

CONJUGATED RADICALS. XI.*

para-SEMIQUINONES

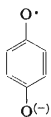
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Czechoslovak Academy of Sciences, Prague 2**Dedicated to the 65th anniversary of the late Academician R. Brdička.*

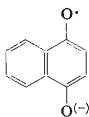
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1,4-Benzosemiquinone, 1,4-naphthosemiquinone, 9,10-anthrasemiquinone, 5,12-tetracenesemiquinone, 6,13-pentacenesemiquinone, 9,10-anthrahydroquinone dianion, 5,12-tetracenehydroquinone dianion and 6,13-pentacenehydroquinone dianion were prepared electrochemically in acetonitrile. Their electronic spectra were interpreted by the open shell and closed shell semi-empirical calculations of the PPP type.

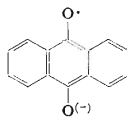
In an earlier paper¹ of this series we attempted to interpret the electronic spectra and disproportionation equilibria of nitrogen-containing radicals with the aid of semi-empirical open shell calculations of the PPP type. A similar study was previously performed on sulphur-containing radical cations².



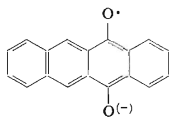
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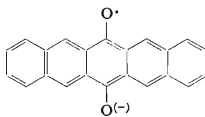
II



III



IV



V

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Results were so encouraging that we extended the treatment to the *p*-semiquinones I–V, chosen because they constitute a series of related radicals containing oxygen (instead of nitrogen or sulfur).

EXPERIMENTAL

Substances and solvents. 1,4-Benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone were obtained commercially and purified by vacuum sublimation. Tetrabutylammonium perchlorate was prepared by mixing a hot aqueous solution of tetrabutylammonium bromide and perchloric acid; the precipitate was repeatedly recrystallized from ethyl acetate and vacuum dried. Acetonitrile was purified by refluxing with calcium hydride, followed by a fractional distillation from calcium hydride³. Dimethoxyethane was similarly treated with a Na-K alloy. Commercial propylene carbonate (Jefferson Chemical Company, Houston) was distilled under reduced pressure and dried over molecular sieves.

Generation of semiquinones. Solutions of semiquinones were prepared by electrochemical reduction at a mercury pool electrode maintained at a potential on the diffusion plateau of the first polarographic wave of quinones. Initial concentration of quinones was $2-7 \cdot 10^{-4}$ M. 0.1M Tetrabutylammonium perchlorate served as a supporting electrolyte. The electrochemical cell (Fig. 1) was placed directly in a cell compartment of an Optica Milano CF-4 spectrophotometer. Besides measuring the electronic spectra, the course of the electrolysis was followed by recording the polarographic curves on an OH-102 polarograph (Radelkis). This experimental arrangement is similar to that used recently⁴ in the electron spin resonance study of the anion radicals of heterocyclic amine N-oxides.

Determination of concentration. The concentration of semiquinone formed in the electrolysis was determined simultaneously from the height of the polarographic anodic oxidation curve⁵ and from the time-dependence of the absorption curves.

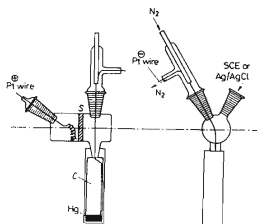


FIG. 1

Electrochemical Cell Used for Generation of Radicals and Recording Electronic Spectra and Polarograms

Dissolved oxygen in the cathode compartment was removed by pure dry nitrogen, which was passed through a polyethylene capillary tube inserted into the quartz cell C. The joint with the Pt-wire in the cathode compartment could be replaced by the dropping Hg electrode, which enabled us to record polarograms during the electrolysis. The optical path of the quartz cell was 1 cm. S sintered glass disk.

Determination of half-wave potentials. For the determination of half-wave potentials, all polarographic curves were recorded in acetonitrile using a silver chloride reference electrode. In order to obtain the values of half-wave potentials *vs* S.C.E., we used a bis-diphenyl chromium(I) iodide as a recommended standard⁶ ($E_{1/2} = -0.640$ V *vs* S.C.E.).

