

THE STABLE RADICAL CATION OF TETRAKIS(DIMETHYLAMINO)-p-BENZOQUINONE¹⁾

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Summary: The electron-rich tetrakis(dimethylamino)-p-benzoquinone exhibits a low first ionization energy of only 7.1 eV and can be oxidized electrochemically at +0.25 V vs. SCE to its purple radical cation, whose spin population differs considerably from that of the corresponding semiquinone radical anion.

The strong donor effect of dimethylamino substituents is a well established device to lower the first ionization potential of π systems³⁾

$X-C\equiv C-X$						
$IE_1(X=H)$	11.40 eV	10.57 eV	10.06 eV	9.25 eV	9.25 eV	
$IE_1(X=NR_2)$	7.70 eV	6.95 eV	7.10 eV	6.75 eV	6.75 eV	(1)

and thus provides access to persistent radical cations³⁾ like famous Wurster's Blue. The black title compound, which has been prepared by reacting tetrafluoro-p-benzoquinone with dimethylamine⁴⁾, therefore, should be a prospective precursor for a hitherto unknown stable "semiquinone radical cation"⁵⁾.

Both the photoelectron spectrum (Figure 1) and the anodic cyclovoltammogram (Figure 2: A) confirm the expectation. Relative to the parent, p-benzoquinone⁶⁾, the first vertical ionization energy is lowered by more than 3 eV

	IE_1^V	$E_{1/2}^{Ox}$	$E_{1/2}^{Red}$	
$X = H$	10.11 eV	+2.85 V	-0.40 V	
$X = N(CH_3)_2$	7.10 eV	+0.25 V	-1.07 V	(2)

Figure 1.

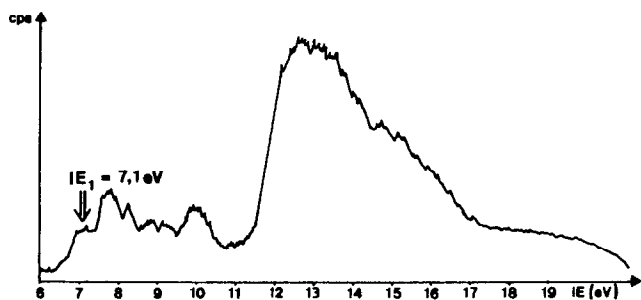


Figure 2.

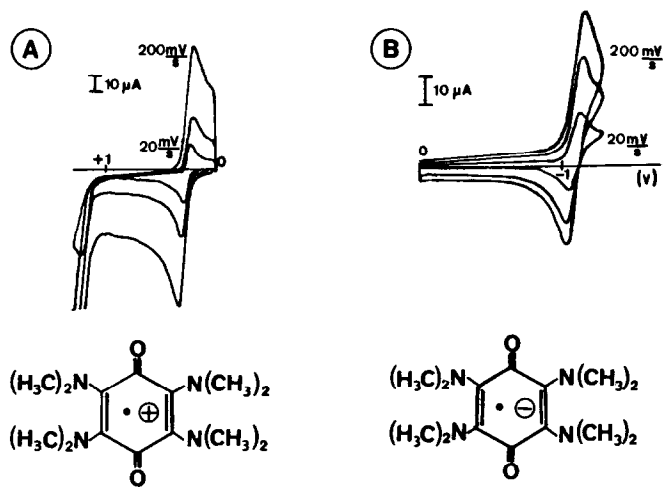
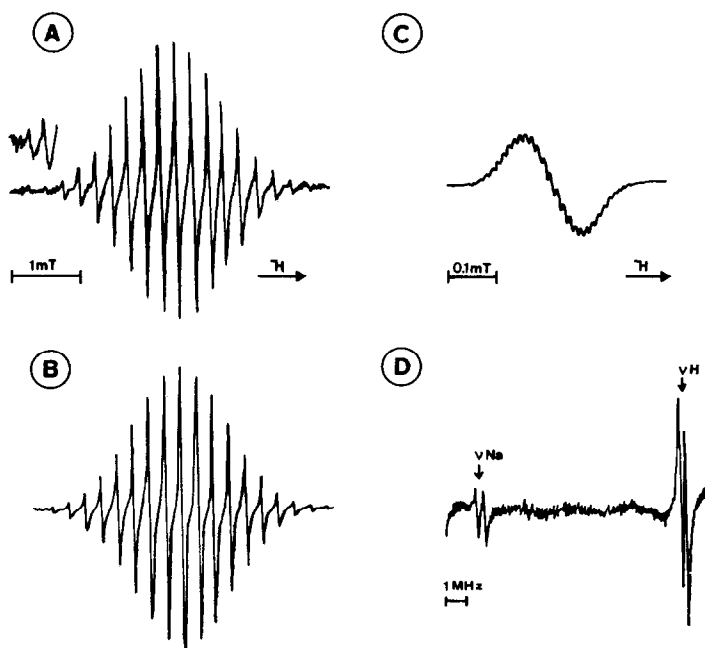


Figure 3.



