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# Application of electron spin resonance spectroscopy to problems of structure and conformational analysis: polysemiquinones and macrocyclic semidiones

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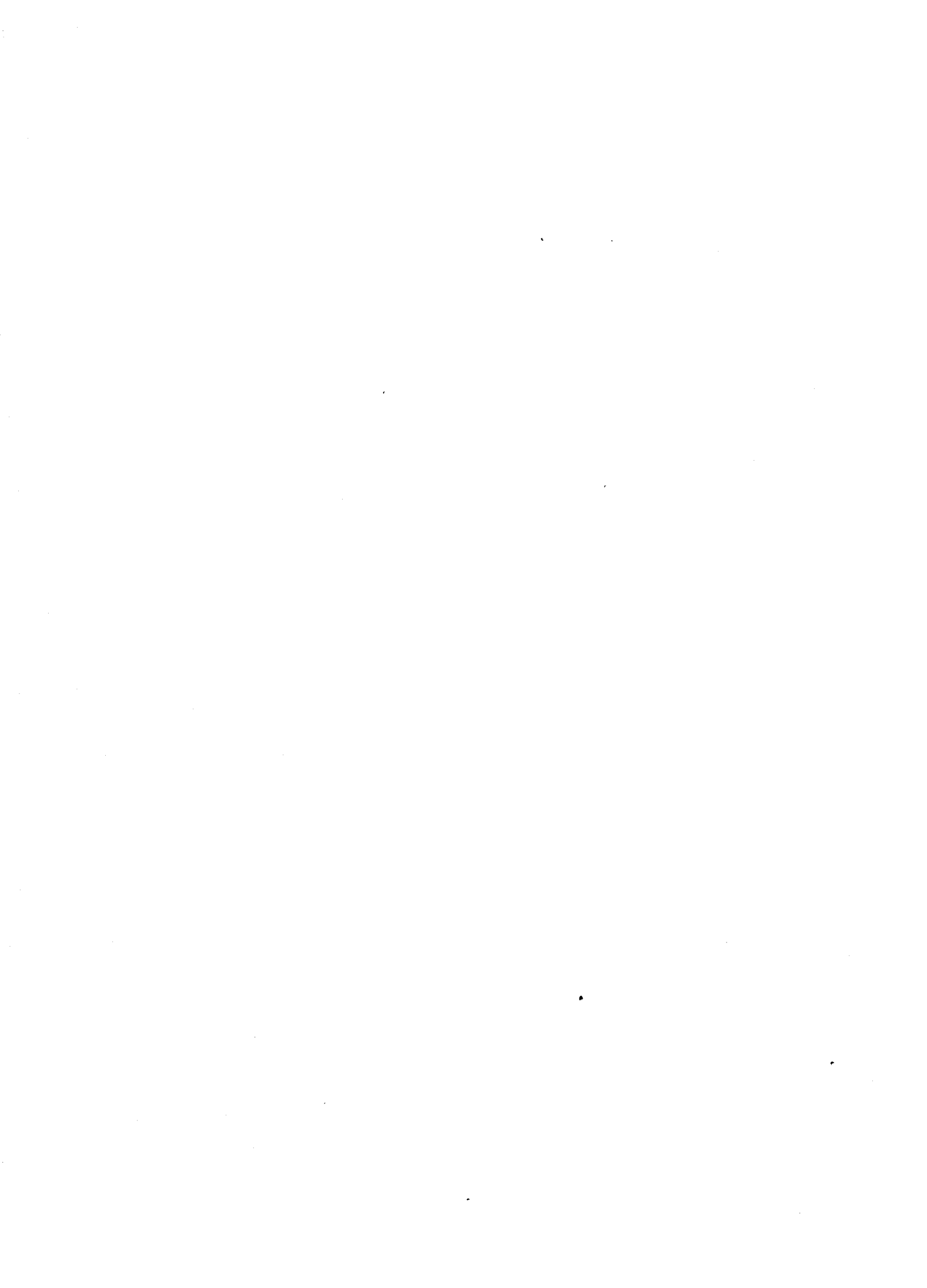
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**APPLICATION OF ELECTRON SPIN RESONANCE SPECTROSCOPY TO  
PROBLEMS OF STRUCTURE AND CONFORMATIONAL ANALYSIS:  
POLYSEMIQUINONES AND MACROCYCLIC SEMIDIONES**

*Iowa State University*

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**Application of electron spin resonance spectroscopy  
to problems of structure and conformational analysis:  
Polysemiquinones and macrocyclic semidiones**

**by**

**Naushadalli Kamrudin Suleman**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Department: Chemistry  
Major: Organic Chemistry**

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iv

**DEDICATION**

**To My**

**Wahala Mataji anē Bapaḡi**

## PREFACE

This dissertation will provide a further exposition to the utility of paramagnetic spin probes in addressing diverse problems in physical organic chemistry. In order to facilitate the presentation, a description of the investigations undertaken will be presented in parts.

Part I deals primarily with the electronic structure of a variety of polysemiquinones as revealed by their Electron Spin Resonance (ESR) spectra. Particular emphasis is placed on considerations such as spin density distribution as a function of temperature, reduction state, geometry and acceptor capability of the interconnected quinone moieties.

Part II addresses the question of conformational preference as a function of temperature in a series of large carbocyclic semidiones. Specific reference is made to the conformational mobility of the semidione spin label with respect to the hydrocarbon chain. Also considered are the isomeric ratios ( $E/Z$ ) of the radical anions as functions of counterion concentration.

Part III explores the possibility of molecular rearrangement in a number of unsaturated 1,2- and 1,4-semidiones. Valence isomerization in 1,4-semidiones derived from the bicyclo[4.1.0]heptane skeleton is discussed. The concluding section provides a treatise on "bullvalene" semidione.

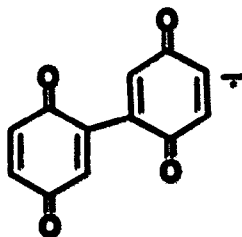
A general experimental section includes synthetic approaches to the various radical ion precursors, sources of samples, and general details of ESR sample preparation and instrument operation.

**PART I. ESR OF POLYSEMIQUINONES**

## I. INTRODUCTION TO THE RADICAL IONS OF MULTIPLE QUINONES

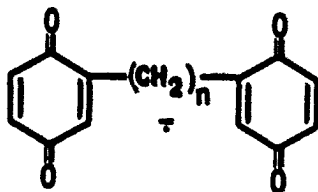
Electron spin resonance studies of the radical anions of quinones, the semiquinones, have over the years been numerous and extensive. Considerable effort has been expended in the elucidation of such phenomena as ion pairing [1-8], restricted motion in the solid state [9,10], and various exchange processes as they occur in these paramagnetic species [11,12]. As semiquinones with complex hydrocarbon appendages often exhibit a wealth of hyperfine structure, the various mechanisms of unpaired spin propagation to distant nuclei also appear well understood [13-19].

In contrast, reports of ESR investigations of Polysemiquinones are scant. Radical anions of type 1 have been described on occasion, but the reports conflict and conclusions are tenuous at best [20-23].



1

Much less is to be found on molecular systems wherein the semiquinone moieties remain proximate but devoid of formal conjugation (type 2) [24]. Radical ions of [2.2]paracyclophanequinone have been observed, but discussions of their magnetic properties have been brief and undetailed [25] (Section III).



It is thus clear that the existing body of experimental data on the radical ions of polyquinones is fragmentary and incomplete. Little is known of their electronic structure, and the effects of subtle changes in geometry, acceptor strength, and reduction state on their spin density distributions are poorly understood.

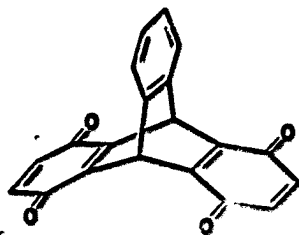
Part I of this dissertation will reveal efforts to address some of these issues.

## II. RADICAL ANIONS OF TRIPTYCENE BIS- AND TRIS(QUINONES) AND DERIVATIVES

### A. Introduction

Radical ions derived from molecular systems explicitly designed for the purpose of facile investigation by ESR spectroscopy ought, in principle, to fulfill certain criteria. The first of these might relate to precursor stability which could render the material pure and available at least in milligram quantities. It is also of vital importance that the precursor be resistant to destruction under conditions of radical ion generation. Once formed, the paramagnetic species in question should be free from rapid decay to facilitate detection under static, isotropic conditions. Consideration may also be given to the judicious location of information bearing termini within the molecular framework. Most often, this is accomplished by placing nuclei of non-zero magnetic (but low quadrupole) moment in the proximity of the spin probe.

9,10-dihydro-9,10[1',2']-benzenoanthracene-1,4,5,8-tetrone, from hereon referred to as triptycene bis(quinone) 3,[26] appeared to meet these criteria. The high symmetry, coupled with the



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flanked quinone moieties in a rigid bicyclic framework, provides a promising structure for investigation without complicating conformational



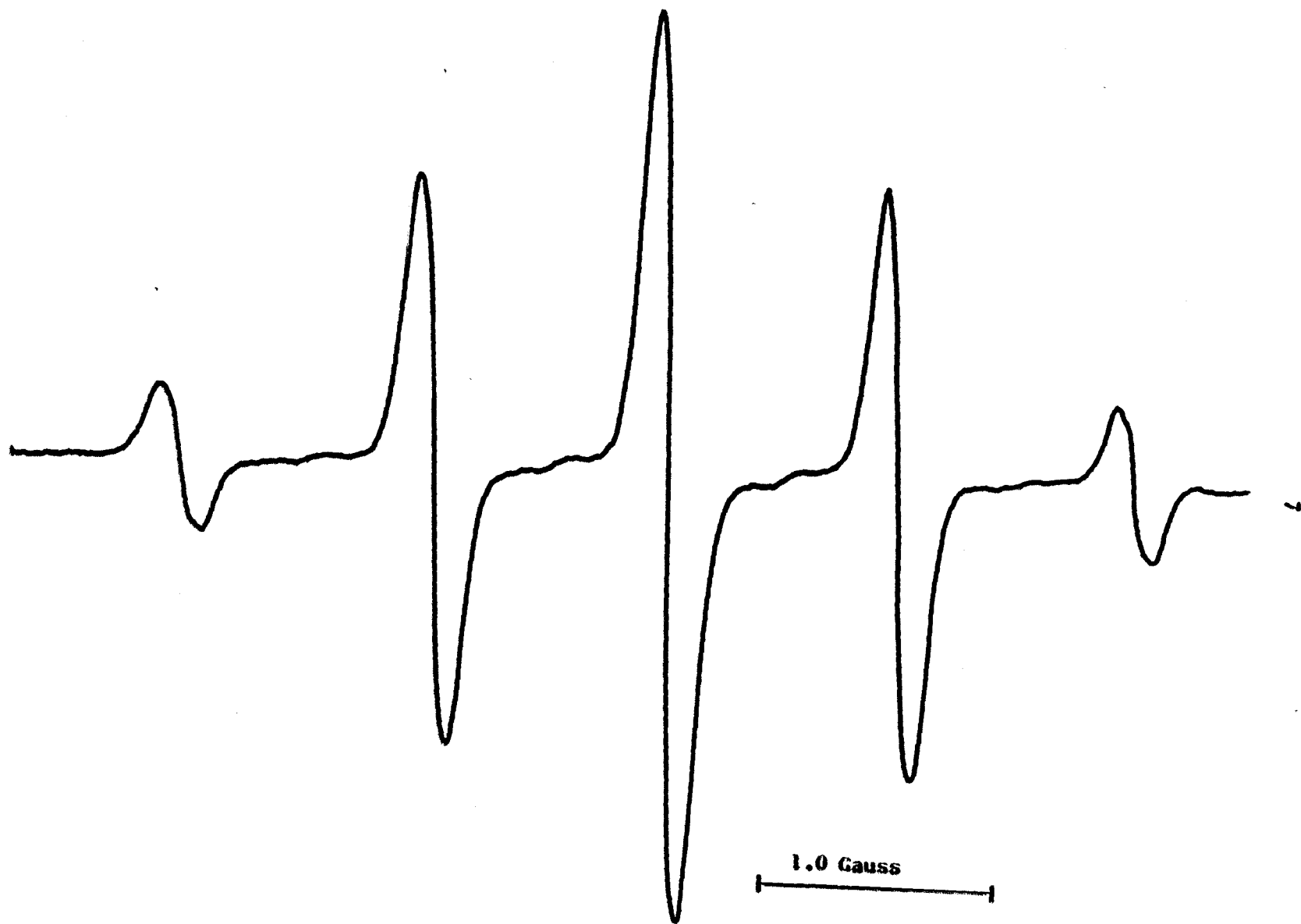
effects and overwhelming hyperfine structure. Additionally, available electrochemical data were indicative of an interesting transannular interaction in 3, since the first and second half-wave potentials ( $E_{1/2}$ ) were found to be  $-0.23$  and  $-0.48\text{v}$  (with respect to the saturated calomel electrode), respectively, in contrast to  $-0.37\text{v}$  for the first  $E_{1/2}$  of triptycene mono(quinone). Our attempts at elucidating the electronic structure of polysemiquinones thus began with the ESR spectra of radical ions derived from triptycene bis(quinone).

### B. Results and Discussion

Continuous electrolytic reduction of 3 in the cavity of an ESR spectrometer at a Hg pool or Pt electrode with TBAP as supporting electrolyte in DMSO or  $\text{CH}_3\text{CN}$  solutions initially gave rise to the binomial pentet of Figure 1 ( $a^{\text{H}}=1.10\text{ G}$  [4 H's],  $g=2.00506$ ). An identical spectrum was seen upon chemical reduction of 3 with trace quantities ( $\sim 0.5\text{ mg}$ ) of potassium tert-butoxide in DMSO.

On the basis of hyperfine coupling constants ( $a^{\text{H}}=2.30\text{ G}$  [2H's] for triptycane mono(quinone)), and by virtue of the fact that the pentet splitting was the first paramagnetic reduction product observed under carefully controlled electrolytic and chemical conditions, the spectrum of Figure 1 was attributed to the radical monoanion of triptycene bis(quinone),  $3^{\cdot-}$ . Thus, at ambient temperature, the ESR spectrum of  $3^{\cdot-}$  reveals a symmetric ion with equal unpaired spin distribution in both quinone rings. The mechanism by which this symmetry is established was clarified by observation of  $3^{\cdot-}$  at subambient temperatures, since cooling of the  $\text{CH}_3\text{CN}$  solutions resulted in

Figure 1. First derivative ESR spectrum of triptycene bis(quinone) radical anion,  $3^{\cdot-}$ .



selective line broadening of the second and fourth peaks of the original pentet (Figure 2a-c).

In analogy to other well-documented time dependent phenomena, these linewidth alternating effects are believed to occur due to fluctuating hyperfine splittings via some inter- or intramolecular exchange process [27]. Intermolecular processes such as electron spin exchange in a bimolecular reaction where the unpaired electrons of the two free radicals exchange their spin states, or instances of electron transfer between a radical and a diamagnetic species, both give rise to similar effects in the ESR spectrum [28]. However, the characteristics of their linewidth effects are concentration dependent and differ dramatically from those observed for  $3^-$ .

Precluding conformational effects for the rigid framework under consideration, a process consistent with the lineshape analysis involves an out of phase modulation of the hyperfine couplings caused by intramolecular jump of the unpaired electron. At 298 K, the hydrogen atoms of  $3^-$  are time averaged by electron migration for which a lower limit of approximately  $10^7 \text{ sec}^{-1}$  for  $k_{\text{ex}}$  may be placed by application of the Heisenberg uncertainty principle. The exchange rate decreases upon lowering the temperature, and at 230 K, the lifetime of a given occupational state becomes comparable to the reciprocal of the difference in coupling constants, resulting in significant broadening of the appropriate peaks [29]. At temperatures below the coalescence point (not attained here due to inhomogeneous line broadening), the odd electron would appear localized on the ESR time scale, and the spectrum is predicted to be a 1:2:1 triplet in the absence of hyperfine

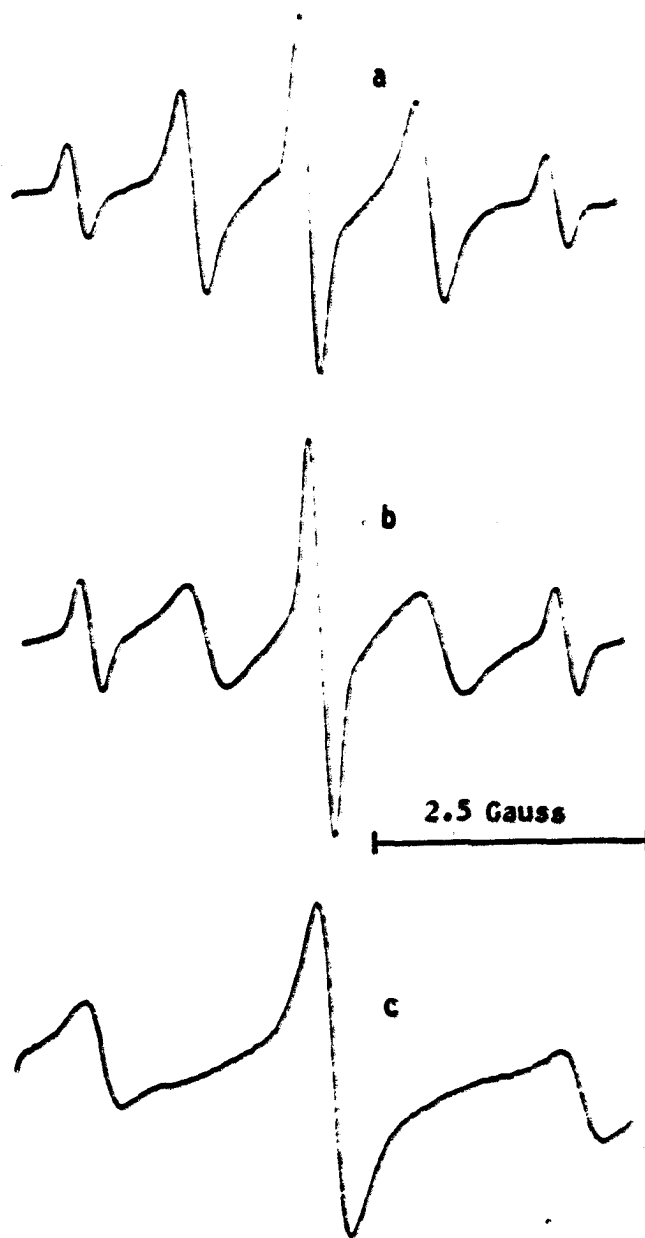
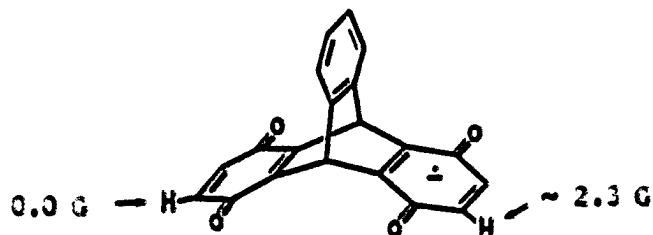


Figure 2. First derivative ESR spectra of triptycene bis(quinone) radical anion, 3°.

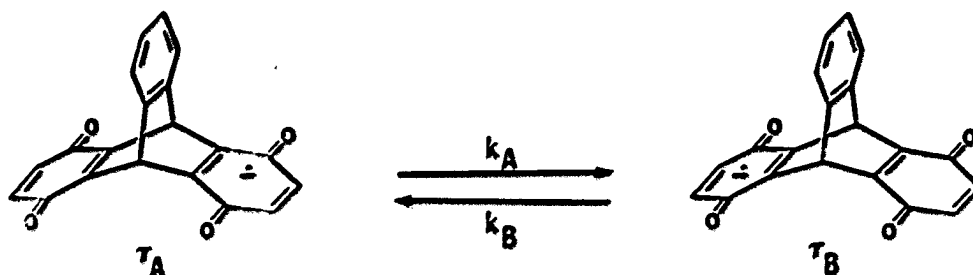
- (a) At 243 K
- (b) At 223 K
- (c) At 213 K

interaction with the unoccupied ring.



Inspection of Figure 3 clarifies the details of the linewidth alternation effect. Under conditions of rapid electron exchange, the spectrum appears as one set of four equivalent protons with the intensity ratio 1:4:6:4:1. At low temperatures when the exchange is slow, the spectrum appears to be that of two sets of two equivalent protons (with one set of  $a^H=0$ ). At intermediate rates of exchange, the positions of the lines in which the two protons have the same quantum numbers do not shift. However, lines where the protons have different quantum numbers become broad since the splitting is changing between the values  $a_1^H$  and  $a_2^H$ . This results in a splitting pattern of 1:4:1 in sharp lines with line separation equaling the sum of the non-interconverting species ( $a_1^H + a_2^H$ ).

Since the occupational states are of equal energy and hence, equally populated, the mean lifetime of a given state ( $\tau_A$  or  $\tau_B$ ) is the reciprocal of the rate constant ( $k_A$  or  $k_B$ ).





Under conditions of fast exchange or intermediate exchange, the rate constant for electron jump,  $k_A$  or  $k_B$  is given by equation (1) [30].

$$k = \frac{\gamma_e}{2\pi} (a_1^H - a_2^H)^2 / 4\sqrt{3} \quad (\Delta \text{ width}) \quad (1)$$

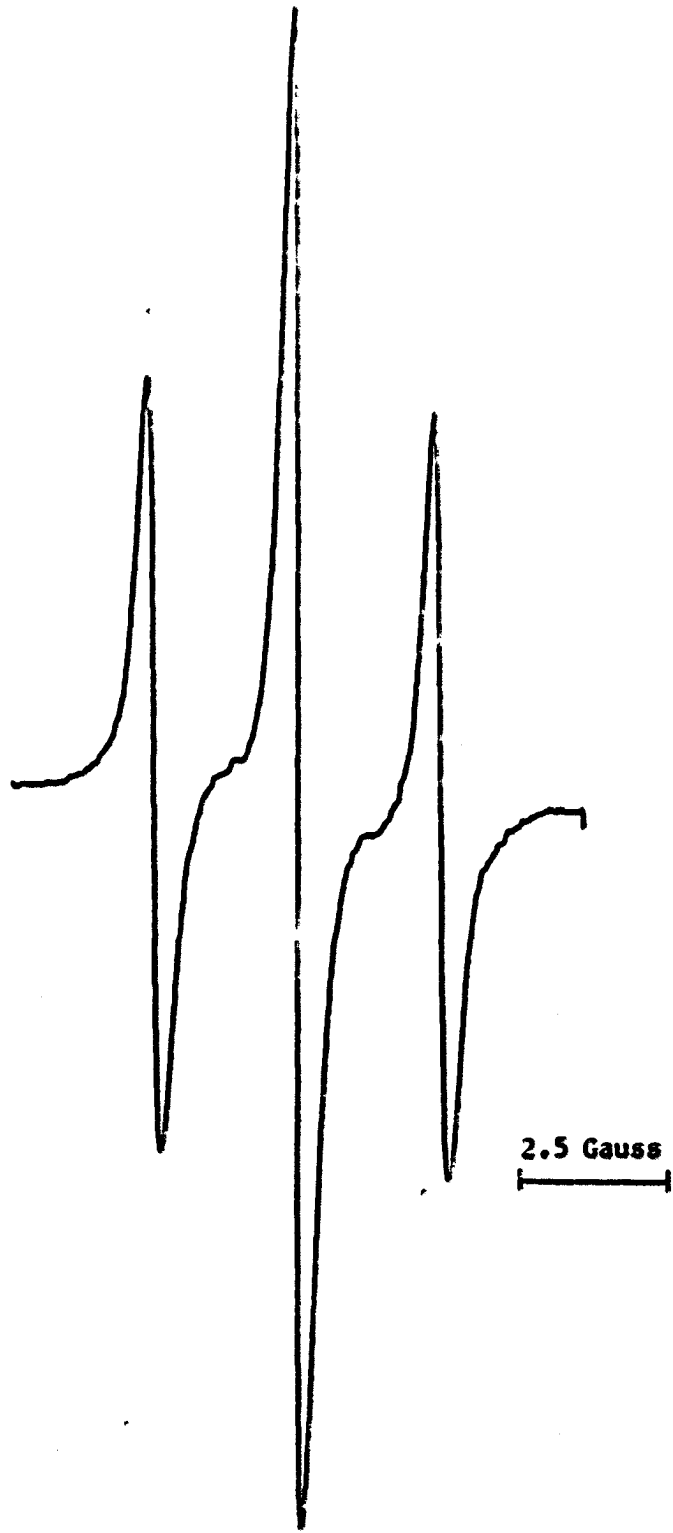
where  $\gamma_e$  is the magnetogyric ratio of the free electron,  $a^{H1}$  and  $a^{H2}$  are the limiting values of the hyperfine splitting frequencies, and  $\Delta$  width is the difference in line width at half height between broadened and sharp peaks. From values of  $\Delta$  width obtained between 273 and 248 K, the energy barrier for electron migration in  $3^{\cdot-}$  was calculated as  $\Delta H^\ddagger = 6.2 \text{ kcal mol}^{-1}$ , with an entropy of activation  $\Delta S^\ddagger = -7.0 \text{ e.u.}$  These values are assumed to reflect the behavior of the free ion  $3^{\cdot-}$  since stoichiometric quantities of [2.2.2]-cryptand were introduced into  $\text{CH}_3\text{CN}$  solutions to scavenge the potassium counterion, thus precluding the existence of ion pairs of the type  $3^{\cdot-}\text{K}^+$ .

Continued electrolytic reduction of solutions containing  $3^{\cdot-}$  resulted in asymmetric ESR spectra due to the appearance of a second paramagnetic species which was not time averaged with  $3^{\cdot-}$ . Upon prolonged reduction (0.5 to 3.0 hours, depending upon the working potential), the pentet disappeared completely to give a 1:2:1 triplet ( $a^H = 2.40 \text{ G}$  [2H's],  $g = 2.00506$  in DMSO, Figure 4). Chemical reductants such as potassium tert-butoxide, when employed in excess ( $\sim 1.0 \text{ M}$  in DMSO), produced similar spectra in solutions containing 3 or  $3^{\cdot-}$ .

The species responsible for the 1:2:1 triplet was stable to



Figure 4. First derivative ESR spectrum of triptycene bis(quinone) diradical dianion  $^{3-}$ .



molecular oxygen and could be observed in both nucleophilic and non-nucleophilic media, in the presence or absence of potassium ions. Electrolysis in protic cosolvents such as DMSO-H<sub>2</sub>O (80:20) appeared to facilitate the formation of the 1:2:1 triplet which was unchanged upon dilution.

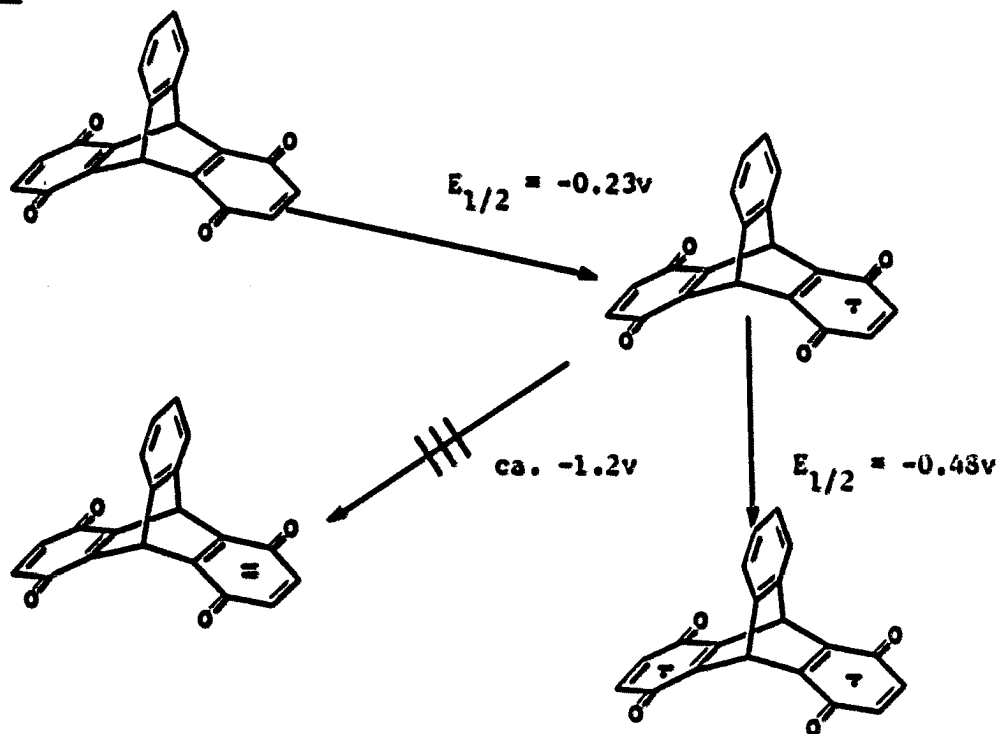
The identity of the species attributed to the 1:2:1 triplet is quite problematic and has been the subject of extensive investigation and debate. A detailed rationale is thus presented here to justify the assignment.

In accordance with the acceptor properties of quinones, triptycene bis(quinone) may in principle, accept a maximum of four electrons. The highest reduction state  $3^{\ominus}$  is diamagnetic, and need not be considered further, while both  $3^{\ominus\cdot}$  and the trianion radical  $3^{\ominus\ominus\cdot}$  (to be discussed subsequently) have been characterized and assigned without difficulty. The remaining two-electron reduction product,  $3^{\ominus\ominus}$  is expected to show diradical rather than dianion character in view of the available electrochemical data (first and second  $E_{1/2}$  of *p*-benzoquinone = -0.35 v and -1.20 v, respectively) [31]. Thus, casual consideration of the data would suggest a straight forward assignment of the 1:2:1 triplet to a diradical species. However, such an assignment poses some difficulty and could appear irreconcilable with the existing body of knowledge pertaining to the ESR spectral characteristics of diradicals.

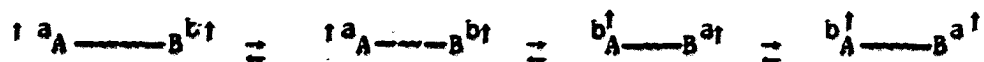
From the large number of organic diradicals that have been studied, it has become clear that the dominant magnetic interactions to be considered in these species are the scalar spin exchange term (J), the

electron-electron dipolar coupling which gives rise to the zero field splitting parameter (D), and the nuclear spin isotropic hyperfine interactions (A) [32].

Scheme I



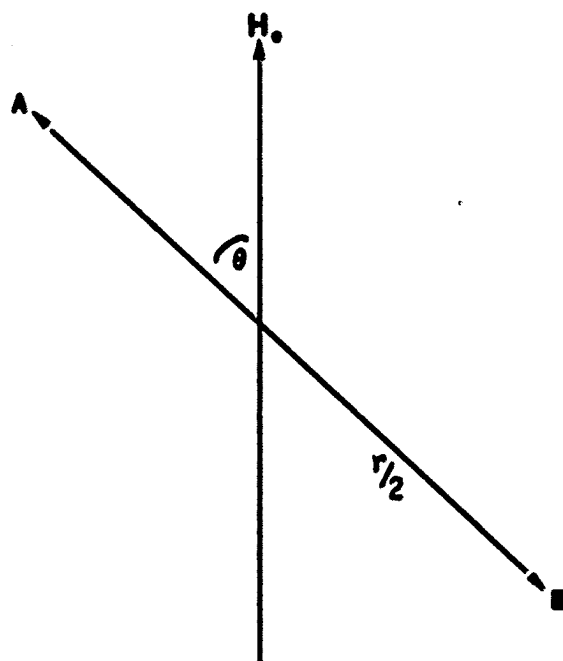
The spin exchange term ( $J$ ) is a measure of the frequency with which the unpaired electrons interchange their respective domains, and thus of the energy separation between the singlet and triplet states. The most common means by which electron-electron spin exchange occurs in these species, is by the spatial encounter of the two moieties of the diradical, each bearing an unpaired electron [33]:



In instances of slow exchange, the weak coupling leads to a degenerate ground state in the diradical (singlet-triplet energy difference of zero), while in cases of fast exchange, the strong interaction gives rise to finite differences in the respective singlet and triplet energy states.

Characteristic magnitudes of the electron-nuclear hyperfine interaction ( $a$ ) in organic radicals assume values between 0-25 Gauss ( $A \leq 7 \times 10^7 \text{ sec}^{-1}$ ). In diradicals where the two electrons are well separated spatially ( $> 10 \text{ \AA}$ ), the possibility exists that  $|J|$  will be small and hence,  $|J| \ll |A|$ , resulting in solution ESR spectra with sharp lines ( $\sim 0.1 \text{ G}$  width) of spacing  $|A|$ , identical to those observed for the corresponding doublet monoradicals [34]. A change in the frequency of electronic exchange between the two paramagnetic spin centers may be brought about by structural modification of the interconnecting medium. A shortening of the mean distance between spin points would presumably mean enhanced values of  $|J|$ , as would modulation of the spin exchange term due to extended intramolecular conformational mobility at elevated temperatures [35]. At a high frequency of electronic exchange (slightly exceeding the frequency of hyperfine interaction), the mean residence time of each electron at the nuclei imparting hyperfine interaction is the same, and results in an ESR spectrum showing hyperfine coupling to both radical fragments with line separation  $|A|/2$ . It is interesting to note, however, that for either case,  $|J| \gg A$  or  $|J| \ll |A|$ , the detection of an ESR signal in fluid solution is entirely contingent upon an important magnetic parameter, the anisotropic electron-electron dipolar interaction [36]. The nature of this

coupling is analogous to the interaction between electron and nuclear dipoles which gives rise to anisotropic hyperfine interaction, and is best presented schematically.



Consider the rigid disposition of radical fragment A with respect to B, separated by a distance  $r$ , and imparting an angle  $\theta$  to the applied field  $H_0$ . The instantaneous magnetic field felt at electron A ( $H_A$ ) is given by equation (2) [32], where  $\mu_B$  is the magnetic moment of the second electron.

$$H_A = H_0 + H_B = H_0 + \frac{\mu_B}{r^3} (3 \cos^2 \theta - 1) \quad (2)$$

The dipolar interaction is thus dependent upon the orientation of the

molecule with respect to the external magnetic field, and in solutions possessing sufficient molecular motion, the random and rapid fluctuation in  $\theta$  may result in the averaging of the anisotropic electron-electron dipolar moment. In instances wherein the dipolar coupling is weak (i.e., at large values of  $r$ ), the anisotropic interaction is averaged out by Brownian motion, and well resolved ESR spectra may be obtained. However, values of the zero field splitting parameter ( $D$ ), much in excess of 100 MHz, result in considerable line broadening of the solution ESR spectra. This increase in linewidth may encompass several orders of magnitude, and has its origins in reduced lifetimes of the spin states, since in solutions of low viscosity, the rapid tumbling of the triplets (with large  $|D|$ ) give rise to strongly oscillating magnetic fields and hence, provide an additional relaxation mechanism, leading to broadened resonances. ESR detection of species with ( $D > 100$  MHz) in solution is thus often unsuccessful, with the resonance absorption broadened over hundreds, or perhaps thousands of Gauss. However, this limitation is partially overcome by the observation of triplets in viscous media wherein the rates of molecular tumbling are somewhat attenuated. In such cases of restricted motion, the spectra are a composite of absorptions from all the individual orientations, and are therefore smeared out over the range of the dipolar splitting.

In summary, the form of the fluid ESR spectrum of a system with  $S=1$  depends critically on the magnitude of the zero field splitting parameter  $D$ , and on the relative magnitude of  $J$  as compared to the hyperfine coupling constant  $A$ . In the limiting case  $|J| \ll |A|$ , simply a superposition of the spectra of the independent monoradical halves is

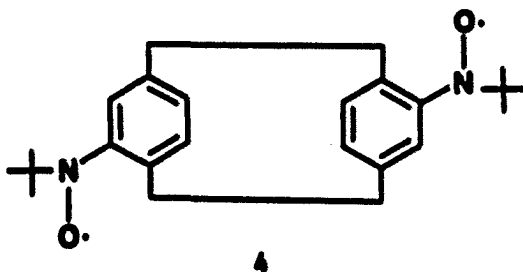
obtained, while in the case where  $|J| \gg |A|$ , hyperfine coupling of each unpaired electron to all the interacting magnetic nuclei is apparent. If  $D$  is smaller than approximately 100 MHz, the anisotropic electron-electron dipolar coupling may be averaged to zero by rapid molecular tumbling, resulting in well resolved spectra [34].

In analogy to numerous ESR studies of diradicals and triplets such as the bis(nitroxides) [37,38] and bis(hydrazyls)[39], the ESR spectrum of the dianion diradical of triptycene bis(quinone)  $^{2-}3^{2-}$ , should without question, show strong manifestations of the characteristic magnetic forces operating in species with  $S=1$ . However, the spectrum (which takes the form of a solution 1:2:1 triplet of sharp lines), if assigned to a diradical, would appear to entail unusual magnetic interactions in this species, since the triplet of Figure 4 would only be consistent with a diradical structure if  $|J| \ll |A|$ , with a singlet-triplet diradical energy separation of approximately zero. In such a case, there are only three  $\Delta M_S = 1$  energy transitions between the  $T_+$ ,  $T_0$  and singlet diradical states, when each electron undergoes hyperfine splitting by two equivalent hydrogen atoms [40,41]. Additionally, the lack of significant line broadening in the solution spectrum indicates the absence of a large zero field splitting parameter  $D$  (certainly much less than 30 Gauss, since the lines do not appear appreciably broader in frozen DMSO solutions at 273 K).

