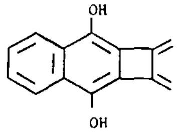
1a′

,



2a′

, and



3a′

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Table 2. Calculated results

Compound	ΔH_a (eV)	Resonance Energy (eV)
1á	- 99.603	1.331
1b	- 94.092	0.551
2á	-113.464	0.954
2b (X=H)	-107.681	-0.097
3á	-132.466	1.193
3b (X=H)	-126.994	0.453
4	- 57.157	0.869
5	- 90.610	1.322
6	- 36.752	-0.774
7	- 42.078	0.027

The calculated heat of atomization for naphthoquinone may be compared with the experimental value[7] of 93.98 ± 0.3 eV. This agreement, well within experimental error, is the sort of accuracy which experience has shown can be expected from this method. Also, the results have already been published for the reference compounds.[3a]


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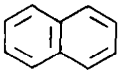
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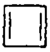
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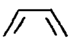
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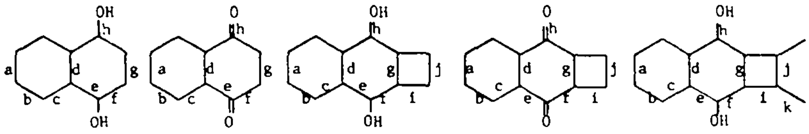
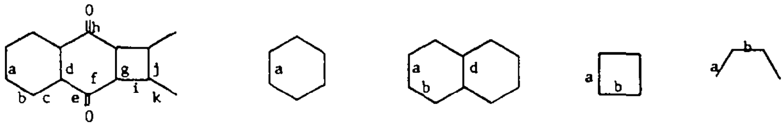
Reviewing these results, we see that naphthohydroquinone, **1á**, has essentially the same resonance energy as naphthalene, **5**. Naphthoquinone, **1b**, however, might have been expected to have a resonance energy like that of benzene since it has a benzene ring intact in its structure. The quinoidal system appears to reduce the aromaticity significantly, lowering it by 0.869 − 0.551 = 0.318 eV. Looking at compound **2á**, we see that its resonance energy is lower than that of **1á** by 0.377 eV. This is, at least in part, due to the cyclobutadiene character in the resonance form **2c**. Compound **2b** is interestingly seen to be nonaromatic. Here the aromaticity of the benzene ring is effectively cancelled by the antiaromaticity of the cyclobutadiene and the destabilizing influence of the quinoidal system seen in naphthoquinone, **1b**.

Next we want to look at the differences between the energies of compounds **1** and compounds **2**. In going from **1á** to **1b**, we calculate a difference in heats of atomization of −5.511 eV; for **2á** to **2b** (X=H) we arrive at −5.783 eV. Thus, as Breslow found, **2a** should be more difficult to oxidize than **1a**. If we look at the resonance energies, we find a difference of 0.780 eV for compounds **1á** and **1b** and



	1á	1b	2á	2b	3á
a	1.42	1.39	1.41	1.39	1.42
b	1.37	1.40	1.38	1.40	1.37
c	1.43	1.39	1.42	1.39	1.43
d	1.40	1.41	1.40	1.41	1.40
e	1.43	1.47	1.44	1.47	1.43
f	1.37	1.47	1.36	1.47	1.38
g	1.42	1.35	1.44	1.51	1.43
h	1.39	1.25	1.39	1.26	1.39
i	-	-	1.48	1.35	1.47
j	-	-	1.35	1.51	1.47
k	-	-	-	-	1.35



	3b	4	5	6	7
a	1.39	1.40	1.42	1.34	1.34
b	1.40	-	1.37	1.51	1.47
c	1.39	-	1.43		
d	1.41	-	1.40		
e	1.47				
f	1.47				
g	1.36				
h	1.26				
i	1.47				
j	1.47				
k	1.35				

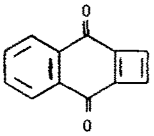
Fig. 2. Calculated bond lengths.

1.051 eV for compounds **2á** and **2b**. Thus, the oxidation of the cyclobutadiene derivative goes against a much greater loss of resonance energy.

We can also get a comparative measure of the amount of destabilization of **2a** due to the resonance form **2c**. The difference in the resonance energies of **1á** and **2á** is 0.377 eV while that between **1b** and **2b** is 0.648 eV. Thus **2b** is destabilized relative to **1b** 1.7 times more than **2á** is relative to **1a**.

The variable β provision of the SCF-PI method used in this work allows calculation of bond lengths. These data are indicated in Fig. 2.