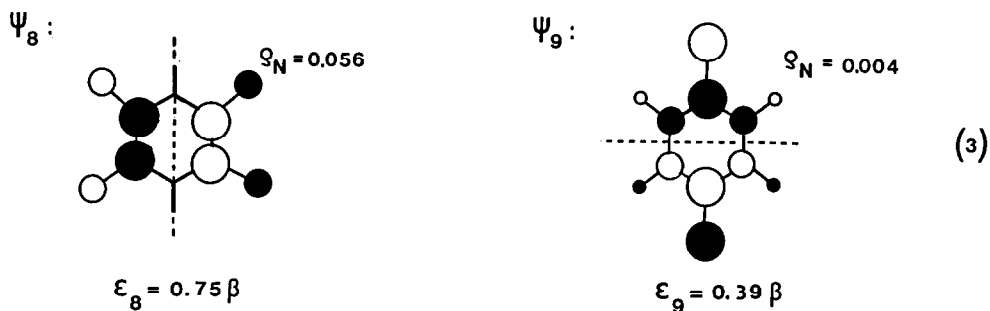
and an almost reversible ($\Delta E = 70$ mV) oxidation wave is recorded at only +0.25 V in DMF/0.1 m TBAP at room temperature. The reversible ($\Delta E = 60$ mV) quinone reduction potential (Figure 2: B), on fourfold dimethylamino substitution moves by -0.67 V in the same direction (2).

The purple radical cation of tetrakis(dimethylamino)-p-benzoquinone, generated advantageously by electrochemical oxidation at a platinum anode in DMF/0.1 m TBAP solution at room temperature, exhibits a well-resolved 19 line multiplet ESR spectrum centered at $g = 2.0032$ (Figure 3:A). Its computer simulation (Figure 3: B) can be accomplished assuming accidental degeneracy of the coupling constants $a_{1H} \sim a_{14N} = 0.332$ mT for sets of 24 1H ($I = 1/2$) and 4 ^{14}N ($I = 1$) nuclei each equivalent within the ESR time scale.

On reduction e.g. of a THF solution using Na at room temperature and adding $Na^{\oplus}B(C_6H_5)_4^{\ominus}$ to enhance ion-pairing, the tetrakis(dimethylamino)-p-benzoquinone radical anion is formed, presumably as a triple ion complex with 2 counter cations $[Na^{\oplus}SQ^{\ominus}Na^{\oplus}]^{\ominus 7}$. Comparison of its "single-wave" ESR spectrum superimposed by a 29 line multiplet (Figure 3: C) with the one of the corresponding radical cation (Figure 3: A) discloses tremendous changes in the spin distribution: the total spectrum width shrinks from about 6 mT for the observed M^{\oplus} signals to only 0.4 mT for the corresponding M^{\ominus} i.e. to one fifteenth(!) and the center is shifted to $g = 2.0046$. The 1H and ^{23}Na (100 % nat. abundance, $I = 3/2$) coupling constants, $a_{1H} = 0.0112$ mT and $a_{23Na} = 0.0143$ mT, respectively, are determined from the ENDOR spectrum (Figure 3: D); both couplings are of same, most probably positive sign as deduced from General Triple experiments and the ESR temperature dependence.

How can one rationalize both the stability of the tetrakis(dimethylamino)-p-benzoquinone radical cation and the ESR spectroscopically detected huge change in the spin population on formally adding 2 electrons to form the corresponding radical anion?

To start with, the surprising "merocyanine" structure of 2.5-bis(dialkylamino)-p-benzoquinones is called back to mind, showing strangely alternating CC bonds flanking each CO group, 141 pm and 150 pm⁸⁾ long, respectively and rather short CN bonds of only 134 pm⁸⁾ lengths. A space-filling model of the tetrasubstituted molecule suggests, in addition, considerable steric overcrowdedness due to the somewhat bulky, lone pair bearing $N(CH_3)_2$ groups, which possibly reduces the maximum n_N/π interaction. With the molecule $C_{14}H_{24}O_2N_4$ being too large for complete and reliable semiempirical treatment including geometry optimization, we retreated to a set of HMO (McLachlan) calculations, varying especially the N perturbation and achieving reasonable correlation with the experimental results using $h_O \sim h_N = 1.5$, $k_{CO} = 1$, $k_{CN} = 0.4$ and $\lambda = 1.2$. The results for the inner orbitals Ψ_8 and Ψ_9



illustrate not only the lowering of the ionization potential relative to parent p-benzoquinone (cf. (2)), $\Delta \epsilon_J = -0.22$) and the radical cation ground state stabilization due to delocalization of positive charge into the 4 NR₂ groups, but also the observed large differences in the spin population g_N at the N centers for radical cation and radical anion due to the spin nodal plane in Ψ_8 crossing both CO groups.

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References and Notes

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