The relative values of  $|J|$  and  $D$  for  $^{2-}3^{2-}$  are therefore in contrast to those for bis-nitroxides of similar, rigid constitution, such as  $N,N'$ -di-*t*-butyl-[2,2]-paracyclophan-4,16-diylbisnitroxide 4, for which an average distance  $r$  of 6.8 Å between paramagnetic centers can



be calculated using a point-dipole approximation. The ESR spectrum of **4** shows fast exchange between the two unpaired electrons ( $|J| \gg |A|$ ), and suffers from considerable line broadening due to the large zero field splitting value of approximately 240 MHz [42].



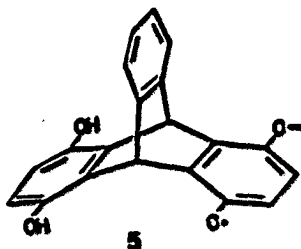
Numerous other examples with similar values of  $r$  (4-8 Å) continue this trend, often showing  $|J| \gg |A|$  and values of  $D$  in excess of 200 MHz [43-45].

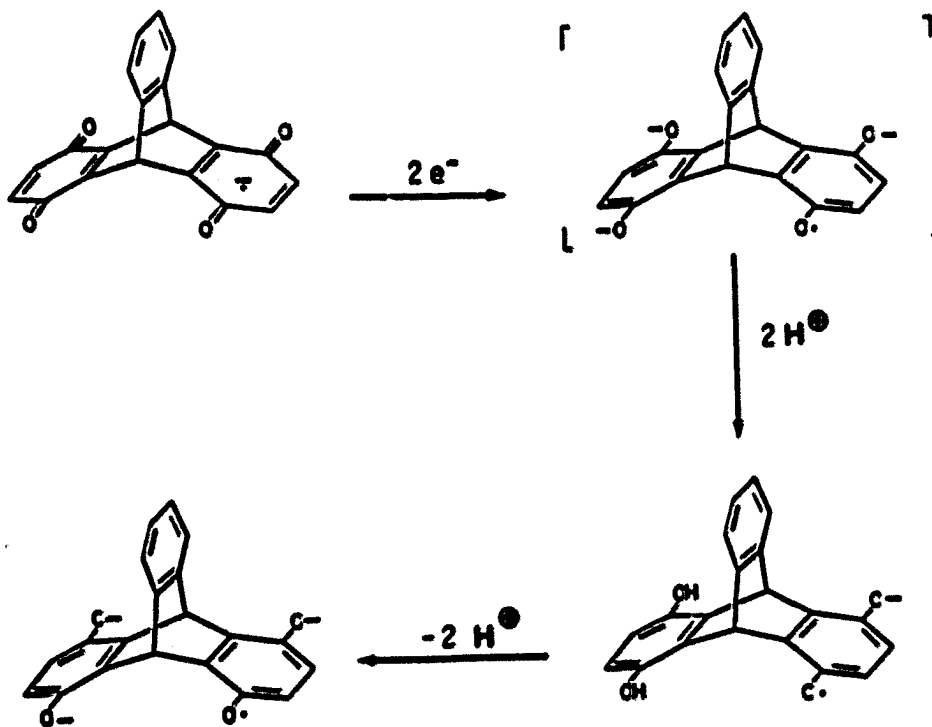
In  $\cdot\bar{3}\bar{\cdot}$ , the average distance between the two unpaired electrons may be estimated at approximately 6 Å. By analogy, therefore, the ESR spectrum of the diradical dianion  $\bar{\cdot}\bar{3}\bar{\cdot}$  might be expected to show properties of fast electronic exchange ( $|J| \gg |A|$ ) and large values of  $D$  so as to broaden the resonance significantly. The solution to this dichotomy may rest in the nature of the molecular orbitals harboring the free electron. In the case of the bis-nitroxides, most of the unpaired spin is localized over the nitroxyl moieties, giving rise to proximate loci of high electron spin density. In contrast, the singly occupied molecular orbitals in  $\bar{\cdot}\bar{3}\bar{\cdot}$  have large pi perimeters over which the electrons are completely delocalized, and it is entirely possible that the lack of significant electron-electron dipolar coupling in  $\bar{\cdot}\bar{3}\bar{\cdot}$  arises from much greater charge and dipole moment

separation than is predicted from a spin point expression.

The low frequency of electronic exchange in  $^{\cdot-}3^{\cdot-}$  ( $J \ll 7 \times 10^7$  MHz) may have its origins in the extremely rigid disposition of the paramagnetic fragments relative to each other. The lack of conformational mobility undoubtedly precludes the close intramolecular approach of the radical containing moieties, thus drastically reducing the probability of direct spin exchange. While indirect mechanisms for spin exchange have, on occasion been put forth to explain electronic interaction between distant spin centers which lack conformational mobility [46], electron exchange via the polarization of core sigma and pi electrons does not appear important in  $^{\cdot-}3^{\cdot-}$ .

The possibilities of assigning the 1:2:1 triplet to structures other than a diradical have been examined. The most plausible alternative appeared to be the quinhydrone radical anion **5**, which could conceivably arise from the spontaneous protonation of the trianion radical  $3^{\equiv-}$ . An observation which supported this hypothesis was the fact that the 1:2:1 triplet could be observed much more readily when the electrolysis was carried out in the presence of possible proton sources such as methanol or water. Further chemical or electrolytic reduction would presumably then lead to deprotonation, giving  $3^{\equiv-}$ , (Scheme II).

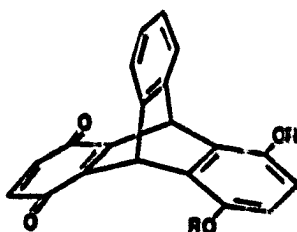


Scheme II

This hypothesis was tested by the generation of  $3^{\cdot-}$ , followed by introduction of water via a fine capillary into the sample chamber under observation. The lack of significant change in the ESR spectrum of  $3^{\cdot-}$  indicated a poor propensity of  $3^{\cdot-}$  to protonate under the given conditions. The quinhydrone radical anion was therefore dismissed as a major source of the 1:2:1 triplet. Attempts to generate **5** directly from the neutral quinhydrone failed due to a disproportionation equilibrium involving the bis(quinone) **3** and the corresponding bis(hydroquinone).

A second alternative regarding the identity of the 1:2:1 triplet arose from the possible presence in trace quantities, of **6**, especially since the final sequence in the synthesis of triptycene

bis(quinone) involved the oxidative demethylation of the dimethyl ether.



R = H  
6

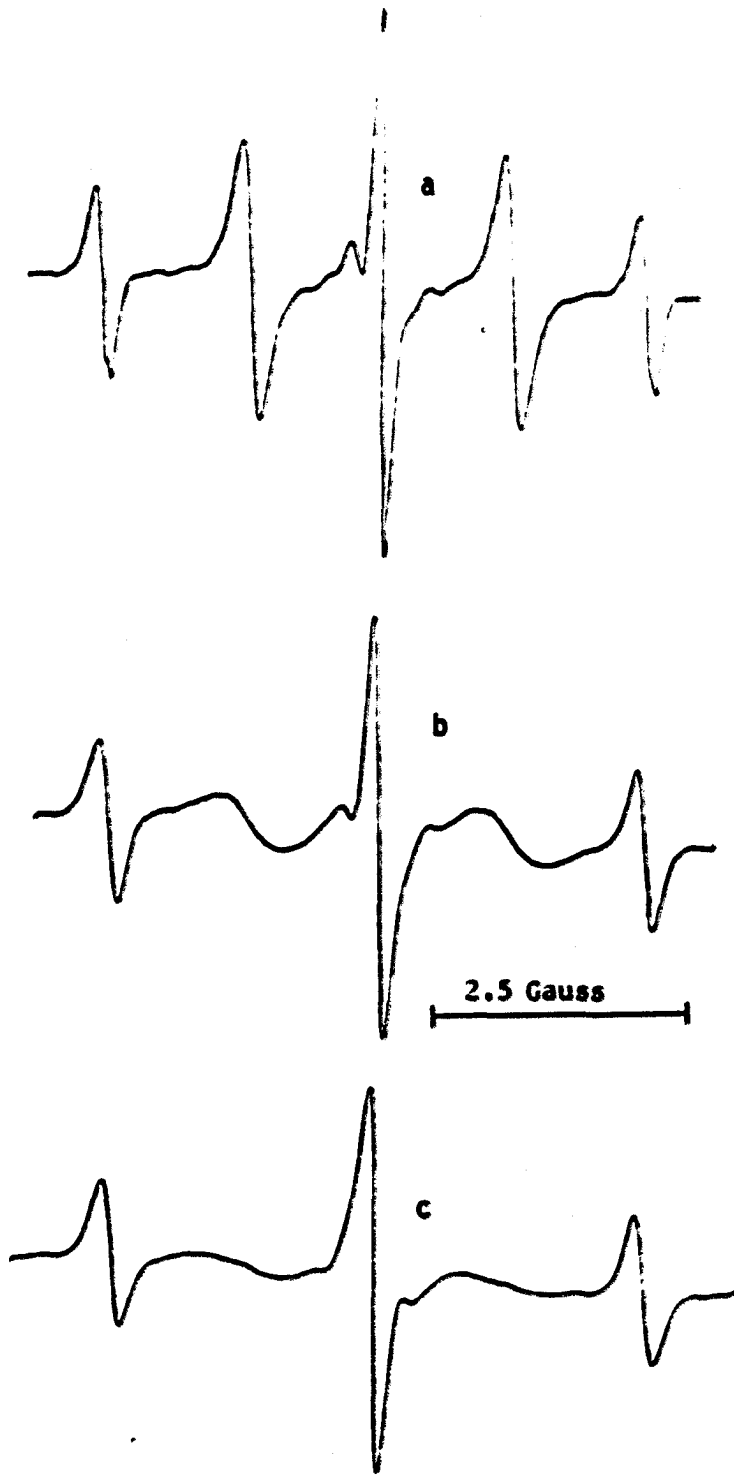
This possibility was ruled out by careful spectroscopic examination, which revealed the bulk sample of 3 to be analytically pure.

It is thus the present author's contention, that in light of the experimental data, assignment of the 1:2:1 triplet is most reasonably made to the dianion diradical of triptycene bis(quinone),  $^{\cdot-}3^{\cdot-}$ .

Extensive electrolysis at high reduction potentials of solutions containing  $^{\cdot-}3^{\cdot-}$  resulted in the appearance of a third paramagnetic species, a new pentet of lower g value than for the composite spectra for  $3^{\cdot-}$  and  $^{\cdot-}3^{\cdot-}$  ( $a^H = 1.30$  G [4H's],  $g = 2.00495$ , DMSO, Figure 5a). This new species could also be generated via the action of (0.1 M) potassium tert-butoxide and [2.2.2]-cryptand/18-crown-6 ether on solutions containing  $3^{\cdot-}$  and  $^{\cdot-}3^{\cdot-}$ . Addition of neutral 3 converted the new spectrum to one containing a mixture of both  $3^{\cdot-}$  and  $^{\cdot-}3^{\cdot-}$ , while trace quantities of molecular oxygen immediately destroyed the highly reactive pentet to give a residual signal analyzed as a doublet of doublets ( $a_1^H = 2.00$  G [1H],  $a_2^H = 2.35$  G [1H],  $g = 2.0020$ ), which is believed to be a semiquinone dianion in which one ring has been substituted by OH or OR.

Ion pairing did not alter the appearance of the low g pentet, which

**Figure 5.** First derivative ESR spectrum of erioptycene bis(quinone) radical trianion,  $3^{\ominus}$ . (a) At 298 K (b) At 260 K (c) At 238 K



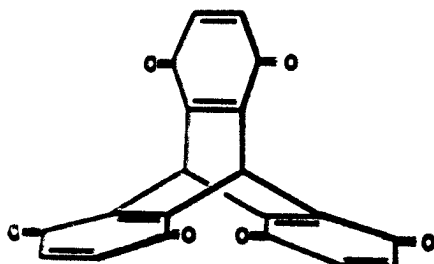
was observed electrolytically in (0.1 M) KI, or in the presence of an excess or deficiency of a complexing agent when generated chemically. The apparent role of the crown ether or cryptand in generating the pentet was thus merely that of extending the reducing capacity, by disruption of ion pairs in the chemical reductant.

The high reactivity, the form of the low g pentet, and the delayed appearance of this species along the reduction sequence are consistent with the expected properties of the trianion radical  $3^{\equiv\cdot}$ . At 298 K, the pentet assigned to the trianion radical  $3^{\equiv\cdot}$  displayed selective line broadening of the second and fourth peaks. Cooling the  $\text{CH}_3\text{CN}$  solution to 253 K resulted in a 1:4:1 triplet of sharp wing and center peaks, while warming caused the splitting pattern to approach the normal binomial ratios of 1:4:6:4:1 (Figure 5b,c). As in the case of the radical monoanion, these temperature dependent alternating linewidth effects were completely reversible, and have been attributed to intramolecular electron jump, rather than to a process involving chemical change.

The energy barrier for electron migration between the quinone moieties in  $3^{\equiv\cdot}$  was calculated from the selective line broadening data obtained between 293 and 253 K, and the values of  $\Delta H^\ddagger = 3.7$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -14.0$  e.u sharply contrast those calculated for  $3^{\cdot-}$  ( $\Delta H^\ddagger = 6.2$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = -7.0$  e.u). The lower activation energy in the trianion may be due to the greater electronic repulsion in the dianion moiety of  $3^{\equiv\cdot}$ , while the highly unfavorable entropy of activation may retard electron migration due to the necessary reorganization that must occur in the solvation sphere of

this highly reduced and ordered species.

The ESR study of polysemiquinones was continued with the radical anions of 9,10-dihydro-9,10[1',2']-benzenoanthracene-1,4,5,8,13,16-hexone, from hereon known as triptycene tria(quinone), 7.



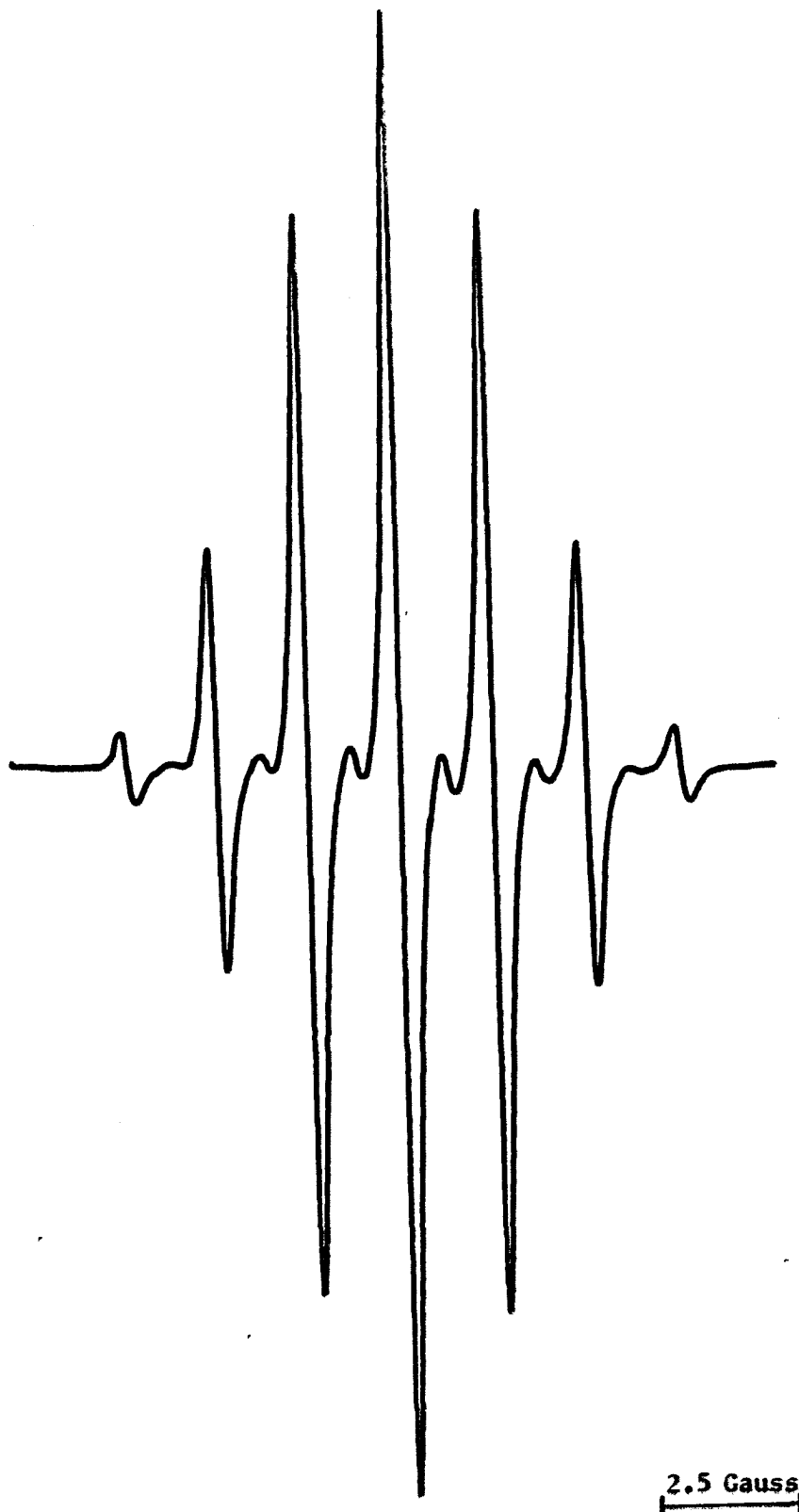
7

Electrolytic reduction of 7 in DMSO or  $\text{CH}_3\text{CN}$  with TBAP as supporting electrolyte at a Hg pool or Pt electrode initially gave a binomial septet which was most reasonably assigned to the radical monoanion,  $7^{\cdot-}$  ( $a^{\text{H}} = 0.66 \text{ G}$  [6H'a],  $g=2.00507$  in DMSO, Figure 6). An identical spectrum could be obtained by treatment of 7 with trace quantities of potassium tert-butoxide in DMSO. The spectrum for  $7^{\cdot-}$  showed no evidence for selective line broadening in the temperature range studied, and the hydrogen atoms in all three quinone rings remain time averaged by rapid electron migration at temperatures as low as 183 K.

Prolonged electrolysis at higher reduction potentials, or reaction of solutions containing  $7^{\cdot-}$  or 7 with (0.1 M) potassium tert-butoxide resulted in a new paramagnetic species showing hyperfine structure due to two equivalent hydrogen atoms, (Figure 7). In analogy to the reduction products observed for triptycene bis(quinone), this ESR



**Figure 6. First derivative ESR spectrum of triptycene tris-(quinone) radical anion, 7<sup>-</sup>.**



spectrum was assigned to the triradical trianion  $\cdot\cdot\cdot\dot{7}^-$  in which the zero field splitting parameter is considerably less than 100 MHz, and there is no correlation between the unpaired electrons ( $|J| \ll |A|$ ). The intermediate paramagnetic reduction state  $\cdot\cdot\dot{7}^-$  could not be identified as a discrete species possibly because the ESR spectrum of the diradical dianion is expected to be a binomial septet, and is perhaps indistinguishable from that due to  $\dot{7}^-$ .

At still higher reduction potentials, a second septet was produced which was not time averaged with the 1:2:1 triplet that preceded it ( $a^H = 0.68$  G [6 H's], Figure 8). This species, tentatively assigned to the diradical tetraanion  $\cdot\cdot\dot{7}^{4-}$  was quite unstable and disappeared immediately upon cessation of electrolysis. Although the form of the septet (not in correct binomial ratio, possibly due to selective line broadening or an overlap of a mixture of species) invited further inquiry, the highly fleeting nature of the species ruled out this possibility.

In summary, the reduction of 7 gave rise to a number of paramagnetic species, three of which have been spectrally isolated and identified. The existence of five possible paramagnetic states prevented the unequivocal assignment of the higher reduction states, especially since the chemical reaction of 7 with potassium tert-butoxide/[2.2.2]-cryptand resulted in complex mixtures rather than in a single, highly reduced component as in the case of the bis(quinone).

In the triptycene tris(quinone) system, intramolecular electron jump occurs more readily than for the bis(quinone). This may have its origins

Figure 7. First derivative ESR spectrum of triptycene tris(quinone) triradical trianion. <sup>7</sup>.

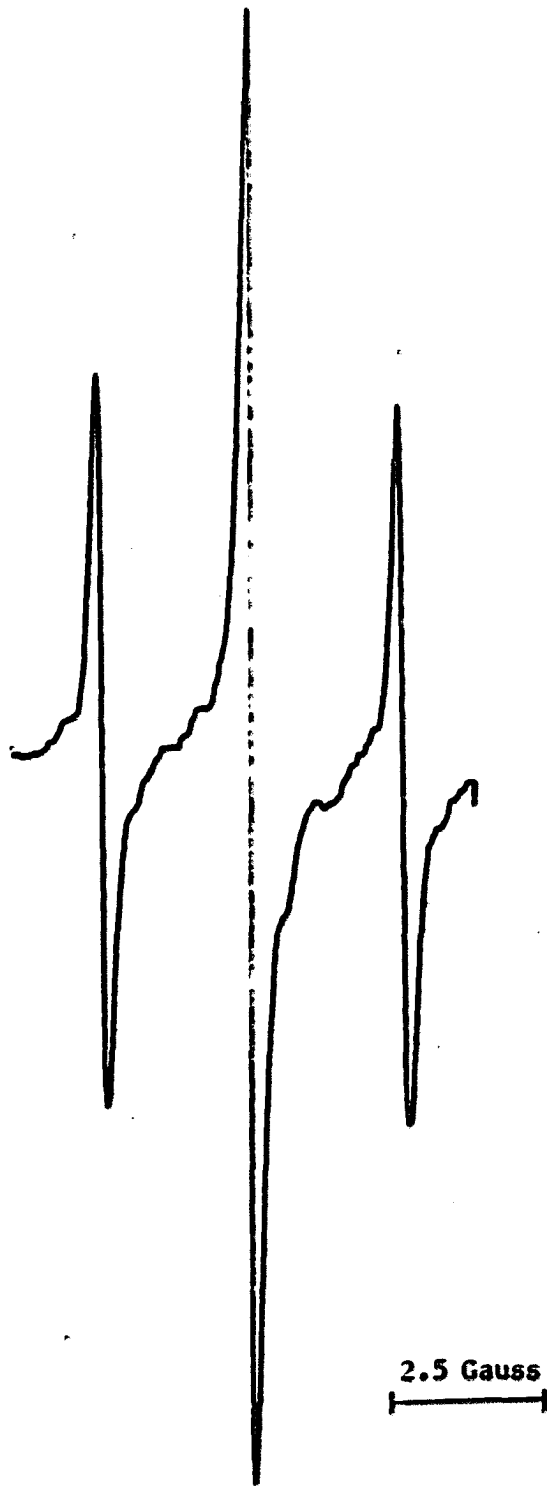
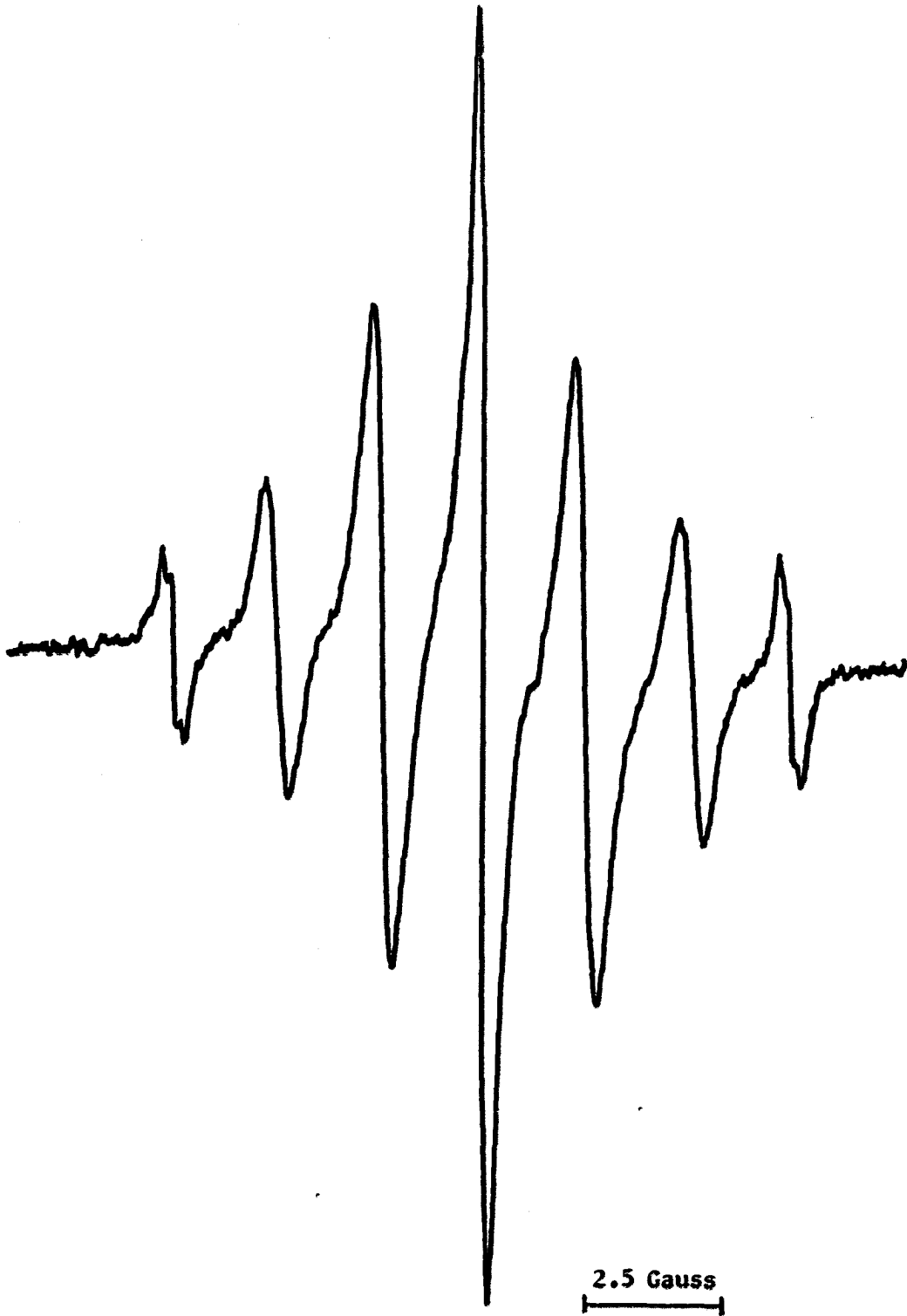
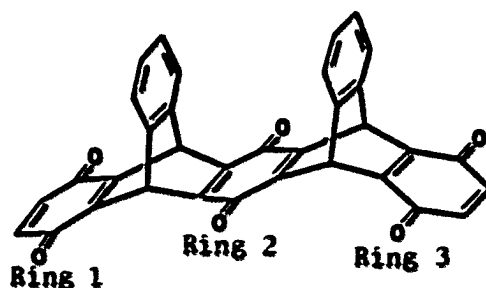


Figure 8. First derivative ESR spectrum of triptycene tris-(quinone) diradical tetraanion,  $^{7-}$ .



in a more favorable  $\Delta S^\ddagger$  for electron migration in  $7^-$ . It is important to note here, that the question of energy barriers for such processes as intramolecular electron transfer in  $7^-$  cannot be addressed satisfactorily in cases where linewidth alternation is not observed. At the lowest attainable temperatures (generally about 180 K), organic radicals with typical linewidths of 0.1 to 1.0 G will exhibit insignificant selective line broadening for exchange processes occurring at a frequency in excess of approximately  $10^8 \text{ sec}^{-1}$  [20]. The term "fast electron exchange" thus makes reference to the ESR time scale, and does not necessarily invoke delocalization of the unpaired electron.

The appenditure of three quinone rings in a triptycene-like framework wherein all the quinone moieties are no longer equivalent may be found in 5,7,12,14-tetrahydro-5,14:7,12-di(1',2')-benzenopentacene-1,4,6,8,11,13-hexone, compound 8 [47].





Electrolytic reduction of **8** (Hg pool, TBAP as supporting electrolyte) or treatment with trace amounts of potassium tert-butoxide in DMSO initially gave the single line ESR spectrum of Figure 9. This species, assigned to the radical monoanion  $\bar{8}^{\cdot}$ , was stable to molecular oxygen and could be observed in the presence or absence of potassium ions. The spectrum remained a one line pattern upon heating to 373 K, and was essentially unchanged upon a one-hundred-fold dilution. From the lack of hyperfine structure in the spectrum for  $\bar{8}^{\cdot}$ , it is apparent that the unpaired electron resides predominantly in the central ring where it remains localized up to 373 K, and to which there are no direct carbon-hydrogen linkages. This peculiar spin density distribution, and the poor migratory aptitude of the unpaired electron in  $\bar{8}^{\cdot}$  [as compared to triptycene bis- and tris(semiquinones)] may be a consequence of enhanced acceptor capacity of the central ring, resulting in a lower  $T_{1/2}$  of the central ring as compared to the peripheral quinone moieties. Although the origins of the described effects in the central ring have not been firmly established, it appears reasonable that the inductive effects of two, electron poor quinone moieties linked to the middle ring result in the latter acquiring much greater electron deficiency, thus rendering it a more powerful electron acceptor. Continued electrolytic reduction at higher potentials, or treatment of solutions containing **8** or  $\bar{8}^{\cdot}$  with (0.1 M) potassium tert-butoxide in DMSO resulted in the appearance of a second paramagnetic species, a 1:2:1 triplet ( $a^H = 2.40$  G [2 H's], DMSO) superimposed on the initial single line, (Figure 10). This new species was most probably the two electron reduction product  $\bar{8}^{2\cdot-}$ , with

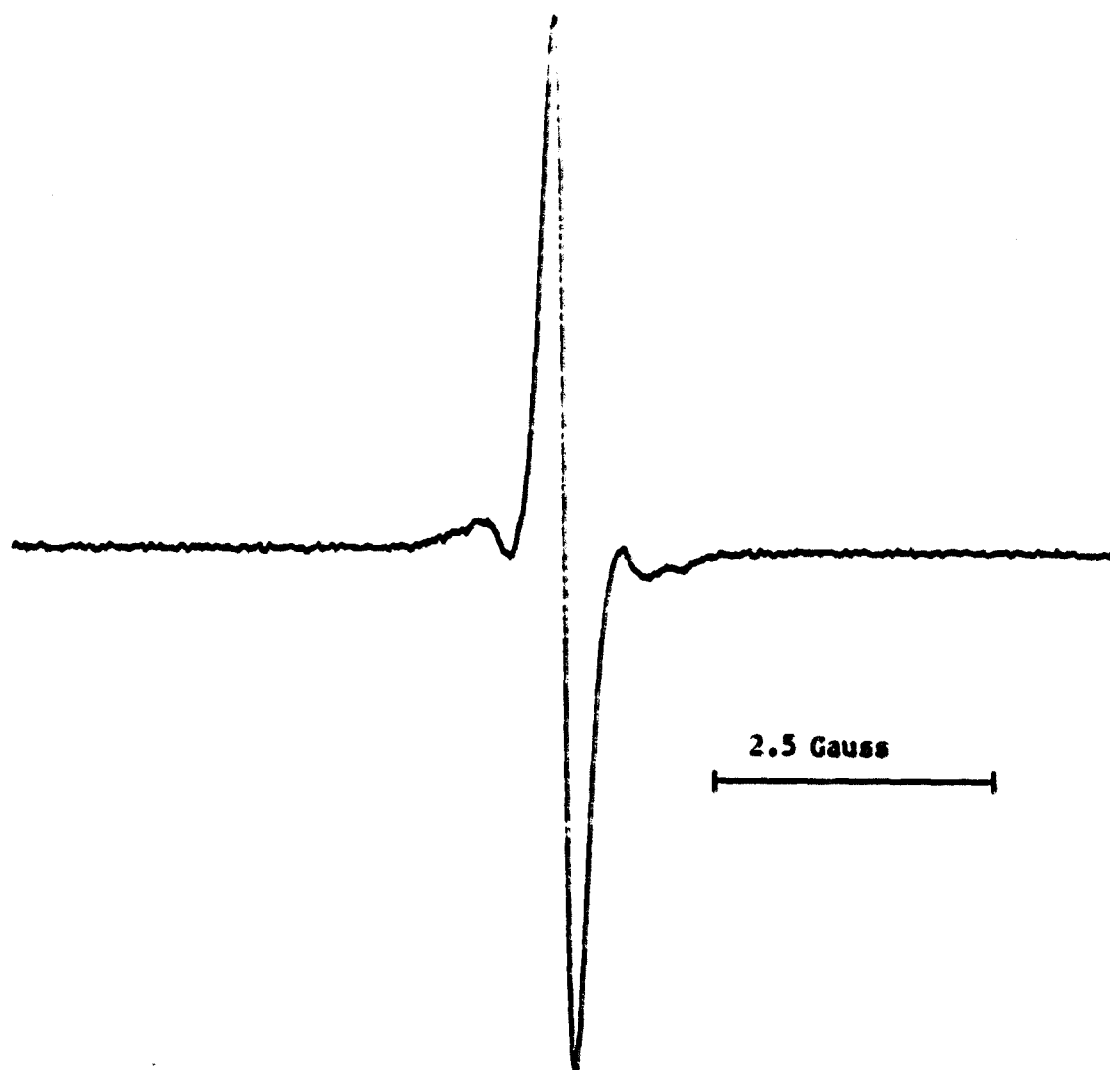


Figure 9. First derivative ESR spectrum of 5,7,12,14-tetrahydro-5,14:7,12-di[1',2']-benzenopentacene-1,4,6,8,11,13-hexone radical anion,  $8^{\circ}$ .



Figure 10. First derivative ESR spectrum of 5,7,12,14-tetrahydro-5,14:7,12-di[1',2']-benzenopentacene-1,4,6,8,11,13-hexone diradical dianion,  $\bar{8}^{\cdot -}$ .

the second electron accepted into one of the peripheral quinone rings, and in which the species satisfies the general trend established for di- and triradical anions in the triptyrene series of  $|J| \ll |A|$ , and  $D \ll 100$  MHz. As expected, the relative proportions of the new triplet and the initial singlet were dependent upon the degree of reduction, with the triplet predominating at higher potentials.

It is interesting to note, however, that the inequivalence of the acceptor groups in **8** result in the superpositioning of transitions from each paramagnetic center, leading to ESR spectra which reflect weighted contributions from the individually occupied states. This has the consequence of eradicating any clear demarcation between the initial reduction states, since the reduction sequence  $\dot{8} \rightarrow \dot{8}^- \rightarrow \cdot\dot{8}^-$  does not manifest itself in discrete ESR spectra, but only in obscure changes in the ratios of the contributing species. Thus, an ESR spectrum showing a 1:2:1 triplet superimposed on a single line may indicate the presence of the diradical dianion  $\ddot{8}^{2-}$ , a mixture of  $\dot{8}^-$  and  $\ddot{8}^-$ , or perhaps even a combination of  $\cdot\dot{8}^-$ ,  $\dot{8}^-$  and  $\cdot\ddot{8}^-$ , with only a qualitative evaluation on the predominating species being possible upon inspection of the 1:2:1/single line ratios, and the prevailing reduction potential.

Further reduction may, in principle, give rise to two possible electronic structures, since the fourth electron may be accepted into either of the outer rings, or into the central quinone group (Table 1). Should the diradical tetraanion ( $\cdot\ddot{8}^{4-}$  or  $\cdot\ddot{8}^{4-}$ ) be the exclusive species in solution, an ESR spectrum showing a perfect binomial triplet (consistent with electronic distribution in 4a), or a superposition of a

1:2:1 triplet on a single line, somewhat similar to that observed for  $\dot{S}^-$  would be seen (consistent with arrangement 4b). The fact that at no time during the reduction was a pure 1:2:1 triplet observed, is indicative of an electronic arrangement as in 4a, although it is recognized that a mixture of three and four electron (4a) products would tend to distort and obscure a binomial triplet, as would a mixture of 4a and 4b.

Extensive electrolysis at still higher potentials gave rise to a reactive species with a well defined ESR spectrum, a new one line pattern of lower g value than for  $\dot{S}$ , (Figure 11). This species was assigned to the monoradical pentaanion  $^{\dot{-}5}S$ , with the fifth electron having entered the available outer ring (Table 1, #5a). The propensity of the five and possibly the four electron reduction products of 8 to assume an electronic distribution wherein the central ring remains partially vacant (#5a and #4a in Table 1, respectively) can once again be rationalized in terms of inductive effects. As discussed previously, the peripheral quinone rings in neutral 8 render the central quinone moiety electron deficient via an inductive polarization mechanism. The triradical trianion  $^{\dot{-}3}S$ , in which the outer rings each harbor an unpaired electron now create reverse polarization effects, rendering the central quinone relatively electron rich. An incoming electron would thus be preferentially accommodated in one of the outer rings. A similar argument may be put forth in the case of the monoradical pentaanion, wherein the electronic repulsion would tend to be minimized should the final electron be taken into the available outer ring, rather than the partially vacant central position.