So far as the geometry of the carbon skeleton is concerned, **1á** is essentially a naphthalene, **5**, and **1b** is essentially a benzene, **4**. Except for a lengthening of the bond at which the cyclobutene ring is fused, **2á** is essentially a naphthalene. The resonance forms drawn in this paper have been dictated by the results of these calculations. That is, the choice as to whether a given bond should be formally drawn as double or single has been determined by its length relative to its neighbors. If it is relatively short it has been drawn as a double bond; if it is long, it is drawn as a single bond. So it is that form **2a** was given instead of **2c** in Fig. 1. This consideration is also interesting with reference to compound **2b**. First we note that the geometry of this compound is that of joined benzene and cyclobutadiene, **6**, rings. However, in all published references to this compound, the cyclobutadiene ring is drawn as in



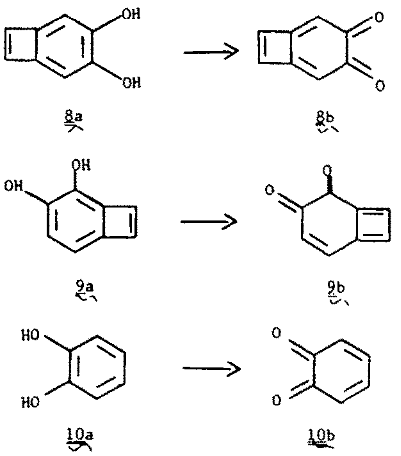
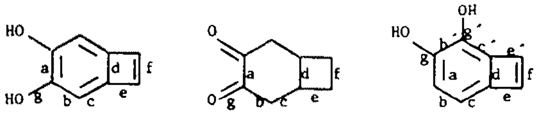


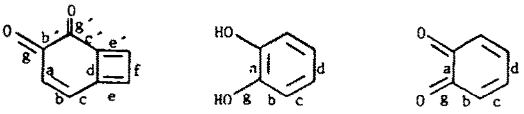
Fig. 3. Orthoquinone reactions.

Our calculation indicates that the alternative "resonance" form for this ring is preferred. The single bonds from the carbonyl carbon atoms are of normal length for sp^2-sp^2 carbons as the butadiene, **7**, reference figures indicate.

In a paper commenting on Breslow's preliminary results,[2a] Pullman[8] suggested that electrochemical oxidation of the two hydroquinones with fused 4-membered rings in Fig. 3 would be an interesting and more direct



	8a	8b	9a
a	1.38	1.48	1.38
b (b′)	1.42	1.47	1.42(1.42)
c (c′)	1.38	1.35	1.38(1.38)
d	1.42	1.47	1.42
e (e′)	1.49	1.47	1.49(1.49)
f	1.34	1.35	1.34
g (g′)	1.39	1.25	1.39(1.39)



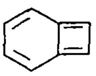
	9b	10a	10b
a	1.47	1.40	1.48
b (b′)	1.35(1.48)	1.40	1.47
c (c′)	1.46(1.46)	1.40	1.35
d	1.51	1.40	1.46
e (e′)	1.36(1.35)	-	-
f	1.50	-	-
g (g′)	1.25(1.25)	1.39	1.25

Fig. 4. Calculated orthoquinone geometries (Å).

Table 3. Calculated orthoquinone energies

Compound	ΔH_a (eV)	Resonance Energy
8a	-79.844	0.334
8b	-74.074	-0.704
9a	-79.855	0.348
9b	-73.504	-1.274
10a	-66.126	0.854
10b	-59.994	-0.546

comparison for the antiaromaticity of the cyclobutadiene ring vs the stability of the dimethylene-cyclobutene moiety. Their carbon skeletons are identical, but the locations of the substituents give them quite contrasting electronic effects. Both starting materials will have the partial cyclobutadiene character imparted by a resonance form analogous to that in **2c**, i.e.



The calculated results for these compounds are given on Tables 3 and Fig. 4. Basically, the calculated quantities for **8a** and **9a** are very similar. Compared with the reference compound **10a**, they show a decrease in resonance energy of 0.5 eV. Dramatic differences arise when these are converted to the orthoquinones. Compound **8a** is forced into the dimethylenecyclobutene derivative, **8b**; **9a** is forced into the vinyl cyclobutadiene derivative **9b**. The difference in the heats of atomization of **8a** and **8b**, 5.770 eV, indicates that this oxidation should go much more easily than **9a**→**9b** where the difference is 6.351 ev. However, as the model calculation for **10a**→**10b** indicates, these results are complicated by the considerable antiaromaticity of the orthoquinone system.

In summary, direct comparison of experimental and theoretical results are complicated by the complex solution chemistry and charged species involved in Breslow's work. However, our calculations confirm that oxidations of hydroquinones to quinones having a fused cyclobutadiene ring should be more difficult to carry out than in analogous cases where this structural feature is missing and that this destabilization is a consequence of the antiaromaticity of cyclobutadiene's electronic structure.

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