Calculations

We used the SCF open shell method of Longuet-Higgins and Pople⁷ combined with configuration interaction. All details have been described previously⁸. The only new feature appearing in the present calculations concerns the employment of the variable β approximation⁹ for C—C bonds

$$\beta_{\mu\nu} = \beta_{\mu\nu}^0 \exp(-1.862r_{\mu\nu} + 2.597),$$

$$r_{\mu\nu} = 1.517 - 0.18p_{\mu\nu}.$$

For β_{CC}^0 we use the value -2.318 eV and $p_{\mu\nu}$ and $r_{\mu\nu}$ stand for bond orders and interatomic distances, respectively. In the choice of the semiempirical parameters for oxygen atoms a fit of the

TABLE I

Semiempirical Parameters for Oxygen Atoms Used in the Calculations (I means ionization potential, γ one center repulsion integral, β resonance integral and Z core charge)

Compound	I_0 , eV	γ_{00} , eV	β_{CO}/β_{CC}	Z_0
Quinone ^a	18.1	14.5	1.15	1
Ionized hydroquinone	21.0	11.5	1	2
Semiquinone	34.0	8.0	1	1

^a Ref. 10.

TABLE II

Half-Wave Potentials

Compound	First wave $E_{1/2}^a$	Second wave $E_{1/2}^a$
1,4-Benzoquinone	-0.60	-1.32
1,4-Naphthoquinone	-0.85	-1.55
9,10-Anthraquinone	-1.04	-1.69
5,12-Tetracenequinone	-1.13	-1.65
6,13-Pentacenequinone	-1.23	-1.55

^a Potentials measured in volts *vs* S.C.E., for details *cf.* Experimental part.

calculated transition energies with the electronic spectrum of *para*-benzosemiquinone served as a criterion. As with hydrocarbon radical ions, we tried a model of a parent closed shell system to which one electron is added or from which one electron is removed. Therefore we started with the parameters which were successful in the interpretation of the electronic spectrum of *para*-benzoquinone¹⁰. However, this attempt failed badly, and equally unsatisfactory results were given by parameters suitable for the ionized hydroquinone (*cf.* Table I). From this it appears a new set of parameters for semiquinones must be selected. We employed the values listed in Table I, which are not necessarily optimal. However, it was not our purpose here to find parameters giving the best fit with the experimental data, but rather to demonstrate the applicability of the open shell theory.

Standard closed shell PPP calculations on the hydroquinone dianions were performed with the parameters listed in Table I.

RESULTS

Experimental data concerning the electronic spectra are discussed separately for each compound. Polarographic half-wave potentials are summarized in Table II.

1,4-Benzoquinone. Electrolytic reduction of 1,4-benzoquinone at -0.8 V *vs* s.c.e. yielded a yellow solution of 1,4-benzosemiquinone. The observed absorption maxima at $22\,300$ and $30\,800$ cm^{-1} are in a good agreement with the data obtained by other methods¹¹⁻¹³.

1,4-Naphthoquinone. Reduction of 1,4-naphthoquinone at -1.1 V *vs* s.c.e. resulted in a yellow-brown solution which displayed absorption maxima at $11\,900$, $17\,500$, $21\,300$, $24\,300$, $25\,500$, $30\,300$ and $32\,800$ cm^{-1} . For the determination of the weak long-wave band at $11\,900$ cm^{-1} the concentration of quinone had to be raised from $3 \cdot 10^{-4}$ M to $5 \cdot 10^{-3}$ M and a cell with an optical path length of 5 cm had to be used.

9,10-Anthraquinone. Electrolytic reduction of 9,10-anthraquinone at -1.25 V *vs* s.c.e. gave a deep purple-red solution. With initial concentrations of quinone above $4 \cdot 10^{-4}$ M, two maxima in the near infrared region (at $10\,200$ and $11\,500$ cm^{-1}) were observed in addition to the ultraviolet and visible absorption. As the calculations indicate that absorption is not due to a $\pi \rightarrow \pi^*$ transition, we tried to obtain further experimental evidence by the following measurements (*cf.* Table III): 1. the 1-chloro and 1,4-dichloro derivatives gave the similar results, 2. dimethoxyethane and propylene carbonate were used instead of acetonitrile and the solvent effect was examined (observed shifts of bands are discussed later).

The highest concentration of semiquinone was reached 20 minutes after the beginning of the electrolysis. As electrolysis proceeded, the bands due to the semiquinone absorption gradually decreased and new bands at $16\,100$, $21\,700$ and $25\,600$ cm^{-1} appeared. The latter were assigned to the anthrahydroquinone dianion, probably formed by the disproportionation of semiquinone. The same absorption maxima

were observed if the electrolysis proceeded at potential -2.0 V, corresponding to the limiting current of the second reduction wave. After exposure of the solution to air, the absorption bands of both semiquinone and hydroquinone disappeared and only the anthraquinone spectrum was observed.