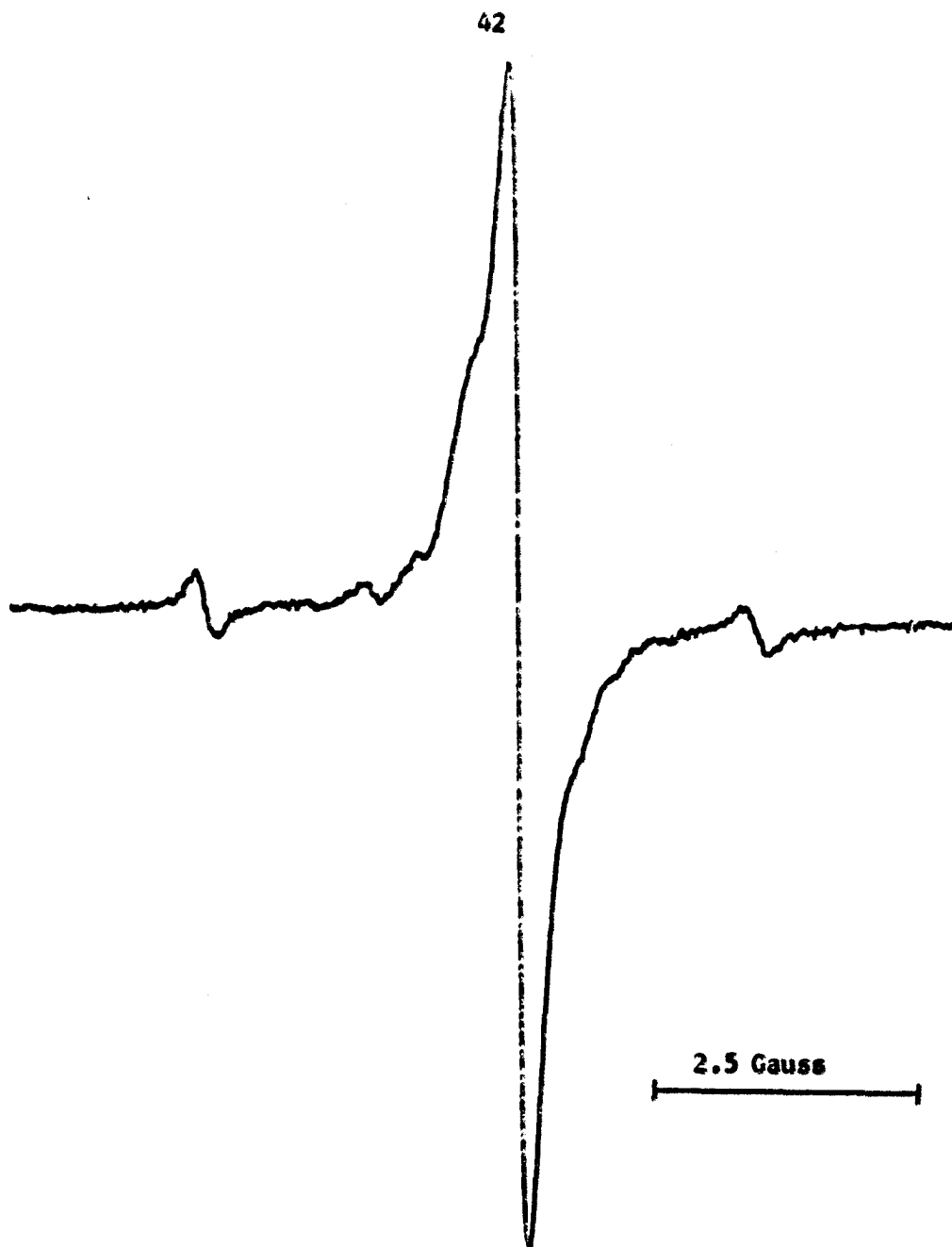


Figure 11. First derivative ESR spectrum of 5,7,12,14-tetrahydro-5,14:7,12-di[1',2']-benzenopentacene-1,4,6,8,11,13-hexone monoradical pentaanion,  $8^{\circ}$ .

In summary, the differing acceptor strengths of the outer and central quinone rings manifest themselves strongly in the spin distribution in the radical anions of 8, and while some of the intermediate reduction states could not be assigned unequivocally, the electronic distributions in the first and final paramagnetic reduction states have been firmly established on the basis of their ESR spectra.

Table 1. Electronic distribution in 8

# of added Electrons	Ring 1	Ring 2	Ring 3	Predicted ESR Spectra
1		↑		Singlet
2	↑ <sup>a</sup>	↑ <sup>a</sup>		Singlet superimposed on Triplet
3	↑	↑	↑	Singlet superimposed on stronger Triplet
4(a)	↑↓	↑	↑	Singlet superimposed on Triplet
4(b) <sup>b</sup>	↑	↑↓	↑	Binomial Triplet
5(a)	↑↓	↑	↑↓	New Singlet
5(b) <sup>b</sup>	↑↓	↑↓	↑	Binomial Triplet

<sup>a</sup> Singlet-Triplet energy difference is zero, relative orientations of spin vectors have no significance.

<sup>b</sup> Not seen spectroscopically.

### C. Conclusion

The radical anions of triptycene bis- and tris(quinones), and those of 5,7,12,14-tetrahydro-5,14:7,12-di[1',2']-benzenopentacene-1,4,6,8,11,13-hexone have been investigated by ESR spectroscopy, and

found to exhibit a number of extremely interesting magnetic and chemical properties. At 298 K, the four hydrogen atoms in triptycene bis(quinone) mono- and trianion radicals are time averaged by electron migration for which an energy barrier was calculated from selective line broadening observed at subambient temperatures. Surprisingly, an intermediate two electron reduction product with a well resolved ESR spectrum was also observed, but is only consistent with the form of the spectrum if  $|J| \ll |A|$ , and  $D \ll 100$  MHz. Alternate explanations for this unexpected species were sought, but have been found to be less satisfactory than the assignment to the diradical dianion structure.

Reduction of triptycene tris(quinone) also gave rise to a number of discrete paramagnetic species. The initially observed spectrum was a binomial septet, again reflecting a species where all the quinone hydrogens are time averaged by intramolecular electron jump. This process remained rapid at temperatures as low as 183 K. Further reduction led to a species assigned to the triradical trianion in which the conditions  $|J| \ll |A|$  and  $D \ll 100$  MHz are fulfilled. At high reduction potentials, a fleeting species consistent with the diradical tetraanion was sometimes observed.

The initial reduction product of the triquinone **8** is best described as a localized structure where the unpaired electron resides primarily in the central ring. This observation is consistent with the enhanced electron deficiency of the middle quinone. Upon further reduction, a mixture of products appeared which may have represented the two, three and four electron reduction products. Finally, a highly reduced species, the radical pentaanion is believed to have been present



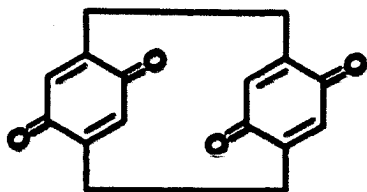
at high potentials. The electronic distribution and the order of electron filling are entirely consistent with minimized electron repulsion in these paramagnetic states.

## III. RADICAL IONS OF [2.2]METACYCLOPHANEQUINONE

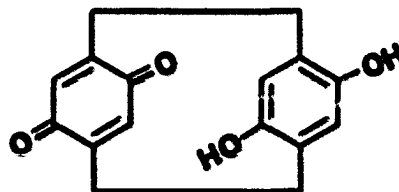
## A. Introduction

Numerous reports have recently appeared on the synthesis and donor-acceptor properties of [2.2]paracyclophanequinones [48-50], [3.3]-[51] and [2.2]-metacyclophanequinones [52]. While it would appear that the intramolecular electronic interaction between the quinone groups in the corresponding radical anions is ideally suited for study by ESR spectroscopy, such efforts have not been forthcoming.

The only existing data in print pertain to the reduction of [2.2]-paracyclophanequinone (9) and the quinhydrone (10) [25].



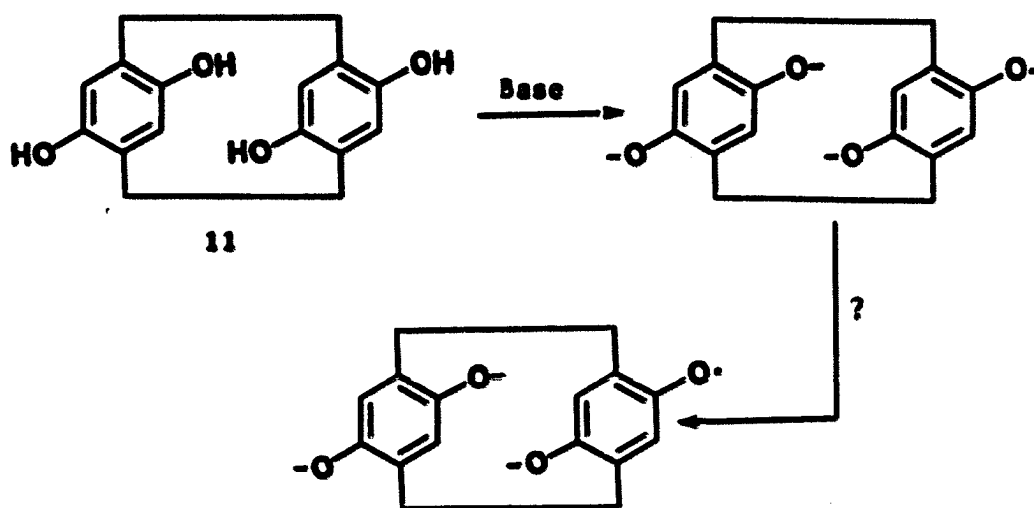
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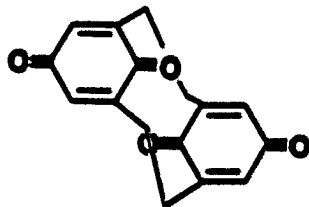
The radical monoanion of 9 shows fast electron exchange between the two acceptor sites. The two electron reduction product is apparently

diamagnetic, with no hint of a thermally excited triplet state, and continued electrolytic reduction is followed by protonation, resulting in the quinhydrone radical anion  $10^{\cdot-}$ . (As demonstrated by voltametry|ESR.) Interestingly, the ESR spectra of  $9^{\cdot-}$  and  $10^{\cdot-}$  are claimed to be identical [53], an observation which necessitates much greater mobility of the hydroxyl hydrogen atoms in  $10^{\cdot-}$ , as compared to the neutral quinhydrone. Thus, while the trianion radical  $9^{\cdot-}$  does not appear to be a major species under conditions of electrolytic reduction, alternate routes via the treatment of 9, 10 or bishydroquinone 11 with chemical reductants such as potassium tert-butoxide/DMSO do not appear to have been investigated.



A report on the synthesis and the ready accessibility of tricyclo[9.3.1.1<sup>4,8</sup>]hexadeca-4,7,11,14-tetraene-6,13,15,16-tetrone

from hereon referred to as [2.2]metacyclophanequinone, prompted an ESR investigation in our laboratories, and although the ESR spectra for



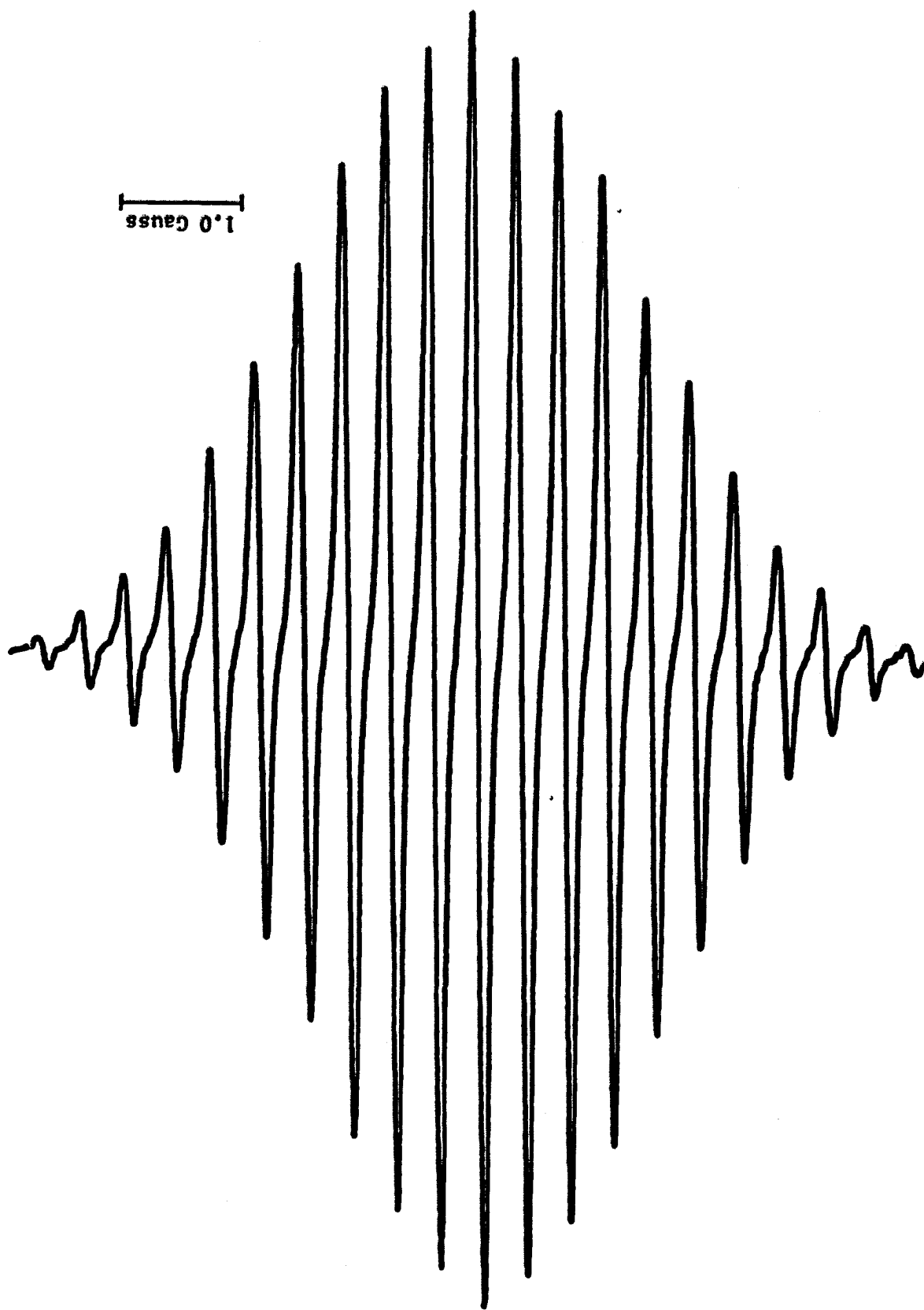
12

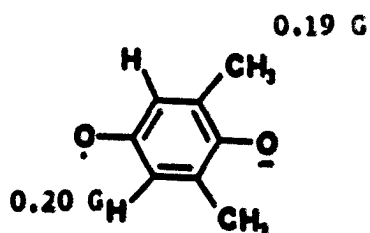
such species as  $12^{\cdot-}$  are predicted to exhibit complex hyperfine structure, it was recognized that the [2.2]metacyclophane skeleton provides the requisite high symmetry and conformational stability. In addition, such a study was expected to provide an important source for comparison to the properties of [2.2]paracyclophanesemiquinones.

#### B. Results and Discussion

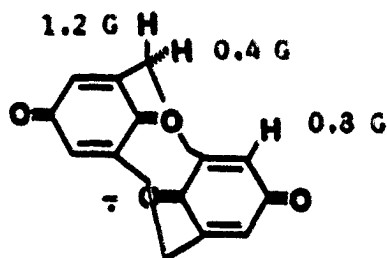
Electrolytic reduction or treatment of 12 with trace quantities of potassium tert-butoxide gave rise to a well resolved ESR signal, a pentet of pentet of pentets ( $a_1^H = 0.4$  G [4 H's],  $a_2^H = 0.8$  G [4 H's],  $a_3^H = 1.2$  G [4 H's],  $g=2.005288$  in DMSO, Figure 12). Assignment of the hyperfine splitting constants in this radical monoanion was made on a qualitative basis by comparison to the semiquinone 13, [54] with the smaller and intermediate

**Figure 12. First derivative ESR spectrum of [2.2]metacyclophanequinone radical anion,  $12^{\cdot-}$ .**





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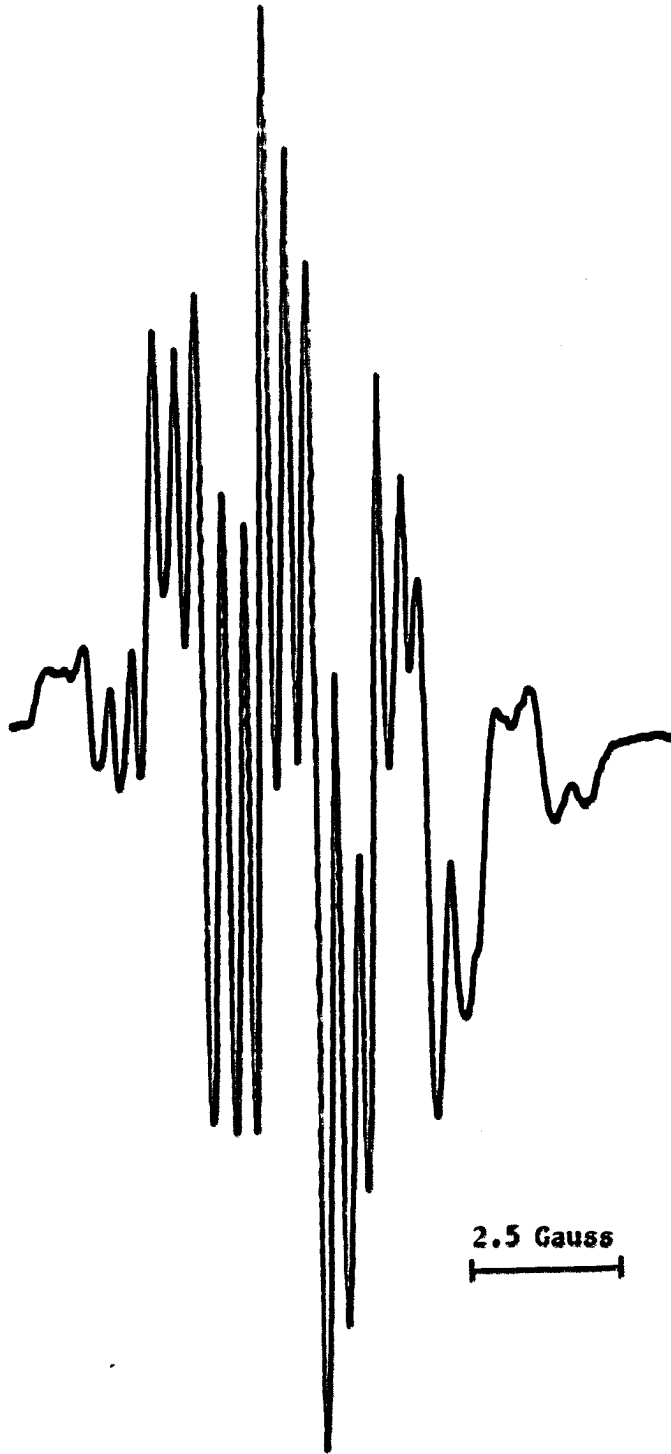
12<sup>-</sup>

coupling constants ( $a_1^H$  and  $a_2^H$ ) being attributed to the hydrogen atoms which reside in the proximity of the nodal plane of the pi system. The larger splitting was assigned to  $a_3^H$ , for which a hyperconjugative mechanism of spin delocalization is possible. The radical monoanion was stable to molecular oxygen, and the spectrum remained essentially unchanged upon addition of potassium iodide, [2.2.2]-cryptand, or upon a one-hundred-fold dilution. The quinone rings in 12<sup>-</sup> are time averaged by intramolecular electron transfer, a process which remains rapid on the ESR time scale since no selective line broadening was observed at temperatures as low as 183 K.

Extensive electrolysis at higher potentials resulted in a complex spectrum due to the appearance of a second species (Figure 13), and upon prolonged reduction, a more favorable ratio of the new radical revealed a poorly resolved spectrum of which a major component could be identified as a pentet of triplets of broad lines (on one occasion, oxidation of the corresponding bishydroquinone resulted exclusively in this species,  $a_1^H = 2.37$  G [4 H's],  $a_2^H = 0.62$  G, [3 H's], DMSO Figure 14). Cessation

**Figure 13.** First derivative ESR spectrum observed upon extensive electrolysis of [2.2]metacyclophanequinone **12**.





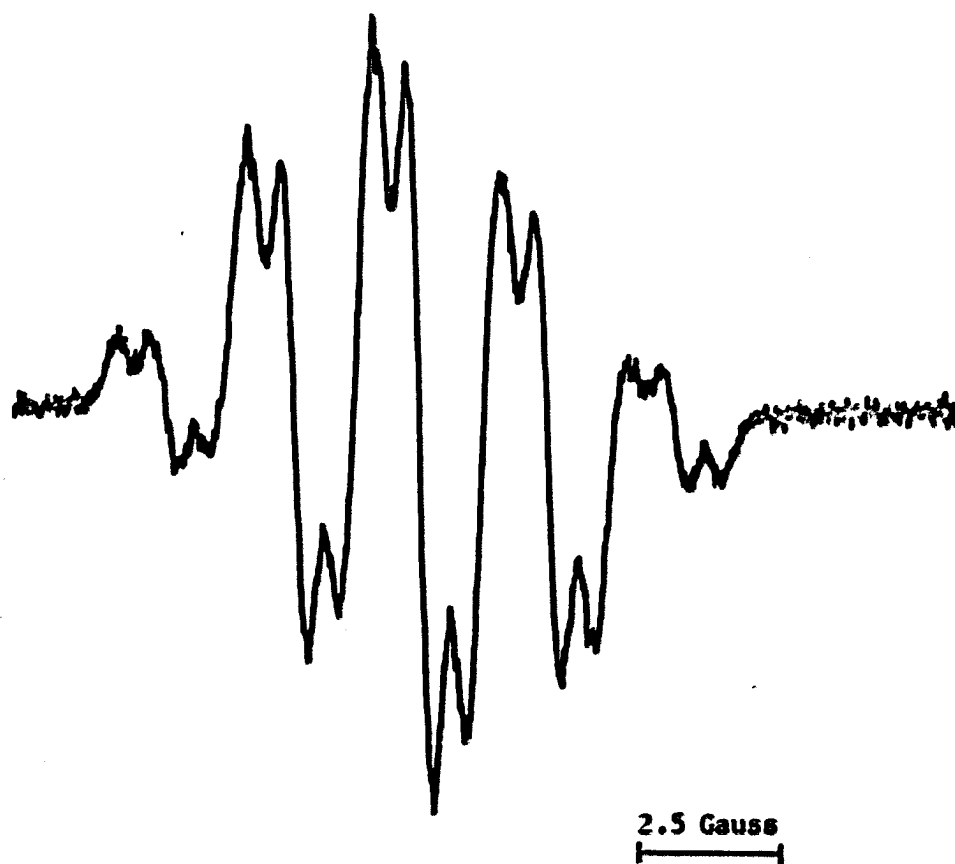
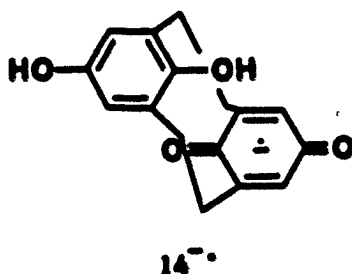


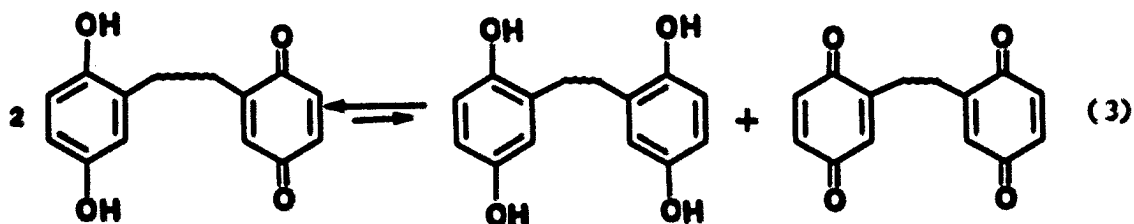
Figure 14. First derivative ESR spectrum assigned to [2.2]metacyclophanequinhydrone radical anion, 14 °

of electrolysis once again led to a complex mixture, followed by a return to the initially observed radical monoanion  $12^{\cdot-}$ . The hyperfine coupling constants for the new species are consistent with the quinhydrone radical anion  $14^{\cdot-}$ , presumably produced through the immediate protonation of the trianion radical, and although this observation would appear consistent with the properties of

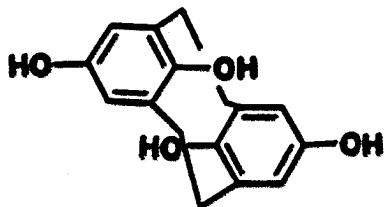


[2.2]paracyclophanequinone, the spectrum for quinhydrone  $14^{\cdot-}$  indicates a localized structure rather than one in which the high mobility of the hydroxyl hydrogen atoms and unpaired electron render both quinone rings equivalent (as is the case for  $10^{\cdot-}$ ). This important difference may be due to the higher local symmetry and degree of electronic overlap in 10 as compared to 14.

Electrolytic or chemical reduction of pure quinhydrone 14 gave rise to spectra identical to those attributed to the bis(semiquinone)  $12^{\cdot-}$ . This observation may immediately be construed as evidence that the quinhydrone radical anion  $14^{\cdot-}$  and bis(semiquinone)  $12^{\cdot-}$  give identical ESR spectra, however such a deduction may, in the authors view, be superficial especially in view of the well recognized disproportionation equilibrium involving quinhydrones, (Equation 3) [26].



Thus, reduction of an equilibrium mixture strongly in favor of the quinhydrone would nevertheless result in preferential reduction of the bis(quinone), since the  $E_{1/2}$  of the latter is often considerably lower than the corresponding quinhydrone, and qualitatively speaking, the appearance of the ESR signal in the reduction of either compound is quite similar. It is therefore apparent that the reduction of 14 failed to produce conclusive data on the structure of the expected quinhydrone radical anion  $14^{\cdot-}$ , and that chemical or electrolytic methods of reduction on bisquinone 12 or quinhydrone 14 did not produce any clearly resolved signal that could be attributed to the trianion radical  $12^{\cdot-}$ . The investigation was thus continued with the bishydroquinone 15, in the hope that deprotonation followed by partial oxidation would lead to the trianion radical.

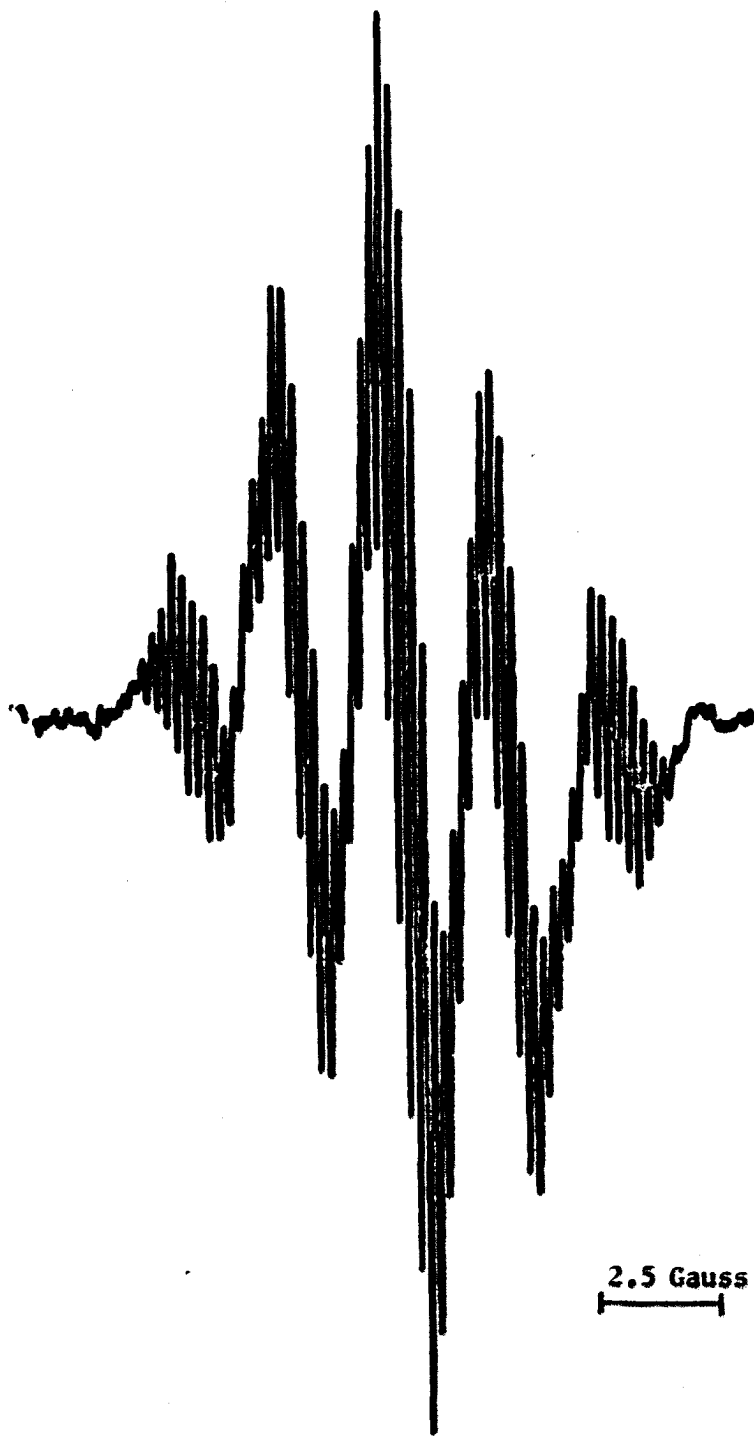


15

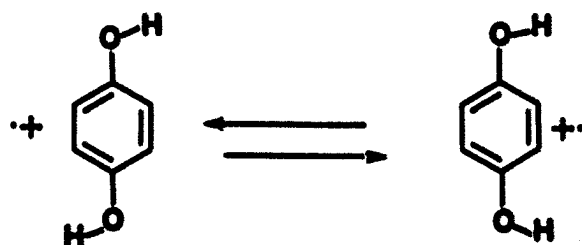
This expectation was realized via the treatment of 15 with excess (~ 0.3 M) potassium tert-butoxide in DMSO/DMF solutions, whereupon an excellent ESR spectrum of sharp lines and extensive hyperfine structure appeared ( $a_1^H = 1.82$  G [4 H's],  $a_2^H = 0.36$  G [4 H's],  $a_3^H = 0.18$  G [4 H's] in DMSO, Figure 15). This new species did not show selective line broadening even at 183 K, and was stable for several minutes at 298 K under a nitrogen atmosphere. However, minute traces of air introduced into the system immediately converted the spectrum to the complex mixture similar to that previously observed in the electrolysis of 12, while additional oxygen resulted in a complete conversion to the spectrum due to the radical monoanion  $12^{\cdot-}$ . The spectral and chemical properties, coupled to the unique precursor requirements and rather basic medium in which this species was generated, collectively indicate a highly reduced species such as the trianion radical  $12^{\cdot-}$ . Thus, a successful search for the various paramagnetic reduction states of the bis(quinone) 12 required the use of the corresponding quinhydrone 14 and bishydroquinone 15, with the trianion radical accessible only through the oxidation of 15 in basic solution.

The electron deficient nature of polyquinones generally restricts the nature of accessible paramagnetic states to electron addition products. In the case of electron rich hydroquinones however, electron ejection to give radical cations may occur in powerfully oxidizing media such as concentrated  $H_2SO_4|K_2S_2O_8$  or  $CH_3NO_2|AlCl_3$ . Thus, ESR studies of radical cations derived from hydroquinone and derivatives have been numerous and revealing in terms of spin density distribution, and dynamic

Figure 15. First derivative ESR spectrum of [2.2]metacyclophanequinone radical trianion,  $12^{\ominus}$ .



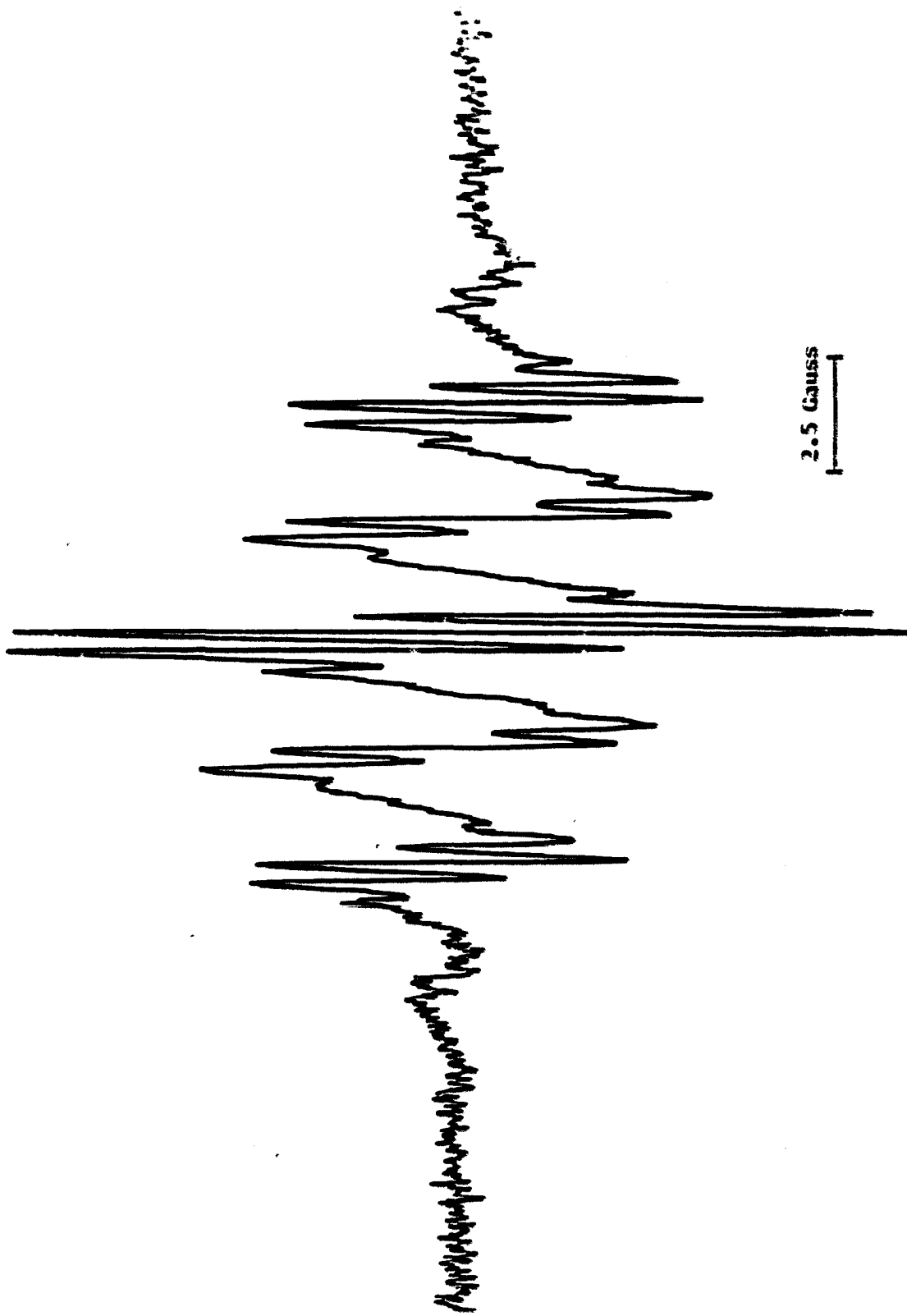
phenomena such as syn-anti isomerism [55,56]:



The ready availability of the bishydroquinone 15 and the expectation that spin distribution in the radical cation  $15^{\cdot+}$  would mimic that in  $15^{\cdot-}$  prompted efforts to oxidize 15.  $\text{AlCl}_3/\text{CH}_3\text{NO}_2$  suspensions consistently failed to produce an ESR signal. However, dissolution of 15 in concentrated  $\text{H}_2\text{SO}_4$  gave rise to a spectrum of fair quality, a nonet of pentets ( $a_1^{\text{H}} = 2.50 \text{ G}$  [8 H's],  $a_2^{\text{H}} = 0.38 \text{ G}$  [4 H's],  $g = 2.002977$  in  $\text{H}_2\text{SO}_4$ , Figure 16). The hyperfine coupling constants in this spectrum (which is presumably due to the radical cation  $15^{\cdot+}$ ) were partially assigned on the basis of isotopic substitution of the hydroxyl hydrogen atoms, since dissolution of 15 in  $\text{D}_2\text{SO}_4$  resulted in a binomial nonet of broad lines ( $a^{\text{H}} = 2.50 \text{ G}$  [8 H's], Figure 17). This result clearly established the pentet splitting in the protium spectrum as being due to the hydroxyl hydrogens, while the nonet splitting is most probably a result of the fortuitous magnetic equivalence of the ring and axial bridging hydrogens. The most interesting feature of this species however, is the selective line broadening displayed by the 2<sup>nd</sup>, 4<sup>th</sup>, 6<sup>th</sup> and 8<sup>th</sup> peaks in the original spectrum of Figure 16. The linewidth altering effects for this species were quite real, although not as dramatic as those observed in previous cases. This was a direct consequence of the rather limited



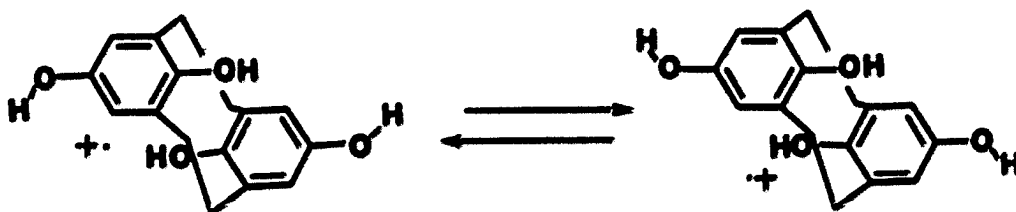
Figure 16. First derivative ESR spectrum of [2.2]metacyclo-  
phanebishydroquinone radical cation,  $15^\circ$  in  
 $\text{H}_2\text{SO}_4$ .



