tion to a double bond, followed by reoxidation. Full details will be presented in a future publication.

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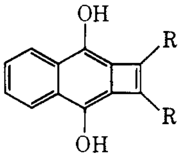
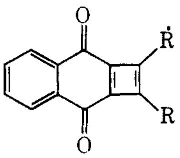
On the Antiaromaticity of the Cyclobutadiene Ring

Sir:

It has been shown recently[1] by polarography measurements that the hydroquinone I (R = CH_3 or C_6H_5), as well as its dianion, was more difficult to oxidize than is naphthohydroquinone or its dianion, the authors stating: "the bulk of the effect is due to the antiaromaticity of the cyclobutadiene ring in II. Such antiaromaticity should raise the energy of I as well as of II, although to a lesser extent."



I



II

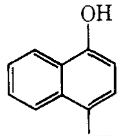
The effects observed can be easily rationalized in a very simple manner, using the theoretical indices which have been shown[2] to be correlated with the red–ox properties of quinone systems, in particular the loss in resonance energy accompanying the oxidation[3] and also the energies of the molecular orbitals involved in the electron transfer.[4] (Although the indices used are defined in the Hückel approximation, we consider that a correlation of the type mentioned may be useful as long as it has not been proven nonexistent. A new case fitting into the correlation here supports its usefulness.) Table I gives the appropriate values for a series of quinones of relevance.

Table I. Energy Indices Related to Oxidation–Reduction[a]

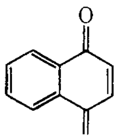
hq/q	R_{hq}	R_q	ΔR	$HOMO_{hq}$	$LEMO_q$
I/II	4.73	3.44	1.29	+0.28	+0.11
III/IV	4.19	3.28	0.91	+0.41	−0.33
V/VI	5.37	4.50	0.87	+0.32	−0.24
VII/VIII	2.88	2.17	0.70	+0.17	−0.42
IX/X	2.49	1.39	1.10	+0.67	−0.21
XI/XII	2.90	1.69	1.21	+0.21	+0.08
XII/XIV	4.89	3.44	1.45	+0.53	+0.04

[a] In Hückel β units. R, resonance energy; ΔR, loss of resonance energy upon oxidation; $HOMO_{hq}$, highest occupied orbital of the hydroquinone; HOMO's are usually *bonding* (+ sign); $LEMO_q$, lowest empty orbital of the quinone; LEMO's are usually *antibonding* (− sign).

It is seen that the oxidation of naphthohydroquinone proceeds against a loss of resonance energy of 0.9 β and that this loss is strongly *increased* in the system I/II, making oxidation more difficult. But still more interesting is the fact that the lowest empty molecular orbital (LEMO) of the quinone II has become *bonding*, a strong indication of an exceptional high tendency to accept electrons. This feature results from the presence of the cyclobutadiene ring, whose degenerate nonbonding orbitals both become bonding in the quinone II, one being filled and the other empty. The occurrence of a bonding LEMO in a quinone is reminiscent of the situation in diphenoquinone (XIV), which indeed is known as a powerful oxidizing agent. Both I and II see their resonance energies increased with respect to the naphthoquinones III and IV, but the increase is larger in the reduced form than in the oxidized form. The number of π electrons in I and III (or II and IV) being different, their relative *thermodynamic* stabilities are not properly measured by R but rather by R divided by the number of π electrons. Then, I and III are practically the same, whereas II appears destabilized. This clearly comes from the fact that, in I, the square cycle can assume, at least partly, a dimethylenecyclobutene structure, which is less, if at all, antiaromatic than a pure cyclobutene.



III



IV

It may be observed that a stabilization (or at least an absence of destabilization) of I from the point of view just developed is not at all incompatible with an increased instability as measured by various properties; for instance, the HOMO value is smaller than in III, making the reduction *per se* easier in I than in III.

The conclusion that no strong destabilization is expected when the square cycle can assume a dimethylenecyclobutene structure could be examined on compounds V and VI; there, ΔR is very similar to its value for III/IV, the quinone appearing as an acceptor only slightly better than IV.

On the other hand, it would seem worthwhile to find a case where the antiaromaticity of the cyclobutene ring would result in an effect opposite to the one observed in ref 1, namely an increased ease of oxidation of a hydroquinone. This should occur in a system where the dimethylenecyclobutene structure is imposed

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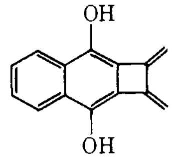
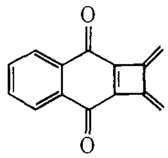
(1) R. Breslow, R. Grubbs, and S.-I. Murahashi, *J. Amer. Chem. Soc.*, **92**, 4139 (1970).

(2) For a detailed discussion, see A. Pullman, *Tetrahedron Suppl.*, **No. 2**, 441 (1963).

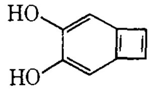
(3) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," New York, N. Y., 1941.

(4) A. Pullman, *C. R. Acad. Sci. Paris*, **253**, 1210 (1961).


