EPR SPECTRA AND ELECTRONIC STRUCTURE OF SEMIQUINONES OF THE TRIPTYCENE SERIES

A. I. Brodskii,* L. L. Gordienko,
A. G. Chukhlantseva, A. A. Balandin,* R. Yu. Alieva,
E. I. Klabunovskii, and L. V. Antik

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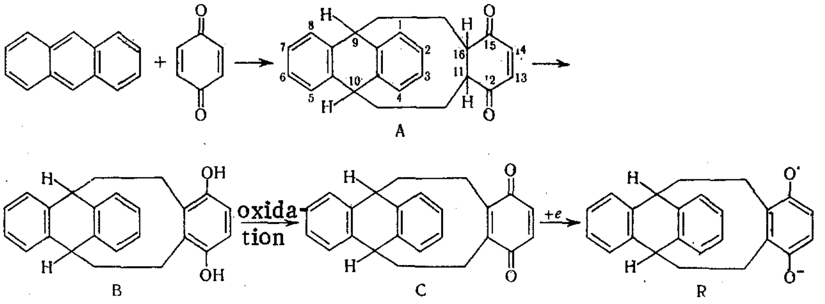
EPR spectra of semiquinones obtained by reduction of quinones of the triptycene series, formed from anthracene and pentacene with benzo-, naphtho-, and anthraquinone, were investigated. It was shown that bridge carbon atoms fully inhibit any coupling between the hydrocarbon and quinoid moieties of these molecules, and that in triptycenes the presence of condensed rings in the quinoid moiety stabilizes neutral nonionized semiquinones.

Triptycene and its derivatives possess special properties due to the presence in their molecules of bridges consisting of carbon atoms C_9 and C_{10} with rigid tetrahedral bonds. The stable noncoplanarity of the benzene rings in the molecules of triptycene derivatives sharply decreases the stability of anions and radicals formed by detachment of hydrogen atoms from the bridge carbon atoms, and strongly depresses the reactivity at the C_9 and C_{10} positions, compared, e.g., with planar derivatives of triphenylmethane. In view of these peculiar features, it seemed to be of interest to investigate the electron coupling in triptycenesemiquinones, which can be produced by cathodic reduction of the corresponding quinones, as described in [1]. For this purpose, we have investigated EPR spectra of radicals produced by reduction of triptycene compounds shown in Table 1.

Triptycenequinones were produced [1] by the addition reaction between the corresponding 1,4-quinones and anthracene or pentacene; the resulting adduct A was isomerized into dihydrotriptycene B; the latter was oxidized to triptycenequinone C. For example:



In the present work, we have investigated the EPR spectra of semiquinones obtained by electrochemical reduction in $0.5\text{-}1.0 \cdot 10^{-3}$ N solutions in dimethylformamide, containing tetrabutylammonium bromide (1.0 N) as a supporting electrolyte, in argon atmosphere (as described in [2]), at the potentials of the first halfwave [1] corresponding to monoelectron reduction to anion radical R. (A minor displacement of the potential caused by the use of another supporting electrolyte instead of KNO_3 employed in [1] could be disregarded.)

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* Deceased.

L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSSR. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 11, No. 4, pp. 604-610, July-August, 1970. Original article submitted April 15, 1968.