2.5 Gauss

temperature range within which  $15^+$  could be observed, since viscosity effects dominated at low temperatures, and the radical decayed rapidly above 348 K.

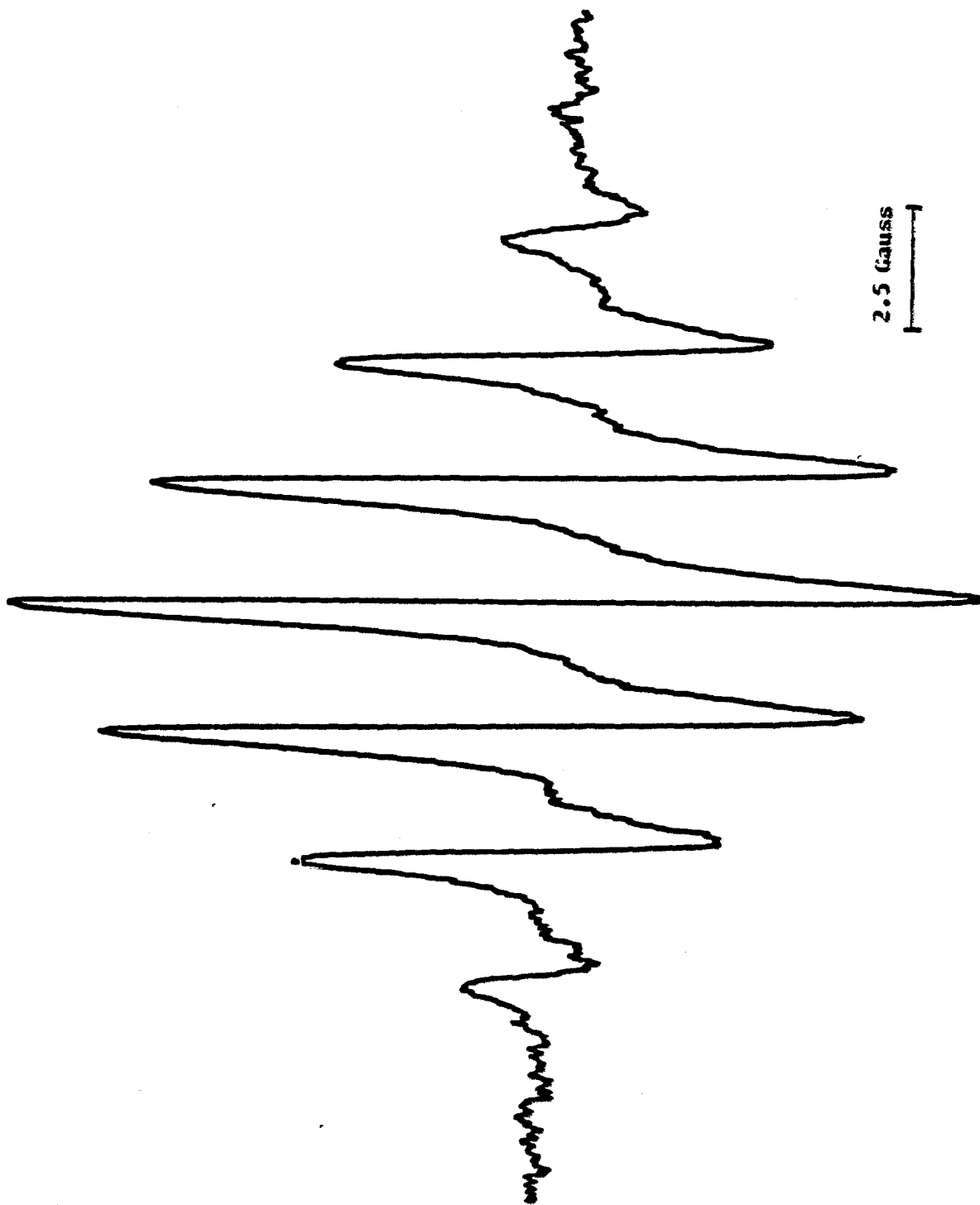
The origin of this selective line broadening is not entirely unambiguous. The most obvious possibility, that of intermediate rate of hole transfer between the hydroquinone rings does not seem reasonable in view of the close proximity of the donor moieties. More importantly, the deuterium substituted  $15^+$  exhibited a binomial nonet, with no evidence for selective line broadening, an observation which does not lend credence to the proposed hypothesis. An alternate possibility invokes an intermediate rate of syn-anti isomerism of the hydroxyl groups in  $15^+$ . Such dynamic behavior would cause a fluctuation in the magnetic environment, leading to an alternation of the hyperfine coupling constants of the ring and bridging hydrogen atoms.



Upon deuteration, equivalent motion of the OD group is expected to give rise to a considerably attenuated fluctuation in the local magnetic environment of the ring and bridging nuclei, which could conceivably eradicate any observable line width alternation. This expectation is based on the much smaller magnetic moment of deuterium as compared to that of hydrogen ( $\mu_D/\mu_H = 1/7$ ).

This investigation has thus revealed important differences in the

Figure 17. First derivative ESR spectrum of [2.2]metacyclo-  
phanebis hydroquinone radical cation,  $15^\circ$  in  
 $D_2SO_4$ .



properties of the radical anions of [2.2]metacyclophanequinone as compared to those derived from the [2.2]paracyclophanequinone and triptycene quinone series. The contrasting behavior of triptycene bis(quinone) and [2.2] metacyclophanequinone upon reduction may stem from differing strengths of the intramolecular electronic interaction, a property closely dependent upon the relative geometric disposition of the acceptor groups. An observation consistent with the stronger interaction in 12 is that intramolecular electron transfer occurs more readily in  $12^{\cdot-}$  and  $12^{\cdot\cdot-}$  than it does in  $3^{\cdot-}$  and  $3^{\cdot\cdot-}$ . Another such observation is the second and third half wave potentials of 12, which are considerably higher and further apart than for 3, resulting in protonation of the higher reduction states of 12 during electrolysis. Further indication of the aforementioned effects may be inferred from the absence of an observable intermediate reduction product such as  $^{\cdot-}12^{\cdot-}$ , which may indicate a species where  $|J| \gg |A|$  and  $D \gg 100$  MHz, consistent with the strong interaction expected for such a species. In the event that the two electron reduction product has a ground state or thermally accessible triplet state, the solution ESR spectrum is predicted to be undetectably broad.

The most important difference between the radical ions of [2.2]metacyclophanequinone and [2.2]paracyclophanequinone appears to be the contrasting form of the ESR spectra for the quinhydrone radical anions  $10^{\cdot-}$  and  $14^{\cdot-}$ . This difference has been discussed in terms of the higher symmetry of  $10^{\cdot-}$ .

### C. Conclusion

The ESR spectrum for the radical monoanion of [2.2]metacyclophane-quinone reveals a symmetric ion due to fast electron exchange between the quinone rings. The hyperfine coupling constants in this species have been assigned in view of the geometries of the interacting nuclei with respect to the plane of the pi system, and on the basis of splitting contents in appropriately substituted monomeric semiquinones. Extensive electrolysis of the bis(quinone) resulted in complex mixtures of the radical monoanion and the diprotonated form of the trianion radical (quinhydrone radical anion). Reduction of the quinhydrone gave a spectrum identical to that observed in the reduction of the bis(quinone). The possibility that both, the quinhydrone and the bis(quinone) lead to identical spectra is viewed as unlikely in light of the rapid scrambling of the hydroxyl hydrogens that would be necessary to establish the required symmetry in the quinhydrone radical anion. The observation of bis(quinone) radical anion in the reduction of the quinhydrone has been attributed to a disproportionation equilibrium. Deconvolution of complex mixtures which arose upon extensive electrolysis of the bis(quinone) reveals a component consisting of a pentet of triplets of broad lines. This spectrum is assigned to the localized quinhydrone radical anion.

The trianion radical of the bis(quinone) was found to be accessible only via the oxidation of the bishydroquinone in basic solution. The spectrum showed fast intramolecular electron exchange, and the properties of this species are consistent with a highly reduced structure.

Important differences in the properties of the radical anions derived from triptycene bis(quinone) and the [2.2]metacyclophanesemiquinones

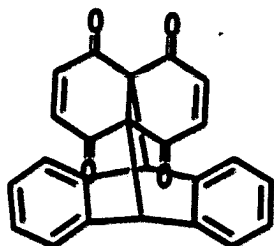
have been rationalized in terms of the greater degree of electronic overlap in the cyclophane.



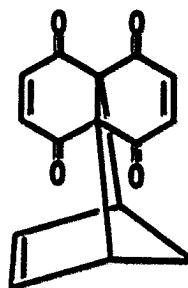
IV. RADICAL ANIONS DERIVED FROM NAPHTHALENETETRONE DERIVATIVES  
AND BRIDGED P-BENZOQUINONES

A. Introduction

ESR spectra of the radical anions derived from the triptycenequinone and metacyclophanequinone series have provided information on the characteristic spin distribution properties in bis- and tris(semiquinones) wherein a specific geometric relationship between the quinone groups is enforced by the rigidity of the bridging carbon skeleton. Questions remain, however, on the properties of radical anions derived from molecules having rigid or semi rigid skeletons wherein the electron acceptors are other than quinone rings. To this end, 9,10-dihydro-9,10[1',2']-benzeno-4a,9a,-[2]butenoanthracene-1,4,17,20-tetrone, compound 16, and 1,4-dihydro-4a,8a-[2]buteno-1,4-methanonaphthalene-5,8,9,12-tetrone, compound 17, were synthesized [57] and their ESR spectra examined upon reduction.



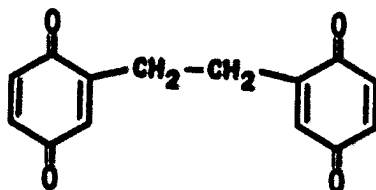
16



17

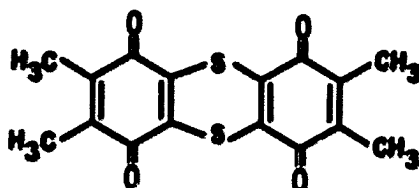
Other important considerations, such as the consequence of increased flexibility of the bridge interconnecting the acceptor groups, have been addressed by the study of the radical anions of 1',2'-bis(2,5-benzo-

quinonyl)ethane [58]  $18^{-\bullet}$ , in which a mutually coplanar arrangement of the quinone rings need not be the preferred conformation.



18

Finally, the effects on the spin density distribution upon substitution by sulphur in place of carbon in the interconnecting bridge has been investigated via the radical anion of 2,3,7,8-tetramethyl-1,4,6,9-thianthranetetrone, 19 [59].



19

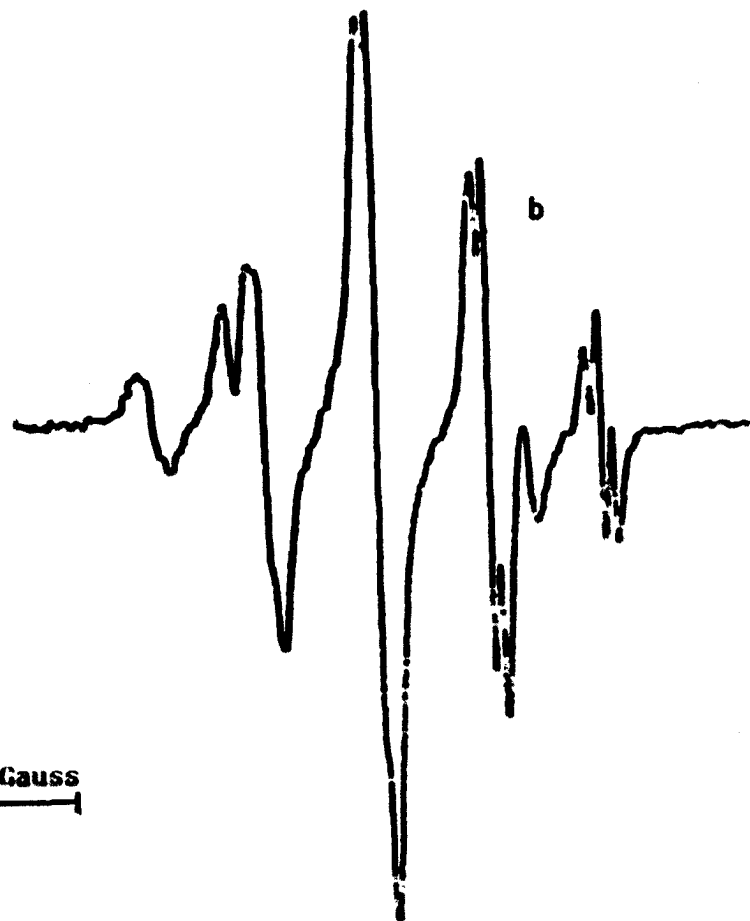
### B. Results and Discussion

Electrolytic reduction or treatment of 16 with trace amounts (~1.0 mg) of potassium tert-butoxide resulted in the spectrum of Figure 18a ( $a_1^H = 2.5$  G [4 H's],  $a_2^H = 0.2$  G [2 H's],  $g = 2.005077$  in DMSO). Assignment of hyperfine coupling constants in this

Figure 1A. First derivative ESR spectrum of 1,4-dihydro-4a,8a-[2]buteno-1,4-methanonaphthalene-5,8,9,12-tetrone radical anion,  $16^-$ . (a) At 298 K (b) At 183 K.



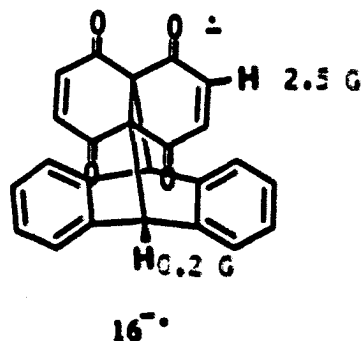
a



b

2.5 Gauss

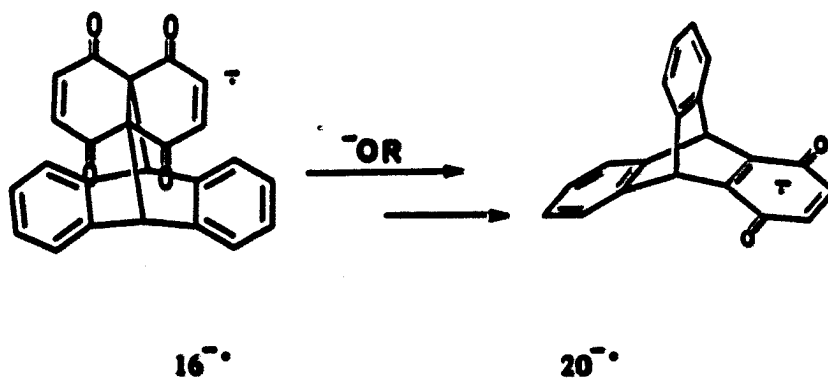
species was straightforward in view of the numbers in each set of interacting nuclei.



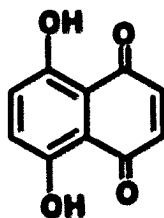
The radical monoanion 16<sup>-•</sup> showed fast electron exchange between the two enedione moieties at temperatures as low as 183 K. At these temperatures, the low field lines of the spectrum appeared significantly broadened (Figure 18b), possibly due to a slow exchange mode involving the ion paired (I.P.) and free ion (F.I.) forms of 16<sup>-•</sup>.



This possibility could not be firmly established since addition of complexing agents such as [2.2.2]-cryptand or 18-crown-6 ether resulted in the cleavage of 16<sup>-•</sup> to give the triptycene mono(quinone) radical anion 20<sup>-•</sup> [14]. This side reaction has been attributed to the increased reactivity of the free alkoxide ion, Me<sub>3</sub>CO<sup>⊖</sup>. The identity of the new species was verified by addition of authentic 20 into the ESR cell, whereupon only an enhancement of signal intensity was observed.

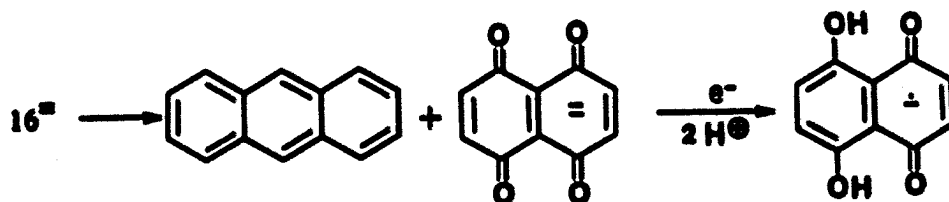


Prolonged electrolysis or reduction of **16** at higher potentials resulted in complex mixtures of which a major component was identified as the naphthazarin radical anion **21**<sup>•-</sup> [60]. The high potentials at which



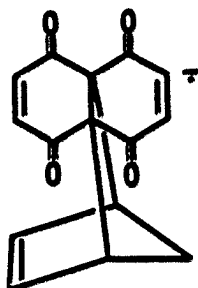
21

this observation was made suggests that the cycloreversion process leading to **21** may occur via the dianion. Thus, although



some of the properties of the radical monoanion  $16^{\cdot-}$  could be readily elucidated from its ESR spectrum, the scope of this study in terms of detection of higher paramagnetic states was severely limited in view of the poor stability of  $16^{\cdot-}$  in highly basic media.

Chemical or electrolytic reduction of adduct 17 resulted in a mixture of species, one of which was a broad pentet, possibly due to the radical monoanion  $17^{\cdot-}$ .



The pentet splitting would be consistent with fast electron exchange between the slightly differing enedione groups, with possible contribution to the overall linewidth from additional hyperfine due to the bridgehead hydrogens. However, as with  $16^{\cdot-}$ , the propensity of the radical ion to undergo cycloreversion and other irreversible

chemical changes precluded a more detailed investigation.

Chemical or electrolytic reduction of bis(quinone) 18 initially resulted in a well resolved ESR spectrum ( $a_1^H = 2.39$  G [2H's],  $a_2^H = 2.59$  G [1 H],  $a_3^H = 1.58$  G [1 H],  $a_4^H = 0.1$  G [1 H] in DMSO, Figure 19). The splitting pattern is consistent with the radical anion  $18^{\cdot-}$  in which the unpaired electron remains localized in one quinone group, possibly due to a preferred conformation where the quinone rings extend a considerable distance whereupon non-bonded interactions are minimized, or one in which a high dihedral angle precludes favorable overlap between the acceptor groups. The spectrum for  $18^{\cdot-}$  remained unchanged upon exposure to molecular oxygen but suffered irreversible change upon heating due to chemical transformation in the basic medium. Thus, spin distribution in the radical monoanion remains uncertain for temperatures in excess of 310 K.

On occasion, extensive electrolysis of solutions containing  $18^{\cdot-}$  resulted in the appearance of a second paramagnetic species of lower g value ( $a_1^H = 2.7$  G [4H's],  $a_2^H = 0.65$  G [4H's],  $a_3^H = 0.20$  G [2H's] in DMSO, Figure 20). While the hyperfine coupling constants could not be assigned unequivocally without isotopic substitution, the overall splitting pattern in this species is consistent with the trianion radical  $18^{3-}$ , this time with the unpaired electron showing fast exchange between the two sites. An interesting observation, thus, is the dramatic difference in spin distribution between the one and three electron reduction products, an occurrence which appears to have precedent for conjugated bis(quinones) of type 1, previously described. The rapid electron transfer in  $18^{3-}$  as compared to  $18^{\cdot-}$  may be due





Figure 19. First derivative ESR spectrum of  $1',2'$ -bis(2,5-benzoquinonyl)ethane radical anion,  $18^\circ$ .

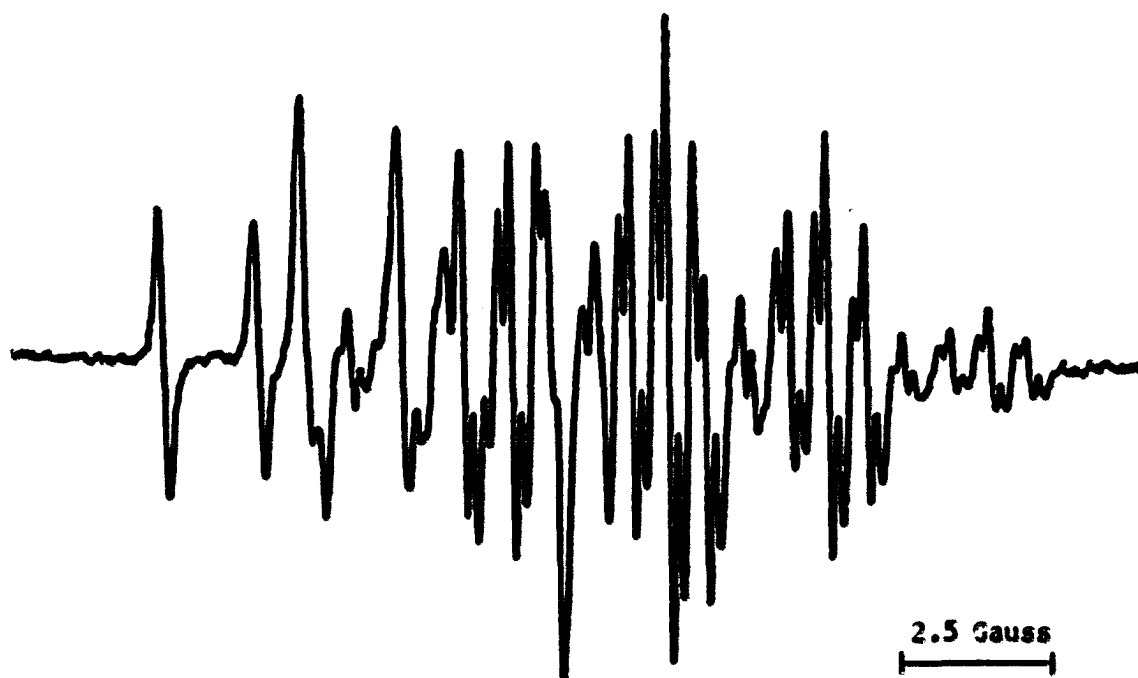


Figure 20. First derivative ESR spectrum of 1',2'-bis(2,5-benzoquinonyl)ethane radical trianion  $18^{\pm 3}$  (major), and radical anion  $18^-$  (minor).

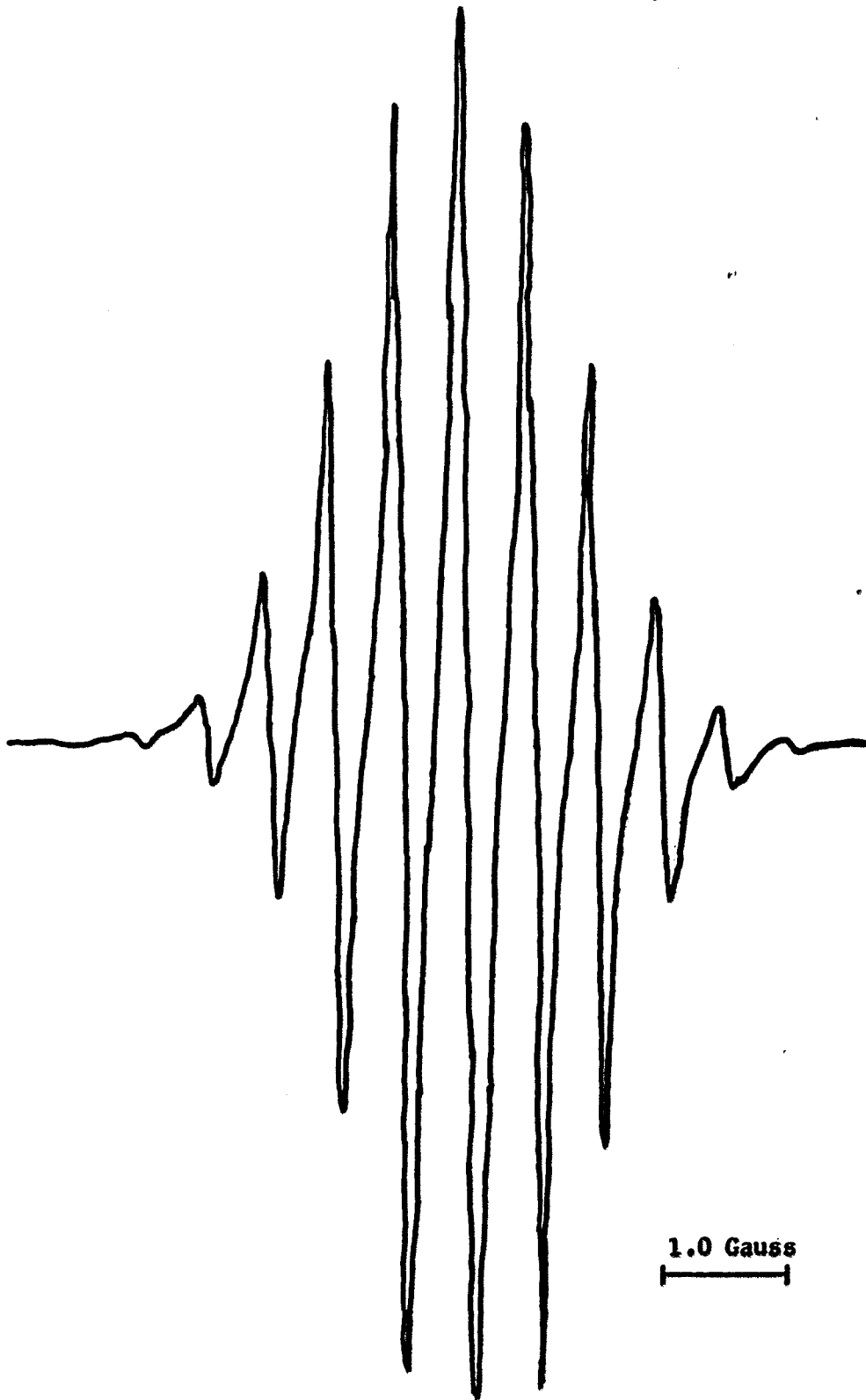
to a more favorable  $\Delta H^\ddagger$  for electron migration in the trianion radical, although other possibilities, such as differing conformational preferences in the two species cannot be ruled out.

Electrolytic or chemical reduction of the thianthrene derivative 19 initially resulted in the binomial tridecate of Figure 21 ( $a^H = 0.52$  G [12H's] in DMSO). This species, assigned to the radical monanion was stable to molecular oxygen, and maintained equal spin distribution in both quinone rings at temperatures as low as 183 K.

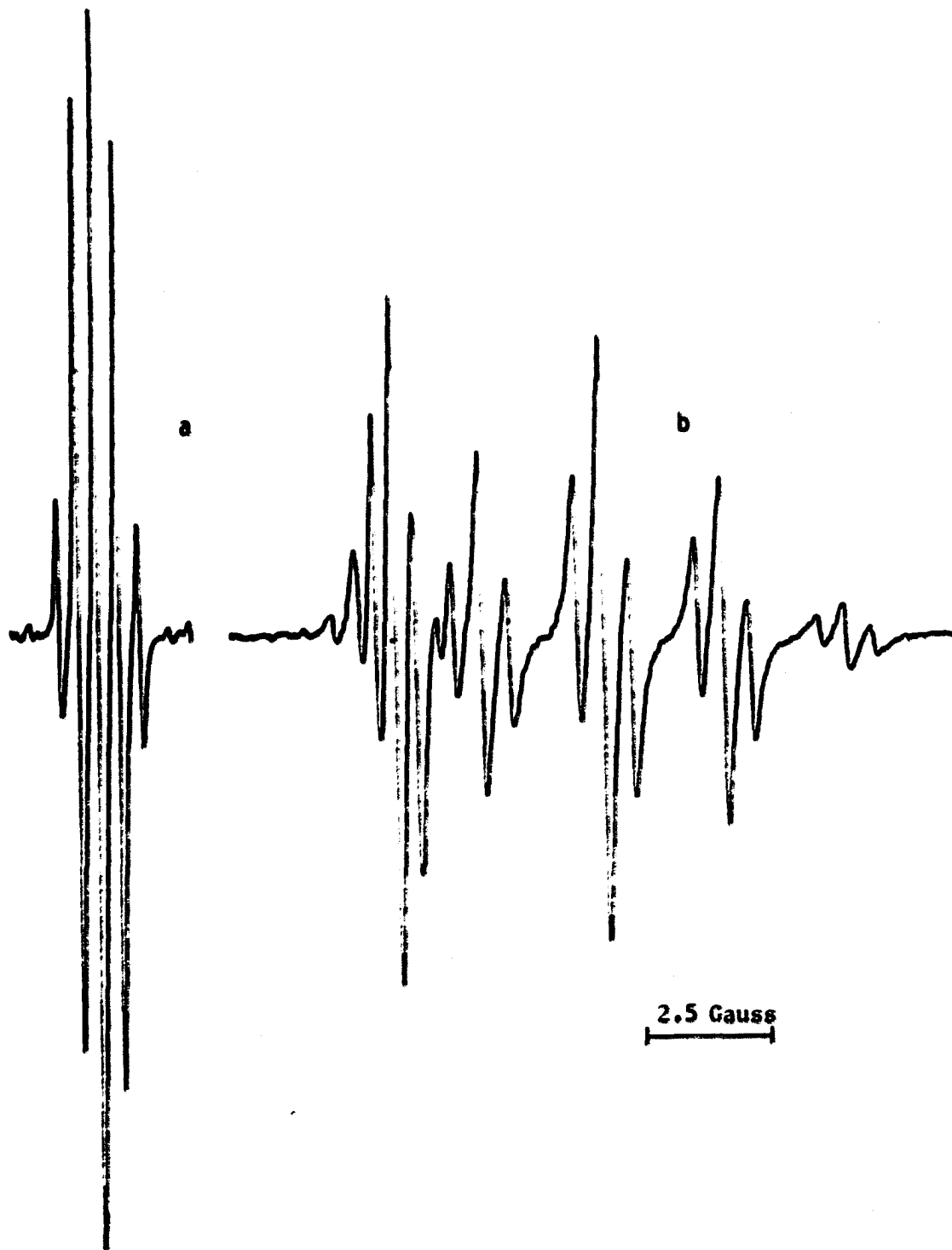
Continued electrolysis at higher reduction potentials or treatment of solutions containing  $19^{\cdot-}$  with (0.1 M) potassium tert-butoxide gave rise to a multitude of species, one of which could be clearly identified as a binomial septet ( $a^H = 2.0$  G [6H's] in DMSO). The identity of this species is unknown, since the form of the spectrum does not appear consistent with a higher reduction product of 19. The possibility that this species arose from cleavage reactions of  $19^{\cdot-}$  has not been ruled out.

Finally, in an attempt to further extend upon the array of highly reduced bis(semiquinones), 1,4,5,8-naphthalenetetrone, compound 22 was prepared and electrolysed. The initially observed spectrum was the well known, formally conjugated radical anion  $22^{\cdot-}$  [60] ( $a^H = 0.44$  G [4H's] in DMSO, Figure 22a). Continued electrolysis at higher potentials resulted in the appearance of a second species which was identified as the naphthazarin radical anion,  $21^{\cdot-}$  (Figure 22b). Thus, it is clear that the highly basic di- or trianions undergo rapid protonation in solution, and that such species are not generally accessible via electrolysis. (Excess quantities of base introduced into the cell prior

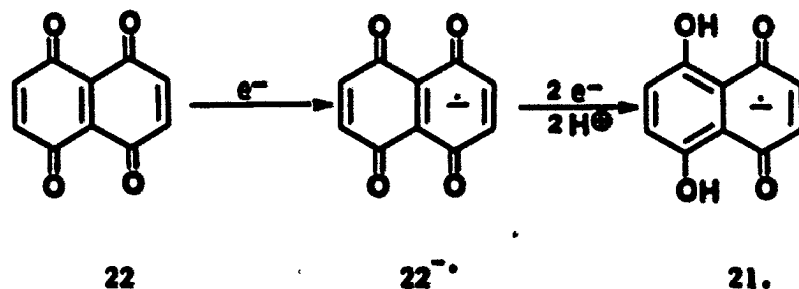
**Figure 21. First derivative ESR spectrum of 2,3,7,8-tetramethyl-1,4,6,9-thianthrene-tetrone radical anion, 19 °.**



**Figure 22.** First derivative ESR spectra observed upon reduction of 1,4,5,8-naphthalenetetrone, 22.  
(a) Electrolysis at low potentials.  
(b) Prolonged electrolysis at high potentials.



to electrolysis generally destroyed the bis(quinone) precursor.)



Treatment of **21** with trace amounts of potassium tert-butoxide gave the previously observed spectrum for **21 $^{\cdot-}$** , Figure 23a. Additional quantities of base often resulted in the appearance of a second species of higher g value which was not time averaged with the first (Figure 23b). At approximately (0.5 M) in potassium tert-butoxide, the spectrum showed a single species ( $a^H = 2.40$  G [4H's] in DMSO, Figure 23c). The ESR signal of Figure 23c disappeared immediately upon exposure to molecular oxygen, and is consistent with the trianion radical **22 $^{3\cdot-}$** .

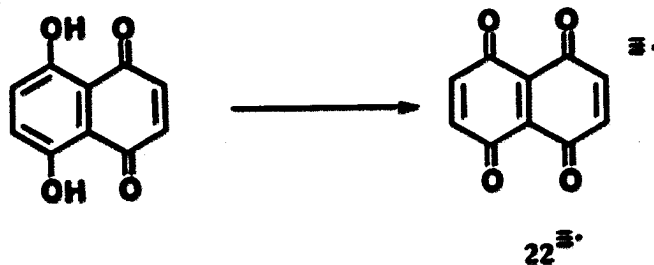
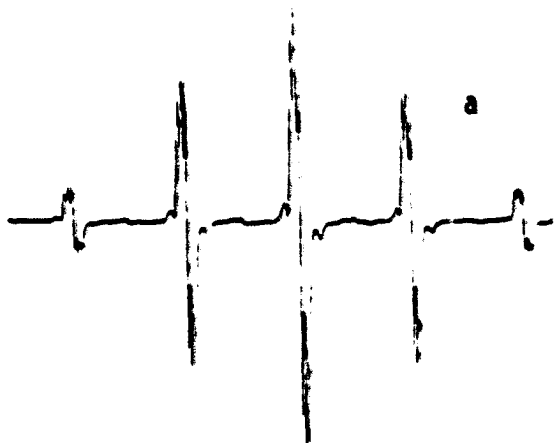


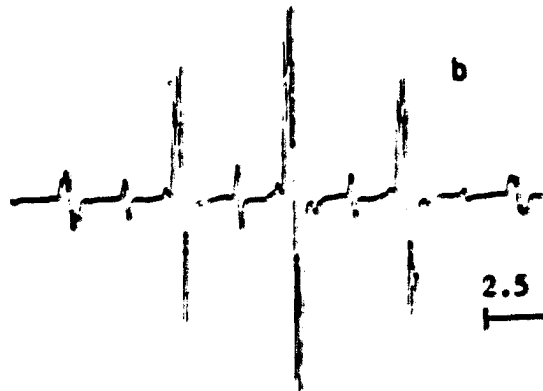


Figure 23. First derivative ESR spectra observed upon reduction of  $d_2$ -naphthazarin, 21.

- (a) Trace potassium tert-butoxide
- (b) (~ 0.2M) in potassium tert-butoxide
- (c) (~ 0.5M) in potassium tert-butoxide.

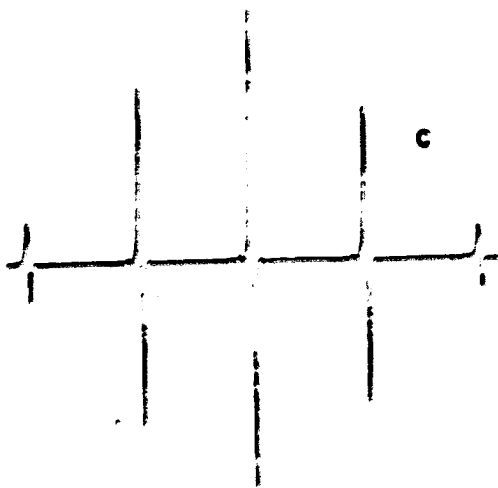


a



b

2.5 Gauss



c

### C. Conclusion

Radical anions of systems with differing acceptor groups and varying interconnecting bridges have been described. Reduction of bis(enediones) 16 and 17 resulted in the corresponding radical monoanions which showed fast electron exchange between the two acceptor sites. Higher paramagnetic reduction states could not be detected since further reduction led to products derived from cycloreversion and cleavage reactions of the radical ions.

The spin distribution in  $18^{\cdot-}$  may best be described by a localized semiquinone structure with limited mobility of the bridging atoms. The weak interaction between the quinone groups has been attributed to poor electronic overlap in the accessible conformations. On occasion, a highly reduced species believed to be the radical trianion  $18^{3\cdot-}$  was observed. The fast electron exchange in  $18^{3\cdot-}$  as compared to the radical monoanion may be due to a lower enthalpy of activation for electron migration in the trianion. No reference has been made to the detection of an intermediate paramagnetic reduction product such as  $^{\cdot-}18^{\cdot-}$ , since the ESR spectrum for such a species is predicted to be indistinguishable from that of  $18^{\cdot-}$ .

The ESR spectrum of  $19^{\cdot-}$  reveals a symmetric ion in the temperature range studied. It is possible that the presence of bridging sulphur atoms effectively conjugate the quinone moieties, and that the unpaired electron is delocalized in this species.

Electrolytic reduction of naphthalenetetrone 22 initially gave  $22^{\cdot-}$ . Higher potentials resulted in further reduction followed

by immediate protonation to yield  $21^{\cdot-}$ . The radical trianion  $22^{\cdot-}$  was found to be accessible via reduction of naphthazarin in basic solution.