TABLE III
Absorption Maxima of Semiquinones Measured in Acetonitrile

Radical	λ_{\max} , m μ	$\tilde{\nu} \cdot 10^{-3}$, cm $^{-1}$	Radical	λ_{\max} , m μ	$\tilde{\nu} \cdot 10^{-3}$, cm $^{-1}$
<i>I</i>	448	22.3	1-Chloro- <i>III</i>	1 031	9.7
	425	23.5		900	11.1
	325	30.8		565	17.1
<i>II</i>	840	11.9		411	24.3
	571	17.5		393	25.4
	469	21.3	301	33.2	
	412	24.3	1,4-Di- chloro- <i>III</i> ^c	—	—
	392	25.5		944	10.6
	333	30.3		592	16.9
	305	32.8		408	24.5
<i>III</i>	980	10.2		392	25.5
	870	11.5	306	32.7	
	546	18.3	<i>IV</i>	685	14.6
	410	24.4		588	17.0
	392	25.5		549	18.2
300	33.3	400		25.0	
<i>III</i> ^a	1 000	10.0		310	32.2
	893	11.2	<i>V</i>	730	13.7
	559	17.9		599	16.7
	412	24.3		410	24.4
	392	25.5		322	31.1
300	33.3	<i>III</i> ^b		980	10.2
870	11.5		870	11.5	
545	18.3		545	18.3	
410	24.4		410	24.4	
385	26.0		385	26.0	
300	33.3	300	33.3		

^a Measured in dimethoxyethane. ^b Measured in propylene carbonate. ^c We were not able to determine the longest-wave maximum owing to the low sensitivity of the spectrophotometer in the region 1040–1100 m μ .

TABLE IV

Observed and Calculated Transition Energies (ΔE) for Hydroquinone DianionsAll values are given in cm^{-13} ; calculated data for forbidden transitions are not included

9,10-Anthrahydroquinone dianion					
ΔE_{obs}	16 100 ^a	21 700	25 600		
ΔE_{calc}	--	21 000	25 700	38 700	
5,12-Tetracenehydroquinone dianion					
ΔE_{obs}	16 700	20 000	25 000		
ΔE_{calc}	16 600	23 100	25 300	31 100	33 500
6,13-Pentacenehydroquinone dianion					
ΔE_{obs}	18 200	22 200			
ΔE_{calc}	14 800	24 800	31 500	35 200	

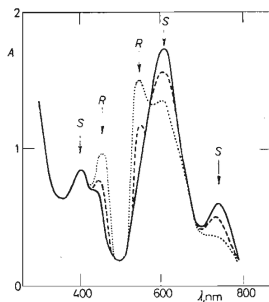
^a We think this band is not due a $\pi \rightarrow \pi^*$ transition of 9,10-anthrahydroquinone dianion (*cf. text*).

FIG. 2

Course of the Electrolysis of 6,13-Pentacenequinone at -1.4 V vs S.C.E.

The full line represents the absorption curve which is displayed by the solution of the highest concentration of semiquinone (*S*). The successively changed curves due to the continued electrolytic reduction are drawn in the dashed and dotted line. *R* is a designation for the hydroquinone dianion.

5,12-Tetracenequinone. Electrochemically, 5,12-tetracenequinone was similar to 9,10-antraquinone. Reduction at -1.3 V vs S.C.E. gave a violet solution of semiquinone, which during prolonged electrolysis gradually turned to the tetracenehydroquinone dianion. Its observed absorption maxima are given in Table IV. The same maxima were observed when the electrolysis was performed at -1.9 V. After exposure to air, solution gave only the quinone absorption.

6,13-Pentacenequinone. Electrolysis of 6,13-pentacenequinone at -1.4 V vs S.C.E. produced a violet-blue solution with absorption maxima at 13 700, 16 700, 24 400 and 31 100 cm^{-1} . Continued electrolysis at the same potential gave the corresponding hydroquinone dianion (Fig. 2) by disproportionation as with 5,12-antraquinone. On electrolysis at -1.9 V, the potential of the second wave, the spectrum again

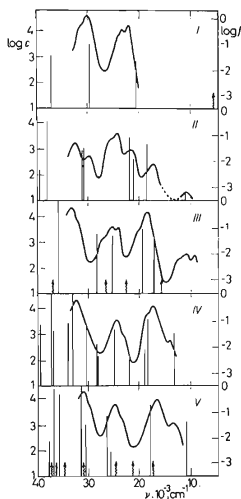


FIG. 3

Electronic Spectra and Results of Semiempirical Calculations for Semiquinones I–V

The calculated transition energies are represented by the vertical lines and the forbidden transitions are indicated by the wavy lines with arrows. The right side scales concern the calculated spectral intensities, f stands for the oscillator strength. As the concentrations could be determined only approximately, the values of $\log \epsilon$ were measured with accuracy ± 0.5 .

exhibited the absorption maxima of hydroquinone ($18\,200$ and $22\,200\text{ cm}^{-1}$ and 549 and 455 nm respectively). On exposure to air, the semiquinone and hydroquinone absorption bands disappeared and formation of the quinone was observed.