TABLE 1. Investigated Compounds of the Triptycene Series

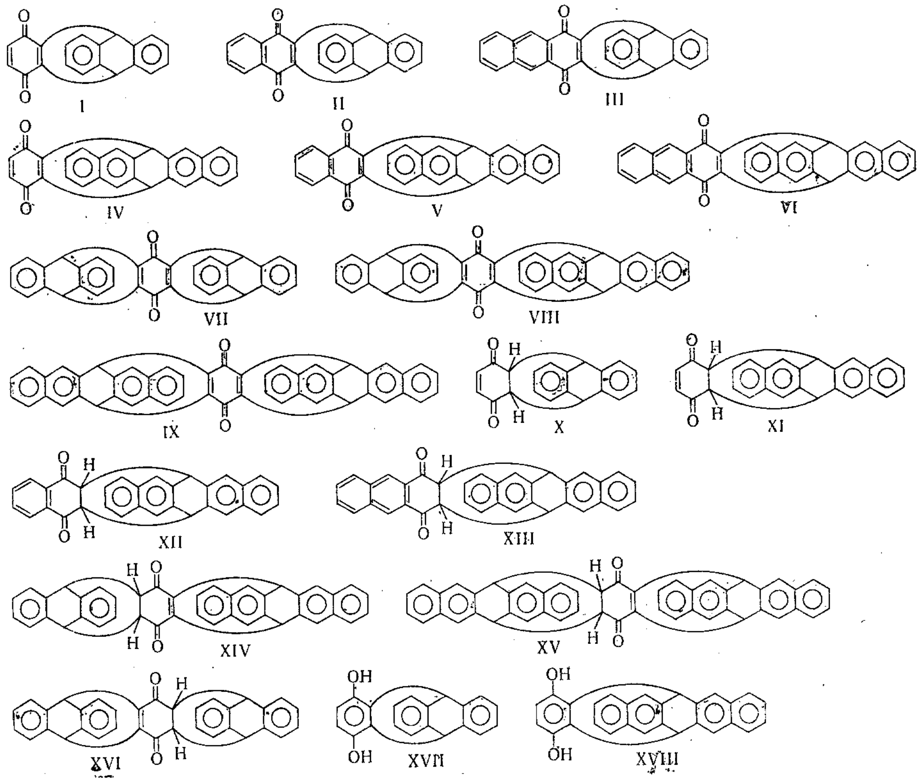


TABLE 2. Results of Polarographic Measurements

Comp.	$-E'_{1/2}$, mV	$-E''_{1/2}$, mV	log K_{sem}	Comp.	$-E'_{1/2}$, mV	$-E''_{1/2}$, mV	log K_{sem}
I	644	1248	10,236	V	806	1352	9,254
II	877	1473	10,102	VI	819	1350	8,988
III	944	1400	7,728	VII	665	1342	11,592
IV	673	1280	10,306	VIII	633	1260	10,644

Semiquinones obtained from quinones I-VI have a pink or brown coloration. Their stability decreases with the increasing number of rings in the quinoid moiety (Table 2), as follows from the results of polarographic measurements [1].

The constant of the formation of the semiquinone is determined by the equation:

$$\log K_{sem} = \frac{2}{0,059} \cdot \frac{1}{2} (E'_{1/2} - E''_{1/2}).$$

Symmetric semiquinones obtained from compounds VII-IX are not colored. They are very stable; the intensity of their EPR spectra did not change after several hours at room temperature.

Anions of triptycenesemiquinone I and its dibenzo analog IV gave, upon electrochemical reduction, identical spectra (Fig. 1) comprising a fully resolved triplet 1 : 2 : 1 with a resolution constant of 2.4 G, which corresponds to two equivalent protons. An analogous spectrum was obtained when the quinone solution was reduced with zinc dust in methanol with 0.1 N CH_3ONa, and also by electrochemical reduction in the same solvent. The resolution constants were in agreement with those obtained for free 1,4-benzosemiquinone anion, for which the splitting was determined by various authors as 2.36-2.42 G, depending on the solvent used, in particular 2.419 G in dimethyl sulfoxide [3]. Apparently, the formation of bonds $C_{10}-C_{11}$ and C_9-C_{16} in the triptycene molecule does not result in

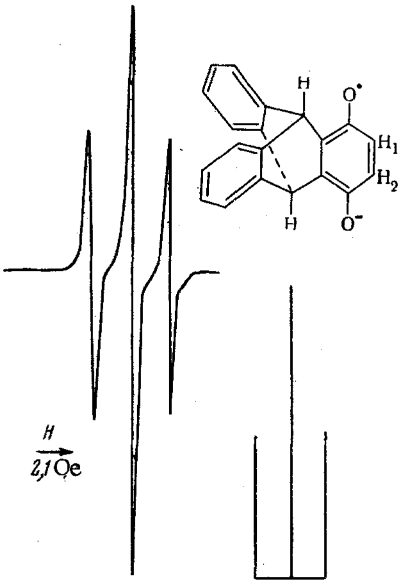


Fig. 1. EPR spectrum of triptycenesemiquinone anion produced by electrochemical reduction of quinone I in dimethylformamide.