## V. CONCLUSION TO PART I

The investigations described in Part I of this dissertation have attempted to address the question of spin distribution as a function of acceptor strength, temperature, and reduction state in polysemiquinones of varying geometric disposition.

The most significant contribution of this study has been the detection of diradical species which exhibit sharp ESR transitions in non-viscous media, an observation that has been attributed to the meager contribution of dipolar relaxation to the overall linewidth due to delocalization of the unpaired electrons.

Also of significance, is the energy barrier for electron migration in triptycene bis(quinone) mono- and trianions, which reveals the importance of solvation in the retardation of the rate of intramolecular electron transfer in highly reduced species. The observation of a general trend of this nature may be contingent upon the conservation of geometry or conformation in the two reduction states.

That small differences in acceptor strengths within molecules results in dramatic changes in the distribution of spin has been clearly shown in the radical ion  $S^{\cdot-}$ , in which the unpaired electron remains localized at the site of greater electron deficiency. The order of electron filling upon subsequent reduction followed a predicted pattern based on the electron affinity of each site.

The form of ESR spectrum invariably failed to distinguish between the initial reduction states such as  $X^{\cdot-}$  and  $^{\cdot-}X^{\cdot-}$  in species where the electronic interaction between the acceptor groups is poor. This

intuitive result is apparent in the reduction of 18, and must be kept in mind in the design of acceptor molecules for which a clear spectroscopic differentiation between radical and diradical is desired.

Finally, the dangers of erroneous assignment of radical anions generated at high electrolytic potentials has been demonstrated, and extreme caution is necessary in view of possible protonation reactions of highly basic semiquinones such as 22<sup>•-</sup>.

**PART II. CONFORMATIONAL ANALYSIS OF LARGE CARBOCYCLIC SEMIDIONES**

## 1. INTRODUCTION TO MACROCYCLIC SEMIDIONES

Radical ions derived from the formal one electron reduction of 1,2-diones are known as 1,2-semidiones.



A vast number of these paramagnetic species have been generated, and have been shown to serve as versatile spin probes in the elucidation of diverse phenomena such as conformational equilibria, ion pairing and radical rearrangements. The first major study of conformational mobility in cyclic 1,2-semidiones was reported [30] in 1967. The ESR spectra of cyclobutane and cyclopentane-1,2-semidiones were shown to consist of sharp pentets with binomial intensities which remained unchanged between 183 and 343 K, revealing planar or less likely, rapidly equilibrating structures. Cyclohexane-1,2-semidione was found to exist as a half-chair conformation with  $\Delta H^\ddagger = 4.0 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -1.0 \text{ e.u.}$  for ring inversion, calculated from linewidth alternation observed between 183 and 305 K. These values compare favorably with a  $\Delta F^\ddagger$  of  $5.3 \text{ kcal mol}^{-1}$  found for ring inversion of cis-3,3,4,5,6,6- $\text{d}_6$ -cyclohexene by N.M.R. Later studies revealed cycloheptane-1,2-semidione to exist as a frozen staggered conformation at 300 K [61]. Cyclooctane-1,2-semidione was found to exhibit a complex splitting pattern at 298 K, possibly due to a mixture of conformations. However, at 370 K, the spectrum merged into a



binomial pentet due to time averaging of the  $\alpha$ -hydrogen atoms [62]. The nine-membered cyclic 1,2-semidione was investigated with the hope that the trans (E) isomer would be detected. However, the ESR parameters indicated a single species, conformationally stable between 250 and 320 K, and consistent with the cis(Z) semidione [63]. Cyclodecane-1,2-semidione was investigated only briefly, and also found to exist only as the Z isomer [61].

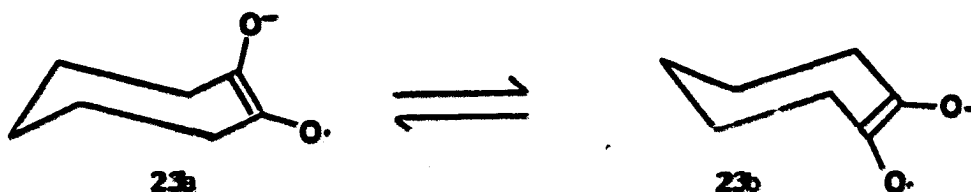
Cycloundecane-1,2-semidione was found to exhibit two contrasting splitting patterns, depending upon the conditions chosen. In the presence of [2.2.2]-cryptand, the spectrum appeared to be a broad triplet at 298 K, possibly due to the E-semidione. Upon addition of excess potassium iodide (KI), a second series of poorly resolved lines, consistent with the Z isomer appeared [61]. The lack of resolution and the complexity of the ESR spectra for both species precluded a more detailed analysis.

Semidiones, derived from twelve to fifteen-membered rings, were found to exhibit a progressive trend toward better resolved ESR spectra in the presence of [2.2.2]-cryptand. Cyclododecane-1,2-semidione showed hyperfine coupling constants due to four different hydrogen atoms at 400 K, indicating a frozen E conformation at that temperature [61]. The thirteen-membered E-semidione showed a similar three-doublet splitting pattern at 310 K. Upon warming to 410 K, the spectrum merged into a reasonably well defined triplet of triplets, indicating partial equilibration of the  $\alpha$ -hydrogens in the E conformation. Cyclotetradecane-1,2-semidione was found to yield similar spectra to those observed for the fifteen-membered ring, and was therefore

Investigated only briefly [61].

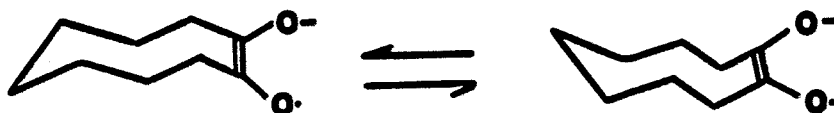
Cyclopentadecane-1,2-semidione gave a well resolved t x t at 300 K in the presence of [2.2.2]-cryptand. At elevated temperatures ( $\approx 400$  K) the spectrum showed selective line broadening, however coalescence of the lines could not be observed due to rapid decomposition of the paramagnetic ions. Addition of KI (0.5 M) to the solution containing the E isomer, resulted in the appearance of a second species, presumably the Z-semidione. At 350 K, this spectrum consisted of a 1:1 mixture of a t x t due to the E-semidione, and a binomial pentet from the Z isomer [62].

The important conformations in medium-large cyclic Z-semidiones may thus be summarized as follows. Cycloheptane-1,2-semidione undergoes observable conformational motion on the ESR time scale at 370 K. A sole process interconverting two degenerate conformations (23a  $\rightleftharpoons$  23b) cannot alone account for the magnitudes of the splitting constants observed at limiting temperatures, a discrepancy best ascribed to the accessibility of additional conformations at elevated temperatures [61].



The ESR spectrum of the eight-membered Z-semidione is complex,

possibly due to a mixture of conformations at 300 K. Warming causes a reversible change to a pentet which has been attributed to the fluxional cyclooctane-1,2-semidione. The nine-membered ring is conformationally stable at 300 K, and its ESR spectrum, like those of the seven- and eight-membered rings also shows a variation with temperature. However, in contrast to the lower homologs, the total spectral width of the nine-membered semidione does not alter dramatically with temperature, an observation consistent with a simple interconversion between two degenerate conformations.



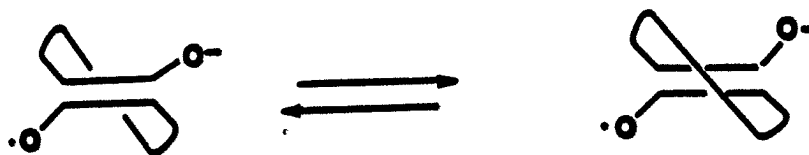
Conformational motion in the larger (eleven- to fifteen carbon) cyclic Z-semidiones is interesting. The  $\alpha$ -hydrogens in the eleven- and twelve-membered rings do not appear completely equilibrated at 380 K. This effect is present, although to a lesser extent in the higher homologs as well, since the thirteen to fifteen-membered rings had to be heated in order to observe binomial pentets of sharp lines [61].

Most remarkable is the observation that cyclohexane-1,2-semidione exhibits a higher rate of conformational interconversion than any of the higher homologs studied. Apparently, the reduced enthalpy of activation

is offset by an exalted (negative) entropy term in the large and "floppy" rings.

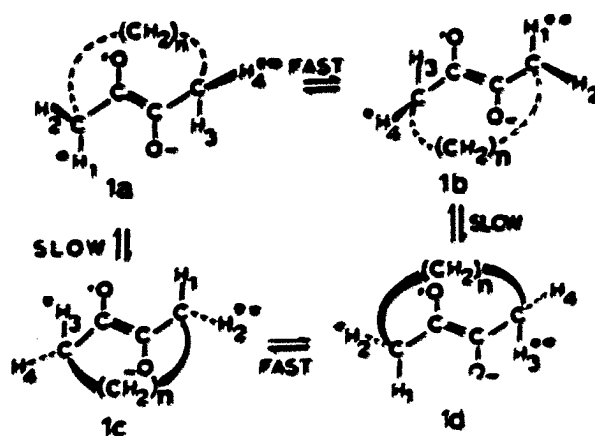
Conclusions regarding conformational mobility in  $C_{11}$ - $C_{15}$  and other heterocyclic  $\underline{E}$ -semidiones have recently been advanced [62-64]. The three-doublet (dxdx) splitting pattern observed for the  $C_{11}$ - $C_{13}$  carbocycles above 300 K, and presumably those arising at subambient temperatures for the  $C_{14}$  and  $C_{15}$  rings have been interpreted in terms of frozen asymmetric conformations, such as la-ld (Scheme III) [62]. For the  $C_{11}$  and  $C_{12}$  carbocycles, the ESR spectrum exhibits four different hydrogen splittings at 400 K, revealing extremely rigid conformations even at high temperatures. In the case of higher homologs, the minor movement of atoms necessary to interconvert la $\rightleftharpoons$ lb becomes possible at modest temperatures, and the spectra coalesce into well defined triplets of triplets. It is important to note, however, that these txt's are not believed to be a result of two pairs of statically equivalent hydrogen atoms, but rather due to the rapid time averaging of  $H_1$  with  $H_4$  and  $H_2$  with  $H_3$ , by a process interconverting la to lb and lc to ld in Scheme III.

At 400 K, the txt due to  $\underline{E}$ -cyclopentadecane-1,2-semidione shows selective line broadening, possibly due to the onset of a process involving the rotation of the semidione moiety through the cavity of the carbocycle [62]. However,



this process, which interconverts  $1e(b) \rightleftharpoons 1c(d)$  in Scheme III, and one which is predicted to result in a binomial pentet when occurring at a rapid rate on the ESR time scale, cannot unequivocally be claimed to be occurring in E-cyclopentadecene-1,2-semidione, since decomposition of the radical ions and loss of signal intensity were found to precede coalescence of the lines in the ESR spectrum.

Scheme III.<sup>8</sup>



<sup>•</sup>H<sub>1</sub>-H<sub>2</sub> refer to the magnetic environments of the protons; <sup>•</sup> and <sup>••</sup> are specific protons. In 1a, H<sub>1</sub>, and H<sub>2</sub>, are in the plane of the semidione double bond. 1a and 1b are superimposable, while 1a(b) and 1c(d) are enantiomers.

## II. SEMIDIONES DERIVED FROM 1-HYDROXY-2-KETOCYCLOTETRACOSANE

## A. Introduction

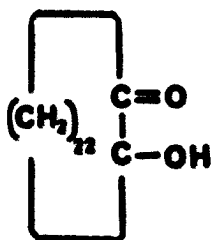
Earlier investigations addressed the issue of conformational preference, and mobility of the hydrocarbon loop in the proximity of the spin label for large ( $C_{11}$ - $C_{15}$ ) carbocycles. These studies revealed two distinct configurations, the more stable and preferred E isomer, and the Z-semidione, detected only as a mixture with the E radical, in the presence of excess quantities of  $K^+$ . Conclusions on the conformational mobility of large ring semidiones in the Z configuration could not be drawn with confidence, since the admixture of species, poor resolution, coupled with unfavorable signal to noise ratios, made analysis of the ESR spectra difficult.

The preferred low temperature conformations in large ring E-semidiones were poorly understood at the inception of the present study. The difficulties arose primarily when cooling the radical containing solutions, whereupon a dramatic loss of resolution and ESR signal intensity often ensued. Additionally, an important question regarding a specific motion of the semidione spin label with respect to the hydrocarbon ring (here termed internal rotation) remained unanswered due to the lack of coalescence in the high temperature E- $C_{15}$  spectrum.

The present investigation was thus undertaken with the explicit purpose of acquiring higher quality ESR spectra of large carbocyclic Z-semidiones, of deriving a better understanding of the preferred conformation in E-semidiones at low temperatures, and most

importantly, of clearly determining the feasibility of internal rotation in the cyclic  $\underline{E}$ -semidiones.

1-Hydroxy-2-ketocyclotetracosane 24, precursor to cyclotetracosane-1,2-semidione was prepared with the expectation the extended perimeter of the twenty-four-membered ring would facilitate internal rotation in the cyclic  $\underline{E}$ -semidione, in addition to serving as a possible access to large carbocyclic  $\underline{Z}$ -semidiones.



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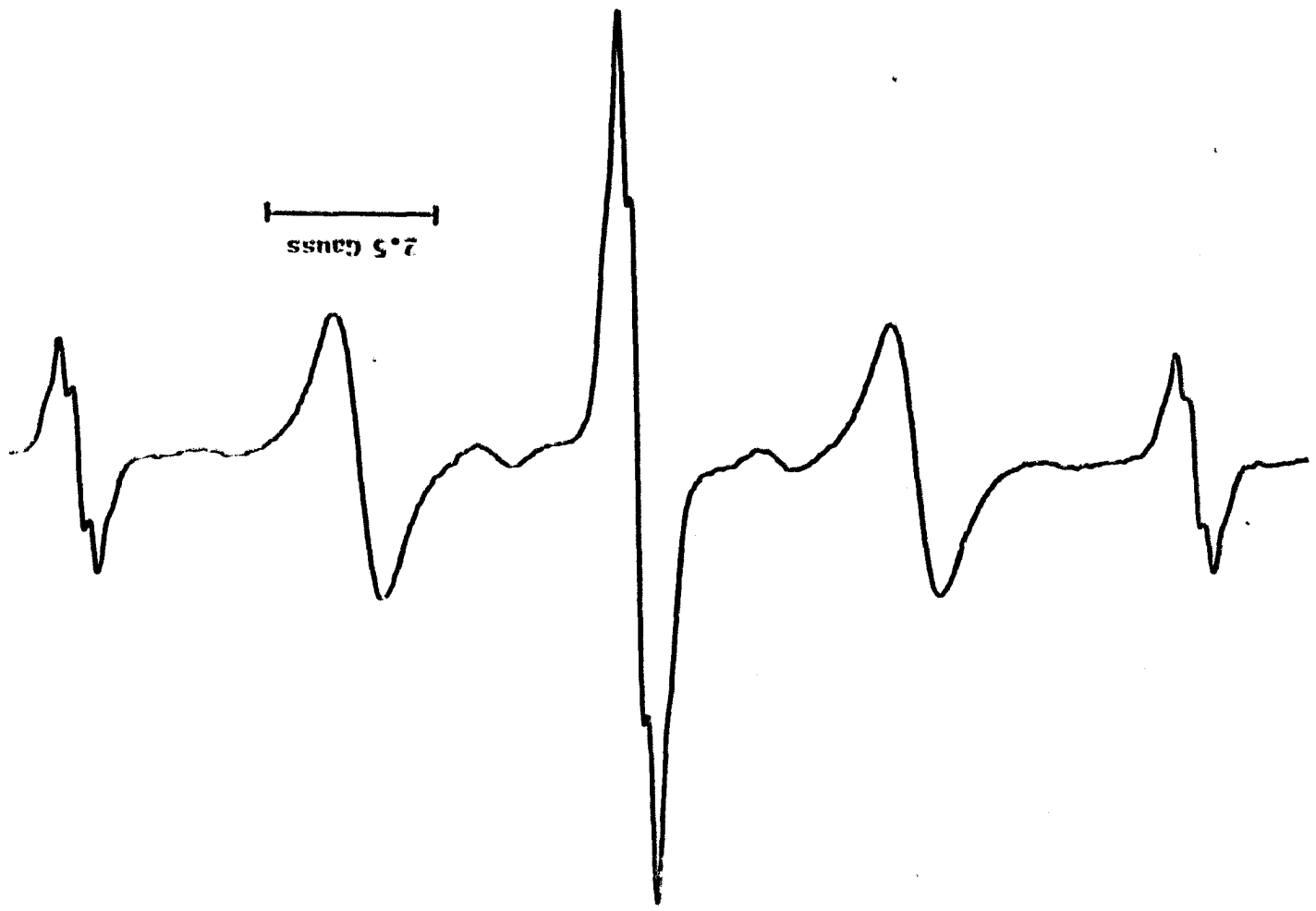
### B. Results and Discussion

Reaction of freshly prepared, unpurified  $\alpha$ -hydroxy ketone 24 with potassium tert-butoxide/[2.2.2]-cryptand (1:1) in anhydrous, deaerated DMSO resulted in an excellent ESR spectrum at 298 K ( $a_1^H = 4.2$  G, [4 H's],  $a_2^H = 0.1$  G, [4 H's],  $g = 2.005046$ , Figure 24). Upon warming, the lines in the spectrum approached binomial intensities of 1:4:6:4:1, (Figure 25a-c), while the cooling of DMSO/DMP solutions resulted in further broadening of the second and fourth peaks, until at 248 K, the spectrum consisted of a 1:4:1 triplet of sharp wing and central peaks. Loss of signal intensity and resolution resulted upon further cooling, however, at 218 K, the spectrum appeared consistent with a species showing hyperfine coupling to four different hydrogen atoms ( $a^H = 8.5$  G [1 H],  $a^H = 6.6$  G [1 H],  $a^H = 1.9$  G [1 H],  $a^H < 0.05$  G [1 H]).

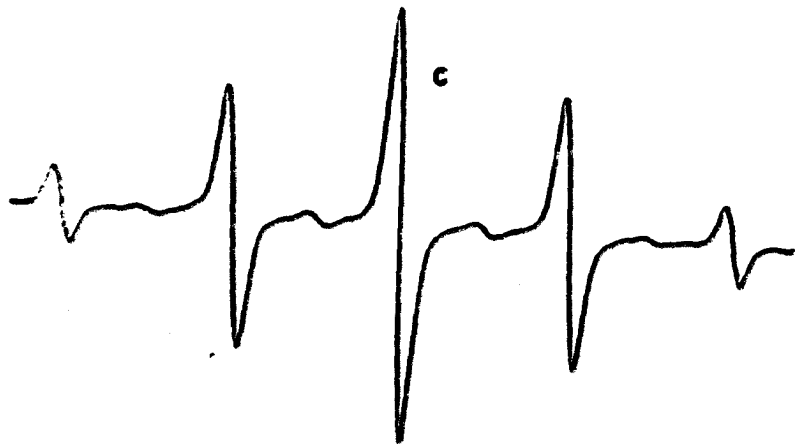
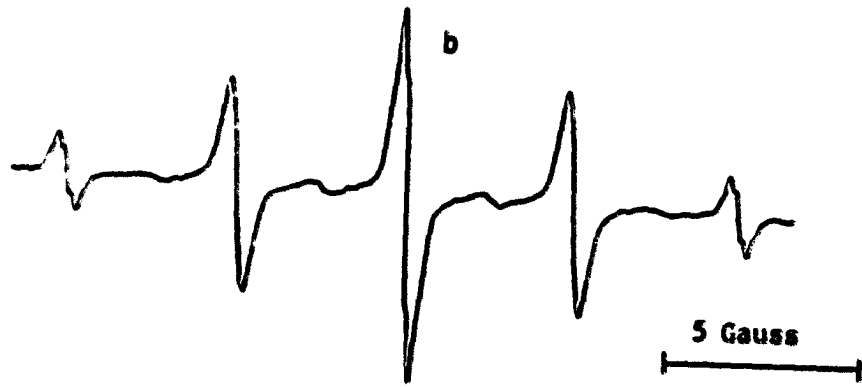
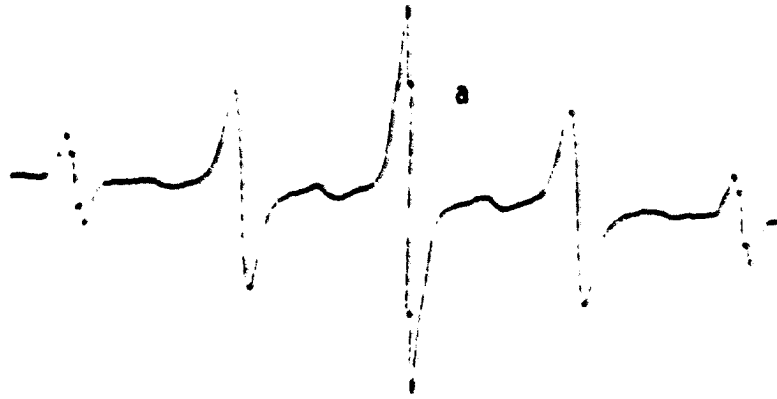
**Figure 24. First Derivative ESR spectrum of E-cyclotetracosane-1,2-semidione at 298K**



101



**Figure 25. First derivative ESR spectrum of E-cyclotetracosane-  
1,2-semidione at  
(a) 318 K  
(b) 338 K  
(c) 358 K**



**Figure 26.** First derivative ESR spectra of E-cyclotetracosane-1,2-  
semidione at  
(a) 288 K  
(b) 248 K  
(c) 208 K

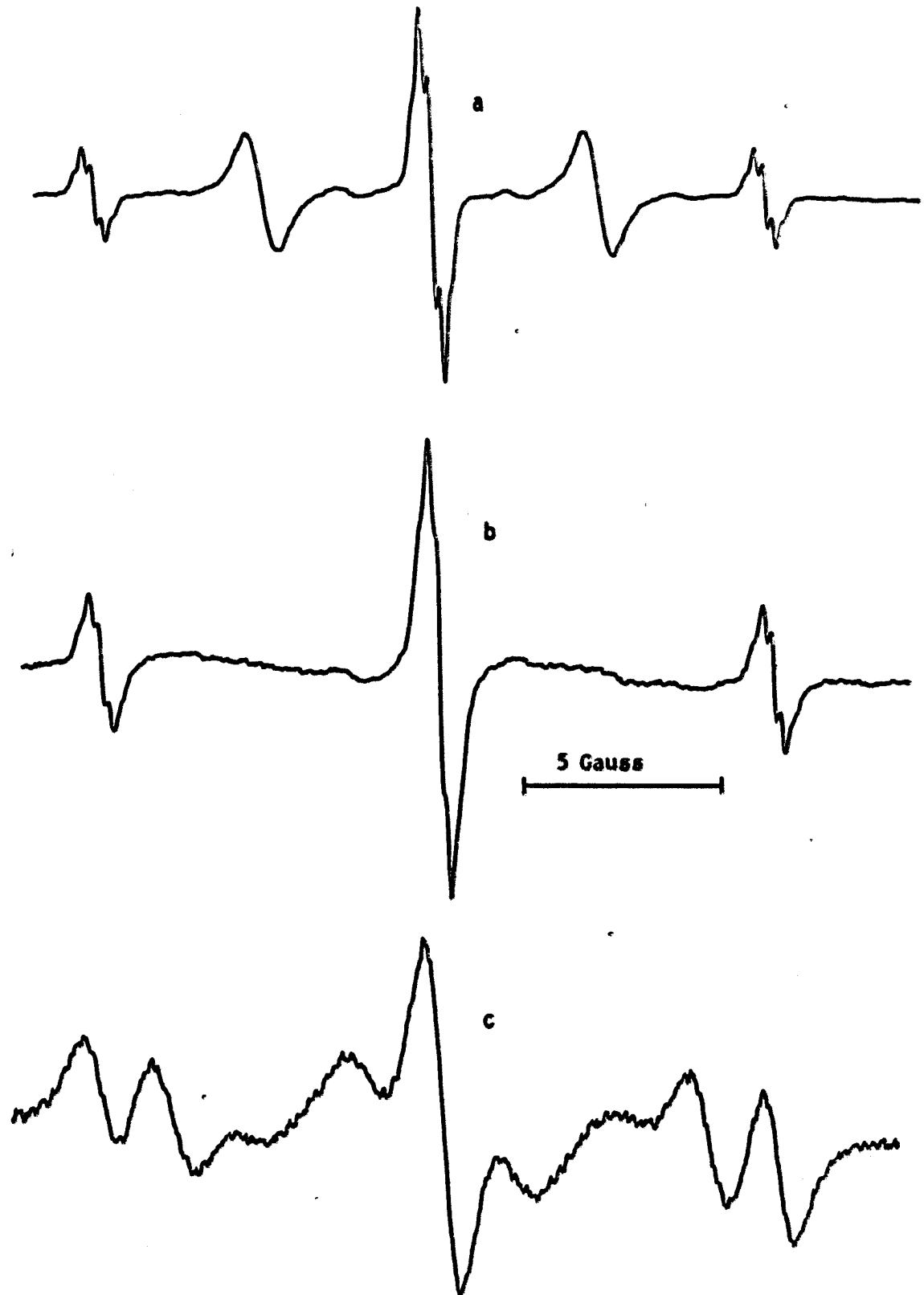


Figure 26c).

Assignment of the radical species observed between 218 and 378 K is made to the cyclic E-semidione on the basis of ESR parameters such as splitting pattern, g value and prior experience with E/Z ratios of large carbocycles observed in the presence of complexing agents. The low temperature (218 K) spectrum of the cyclic  $C_{24}$  E-semidione is thus consistent with frozen, asymmetric conformations of type Ia-Ic previously described in Scheme III. At 248 K, the spectrum displays selective line broadening due to an intermediate rate of the process interconverting the superimposable structures Ia(c)  $\rightleftharpoons$  Ib(d) which time averages the  $\alpha$ -hydrogens  $H_1$  with  $H_4$  and  $H_2$  with  $H_3$ . Upon warming the solutions further, the second and fourth peaks appear and gain intensity, and at 378 K, the spectrum closely exhibits binomial intensities of 1:4:6:4:1. Of important consequence, is the observation that the transition from a temperature at which the conformational equilibrium Ia(b)  $\rightleftharpoons$  Ic(d) is intermediate, to a temperature at which this interconversion is rapid on the ESR time scale does not involve the interplay of a well defined triplet of triplets splitting, as is the case for the previously studied  $C_{15}$  E-semidione.

The absence of a txt spectrum, and the direct passage from the low temperature 1:4:1 splitting to a near binomial pentet at 378 K has the unfortunate effect of eradicating any clear distinction between the process interconverting Ia(c)  $\rightleftharpoons$  Ib(d), and one involving internal rotation of the semidione moiety (the interconversion Ia(b)  $\rightleftharpoons$  Ic(d)). The ambiguity arises due to the fact that the observed pentet need not necessarily arise solely from the process of internal rotation, since a

1:4:6:4:1 pentet does not require four chemically equivalent (on a time average) hydrogen atoms. The splitting pattern at 378 K could conceivably occur due to the process  $1a(c) \rightleftharpoons 1b(d)$ , since, when four magnetically nonequivalent hydrogen atoms are time averaged to yield two pairs of equivalent hydrogens, ( $H_1$  and  $H_4$ ,  $H_2$  and  $H_3$ ), a binomial pentet may fortuitously result if  $a_1^H + a_4^H = a_2^H + a_3^H$ . Inspection of the low temperature splitting constants (6.6 G [1 H], 1.9 G [1 H], 8.5 [1 H]), and the equation  $(8.5 + 0.0 = 6.6 + 1.9)$  reveal that this possibility cannot be dismissed in the case of E-cyclotetracosane-1,2-semidione.

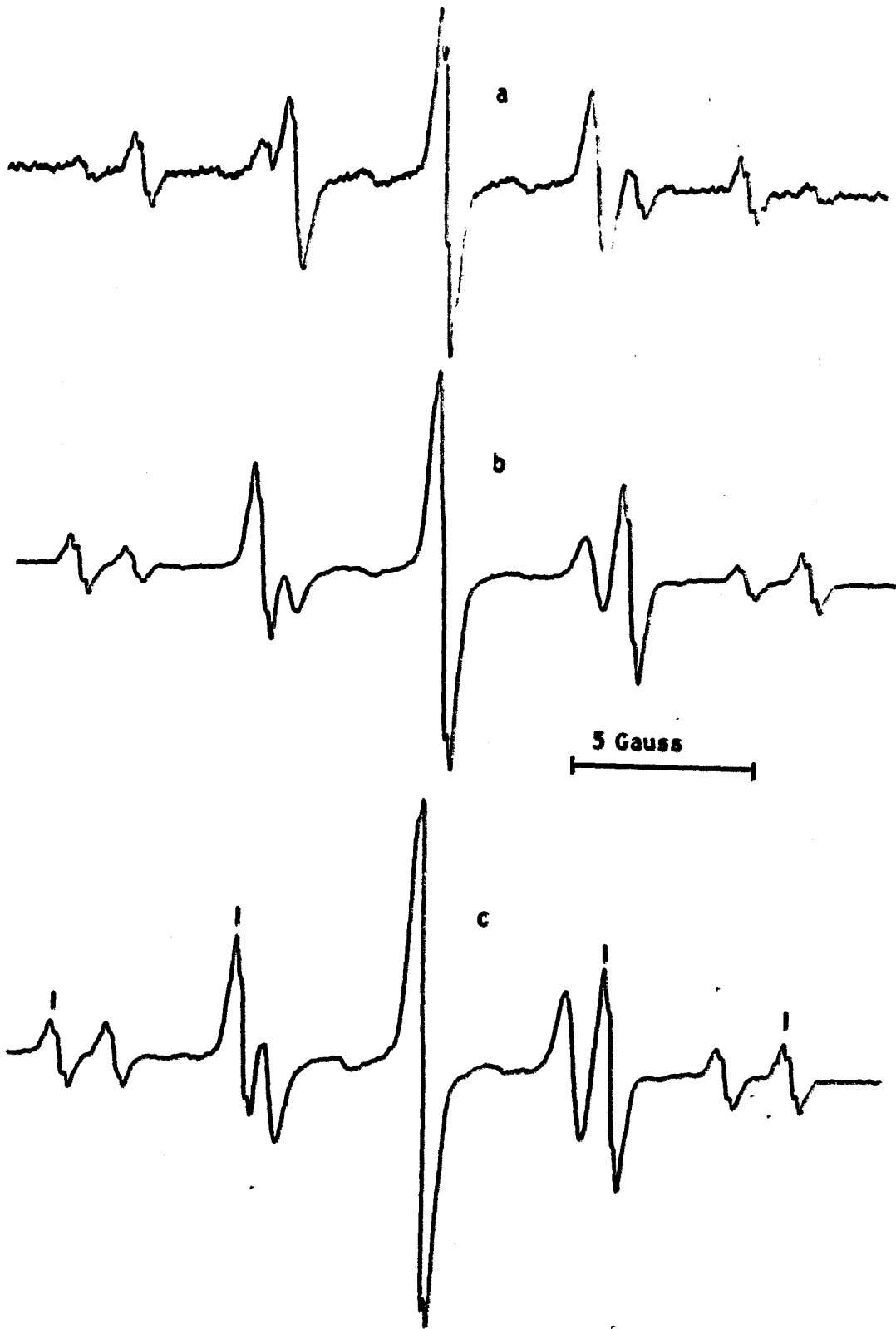
#### C. Effects of Ion Pairing on E/Z Ratios

The  $C_4$ - $C_9$  cyclic semidiones were found to exist as the Z isomers with ion pairing constants ( $K^+$ , 298 K, DMSO) increasing from 14( $C_4$ ) to 87( $C_5$ ) to 220 ( $C_6$ ), 190 ( $C_7$ ) and 260( $C_9$ )  $M^{-1}$ . For the  $C_{11}$ - $C_{15}$  carbocycles in the presence of  $K^+$ , [2.2.2]-cryptand, the E isomer was found to predominate, whereas in the presence of  $K^+$ , the Z isomer was preferred in some instances [62]. Complete time averaging of the  $\alpha$ -hydrogens to give a binomial pentet in the Z-semidiones was found to occur only upon heating, while cooling generally resulted in a reversible loss of signal intensity from the Z isomer.

Addition of KI to solutions showing hyperfine coupling due to the E-cyclotetracosane-1,2-semidione resulted in the appearance of a second species (of lower  $g$  and larger  $a^H$  values) which did not time

**Figure 27.** First derivative ESR spectra of E/Z mixtures of cyclo-  
tetracosane-1,2-semidione at 338 K  
(a) Solution 0.4 M in KI  
(b) Solution 0.6 M in KI  
(c) Solution 0.8 M in KI  
The Z isomer is marked with vertical lines





average with the initial radical present. The relative abundance of each species appeared to be strongly dependent upon the concentration of potassium ions in the medium, with the new species being preferred at high  $[K^+]$ , (Figure 27a-c,  $a_1^H = 5.2$  G [4 H's],  $a_2^H = 0.08$  G [4 H's],  $g = 2.00485$ , DMSO). These observations and prior experience [65] with splitting patterns of isomeric semidiones collectively support the assignment of the new species to Z-cyclotetracosane-1,2-semidione.

At 338 K, the spectrum due to a mixture of E- and Z-semidiones reveals both species to be undergoing selective line broadening. The origins of this effect in the E isomer have been discussed in the previous section. In the case of the Z-semidione, the observation that complete time averaging of the  $\alpha$ -hydrogen atoms to yield a binomial pentet only occurs at  $\sim 368$  K is remarkable, although in keeping with the behavior of the previously studied  $C_{11}$ - $C_{15}$  Z-carbocycles.

Conformational motion at low temperatures in the Z-semidione could not be studied, since cooling of DMSO/DMF solutions containing mixtures of the E- and Z-semidiones invariably resulted in a dramatic, reversible loss of signal intensity from the Z isomer, an occurrence that has been attributed to disproportionation of the semidione to the dione an. the enediol dianion.

In summary, the E/Z ratio of cyclotetracosane-1,2-semidione changes from an estimated one hundred for the free ion, to approximately one for a solution 0.4 M in  $K^+$  at 298 K. Conformational motion in the Z-semidione mimics that in the Z- $C_{15}$  carbocycle, since warming causes the pentet due to the Z isomer to attain binomial

intensities, while cooling below 298 K results in reversible loss of the ESR signal due to disproportionation of the radical ions.

#### D. Conclusion

Cyclotetracosane-1,2-semidione exists primarily as the E isomer in the presence of  $K^+$ [2.2.2]-cryptand, with an E/Z ratio of approximately 100 at 298 K. Addition of KI results in the appearance of the Z isomer which can be detected as a 1:1 mixture with the E-semidione at a potassium ion concentration of approximately 0.4 M.

Conformational motion time averaging the  $\alpha$ -hydrogens in the large cyclic Z-semidione, occurs less readily than in some of the lower homologs studied, an observation that has been ascribed to the offsetting of a more favorable  $\Delta H^\ddagger$  term by an exalted negative entropy of activation in the extreme "floppy" carbocycle. Conformational preference and mobility in the Z-semidione at low temperature remains uncertain due to loss of the ESR signal upon cooling.

The low temperature spectra recorded for E-cyclotetracosane-1,2-semidione further substantiate the claim of frozen, asymmetric conformations in large carbocyclic E-semidiones. The observed conformational preference may be a consequence of enhanced solvation of the asymmetric structure.

At elevated temperatures, coalescence of the lines due to the E isomer to give a binomial pentet has been shown possible for conformational equilibria involving minor movement of the  $\alpha$ -hydrogen atoms. The high temperature ESR spectrum of E-cyclotetracosane-

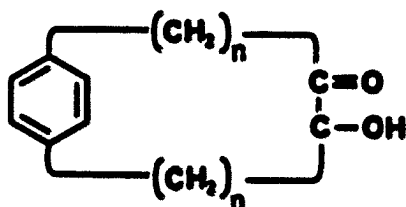
1,2-semidione thus fails to provide unequivocal evidence for internal rotation in the cyclic 1,2-semidione.

### III. SEMIDIONES DERIVED FROM ACYLOINS OF P-CYCLOPHANES

#### [1,4-(n'-HYDROXY-(n'+1)-KETOPOLYMETHYLENE) BENZENES]

##### A. Introduction

The high temperature ESR spectrum of E-cyclotetracosene-1,2-semidione was found not to provide an unambiguous example of internal rotation in cyclic 1,2-semidiones. The study was thus continued, and extended to include semidiones derived from the more readily accessible acyloins 25 (a-d).