DISCUSSION

Results of the semiempirical calculations are presented together with the absorption curves of semiquinones *I–V* in Fig. 3. It can be seen that the nature of the electronic spectra is well interpreted by the calculations, except for two unsatisfactory points: 1. the absorption curve for 1,4-naphthosemiquinone does not fit the calculation as well as the other systems under study. Perhaps another set of parameters could provide better agreement for the whole series *I–V*. We explained in the theoretical section why no such attempt was made, 2. from the point of view of calculations, there is a puzzling long-wave band in the electronic spectrum of 9,10-anthrasemiquinone. In view of the results obtained with the other systems, we believe that this band is not due to a $\pi \rightarrow \pi^*$ transition. If it does not represent another species, it might possibly be assigned to an $n \rightarrow \pi^*$ transition. We think this not unreasonable, inasmuch as anthraquinone shows an $n \rightarrow \pi^*$ band of rather high intensity¹⁴ ($\log \epsilon \sim \sim 2$). We found evidence to support this suggestion. On going from dimethoxyethane

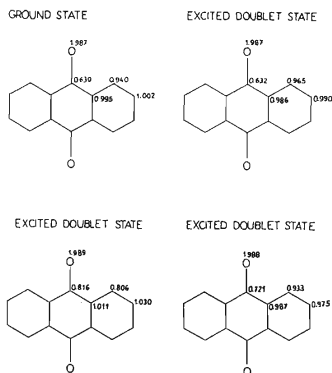


FIG. 4

Molecular Diagrams Based on the LCI-SCF Calculations

Only the second (right top), third (left bottom) and fifth (right bottom) excited states are considered because the first and the fourth excited states arise from forbidden transitions (cf. Fig. 3).

(dielectric constant $D = 2.7$) to acetonitrile ($D = 37.5$), *i.e.* from a nonpolar solvent to a polar one, a hypsochromic shift is observed, as expected for $n \rightarrow \pi^*$ bands^{15,16} with closed shell systems. Further increase in polarity on going from acetonitrile to propylene carbonate ($D = 69.0$) was ineffective, but this can be understood from an examination of a formula for estimating solvation energies¹⁷

$$-E_{\text{sol}} = \left\{ \sum_{\mu} \frac{q_{\mu}^2}{2r_{\mu}} + \sum_{\mu < \nu} \frac{q_{\mu}q_{\nu}}{r_{\mu\nu}} \right\} \left(1 - \frac{1}{D} \right).$$

The absorption band at $18\,300\text{ cm}^{-1}$ is also seen, from Table III, to exhibit a hypsochromic shift on going from a nonpolar solvent to a more polar one. From the inspection of electron distributions in the seven lowest excited doublet states we found that the third excited state is the only one, which arises from an allowed electronic transition and in which polarity of the C—O bonds is decreased significantly with respect to the ground state (Fig. 4). This fact appears to afford an explanation, why among the bands which are due to $\pi \rightarrow \pi^*$ transitions, only the one at $18\,300\text{ cm}^{-1}$ is solvent dependent.

In order to confirm the assignment of the measured absorption maxima after a prolonged electrolysis to hydroquinone dianions, we carried out the standard PPP calculations on the latter. Calculated transition energies are seen, from Table IV, to be in a satisfactory agreement with the experimental findings. 9,10-Anthrahydroquinone dianion again gives a long-wave band which is not interpreted by the calculation. If that absorption is not due to other species, its assignment to a $n \rightarrow \pi^*$ transition appears to afford the most reasonable interpretation.

Our thanks are due to Dr V. Štěpán of this Institute for the samples of 5,12-tetracenequinone and 6,13-pentacenequinone and to Professor M. Večeřa Institute of Chemical Technology, Pardubice for the samples of 1-chloroanthraquinone and 1,4-dichloroanthraquinone.

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Translated by the author (P. Č.).

Note added in proof: Recently the electronic spectrum of the electrogenerated 9,10-anthra-semiquinone has been recorded by R. Sioda (submitted for publication in *J. Electroanal. Chem.*)