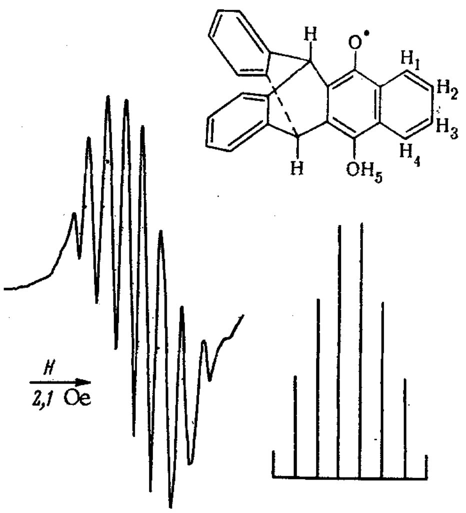


Fig. 2. EPR spectrum of benzotriptycenesemiquinone produced by electrochemical reduction of quinone II in dimethylformamide.

an appreciable rearrangement of the density of the unpaired electron. This observation can be compared with the fact that in 1,4-benzosemiquinone anion the replacement of two adjacent hydrogen atoms by methyl groups leads to a change in the splitting of the remaining two hydrogen atoms by 0.23 G only [4].

In contradiction to the benzo- and naphthotriptycenesemiquinones described hereinafter, we have not found any indication of splitting associated with the third hydrogen atom belonging to the hydroxyl group of nonionized semiquinone. This is in accordance with the well known high instability of the free benzosemiquinone compared with its anion.

The well resolved spectra comprised two satellites symmetrically disposed on both sides of the central line of the triplet at a distance of 0.9 G; their intensity was about 2% of that of the central line. These satellites were associated with the splitting on C^{13} of natural origin. This is in accordance with earlier findings in [3, 5], where $a_{C^{13}}$ values of 0.6-2.1 G were determined for 1,4-benzosemiquinone in different solvents.

Stock and Suzuki [6] have also investigated the EPR spectrum of the semiquinone anion obtained by oxidation of hydroquinone XVII with atmospheric oxygen in alkaline methanol solution. Apart from the triplet with a_{H} = 2.32 G, they found a doublet with a = 1.1 G, which was superimposed on the triplet. They ascribed it to another radical with one splitting hydrogen atom, in particular a semiquinone substituted with methyl at the position 9 or 10. We have also observed a temporary appearance of this doublet during the oxidation of hydroquinones XVII and XVIII with oxygen in 2 N KOH or CH_3ONa in methanol. Later, the spectrum became more complex, but the original 1 : 2 : 1 triplet with a = 2.4 G was preserved. During oxidation with atmospheric oxygen in more dilute solutions (0.1 N CH_3ONa) there appeared a stable seven-component spectrum. A similar spectra can be obtained from adducts X and XI, apparently because of their isomerization to XVII and XVIII.

Benzotriptycenequinone II and its dibenzo analog V gave, upon electrochemical reduction, identical spectra comprising eight equidistant lines with an intensity ratio of 1 : 4 : 7 : 10 : 10 : 7 : 4 : 1 (Fig. 2), which were in good agreement with calculations for two groups of equivalent protons with a splitting of 1.2 G (two H atoms) and 0.6 G (three H atoms). This spectrum cannot be explained otherwise than by assuming the participation of five hydrogen atoms in the splitting. However, the results of our investigations indicate that in this anion radical there are only four hydrogen atoms at the quinoid nucleus, which can participate in the formation of fine structure. Therefore, we postulate that this spectrum belongs not to the anion, but to the neutral nonionized semiquinone, in which the fifth hydrogen atom contributing to the splitting is that of the hydroxyl group. This semiquinone can be formed from the original cathodic semiquinone anion by reaction with the residue of the nonoxidized benzotriptycenehydroquinone according to the scheme:

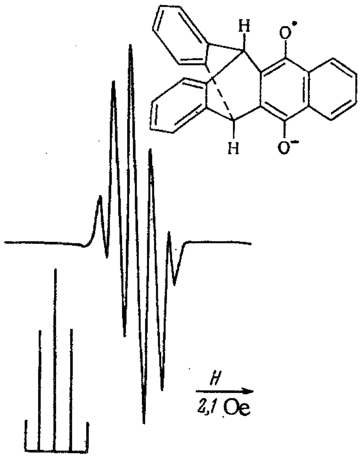


Fig. 3

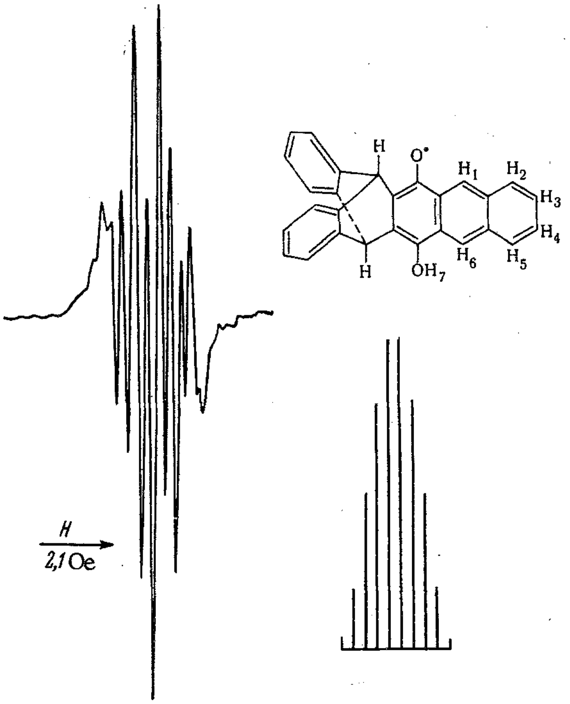
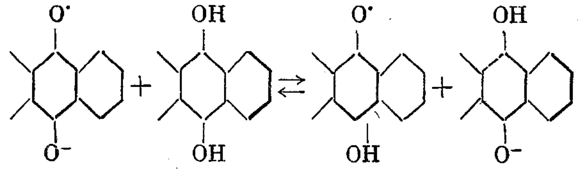


Fig. 4

Fig. 3. EPR spectrum of benzotriptycenesemiquinone anion produced by reduction of quinone II with zinc in alkaline methanol.

Fig. 4. EPR spectrum of naphthotriptycenesemiquinone produced by electrochemical reduction of quinone III in dimethylformamide.



In distinction from triptycenesemiquinones obtained from I and IV, the presence of the second condensed ring in the quinoid moiety increases the stability of the neutral semiquinone to such a degree that in the presence of excess hydroquinone* the equilibrium of this reaction is shifted to the right.

This assumption was confirmed by the fact that the same quinone II, when reduced in alkaline methanol (0.1 N CH_3ONa), where the equilibrium was shifted towards the semiquinone anion, gave the appropriate distinct quintuplet 1 : 4 : 6 : 4 : 1 with a = 0.6 G due to the splitting on four equivalent protons (Fig. 3). The same spectrum was obtained by either electrochemical or chemical (with zinc dust) reduction of quinones II and XII.

This spectrum was in agreement with that obtained in [7] from 1,4-naphthosemiquinone in alcohol. In this case, splitting on three pairs of equivalent protons took place at 3.230, 0.655, and 0.513 G; the largest splitting was due to hydrogen atoms in positions 2 and 3, which are absent in the triptycene derivative; the remaining two, giving an average of 0.58 G, were in accordance with the 0.6 G splitting found by us when an apparatus with a small resolution was used. For 1,4-naphthosemiquinone anion in dimethylformamide the values of 3.35, 0.64, and 0.32 G were obtained [8]. The latter splitting amounted to about half of that obtained by us for the triptycene derivative. Taking into account the data on triptycenequinone, we are inclined to ascribe this difference not to a change in the distribution of the density of the unpaired electron during the formation of bonds with bridge carbon atoms, but to the fact that in one case the spectrum belonged to undissociated semiquinone and in the other case to its anion.

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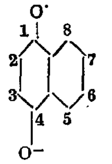
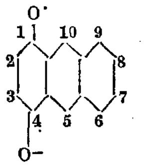
*The purity of the preparations was controlled by IR spectra with an accuracy of a few per cent [1]. A small quantity of residual hydroquinone undetected by this method can still represent a concentration higher by a few orders of magnitude than the concentration of radicals being generated, which does not exceed 10^{-4} N.