25

a: n=4	c: n=9
b: n=7	d: n=11

The choice of hydrocarbon skeleton in compounds 25 (a-d) was made primarily on the basis of the expected ease of synthesis of the paracyclophanes as compared to polymethylene macrocycles such as 24. The presence of a 1,4-benzene linkage in the ring was not expected to dramatically alter conformational mobility of the corresponding E-semidiones, and it was hoped that suitable choice of chain length in

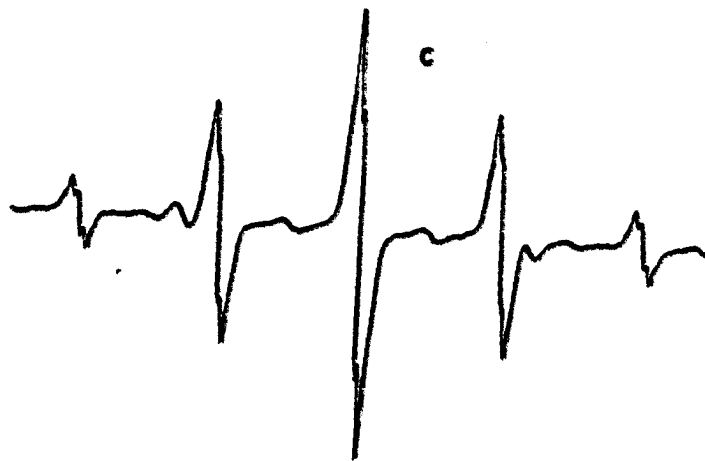
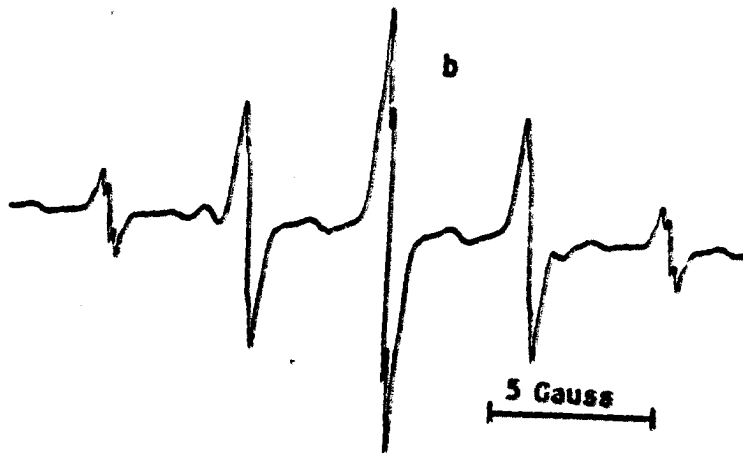
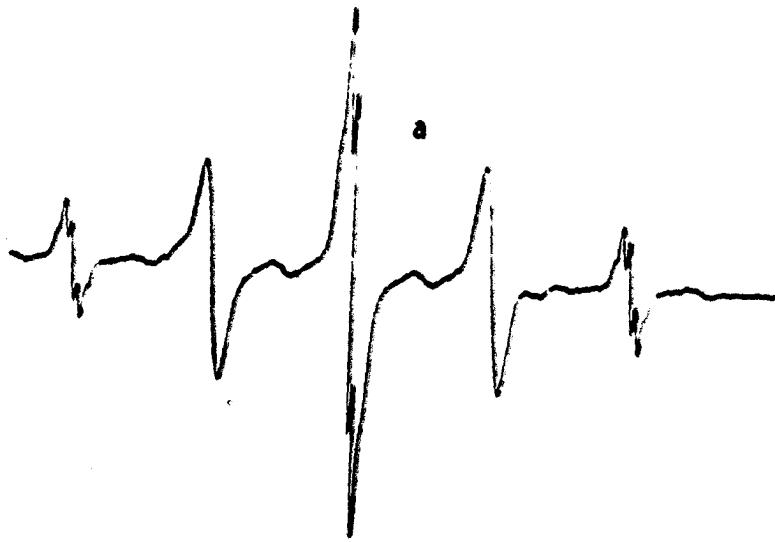
a macrocyclic semidione would result in a radical in which the occurrence of a fortuitous pentet would be replaced by a splitting pattern unique to a process involving internal rotation.

### B. Results and Discussion

Disproportionation of crude  $\alpha$ -hydroxy ketone 25d in potassium tert-butoxide/[2.2.2]-cryptand (1:1) in dry, oxygen free DMSO resulted in the ESR spectrum of Figure 28a ( $a_1^H = 4.25$  G [4 H's],  $a_2^H = 0.12$  G [4 H's],  $g = 2.005045$ ). At 298 K, the spectrum due to E-semidione displayed selective line broadening, however upon warming, the second and fourth peaks gained intensity and coalesced to give a binomial pentet at 348 K, (Figure 28 b,c). Cooling of DMSO/DMF solutions below 298 K resulted in further broadening of the second and fourth peaks, until at 238 K, the spectrum consisted of a 1:4:1 triplet of sharp central and wing peaks. Continued cooling was accompanied by loss of resolution and signal intensity, however at 208 K, the observed signal was consistent with hyperfine coupling to four different hydrogen atoms, similar to that observed for the low temperature 24-membered E-semidione ( $a^H = 7.9$  G [1 H],  $a^H = 5.9$  G [1 H],  $a^H = 1.9$  G [1 H],  $a^H < 0.05$  G [1 H], Figure 29 a-c).

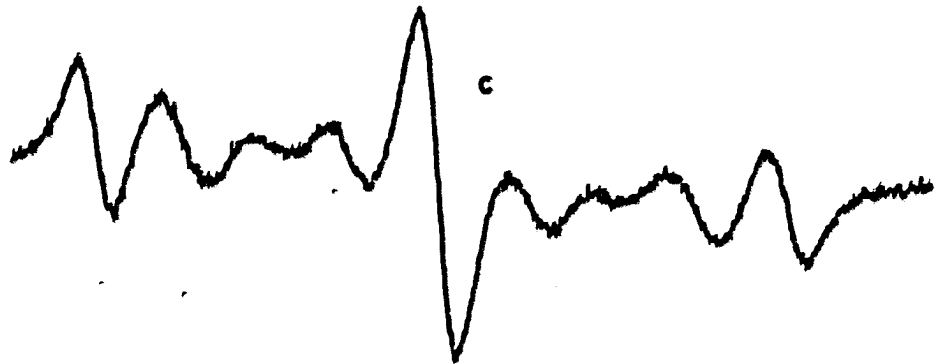
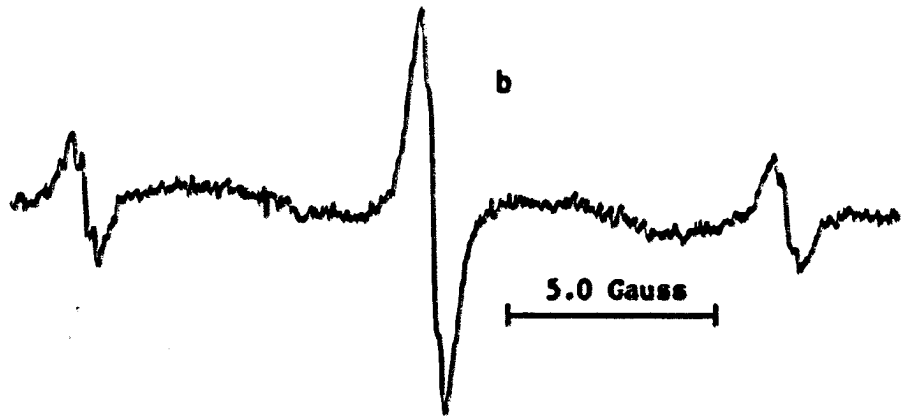
Addition of KI to solutions showing hyperfine coupling primarily due to the E isomer, resulted in the appearance of a second species, presumably the Z-semidione, Figure 30a ( $a_1^H = 5.2$  G [4 H's],  $a_2^H = 0.08$  G [4 H's]  $g = 2.00485$ ). At 298 K, the spectrum showed selective line broadening, indicating incomplete equilibration of the four  $\alpha$ -hydrogen atoms in the Z-semidione. Warming to 358 K caused the

**Figure 28. First derivative ESR spectra of the E-semidione  
derived from 25d at**  
**(a) 298 K**  
**(b) 328 K**  
**(c) 348 K**



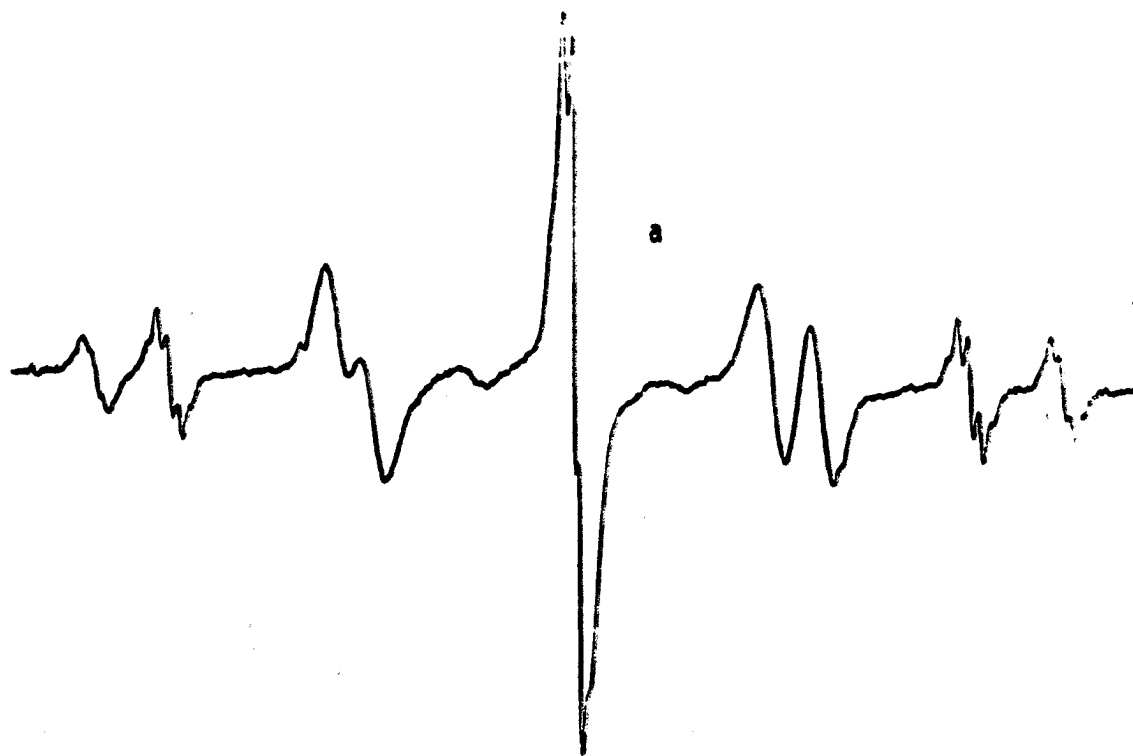


**Figure 29.** First derivative ESR spectra of the E-semidione derived from 25d at  
(a) 258 K  
(b) 238 K  
(c) 208 K



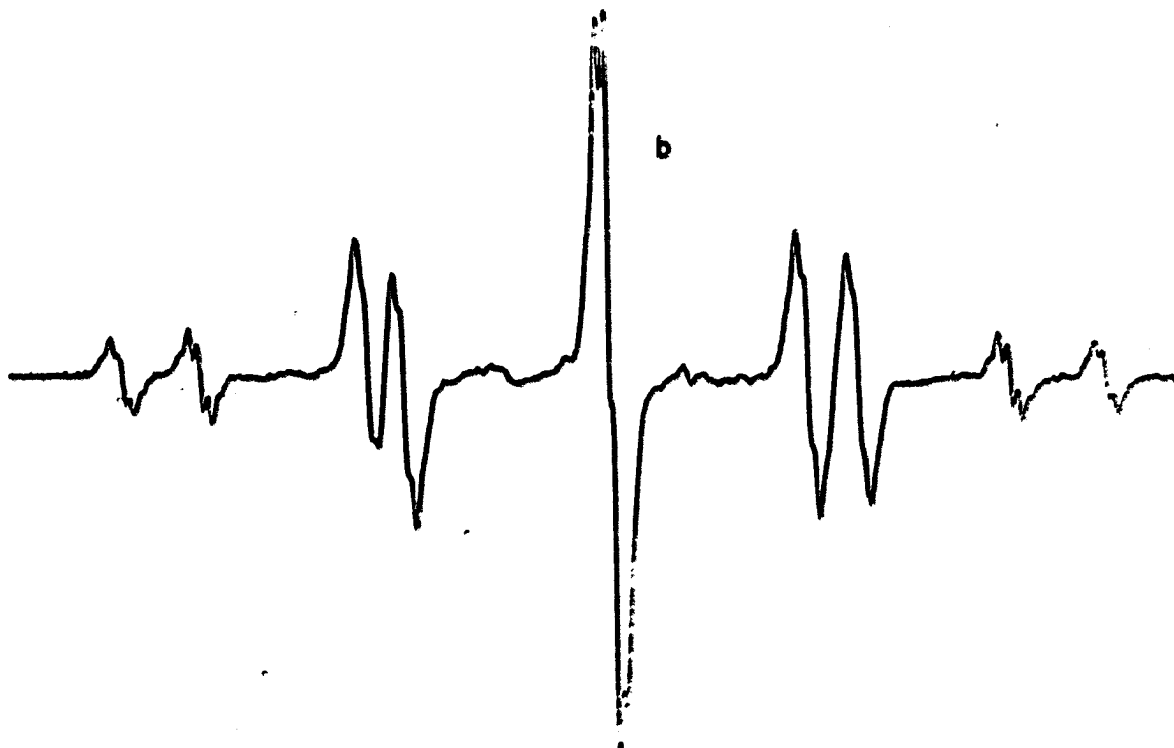
**Figure 30.** First derivative ESR spectra of the E- and Z-semidiones derived from 25d at  
(a) 298 K  
(b) 358 K

120



a

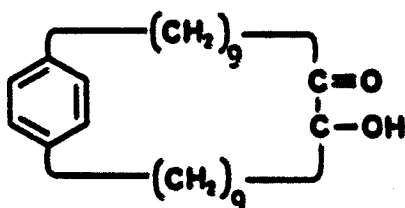
5 Gauss



b

lines to approach binomial intensities of 1:4:6:4:1, while cooling below 298 K was found to result in the reversible loss of signal due to the Z isomer.

It is thus apparent that conformational motion in the E- and Z-semidiones derived from 25d closely resembles that in the E- and Z-cyclotetracosane-1,2-semidiones. Complete time averaging of the  $\alpha$ -hydrogen atoms in the Z isomer could only be accomplished upon heating, in keeping with the previously established behavior of macrocyclic Z-semidiones. Of greater significance, however, is the observation that the ESR spectra recorded between 208 and 348 K for the E-semidione derived from 25d fail to provide unequivocal evidence for internal rotation in the macrocycle, due to, in much the same fashion, the ambiguity that arose in the case of E-cyclotetracosane-1,2-semidione. Inspection of the hyperfine coupling constants for the frozen, asymmetric structures reveals that a fortuitous pentet may result at high temperatures via simple rocking motion of the  $\alpha$ -methylene groups in the E-semidione (the motion described by the interconversion  $1a \rightleftharpoons 1b$  in Scheme III), since the largest and smallest coupling constants, may in principle, average to give a number close to the value of the intermediate coupling constants, time averaged ( $7.9 + 0.0 \approx 1.9 + 5.9$ ). Further elucidation of the properties of this radical was thus not pursued, and the search for internal rotation was continued with the semidione derived from 25c.



25c

Treatment of pure  $\alpha$ -hydroxy ketone 25c with potassium tert-butoxide/[2.2.2]-cryptand (1:1) in anhydrous, degassed DMSO gave rise to the well resolved spectrum for the E-semidione ( $a^H = 4.19$  [4 H's],  $e^H = 0.2$  G [4 H's],  $g = 2.005061$ , Figure 31a). Upon warming to 378 K, the lines in the spectrum were found to approach binomial intensities (Figure 31 b,c), while cooling resulted in further broadening of the second and fourth peaks (Figure 32a), until at 233 K, these lines were essentially unobservable to yield a 1:4:1 triplet of sharp central and wing peaks (Figure 32b). Continued cooling resulted in a spectrum consistent with the frozen, asymmetric conformation previously described for macrocyclic E-semidiones ( $a^H = 7.75$  G [1 H],  $a^H = 5.7$  G [1 H],  $a^H = 1.8$  G [1 H],  $a^H < 0.05$  G [1 H], Figure 32c).

Addition of KI to solutions showing hyperfine primarily from the E-semidione, resulted in the appearance of the Z isomer in a more favorable ratio (at 0.4 M in KI, the E/Z was found to be

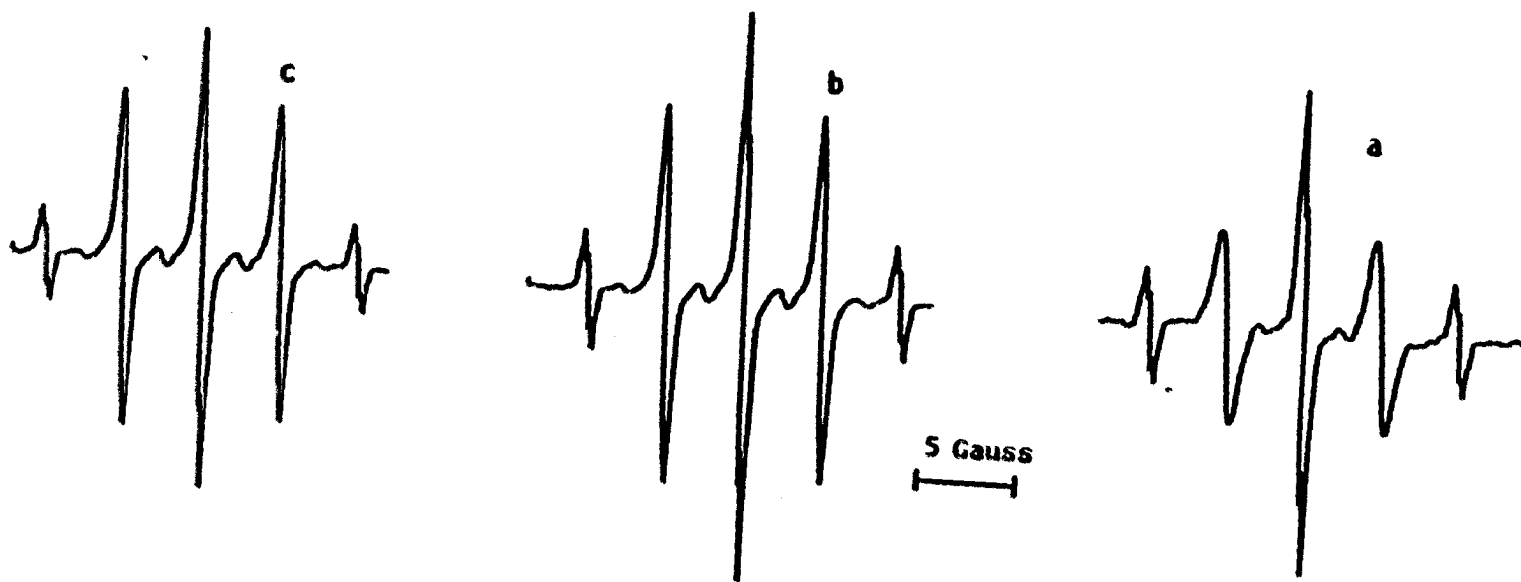
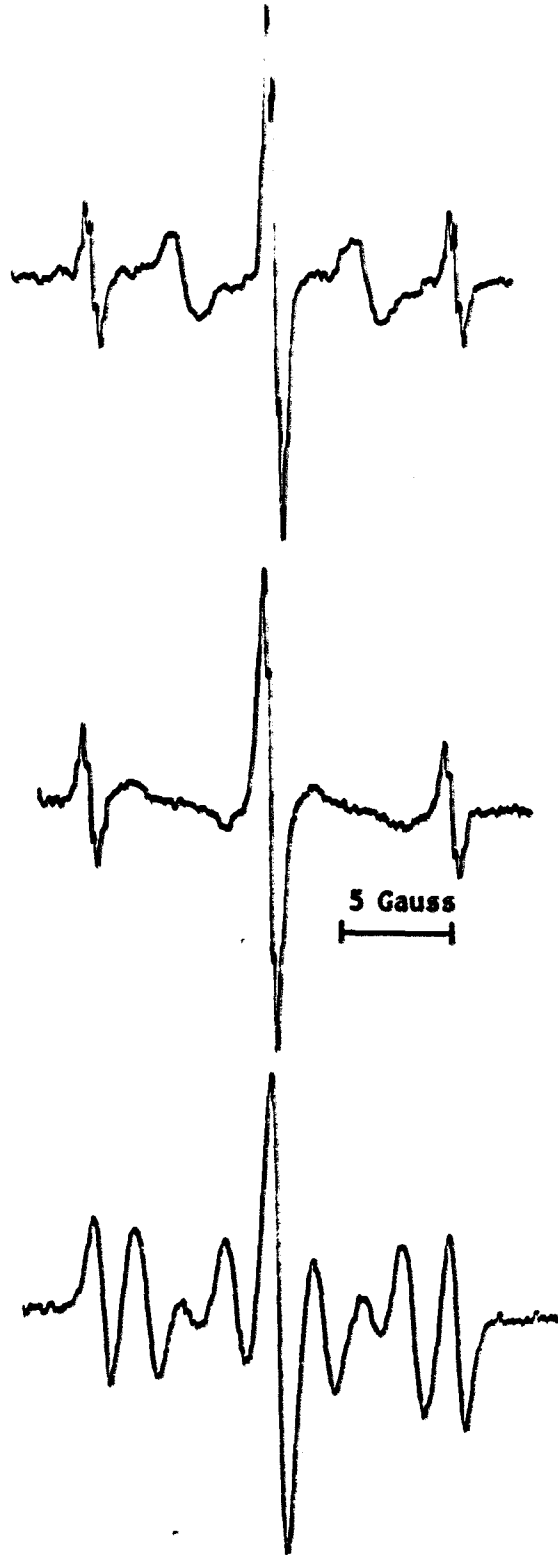


Figure 31. First derivative ESR spectra of the E-semidione derived from 25c at  
(a) 298 K  
(b) 348 K  
(c) 378 K

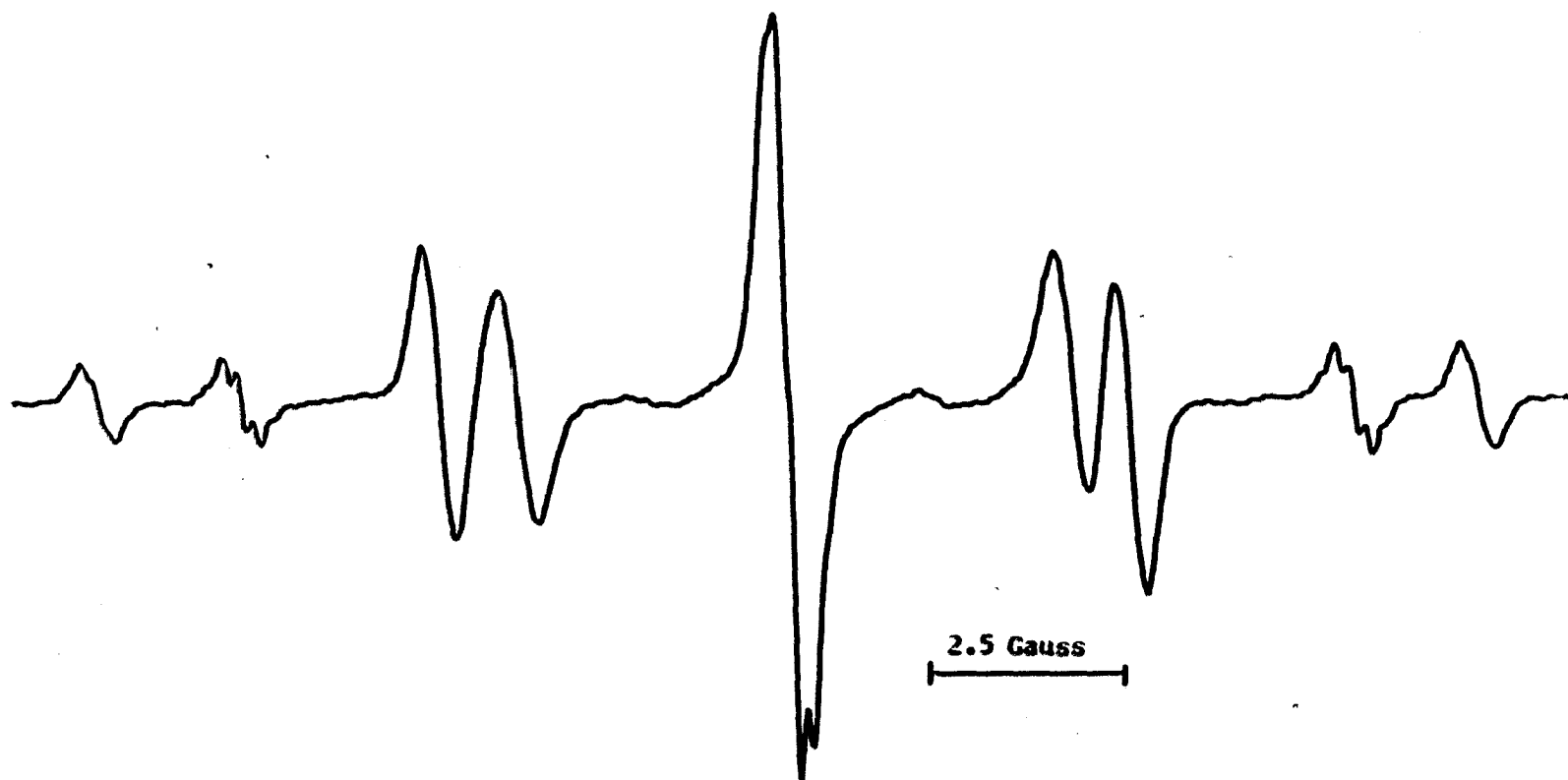
**Figure 32.** First derivative ESR spectra of the E-semidione derived from 25c at  
(a) 253 K  
(b) 233 K  
(c) 173 K





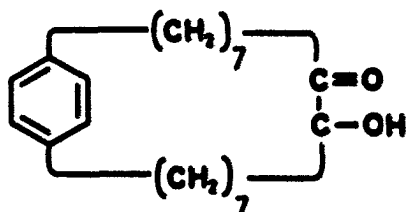
approximately 1,  $a_1^H = 5.1$  G [4 H's],  $a_2^H = 0.1$  G [4 H's]  
 $g = 2.00485$ , Figure 33). As observed for the previously studied  
 macrocycles, complete coalescence of the lines to give binomial  
 intensities could only be accomplished upon warming the solution.

Inspection of the low temperature hyperfine coupling constants for  
 the E-semidione derived from 25c once again reveals the possible  
 occurrence of a pentet due to a process other than one involving internal  
 rotation, since the sum of intermediate coupling constants approaches  
 that of the largest and smallest splitting ( $7.8 + 0 \approx 5.7 + 1.8$ ).  
 Thus, the ESR spectra recorded for the E-semidiones derived from 24,  
 25d and 25c failed to provide unequivocal evidence for internal  
 rotation in the macrocycles. It was subsequently suggested [66] that  
 possible cause for the absence of a triplet of triplets spectrum in the  
 said macrocycles may have had its origins in the near equivalence of the  
 energy barriers for the processes involving rocking motion of the  $\alpha$ -methyl-  
 ene group and internal rotation of the semidione moiety (processes  
 $1a \approx 1b$  and  $1a \approx 1c$ , respectively, Scheme III). In such instances, the  
 transition from the frozen, asymmetric conformations recorded at low  
 temperatures, to temperatures at which equilibration of the  $\alpha$ -hydrogen  
 atoms to give two sets of time averaged nuclei is expected, would be  
 obscured by the intervention of internal rotation due to the relative  
 facility of this motion in the macrocycle. Constriction of the  
 macrocycle would predict a lifting of the degenerate energy barriers,  
 since internal rotation is expected to be considerably less facile in  
 smaller carbocycles. Thus, the  $\alpha$ -hydroxy ketone 25b was synthesized  
 and the properties of the corresponding E-semidione examined.



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Figure 33. First derivative ESR spectrum of E- and Z-semidiones derived from 25c at 333 K.



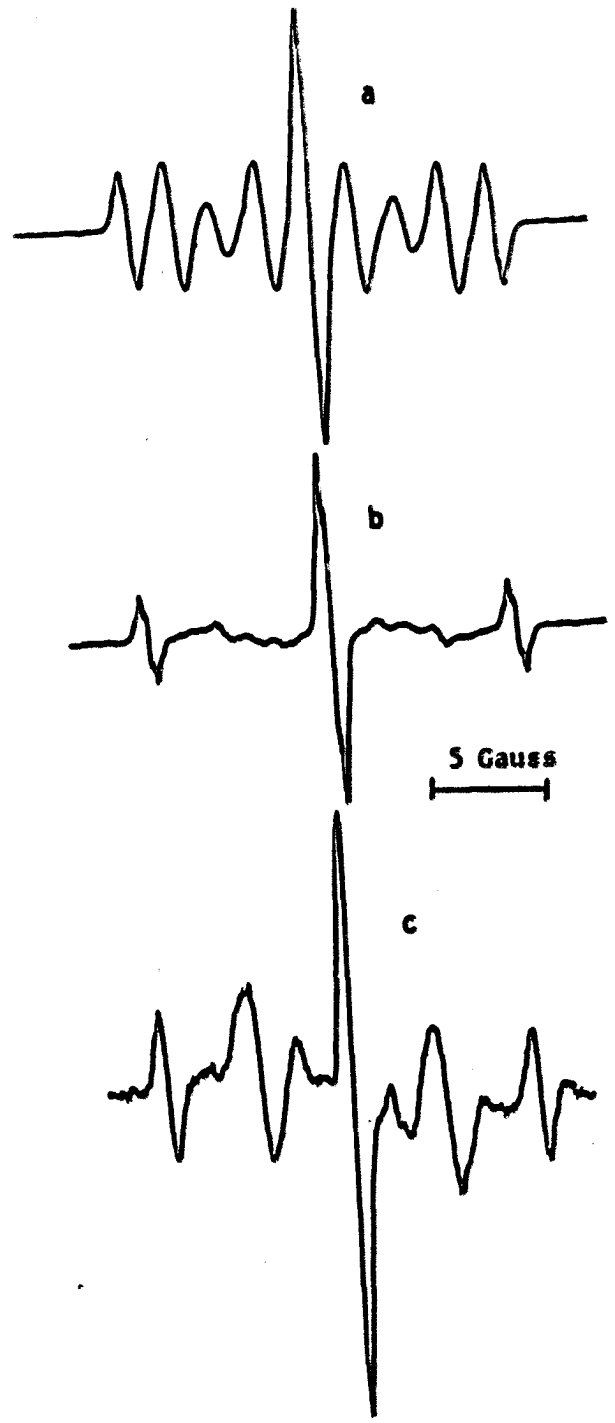
25b

Reaction of freshly prepared, unpurified  $\alpha$ -hydroxy ketone 25b with potassium tert-butoxide/[2.2.2]-cryptand (1:1) in anhydrous, deaerated DMSO resulted in the spectrum for the E-semidione, Figure 34a. Warming caused the lines in the spectrum to merge into a 1:4:1 triplet of sharp wing and central peaks, Figure 34b. Further heating resulted in the appearance of the second and fourth peaks, and at 378 K, the spectrum was found to approach the binomial intensities in a pentet ( $a^H = 3.9$  G [4 H's], Figure 34c).

Cooling to 263 K of solutions containing the E-semidione led to the predicted splitting pattern, a well-defined triplet of triplets ( $a_1^H = 6.10$  G [2 H's],  $a_2^H = 1.7$  G, [2 H's], Figure 35a). Further cooling to 223 K resulted in a spectrum showing hyperfine coupling to four different hydrogen atoms ( $a^H = 7.6$  G [1 H],  $a^H = 6.3$  G [1 H],  $a^H = 1.3$  G [1 H],  $a^H \leq 0.05$  G [1 H], Figure 35b).

Addition of KI to solutions containing the E-semidione resulted

**Figure 34.** First derivative ESR spectrum of the E-semidione derived from 25b at  
(a) 298 K  
(b) 348 K  
(c) 378 K



**Figure 35. First derivative ESR spectrum of the E-semidione derived from 25b at**  
**(a) 263 K**  
**(b) 223 K**



a

2.5 Gauss



b



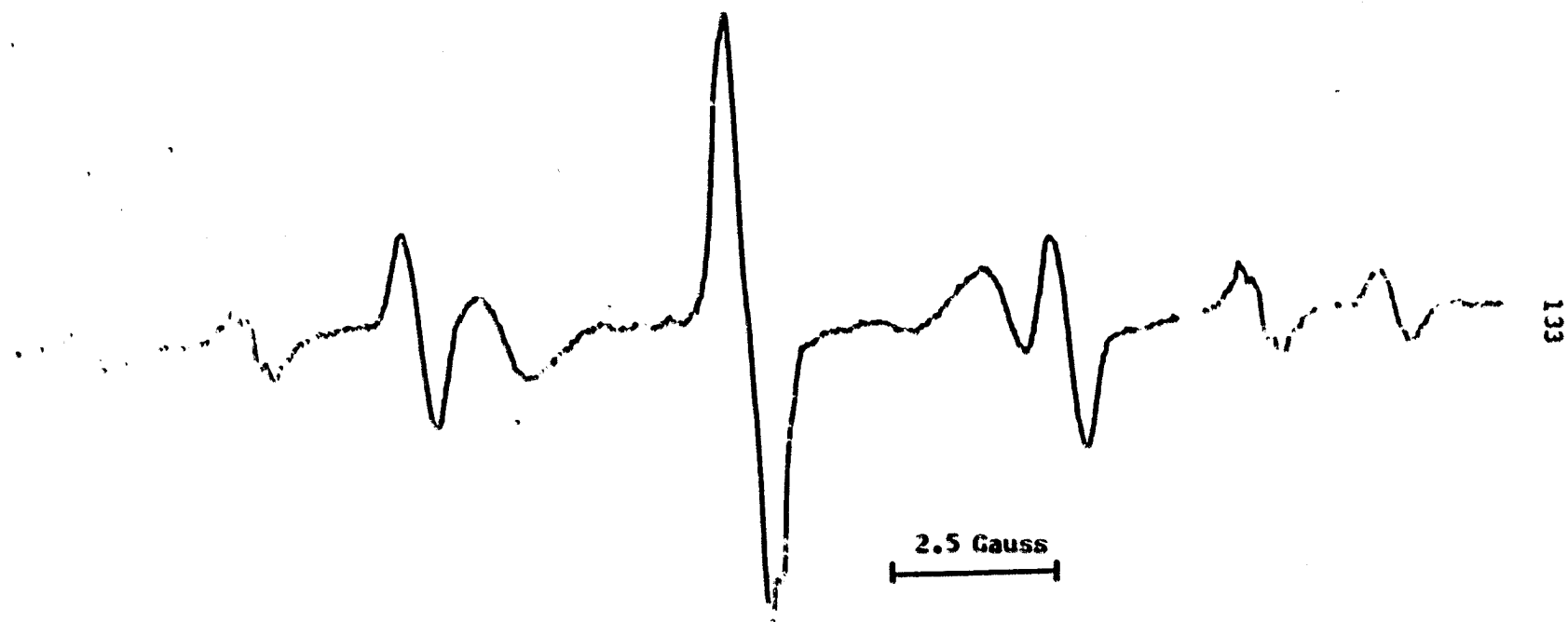


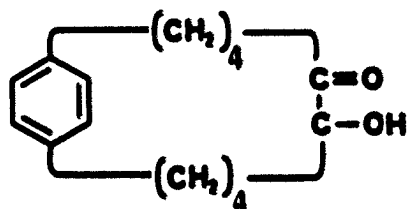
Figure 36. First derivative ESR spectrum of E- and Z-semidioxes derived from 25b at 393 K

in the appearance of the Z-isomer. At 393 K, the spectrum was found to exhibit a binomial pentet ( $a^H = 5.0$  G [4 H's] Figure 36), indicating complete equilibration of the  $\alpha$ -hydrogen atoms in the Z-semidione.

Conformational motion in the E-semidione derived from 25b may thus be summarized as follows. At 233 K, the spectrum shows hyperfine coupling from four different hydrogen atoms, due to non-equilibrating, asymmetric structures of the type previously discussed (structures la-ld in Scheme III). Upon warming to 268 K, the interconversion la(c)  $\rightleftharpoons$  lb(d) which time averages  $H_1$  with the  $H_4$  and  $H_2$  with  $H_3$  (a process that has been previously described as "rocking motion") becomes rapid on the ESR time scale, leading to a well defined triplet of triplets. Further warming results in selective line broadening, due to the onset of internal rotation, a process which equilibrates  $H_1$  with  $H_2$  and  $H_3$  with  $H_4$  (the interconversion la(b)  $\rightleftharpoons$  c(d)). At 378 K, internal rotation in the E-semidione is occurring at a rate intermediate-rapid on the ESR time scale, as observed by the approach of a binomial pentet. The values of  $\Delta H^\ddagger = 10$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = + 1.0$  e.u were estimated for this process from selective line broadening observed between 355 and 385 K. The E-semidione derived from 25b thus serves as the first clear case wherein internal rotation may be unambiguously invoked in cyclic E-1,2-semidiones.

While the primary goal of this investigation was achieved with the assignment of internal rotation in the E-semidione derived from 25b, it was deemed desirable, in the interests of completeness to undertake the study of conformational motion in a more rigid cyclic

semidione, one derived from a medium sized carbocycle of the type **25a**.



**25a**

Disproportionation of freshly prepared, crude  $\alpha$ -hydroxy ketone **25a** with potassium tert-butoxide/[2.2.2]-cryptand (1:1) in degassed DMSO resulted in a poorly resolved spectrum of broad lines which remained essentially unchanged upon warming to 353 K. Analysis of the spectrum reveals a doublet of doublet of triplet splitting ( $a^H = 6.5$  G [1 H],  $a^H = 1.7$  G [1 H],  $a^H = 4.8$  G [2 H's]), consistent with hyperfine coupling in a rigid Z-semidione.

