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ELECTRONIC SPECTRA OF *ortho*-SEMIQUINONES AND A REMARK ON THE APPLICABILITY OF THE LCI-CNDO METHOD TO QUINONES AND SEMIQUINONES

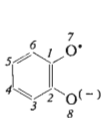
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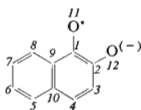
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Electronic spectra of electrochemically generated 3,5-di-*tert*-butyl-1,2-benzosemiquinone, 1,2-naphthosemiquinone, and 9,10-phenanthrenesemiquinone are compared with the results of semiempirical open shell PPP-like calculations. Results of LCI-CNDO calculations on 1,4-benzoquinone, 1,2-benzoquinone, and on the corresponding semiquinones, are briefly discussed.

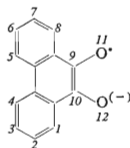
In an earlier paper¹ of this series, electronic spectra of five *para*-semiquinones were interpreted by the open shell semiempirical calculations of the PPP type. Using the same computational scheme, we attempted in this paper to interpret the electronic spectra of electrochemically generated *ortho*-semiquinones I–III.



I



II



III

EXPERIMENTAL

3,5-Di-*tert*-butyl-1,2-benzoquinone was prepared from 3,5-di-*tert*-butylcatechol** following the procedure reported² for 1,2-benzoquinone. 1,2-Naphthoquinone was kindly furnished from the collection of Dr J. M. Bruce, University of Manchester. 9,10-Phenanthrenequinone was obtained commercially.

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** A sample of 3,5-di-*tert*-butylcatechol was kindly provided by Dr J. Pospíšil, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague.

Semiquinones were prepared by electrochemical reduction of quinones in acetonitrile, using tetrabutylammonium perchlorate as a supporting electrolyte. Purification of solvent³, electrochemical devices, and determination of semiquinone concentration are described elsewhere¹.

Our absorption spectrum for 9,10-phenanthrenesemiquinone is in excellent agreement with that of Staples and Szwarc⁴, who prepared the compound by alkali metal reduction *in vacuo*.

Calculations

Both for semiempirical π -electron and CNDO calculations we used the SCF open shell method of Longuet-Higgins and Pople⁵ combined with the limited configuration interaction. In π -electron calculations we employed the variable β -approximation⁶ for C—C bonds. Otherwise the calculations were of the standard PPP-type. For computational details see refs^{1,7}; here we present only semiempirical parameters adopted (Table I). In CNDO calculations we followed the computational scheme of Del Bene and Jaffé⁸.

RESULTS AND DISCUSSION

A problem arising in semiempirical π -electron calculations on semiquinones is that of estimating empirical parameters for oxygen atoms. Previously we found¹ that neither the parameter set typical for quinones nor that for ionized hydroquinones yielded reasonable transition energies for semiquinones when employed in open shell

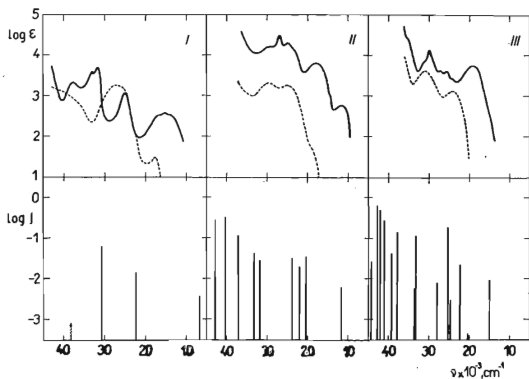


FIG. 1

Electronic Spectra of Electrogenerated Semiquinones *I*–*III* (solid lines) and of the Parent Quinones (dashed lines)

The results of semiempirical calculations are indicated at the bottom by vertical lines; a symmetry forbidden transition for *I* is indicated by a wavy line with arrow. Intensities of calculated transitions are given by $\log f$, f being calculated oscillator strength.

calculations. Obviously, a special parameter set for semiquinones must be selected. We attempted to find such a set by a least-squares fit to transition energies of *o*-semiquinones I–III and five *p*-semiquinones studied previously¹. Unfortunately a strong dependence of calculated transition energies on parameters prevented this optimization, because the theoretical electronic transitions could not be unambiguously assigned to absorption maxima. Hence we adopted a parameter set (Table I) which was tentatively chosen for *p*-semiquinones¹. The results of calculations are seen, in Fig. 1, to reproduce the main features of the absorption curves, although the theory underestimates the transition energies of 1,2-benzosemiquinone.

Recently a LCI-CNDO calculation based on the CNDO version of Del Bene and Jaffé has been published⁹ which interpreted fairly well the electronic spectrum of 1,4-benzoquinone. We found this result very promising, as the CNDO method should be amenable to semiquinones without change in empirical parameters. Following the same computational scheme, we performed the closed shell calculation on 1,2-benzoquinone and open shell calculations on 1,4-benzosemiquinone and 1,2-benzosemiquinone. The results can be characterized as follows. Calculated $\pi \rightarrow \pi^*$ transition energies of 1,2-benzoquinone and 1,4-benzoquinone⁹ are too short-wave (by about 3000–7000 cm^{-1}); but the $n \rightarrow \pi^*$ transitions agree well

TABLE I

Semiempirical Parameters for Atoms Used in the PPP-like Calculations

IP ionization potential, γ one center repulsion integral, β resonance integral and Z core charge.

Atom	IP, eV	$\gamma_{\mu\mu}$, eV	β_{CX}/β_{CC}	Z
C	11.22	10.53	1	1
O	34.0	8.0	1	1

TABLE II

LCI-CNDO Transition Energies for 1,2-Benzosemiquinone

Transition	ν , cm^{-1}	Type of transition	Transition	ν , cm^{-1}	Type of transition
1	10 539	$\sigma-\pi^*$	6	27 867	$\sigma-\pi^*$
2	16 347	$\pi-\pi^*$	7	29 248	$\pi-\pi^*$
3	18 749	$\sigma-\pi^*$	8	31 291	$\sigma-\pi^*$
4	19 640	$\pi-\pi^*$	9	34 651	$\pi-\pi^*$
5	19 791	$\pi-\pi^*$	10	42 337	$\pi-\pi^*$

with experimental data. The first $\pi \rightarrow \pi^*$ transition energies of both semiquinones are underestimated by about 5000 cm^{-1} , which is comparable to accuracy achieved with quinones, but the over-all correspondence between calculated and observed transition energies of *I* is unsatisfactory (Table II).

We attempted to improve the CNDO results by the only justifiable change in the parameter set of Del Bene and Jaffé – by varying the κ constant (in the expression for resonance integrals). With quinones a lower κ lead to an improvement, *i.e.* for $\kappa = 0.535$ the error in calculated first $\pi \rightarrow \pi^*$ transition energies reduced to about $500\text{--}2000 \text{ cm}^{-1}$; whereas the $n \rightarrow \pi^*$ transition energies were practically unaffected. Unfortunately, with semiquinones an improvement was achieved only for unreasonably high κ .

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