TABLE 3. Constants of Superfine Splitting

Semiquinone	Position of H	a_H of semiquinone anion		Measured a_H of neutral triptycenesemiquinone
		calc.	measured	
	2,3 5,8 6,7 OH	3,23* 0,58 0,69	3,1* 0,6 0,6 —	— 1,2 0,6 0,6
	2,3 5,10 6,9 7,8 OH	3,52 1,24 0,15 0,22	2,6 1,1 0,4 0,4 —	— 0,6 0,3 0,3 0,3

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* Our measurements and calculations gave results conforming to [7].

Bolton and co-workers [9] have observed the splitting on hydrogen atoms of hydroxyl groups of doubly protonized cation semiquinones. We have also obtained an analogous radical by reducing benzotriptycenesemiquinone V with zinc dust in a 1 : 1 mixture of dimethylformamide with concentrated sulfuric acid. The spectrum of this radical consisted of nine equidistant components with an intensity ratio of 2 : 3 : 6 : 8 : 8 : 8 : 6 : 3 : 2 and a splitting of 0.8 G; it was in good agreement with that reconstructed for three pairs of equivalent protons (two in positions 5 and 8; two at 6 and 7; and two at OH groups) with a splitting of 2.40, 1.80, and 0.86 G, obtained in [9] for doubly protonized cation radical of 1,4-naphthosemiquinone. Thus, also in this case the formation of triptycene bridge bonds does not affect the distribution of the density of electron charge in the quinoid ring.

On electrochemical reduction naphthotriptycenequinone III gave a spectrum consisting of 10 equidistant lines with an intensity ratio of 3 : 4 : 8 : 10 : 10 : 8 : 4 : 3 for eight middle components and two just noticeable lines at each end. This spectrum corresponded to a calculated spectrum of the type (0.4) : 2 : 5 : 8 : 10 : 10 : 8 : 5 : 2 : (0.4) for two groups of five equivalent protons 6, 7, 8, 9, and OH with a = 0.3 G, and two protons (5 and 10) with a = 0.6 G (Fig. 4). The meaning of this spectrum is the same as that of benzotriptycenesemiquinone, namely, it is associated with neutral semiquinone formed by the reaction between the anion and the excess of nonoxidized residue of hydroquinone.

Unfortunately, we were unable to obtain a sufficiently resolved spectrum of reduced quinone VI. However, by analogy with I and IV, and also II and V, we can assume that this spectrum should be analogous to that of the semiquinone derived from III.

As data on the EPR spectrum of free 1,4-anthrasemiquinone were lacking, we produced this compound by reducing anthraquinone with zinc in an alkaline medium, and recorded its spectrum. The splitting constants obtained are given in Table 3. Their ratio was confirmed by quantum mechanics calculations according to Hückel's MO LCAO method [10], using the M-20 computer of the Institute of Cybernetics, Academy of Sciences of the Ukrainian SSR. For the Coulomb integral $\alpha = \alpha^0 + b_0\beta^0$ and the exchange integral $\beta = b_{CO}\beta^0$, we adopted parameters b_0 = 1.60 and b_{CO} = 1.55, used for similar calculations in [11]. The charge density was calculated with a correction for configuration interaction according to McLachlan [12] ($\rho = \rho^0 + \lambda\Delta$, with λ = 1.2 and Δ calculated from the atom-atom polarizability matrix for closed shells). The splitting was calculated from Q = 23.7 G [11]. A comparison of the experimental and calculated splitting constants is given in Table 3.

Reduction of quinones III and XII with zinc in alkaline alcohol gave the basic 1 : 2 : 1 triplet with a = 1.1G, which could not be further split. Analogous results were obtained with electrochemical reduction under the same conditions.

All the symmetric triptycenequinones VII, VIII, and IX, in which the quinoid moiety did not contain any hydrogen atoms, gave narrow singlets with a distance of 0.5-0.6 G between the points of maximum slope. The absence of fine structure confirms again the absence of any coupling of the unpaired electron with the hydrocarbon ring system. Analogous spectra were obtained from adducts XIV, XV, and XVI, by electrochemical reduction in dimethylformamide and reduction with zinc in alkaline methanol.

All the above considerations confirm the assumption that in triptycene derivatives the bridge carbon atoms with a stable tetrahedral configuration of bonds fully inhibit any electron coupling between the hydrocarbon moiety and the other part of the molecule, in this case the quinoid moiety.

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