Generation of the radical ions with 0.1 M potassium tert-butoxide or addition of KI to  $K^+$ /[2.2.2]-cryptand solutions resulted in the appearance of the Z-semidione, and at approximately 0.8 M in  $K^+$ , the Z isomer could be observed exclusively ( $Z/E > 10$  in DMSO). At 298 K, the spectrum due to the Z-semidione was found to be a 1:4:1 triplet of sharp wing and central peaks due to selective line broadening from an intermediate rate of a process equilibrating the  $\alpha$ -hydrogen atoms

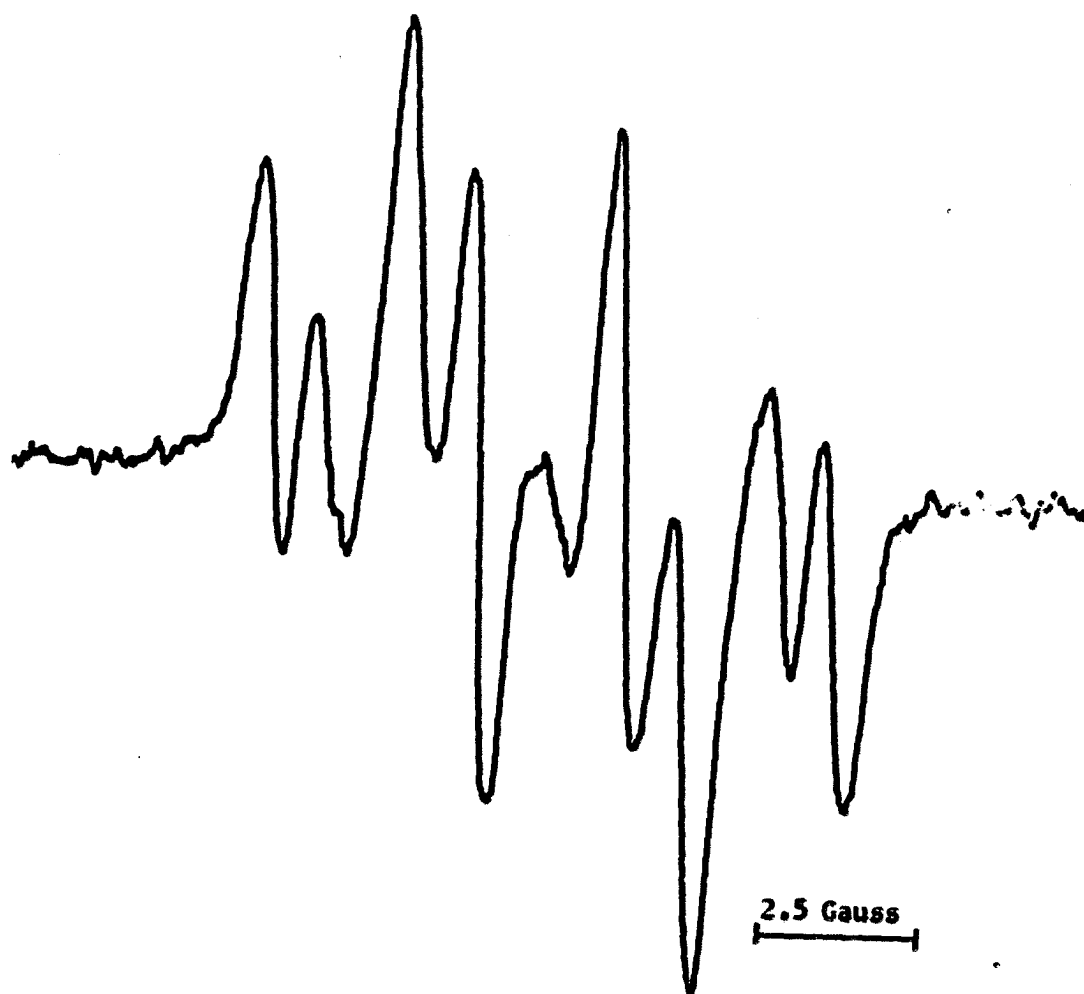
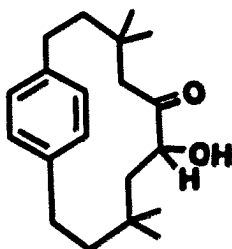


Figure 37. First derivative ESR spectrum assigned to the E-semidione corresponding to 25a at 298 K

(Figure 38a). Cooling to 253 K led to the appearance of a well-defined triplet of triplets spectrum expected for a Z-semidione at low temperatures ( $a_1^H = 5.5$  G [2 H's],  $a_2^H = 1.5$  G [2 H's]) Figure 38b), while heating above 298 K resulted in the approach of binomial intensities in a pentet, indicating near complete equilibration of the  $\alpha$ -hydrogen atoms. Conformation motion in the E- and Z-semidiones derived from 25e thus closely mimicks that in the  $C_{11}$  and  $C_{12}$  polymethylene carbocycles previously studied.

The effects of geminal substitution at the carbon atoms  $\beta$  to the semidione moiety on conformation motion in cyclic semidiones were briefly investigated via the radical ions derived from 25e.



25e

Reaction of 25e with potassium tert-butoxide in deaerated  $D_6$ SO gave rise to a spectrum showing hyperfine coupling from two sets of two equivalent hydrogen atoms ( $a^H = 6.25$  G [2 H's],  $a^H = 13.75$  G [2 H's])  $g = 2.00488$ , Figure 39). The triplet of triplets splitting in

**Figure 38.** First derivative ESR spectra of the Z-semidione  
derived from 25a  
(a) 298 K  
(b) 263 K  
(c) 363 K

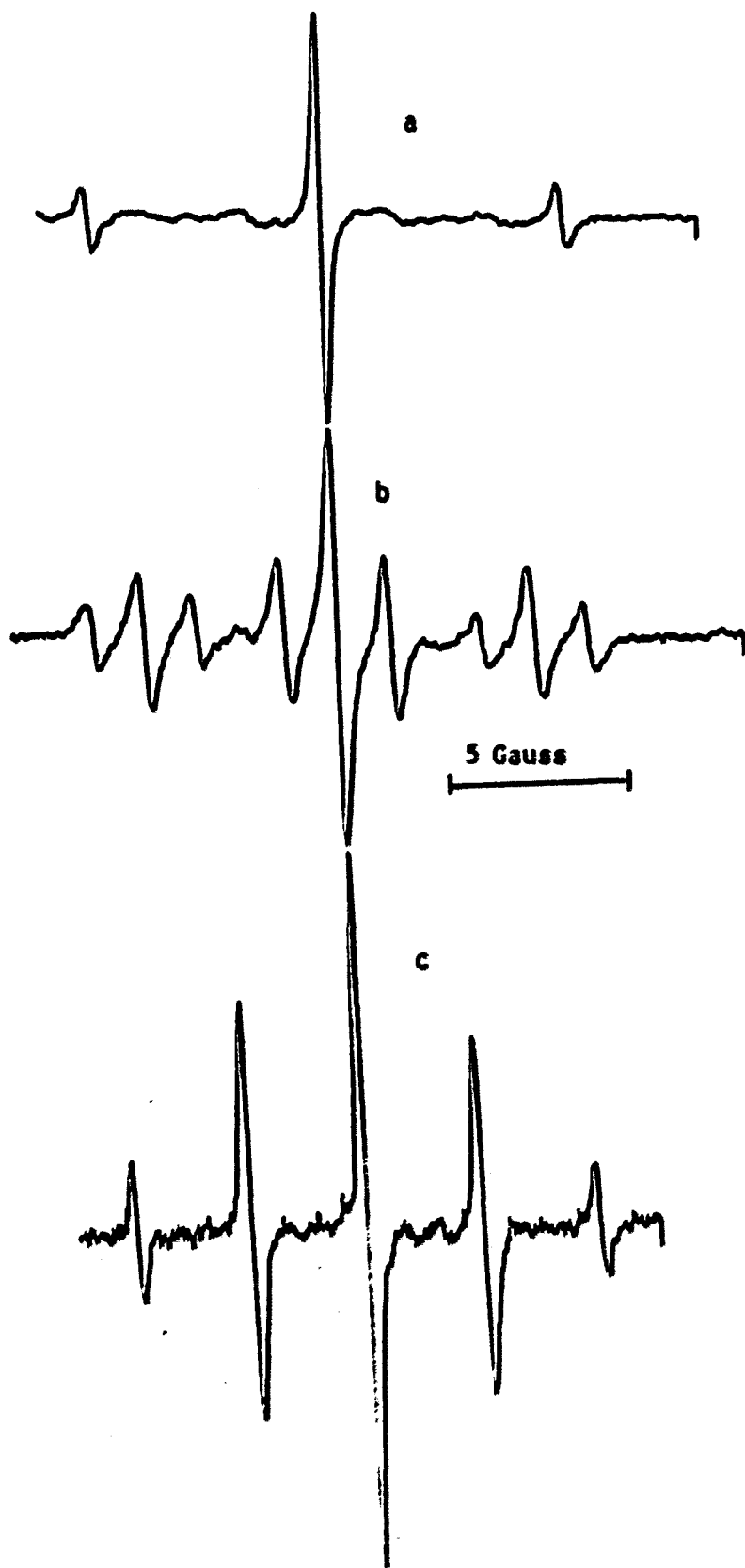




Figure 39. First derivative ESR spectrum of the z-semidione from 25e at 298 K



Figure 39 remained essentially unchanged between 253 and 373 K, and upon addition of excess quantities of KI or [2.2.2]-cryptand. These observations, coupled with the form of the spectrum, collectively indicate a semidione with the Z configuration. The lack of conformational motion time averaging the  $\alpha$ -methylene groups is in keeping with the serious steric interactions that such a motion would provoke. Absence of the E-isomer may also be ascribed to severe non-bonded interactions in the semidione. Examination of molecular models substantiates this premise.

### C. Conclusion

Conformational motion in cyclic E- and Z-1,2-semidiones derived from acyloins 25a-d has been investigated by ESR spectroscopy. Variable temperature spectra obtained for the E-semidione upon disproportionation of 25a revealed an extremely rigid, asymmetric conformation, similar to that observed in the medium-sized  $C_{11}$  and  $C_{12}$  polymethylene carbocycles previously studied.

The E-semidione derived from 25b was found to be considerably more flexible, since equilibration due to rocking motion (resulting in a well-defined triplet of triplets) was found to occur at subambient temperatures. Upon further heating, the ESR spectra were consistent with the onset of internal rotation in the cyclic E-semidione. At 378 K, this process (which time averages all four  $\alpha$ -hydrogens) was found to be intermediate-rapid on the ESR time scale, resulting in a near binomial pentet.

At low temperatures, the E-semidiones corresponding to the macrocycles 25c and 25d gave rise to spectra due to frozen, asymmetric structures of the type 1a-1d. Warming resulted in selective line broadening to give a 1:4:1 triplet, which coalesced into a binomial pentet at high temperature. The absence of a well-defined triplet of triplets splitting in these variable temperature spectra has been attributed to the near equivalence of the energy barriers for rocking motion and internal rotation in the semidiones.

Conformational motion equilibrating the  $\alpha$ -hydrogen atoms in the Z-semidiones derived from 25b-d was found to occur less readily than in some of the lower homologs studied. The low temperature conformations of these species could not be studied, due to loss of ESR signal intensity upon cooling, an occurrence that has been ascribed to disproportionation of the radical ions.

## IV. CONCLUSION TO PART II

The principal objectives of this investigation included those of acquiring high quality ESR spectra of macrocyclic Z-semidiones, of gaining a better understanding of the preferred low temperature conformation in cyclic E-semidiones, and most importantly, of clearly determining the feasibility of internal rotation in cyclic E-semidiones. These objectives have been met.

ESR spectra of macrocyclic Z-semidiones derived from 24 and 25b-d further substantiate previous observations that the rate of conformational motion equilibrating the  $\alpha$ -hydrogens need not be commensurate with ring size. An increase in the ring size results in a lower  $\Delta H^\ddagger$ , but also has the consequence of introducing configurational pathways of low probability involving rotations among the single bonds in the ring in a rigid time sequence.

ESR spectra recorded at low temperature for E-semidiones derived from 24 and 25b-d are consistent with conformations of the type 1a-1d. This conformational preference has been attributed to enhanced solvation in the asymmetric structure.

At modest temperatures, the ESR spectra of E-semidiones corresponding to 24 and 25b-d display selective line broadening due to a process involving rotation of the semidione moiety through the cavity of the carbocycle. In the case of the E-semidione derived from 25d, complete equilibration of the  $\alpha$ -hydrogen atoms indicates that internal rotation in the macrocycle is rapid on the ESR time scale at 378 K.

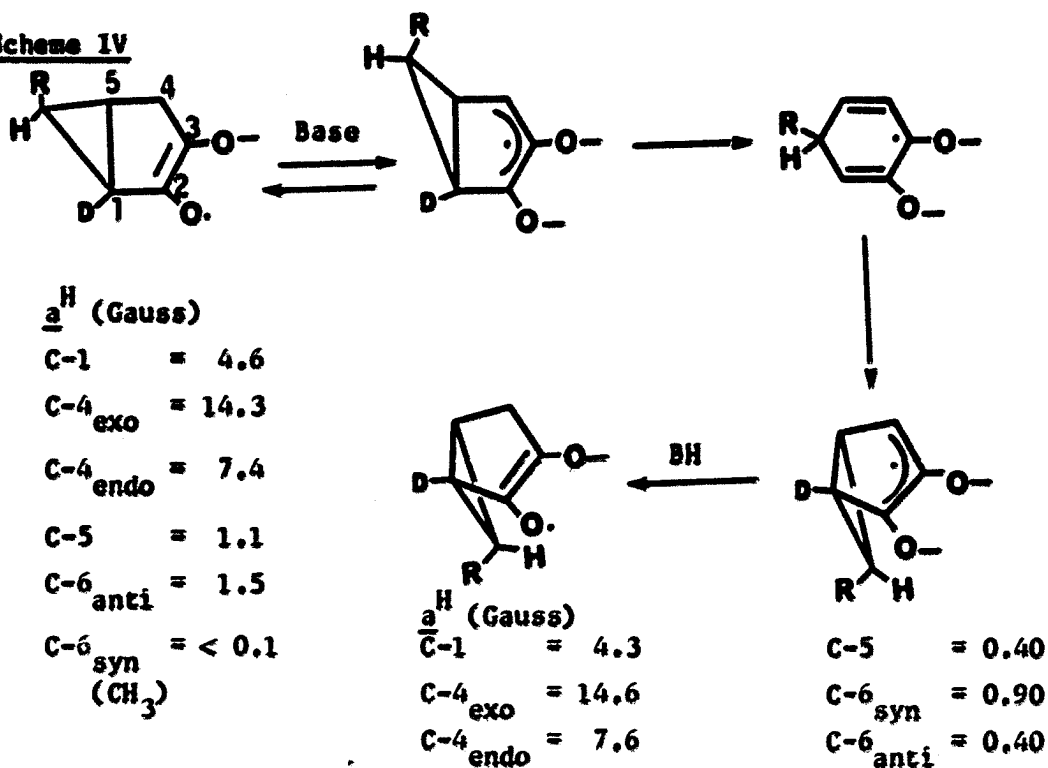
**PART III. MOLECULAR REARRANGEMENTS IN 1,4- AND 1,2-SEMIDIONES**

I. INTRODUCTION TO VALENCE ISOMERIZATION STUDIES OF SOME BICYCLIC AND TRICYCLIC SEMIDIONES

Valence isomerizations involve molecular rearrangements which occur without migration of atoms or groups of atoms [67]. In instances where this process is dynamic, the term valence tautomerism is often employed [68]. The phenomenon continues to be of considerable interest, and has been reviewed [69,70].

The first example of valence isomerization in an aliphatic semidione was encountered fortuitously in an investigation of the long range hyperfine splitting in bicyclo[3.1.0]hexane-2,3-semidione, [71] Scheme IV.

Scheme IV

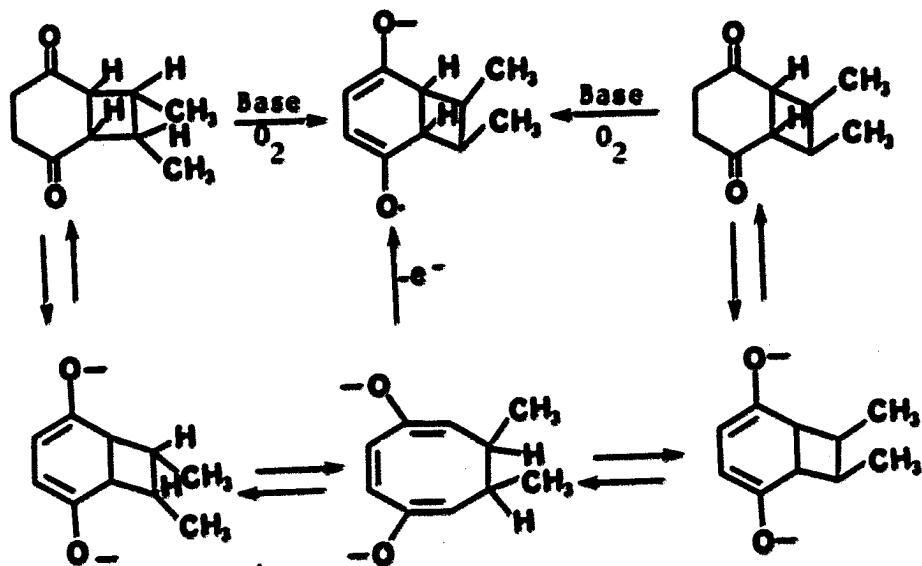


The rearrangement in Scheme IV was found to be strongly dependent upon the concentration and strength of the base, in addition to requiring a steric driving force at 298 K, since the isomerization was not observed

when  $R=D$ , and occurred more rapidly when  $R=C_2H_5$  than when  $R=CH_3$ . In the case of  $R=CH_3$ , the rearrangement proceeded to completion, driven presumably by the thermodynamic preference for the anti methyl group at C-6. These observations prompted further investigations into similar bicyclic-monocyclic equilibria in systems analogous to the classical cycloheptatriene-norcaradiene and cyclooctatetraene-bicyclo[4.2.0]octatriene systems.

The generation of 2,5-semidiones in the bicyclo[4.2.0]octane system was accomplished via base-catalyzed oxidation of two isomeric, saturated diones [72]. Reaction of both isomers led to the same semidione, possibly due to valence isomerization at the dianion stage (Scheme V).

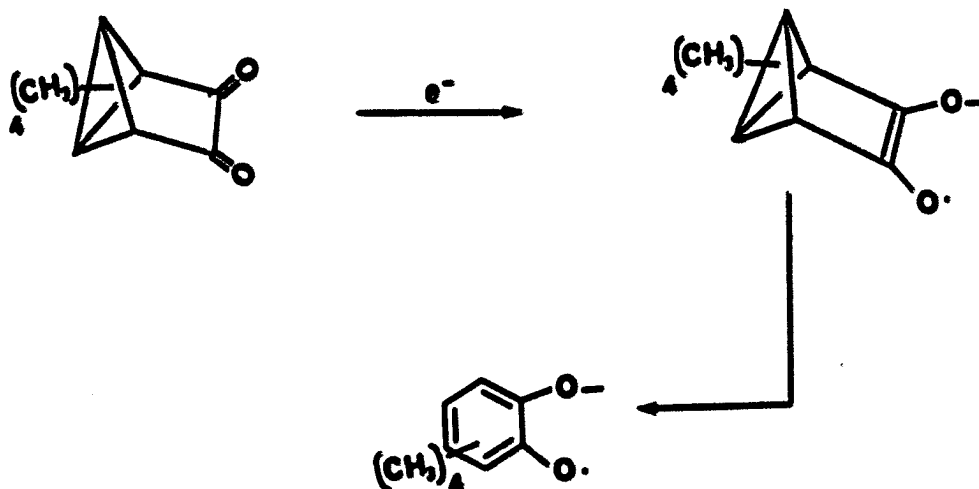
Scheme V



Molecular rearrangement in 1,2-semidiones derived from  $(CH)_6$

hydrocarbons was investigated via the reduction of the benzvalene derivative [72] in Scheme VI.

Scheme VI

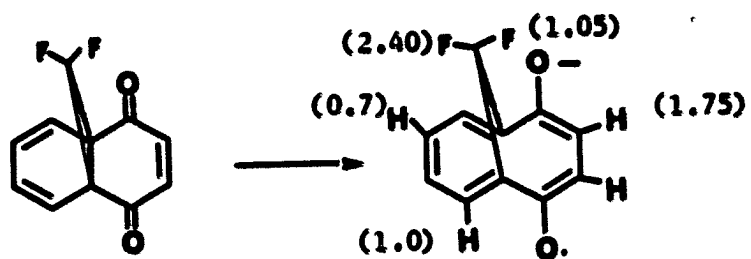
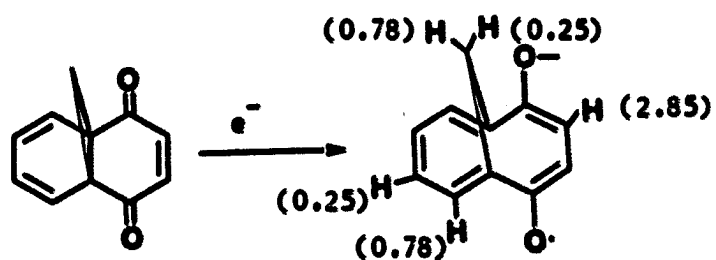


Electrolytic reduction of the stable dione at 235 K gave a broad, unresolved singlet, possibly due to the unrearranged 1,2-semidione. This radical ion was found to be quite unstable, and disappeared immediately upon cessation of electrolysis. At 298 K, electrolysis of the dione produced only the o-benzosemiquinone. Thus, valence isomerization in this system occurs readily at ambient temperatures.

Treatment of the tricyclic diketones in Scheme VII with mild reducing agents such as propiophenone enolate resulted in paramagnetic species with extensive hyperfine structure [73,74]. The splitting pattern in these species is consistent with the ring opened bicyclic

semiquinone wherein the unpaired electron has been extensively delocalized into the entire pi framework.

$s^H$  in G

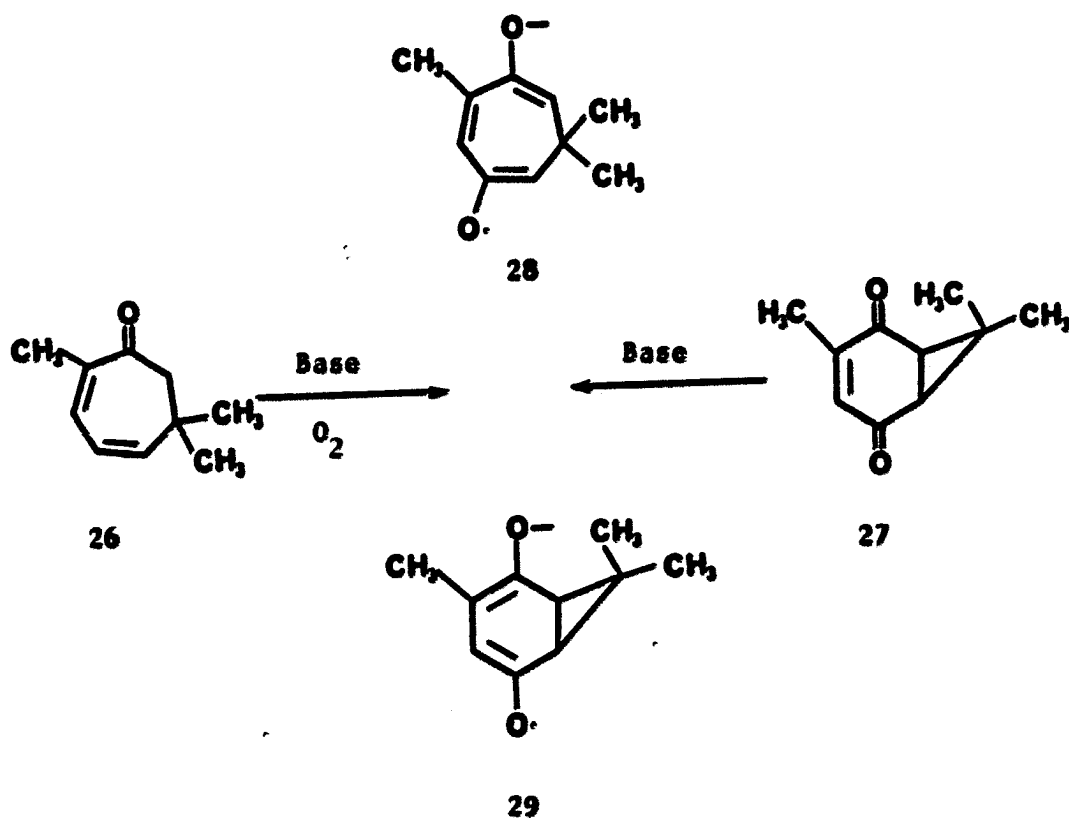




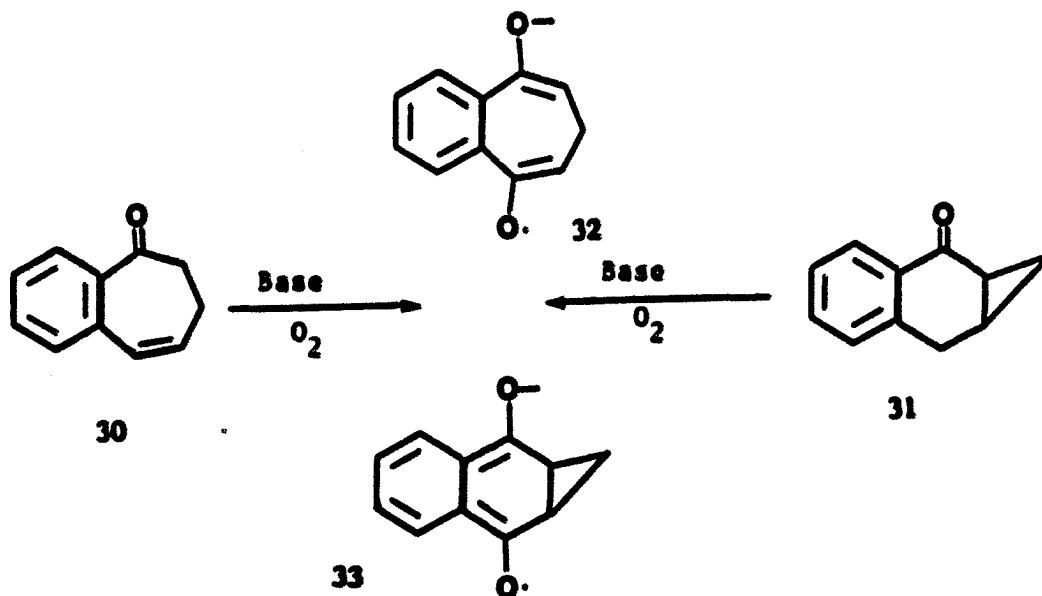
## II. DERIVATIVES OF BICYCLO[4.1.0]HEPTANESEMIDIONE

## A. Introduction

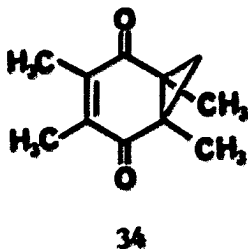
The possibility of molecular rearrangement in paramagnetic analogues of the cycloheptatriene-norceradiene equilibrium has been investigated via the reduction of bicyclo[4.1.0]heptane-2,5-dione derivatives. Reaction of eucervone 26, with base, followed by a trace of oxygen, and treatment of 27 with potassium tert-butoxide in DMSO resulted in the same semidione, having the possible structure 28 or 29 [75].

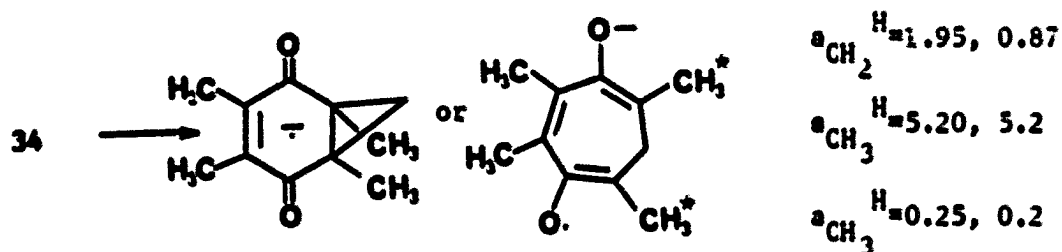


Analogously, reaction of 30 and 31 with base followed by a trace of oxygen resulted in a semidione that could have the structure 32 or 33.

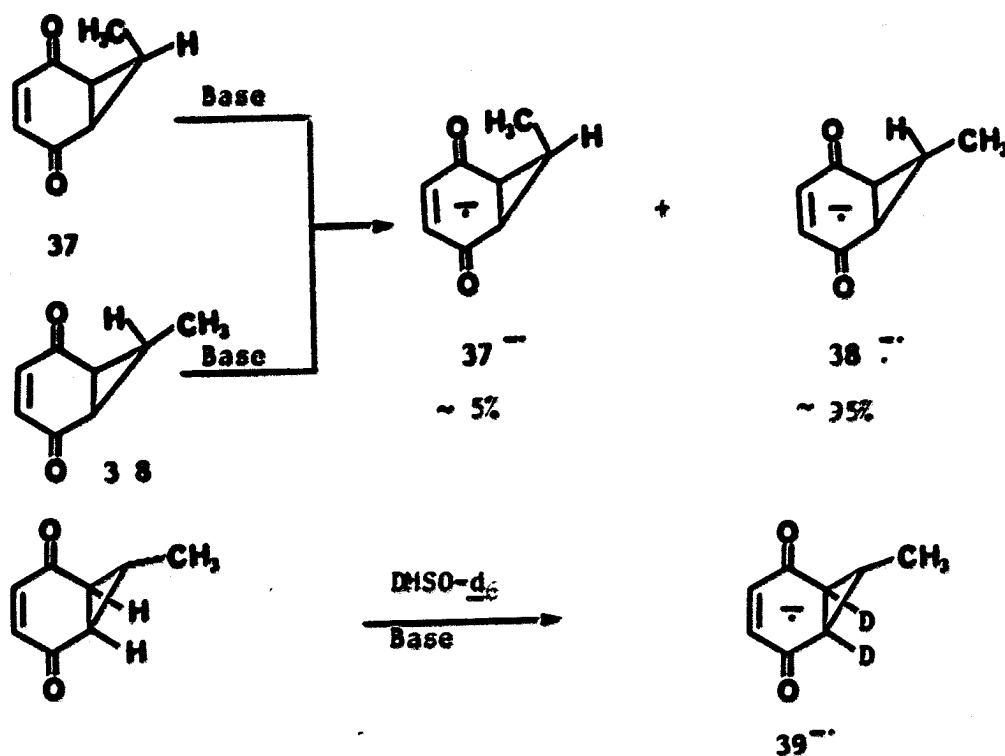


Magnetic nonequivalence of the methylene hydrogens in 32 or 33 or of the gem-dimethyl groups in 28 or 29 is more consistent with the structure 29 and 33. Further evidence for the bicyclic structure was furnished upon reduction of dione 34, since the monocyclic structure requires the value of  $a_{\text{CH}_2}^{\text{H}}$  and  $a_{\text{CH}_3}^{\text{H}}$  be roughly equivalent because hyperconjugation of the methylene and starred methyl hydrogens is expected to be near equal. The large difference in  $a_{\text{CH}_2}^{\text{H}}$  and  $a_{\text{CH}_3}^{\text{H}}$  thus demands the bicyclic structure [73].

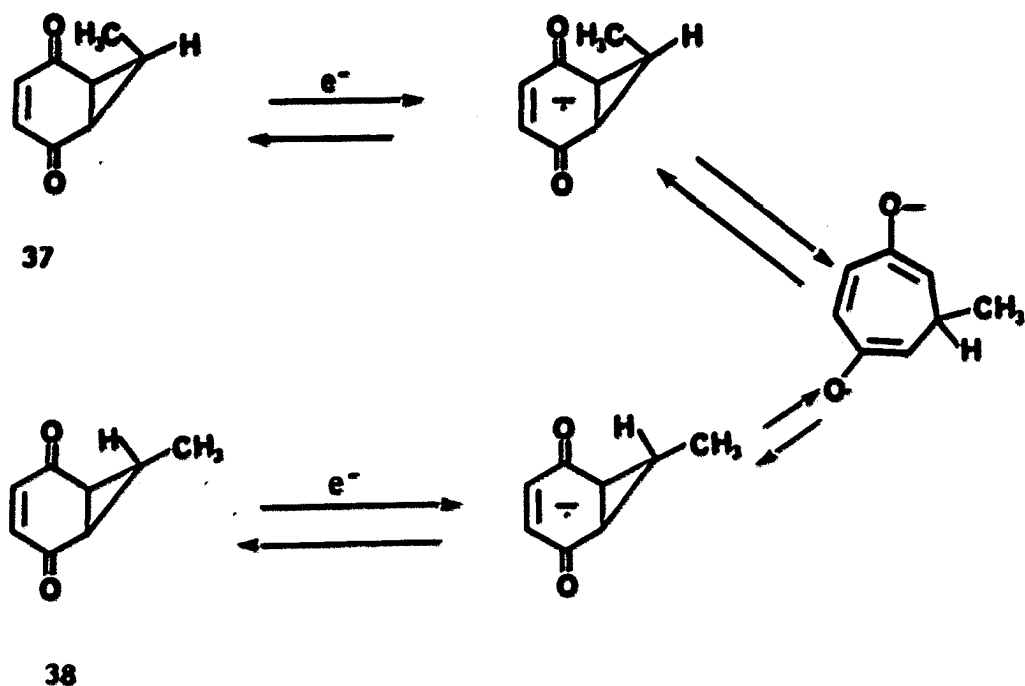




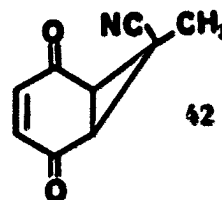
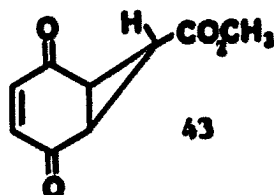
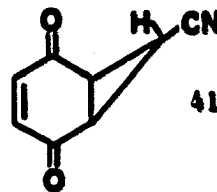
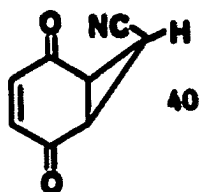
Reaction with potassium tert-butoxide in DMSO of syn- or anti-7-methyl derivatives of bicyclo[4.1.0]hepta-2,5-diones (37 or 38, respectively) resulted in the same mixture of ~5% of 37<sup>-</sup> and ~95% of 38<sup>-</sup>. The results are indicative of interconversion at the radical ion, dianion or enolate dianion steps. Evidence for ionization of the bridgehead protons to give enolate anions was provided by the observation that in basic DMSO-d<sub>6</sub>, 37 gave the semidione 39<sup>-</sup> [74].



Electrolytic reduction of the anti-7-methyl dione 38 led to a strong ESR signal due exclusively to the anti-semidione 38<sup>-•</sup>. Upon cessation of electrolysis, the strength of the ESR signal decreased to reveal additional hyperfine due to approximately 4% of the syn-semidione. Electrolysis for a brief period of the syn-dione 37 resulted in the spectrum due only to the semidione 37<sup>-•</sup>. However, the final spectrum upon extensive electrolysis of 37 was clearly that of the anti-semidione 38<sup>-•</sup>, with a few percent of the syn isomer. These observations are consistent with valence isomerization involving the equilibrium 37<sup>-•</sup>  $\rightleftharpoons$  39<sup>-•</sup>  $\rightleftharpoons$  38<sup>-•</sup>, together with rapid electron transfer between the diones and semidiones, although it is also possible that the syn-anti interconversion involves the dianion species 37<sup>2-</sup>  $\rightleftharpoons$  39<sup>2-</sup>  $\rightleftharpoons$  38<sup>2-</sup> [74].



The present study was initiated with the purpose of further investigating the possibility of valence isomerization in 7-substituted bicyclo[4.1.0]hepta-2,5-semidiones. It was hoped that the radical ions derived from 40-43 [76,77] would extend upon the array of known paramagnetic analogues to the norcaradiene-cycloheptatriene equilibrium.

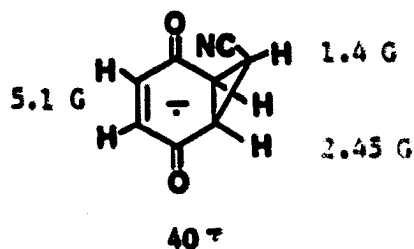
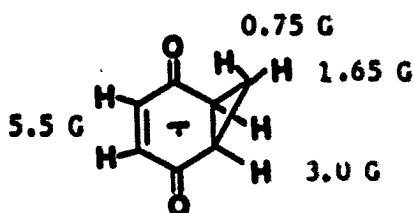


### B. Results and Discussion

Electrolytic reduction of *syn*-7-cyanobicyclo[4.1.0]hept-3-ene-2,5-dione 40, in  $\text{CH}_3\text{CN}$  solution at a Hg pool with TBAP as supporting electrolyte resulted in the well resolved ESR spectrum of Figure 40 ( $a^{\text{H}} = 5.1 \text{ G}$  [2 H's],  $a^{\text{H}} = 2.45 \text{ G}$  [2 H's],  $a^{\text{H}} = 1.4 \text{ G}$  [1 H]). Assignment of hyperfine coupling constants in the unrearranged *syn* semidione could be made without difficulty in view of the established splitting constants in the unsubstituted system.