V


VI

in the quinone instead of in the hydroquinone; this could happen in an appropriate orthoquinone. Indeed, Table I suggests that oxidation of VII to VIII should be easier than that of IX to X. The loss of ΔR upon oxidation is strongly diminished and the effect of the cyclobutadiene ring appears here in the HOMO of the hydroquinone which originates in the zero HOMO of the square cycle. Loss of electrons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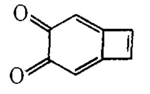
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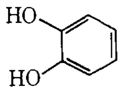
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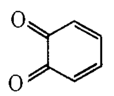
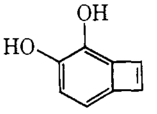

X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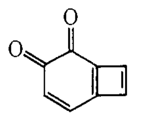
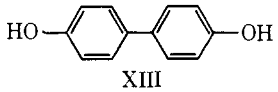

XII

is thus facilitated in VII, and at the same time the electron-accepting tendency of the quinone produced is decreased (LEMO much more antibonding than in X).

In fact, the comparison of VII/VIII to XI/XII should be even more striking since the quinone XII shows the same effect as observed for II, namely a strong destabilization (ΔR = 1.21) and a bonding LEMO, which should tend to make the hydroquinone much more difficult to oxidize than VII.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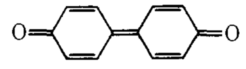
XIV

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Crystal Structure of an Iridium–Tetrazene Complex Formed in the Reaction of Diazonium Salts with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I)

Sir:

The reactions of aryldiazonium salts are receiving considerable attention at the present time, inasmuch as arylazo complexes of transition metals afford model systems for the bound nitrogen complex believed to be the initial step in atmospheric nitrogen fixation.[1,2] In all cases, it appears that the arylazo group binds to the metal through the unsubstituted nitrogen atom.[2–6]

As part of a systematic study of these complexes, we have carried out the reaction of several para-substituted phenyldiazonium tetrafluoroborate salts with Vaska's complex, *trans*-$IrCl(CO)(Ph_3P)_2$. The red crystals readily isolated from these reactions are now shown by a single-crystal X-ray structure analysis for the *p*-fluoro compound to consist of the iridium-1,4-*p*-fluorophenyltetrazene complex, $[Ir(N_4(C_6H_4F)_2)(CO)(Ph_3P)_2]BF_4 \cdot C_6H_6$, rather than the closely related bisarylazo complex we at first expected to be present from chemical considerations. The possibility of the formation of tetrazene complexes in the reactions of aryldiazonium salts does not generally seem to have been recognized. Deeming and Shaw[5] reported the arylazo complex $[IrCl_2(PhN_2)(CO)(PhMe_2P)_2]$ from a similar synthesis in the presence of LiCl, and we are currently investigating other products in our reaction which we believe to be arylazo complexes.

In a typical preparation, a benzene–ethanol solution of $IrCl(CO)(Ph_3P)_2$ was treated at room temperature under argon with an equimolar quantity of the diazonium salt. Red, air-stable, diamagnetic crystals of the product were deposited from the deep red solution at 8°. *Anal.*[7] Calcd for $[Ir\{N_4(C_6H_4F)_2\}(CO)(Ph_3P)_2]BF_4 \cdot C_6H_6$: C, 57.1; H, 3.81; N, 4.85; P, 5.36; F, 9.86. Found: C, 54.9; H, 3.80; N, 5.30; P, 5.10; F, 9.56. Conductivity measurements in nitromethane solution showed typical 1:1 electrolyte behavior (Λ_M = 100 ohm^{-1} cm^2 mol^{-1} at 1.5×10^{-4} *M*). The proton nmr spectra ($CDCl_3$ solution) showed multiplet peaks centered at τ 2.9 (triphenylphosphine and benzene) and 3.8 (*p*-fluorophenyl). ^{19}F nmr spectra in $CDCl_3$ solution (at 56.4 MHz using CAT) confirmed the presence of *p*-F (−6230 cps, weak) and BF_4^- (−8778 cps, strong) relative to a CCl_3F internal standard.[2] In the ir spectrum ν(CO) occurs at 2060 cm^{-1}, but we have been unable to detect bands due to nitrogen vibrations. Raman spectra are unavailable owing to decomposition in He–Ne laser radiation.

The compound crystallizes in the triclinic space group $P\bar{1}$; M = 1156, a = 13.669 (5), b = 17.423 (7), c = 10.852 (4) Å, α = 104.57 (3), β = 98.07 (5), γ = 88.43 (3)°, U = 2477 Å^3, D_m = 1.53 (3), Z = 2, λ 0.70926 Å, D_c = 1.549 g cm^{-3}. Intensities were measured using an automated Picker four-circle diffractometer and Mo Kα radiation (λ 0.7107 Å) up to 2θ = 45°. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure. At present, R = 0.043 on 1396 independent reflections above background in the range 2θ 0–30°, with only the iridium atom allowed anisotropic thermal parameters. Further refinement, incorporating the remaining outer-sphere reflections, is continuing.

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(1) R. Murray and D. C. Smith, *Coord. Chem. Rev.*, **3**, 429 (1968).

(2) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967); **87**, 2133 (1965).

(3) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

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(5) A. J. Deeming and B. L. Shaw, *ibid.*, *A*, 1128 (1969).

(6) V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970).

(7) Analyses were performed independently by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and A. Bernhardt, Munich. The C, N, and P results showed persistent and reproducible deviation, even after repeated recrystallization from benzene–acetone.