

but decomposes to unidentified products in a secondary reaction.

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Radical Anions of Triptycene Bis- and Tris(quinones)¹

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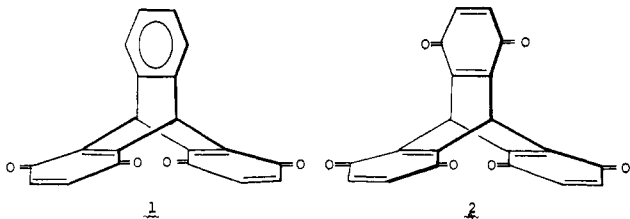
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The formation of radical ions upon reduction of **1** and **2** has been investigated in MeCN and Me₂SO solutions by ESR spectroscopy. We were interested in ascertaining if both radical mono-



and trianions could be detected and if their unpaired electrons are delocalized over all quinone rings, since the first reduction potential of **1** is reported to be considerably lower than the reduction potential of triptycene monoquinone.² We were surprised to observe, in addition to $1^{\cdot-}$ and 1^{3-} , an intermediate paramagnetic reduction product with a well-resolved ESR spectrum which appears to be the diradical ($\cdot 1^{2-}$), while for **2** at least three discrete paramagnetic radical anions can be detected by ESR spectroscopy.

Radical Monoanion of 1. Electrolytic reduction at Hg or Pt of **1** in MeCN or Me₂SO gave initially the 1:4:6:4:1 pentet of Figure 1a ($a^H = 1.10$ G, $g = 2.00506$ in Me₂SO). Occasionally a further hyperfine splitting of ≈ 0.05 G by two hydrogens was observed. This species does not have the electron delocalized over both rings, because cooling the MeCN solution resulted in selective line broadening of the second and fourth peaks. At -55 °C these peaks were essentially unobservable, and a $\sim 1:4:1$ triplet of sharp lines was observed (warming to 25 °C restored the 1:4:6:4:1 pentet). The hydrogen atoms of the bis(quinone) rings of $1^{\cdot-}$ are time averaged by electron migration for which an energy barrier of $\Delta H^\ddagger = 6.2$ kcal/mol ($\Delta S^\ddagger = -7$ eu) was calculated from the selective line broadening observed between -50 and 0 °C. Dilution of solutions giving spectrum **1a** by 200-fold did not affect the line widths or intensities of the 1:4:6:4:1 pentet. The pentet was not immediately destroyed by exposure to oxygen.

Diradical Dianion of 1. Continued electrolysis of **1** in Me₂SO ($\text{Bu}_4\text{N}^+\text{ClO}_4^-$) at a Hg pool or Pt electrode resulted in the appearance of a 1:2:1 triplet, which was not time averaged with the pentet of $1^{\cdot-}$. After a sufficiently long period of electroreduction, the pentet disappeared completely to give the spectrum as shown

(1) Electron Transfer Processes. 26. This work was supported in part by Grant CHE-7823866 from the National Science Foundation.

(2) Iwamura, H.; Makino, K. *J. Chem. Soc., Chem. Commun.* 1978, 720.

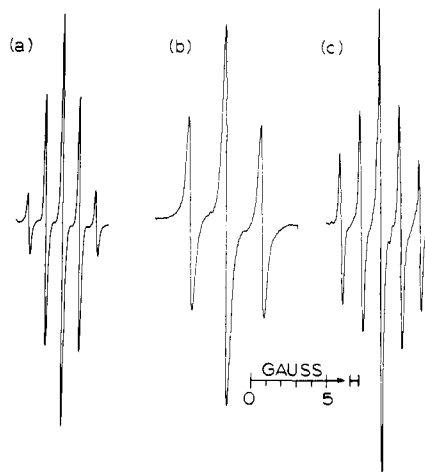


Figure 1. Radical anions derived from triptycene bis(quinone) in MeCN at 25 °C. (a) $1^{\cdot-}$, (b) $\cdot 1^{2-}$, and (c) 1^{3-} containing a trace of $\cdot 1^{2-}$ (shoulders on center and high-field peak).

in Figure 1b ($a^H = 2.45$ (Me₂SO), 2.40 (MeCN) G) with a g value equal to that of $1^{\cdot-}$. The triplet of Figure 1b would be consistent with a diradical structure if $J \ll a_H$ (i.e., no correlation between the electrons).^{3,4} Time averaging of the two rings in the diradical state by a concerted migration of the two electrons would be highly improbable, and up to 100 °C the spectrum was a sharp 1:2:1 triplet with lines not appreciably broader than for $1^{\cdot-}$. Exchange of the two electrons by way of the dianion in which both electrons are in the same quinone ring does not occur rapidly. Frozen Me₂SO solutions of the species responsible for the 1:2:1 triplet still gave the 1:2:1 hyperfine splitting, and no $\Delta m = 2$ transition could be observed. The species responsible for the 1:2:1 triplet was observed in the presence or absence of excess base, the presence or absence of K^+ , and was not converted to another species by dilution. The diradical reacted with an excess of the bis(quinone) to regenerate $1^{\cdot-}$ but was stable to molecular oxygen. The biradical was more easily observed at very low free quinone concentrations. Thus electrolysis in Me₂SO-H₂O (80:20), MeCN-H₂O (85:15), MeCN-MeOH, or MeCN-Et₃N mixtures either gave rise to spectrum 1b as the initial species or greatly shortened the period required for the complete conversion of $1^{\cdot-}$ to $\cdot 1^{2-}$.⁵

In MeCN or Me₂SO **1** was reduced by KI in the presence of Hg or in MeCN by KI in the presence of [2.2]cryptand to give $1^{\cdot-}$. The cryptand had no effect upon the spectra but only served to make KI a better reducing agent (without the cryptand and in the absence of Hg, the formation of radical anions from **1** and KI was not observed). As the amount of KI in the presence of Hg was increased, the initial pentet (Figure 1a) was slowly converted to the triplet (Figure 1b). Another reducing agent, potassium *tert*-butoxide, had the same effect in MeCN or Me₂SO.⁶ Traces of *tert*-butoxide gave the 1:4:6:4:1 pentet, while larger amounts yielded the 1:2:1 triplet.

Radical Trianion of 1. More extensive electrolytic or chemical reduction of **1** led to a species with a lower g value than $1^{\cdot-}$ or $\cdot 1^{2-}$. Continued electrolytic reduction at high voltages in Me₂SO or MeCN (Hg pool, $\text{Bu}_4\text{N}^+\text{ClO}_4^-$) produced a new pentet in addition to the composite spectra of Figure 1a and 1b. There was

(3) The value of a^H for triptycene monoquinone radical anion is the same as for $\cdot 1^{2-}$.

(4) The 1:2:1 pattern of ESR lines results because for the case where the singlet-triplet diradical energy separation (J) is zero (or $\ll a_H$), there are only three $\Delta M_S = 1$ energy transitions between the T_{\pm} states and the T_0 and singlet diradical states when each electron undergoes hyperfine splitting by two equivalent hydrogen atoms. See, for example: Lemaire, H.; Levy, B.; Rassat, A. *Colloq. Int. C. N. R. S.*, 1966, No. 164, 401. Lemaire, H. *J. Chim. Phys.* 1967, 64, 559. Briere, R.; Dupeyre, R.-M.; Lemaire, H.; Morat, C.; Rassat, A.; Rey, P. *Bull. Soc. Chim. Fr.* 1965, 3290.

(5) Presumably due to a reduced quinone concentration as a result of the formation of addition products.

(6) Russell, G. A.; Blankespoor, R. L. *Tetrahedron Lett.* 1971 4573.