Figure 40. First derivative ESR spectrum of syn-7-cyanobicyclo[4.1.0]hept-3-ene-2,5-dione radical anion, 40°





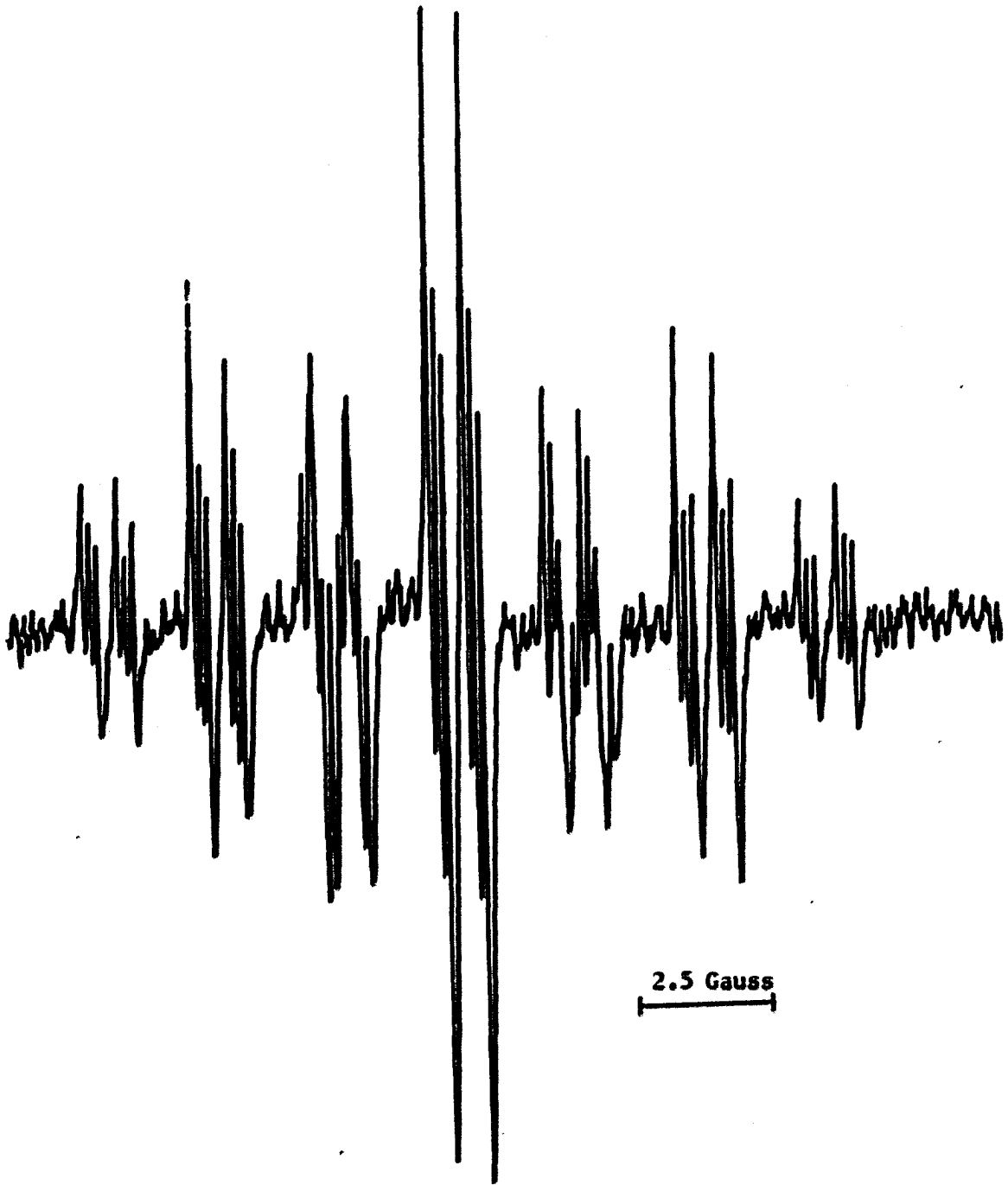
Prolonged reduction at higher potentials led to no significant change in the ESR spectrum, except for diminishing signal intensity, due possibly to depletion of the starting quinone. Cessation of electrolysis and introduction of oxygen followed by continued reduction, once again resulted only in the spectrum for the syn semidione. No signal could be observed in the absence of continued electrolysis.

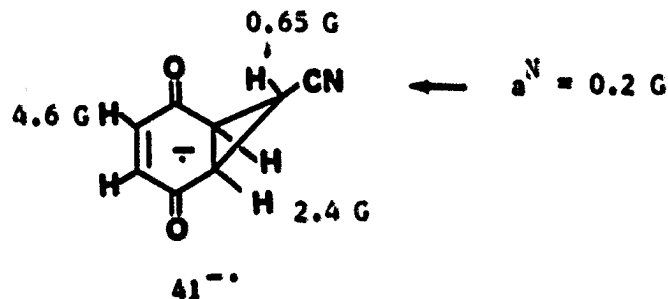
Reaction of dione 40 with potassium tert-butoxide in DMSO resulted in a poorly resolved signal due to the syn isomer. The spectrum remained unchanged over the period of thirty minutes that the signal could be observed. At no time during the chemical or electrolytic reduction of 40 was there any evidence for a long lived paramagnetic species other than the bicyclic syn semidione  $40^{\cdot-}$ .

Electrolytic reduction of anti-7-cyanobicyclo[4.1.0]hept-3-ene-2,5-dione 41, in DMF solution at a Pt electrode with TBAP as supporting electrolyte gave rise to an excellent ESR spectrum ( $a^H = 4.6$  G [2 H's],  $a^H = 2.4$  G [2 H's],  $a^H = 0.65$  G [1 H],  $a^N = 0.2$  G [1 N], Figure 41). Hyperfine splitting constants in this species were found to be consistent with the unrearranged anti semidione,  $41^{\cdot-}$ .



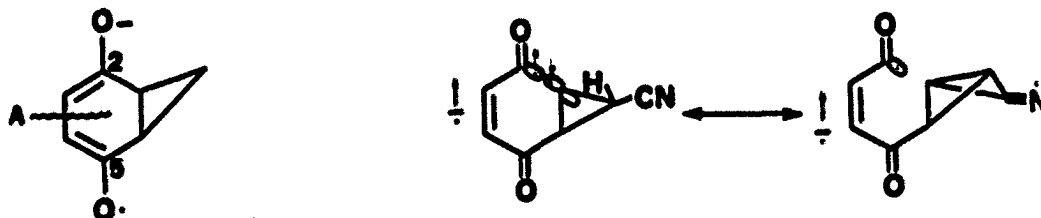
**Figure 41. First derivative ESR spectrum of anti-7-cyanobicyclo [4.1.0]hept-3-ene-2,5-dione radical anion, 41<sup>-•</sup>**



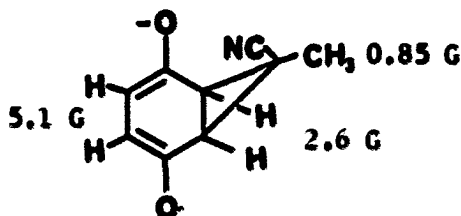


The signal due to 41<sup>-•</sup> remained unchanged upon prolonged reduction, but disappeared immediately upon cessation of electrolysis. Recharging the solution produced the previously observed spectrum for the anti isomer. Chemical reduction of 41 with potassium tert-butoxide in DMSO resulted in a weak and fleeting signal which could not be recorded in its entirety. The behavior of dione 41 upon reduction is thus in keeping with the properties of the syn semidione 40<sup>-•</sup>, which showed no perceptible propensity for rearrangement.

The long range nitrogen hyperfine coupling observed in 41<sup>-•</sup> is remarkable since the singly occupied molecular orbitals in semidiones derived from bicyclo[4.1.0]hept-3-ene-2,5-diones are anti symmetric with respect to the plane bisecting the cyclopropyl ring. The opposite signs of the coefficients at C-2 and C-5 in  $\psi_4$  prevents a homohyperconjugative interaction delocalizing unpaired spin into the cyclopropyl methylene position, because such an interaction takes the form  $a^H = Q(c_2 + c_5)^2$ . The observation of nitrogen hyperfine from the 7-position in 41<sup>-•</sup> thus requires a spin polarization mechanism to introduce unpaired spin from the pi system into the sigma framework. This mechanism allows transmittal of spin density to the 7-position, as the interaction assumes the form  $a^H = Q(c_2^2 + c_5^2)$ .



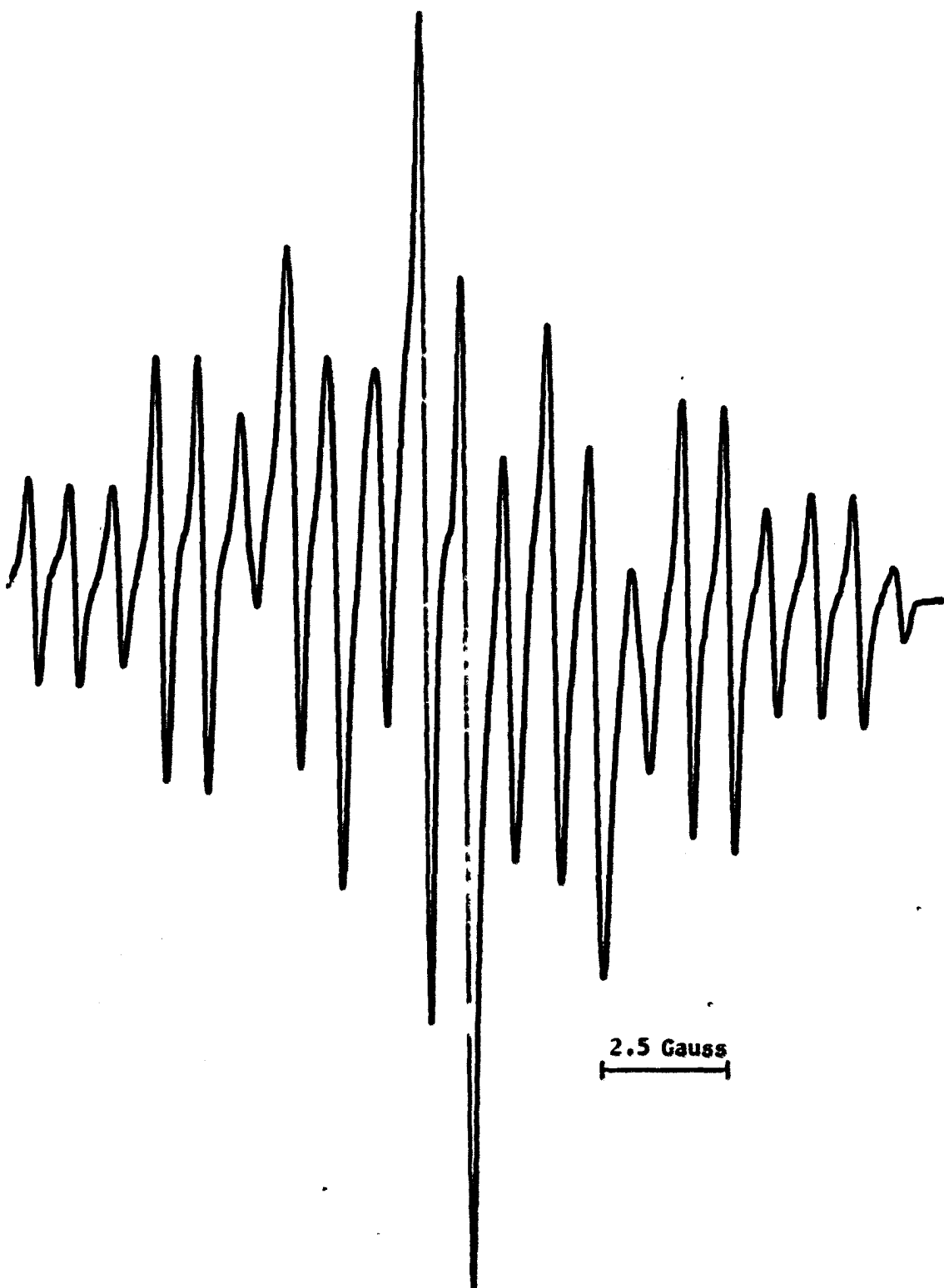
Electrolytic reduction of *syn*-7-cyanomethylbicyclo[4.1.0]hept-3-ene-2,5-dione **42** at a Hg pool in DMSO solution with TBAP as supporting electrolyte resulted in the ESR spectrum of Figure 42 ( $a^H = 5.1$  G [2 H's],  $a^H = 2.6$  G [2 H's],  $a^H = 0.85$  G [3 H's]).

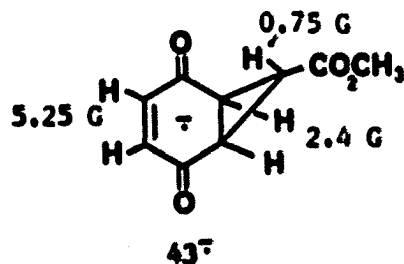
42<sup>r</sup>

The signal due to the unrearranged semidione underwent loss of resolution upon extensive reduction, but the spectrum showed no evidence for the appearance of a second species. A weak and unresolved signal persisted for several minutes after cessation of electrolysis.

Electrolytic reduction of *anti*-7-carbomethoxybicyclo[4.1.0]hept-3-ene-2,5-dione, **43** at a Pt electrode in DMF solution with TBAP as supporting electrolyte gave rise to the ESR spectrum of Figure 43 ( $a^H = 5.25$  G [2 H's],  $a^H = 2.4$  G [2 H's],  $a^H = 0.75$  G [1 H]).

Figure 42. First derivative ESR spectrum of syn-7-cyanomethylbicyclo  
[4.1.0]hept-3-ene-2,5-dione radical anion, 42°





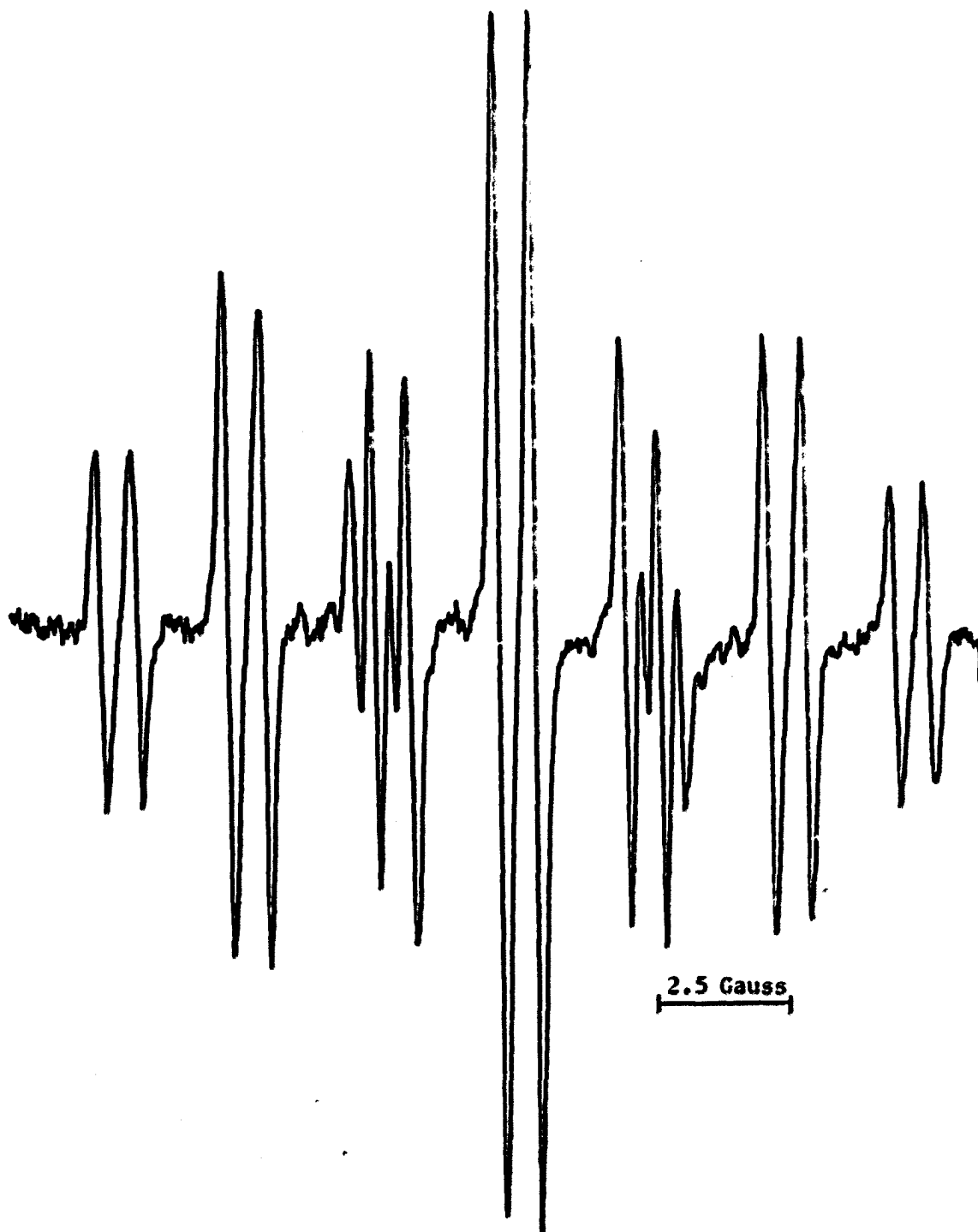
The signal due to the semidione 43<sup>•-</sup> weakened upon prolonged reduction, and disappeared upon cessation of electrolysis. No evidence for rearranged paramagnetic products could be found.

Thus, in contrast to the observed behavior of reduced syn- and anti-methyl derivatives 37<sup>n-</sup> and 38<sup>n-</sup>, close examination of ESR spectra reveal no detectable isomerization upon chemical or electrolytic reduction of diones 40-43.

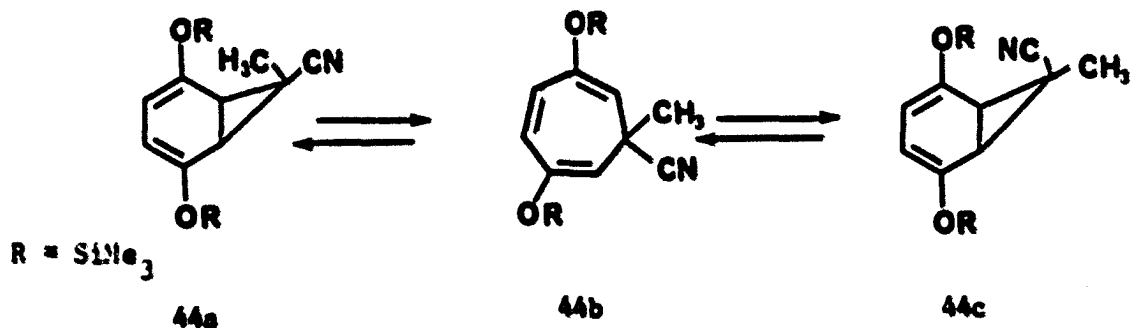
Possible cause for the absence of rearranged paramagnetic species may be found in the reduced lifetime of the bicyclic semidione, once formed. Rapid decay (to diamagnetic products) of the radical anion would preclude valence isomerization, or further reduction to the dianion stage possibly requisite for rearrangement. An observation in support of this hypothesis is that no stable paramagnetic species could be detected in the absence of continuous reduction. Alternatively, rapid destruction to non-radical products of the ring opened cycloheptatriene radical ion or dianion would prevent reclosure to the isomeric species. A third rationalization invokes unusual stability of the cyclopropyl moiety to ring opening in the semidione or dianion. That the resistance to valence isomerization is conferred upon by the presence of electronegative substituents at the 7-position is viewed as unlikely in light of the

Figure 43. First derivative ESR spectrum of anti-7-carboethoxybicyclo [4.1.0]hept-3-ene-2,5-dione radical anion, 43<sup>-•</sup>.





rapid equilibrium observed in the (bis)-trimethylsiloxy derivative 44a, [76] and in view of the long established fact that an equilibrium favoring the norcaradiene structure requires the presence of two electron-withdrawing substituents at the 7-position [78-80].



### C. Conclusion

ESR spectra of paramagnetic species produced upon reduction of diones 40-43 have been recorded. Hyperfine coupling constants in these radical anions are consistent with a bicyclic structure in a norcaradiene/cycloheptatriene ratio of greater than ten. The ESR spectrum of anti-7-cyano derivative  $41^{\cdot-}$  showed hyperfine coupling of the unpaired electron to the  $^{14}\text{N}$  nucleus. This unexpected interaction has been ascribed to a spin polarization mechanism of spin propagation from the pi system to the sigma framework.

Close examination of the ESR spectra revealed no rearrangement products in the reduction of 40-43. This observation is consistent with rapid destruction of the radical ions, once formed.

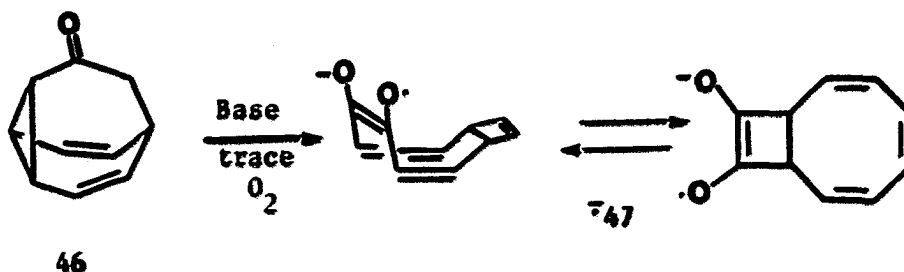
## III. BULLVALENE SEMIDIONE

## A. Introduction

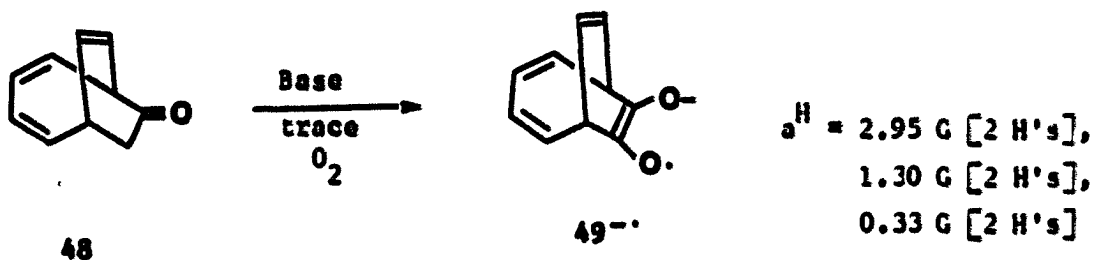
Dynamic valence isomerism in the theoretically interesting  $(\text{CH})_{10}$  hydrocarbon, tricyclo[3.3.2.0<sup>2,8</sup>]deca-3,6,9-triene [81] (commonly known as "bullvalene") has been established by N.M.R. spectroscopy and is well-documented [82,83]. That such fluxional behavior may be present and detectable by ESR spectroscopy in paramagnetic analogues prompted extensive efforts to generate the spin label 45<sup>±</sup>.

45<sup>±</sup>

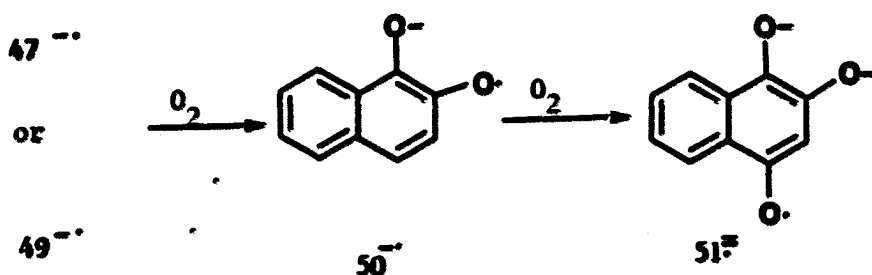
Reaction of ketone 46 with potassium tert-butoxide in DMSO in the presence of limited quantities of molecular oxygen gave rise to an ESR signal due possibly to the rearranged semidione 47<sup>±</sup> [72].



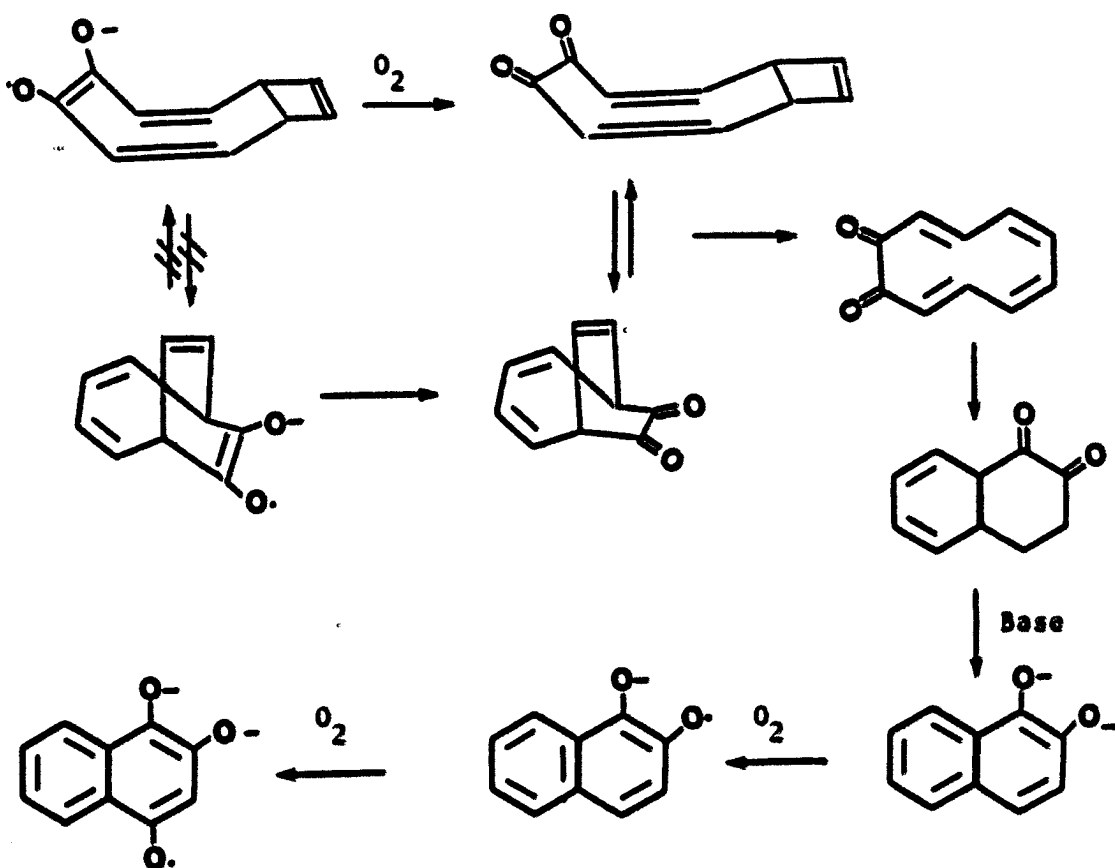
Treatment of the isomeric ketone 48 with basic DMSO in the presence of trace amounts of oxygen resulted in the corresponding semidione 49<sup>-•</sup> [72].



No evidence for interconversion between 47<sup>-•</sup> and 49<sup>-•</sup> could be found. However, further exposure of either 47<sup>-•</sup> or 49<sup>-•</sup> to molecular oxygen led to the same semiquinone 50<sup>-•</sup>, which upon continued contact with oxygen underwent further oxidation to the stable dianion radical 51<sup>2-•</sup>.



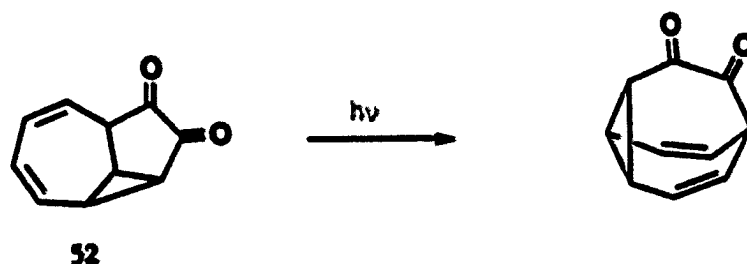
A mechanism consistent with all the experimental data, and one involving molecular rearrangement of the free diones was thus proposed [72]:



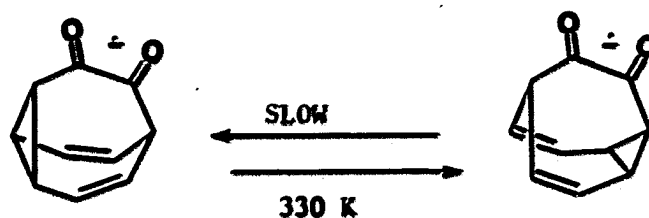
## B. Results and Discussion

Attempts to generate bullvalene semidione from 46 or the corresponding  $\alpha$ -acetoxy ketone failed due to the predominance of competing rearrangements [84]. Successful generation of 45<sup>-</sup> thus appeared contingent upon the availability of a specific precursor requiring less stringent conditions for reduction. Access to such a precursor, tricyclo[3.3.2.0<sup>2,8</sup>]deca-6,9-diene-3,4,-dione "Bullvalenedione" 45, a fluxional molecule on the NMR time scale (with  $E_a \approx 12$  Kcal mol<sup>-1</sup>, Log A = 10.8 for the degenerate Cope rearrangement calculated between 260-400 K) was made possible via a

novel photochemical transformation of the fused homotroplidene 52 [85].



Electrolytic reduction of bullvalenedione 52 at a Hg pool with TBAP as supporting electrolyte in DMSO resulted in a well-resolved spectrum ( $a_1^H = 0.63$  G [2 H's],  $a_2^H = 0.36$  G [2 H's],  $a_3^H = 0.08$  G [1 H], and occasionally an additional doublet splitting  $a_4^H = 0.05$  G [1 H], Figure 44). No signal could be observed in the absence of electrolysis. Although the hyperfine coupling constants in the spectrum of Figure 44 could not be assigned with certainty, the multiplicity and magnitude of the splittings are strongly indicative of the unrearranged bullvalene semidione structure 45<sup>-</sup>. Consideration of the hyperfine splitting constants reveals the radical anion as a frozen, non-interconverting species at 298 K. Efforts to promote and detect fluxional behavior in the semidione by observation at elevated temperatures failed due to rapid decay of the ESR signal above 330 K.



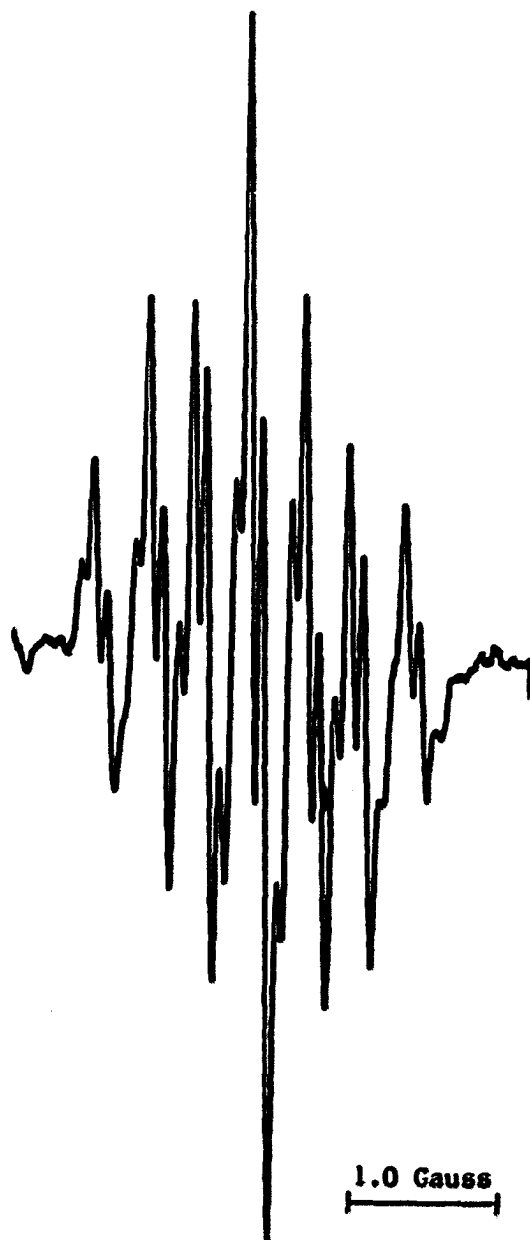
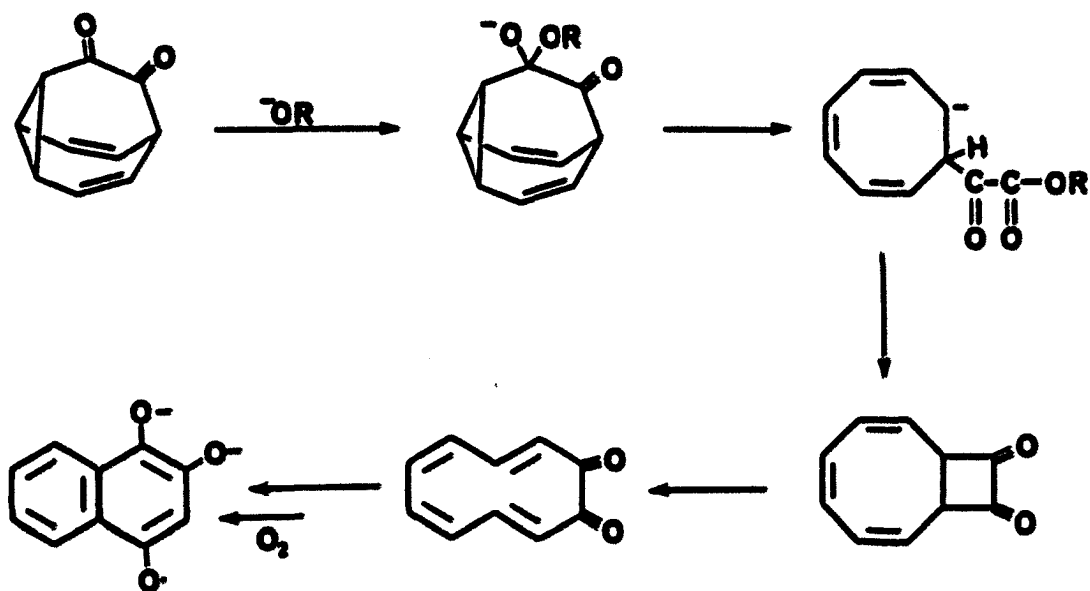


Figure 44. First derivative ESR spectrum of Bullvalene semidione,  
45°

Reaction of dione 45 with potassium tert-butoxide in DMSO gave no observable signal. However, upon addition of oxygen, a weak signal due to the semiquinone  $51^{\cdot-}$  appeared. A possible pathway for the formation of  $51^{\cdot-}$  is given below:



Unsuccessful previous attempts to generate  $45^{\cdot-}$  thus appear explicable in terms of the poor stability of dione 45 in basic media.

### C. Conclusion

Electrolytic reduction of bullvalenedione resulted in an ESR spectrum due to a species believed to be the unrearranged bullvalene semidione  $45^{\cdot-}$ . Inspection of the hyperfine coupling constants obtained at 298 K revealed a non-fluxional radical ion, with no indication of change in the essential features of the spectrum at the highest attainable temperature of 330 K. This result clearly establishes



an upper limit of  $\leq 10^7 \text{ sec}^{-1}$  at 330 K for the rate constant of the degenerate Cope rearrangement in bullvalene semidione,  $45^\circ$ .

## IV. CONCLUSION TO PART III

The investigations described in Part III of this dissertation were undertaken with the intention of further expanding the number of known examples of paramagnetic analogues to the norcaradiene-cycloheptatriene equilibrium. Radical ions generated from the bicyclic diones 40-43 failed to serve as such analogues, possibly due to limited stability of the paramagnetic ions, once formed. The primary objectives of this study thus remain largely unrealized.

Hyperfine coupling constants in bullvalene semidione indicate a non-fluxional ion at 330 K. Degenerate valence isomerization in the semidione is thus slow on the ESR time scale at modest temperatures, a conclusion consistent with the properties of the parent dione (assuming a similar propensity for rearrangement in dione and semidione) for which a rate constant of  $2.93 \times 10^2 \text{ sec}^{-1}$  for the degenerate Cope rearrangement was calculated at 330 K.

## EXPERIMENTAL

## Reagents

Dimethyl sulfoxide (DMSO) was distilled from  $\text{CaH}_2$  at reduced pressure and stored over molecular sieves. N,N-Dimethylformamide (DMF) was distilled from  $\text{CaH}_2$ . Acetonitrile ( $\text{CH}_3\text{CN}$ ) was distilled from  $\text{P}_2\text{O}_5$ . Potassium tert-butoxide, [2.2.2]-cryptand and potassium iodide were obtained commercially and used directly without further purification.

## Preparation of Semidiones and Semiquinones

Fused silica flat cells with inverted U-type mixing chambers were used for the generation of radical anions under static conditions by methods previously described [86].

Electrolytic reductions were carried out in fused silica flat cells with a platinum anode and a mercury pool extending into the cell window as the cathode. Occasionally, a platinum spoon was employed as the cathode. Deoxygenation of electrolytic solutions was accomplished by nitrogen bubbling. A Heathkit L.V. Power Supply Model 1P-27 was used as the current source.

## Recording and Simulation of ESR Spectra

ESR spectra were recorded using either a Varian E-3 spectrometer with a 4-inch magnet and 100 KHz field modulation, or a Bruker ER 200D-SRC with a 10-inch magnet and 100 KHz field modulation. g-values were taken with a Systron Donner Frequency Counter Model 6245A set at 100

Hz resolution and which had been calibrated to better than one part in ten million. Used in conjunction with the frequency counter was an ER035 NMR Gaussmeter with an auto-lock self-tracking proton NMR field measuring device providing direct 7-digit readout. Prior to each g-value determination, the gaussmeter was calibrated for the difference in absolute field between the sample and the probehead. Perylene radical cation with  $g = 2.002569$  [87,88] was used as a standard, and characteristic shifts ranged between 30-100 mG. NMR lock was maintained during the course of a single experiment to ensure a constant correction factor. Simulation of ESR spectra was executed on an Aspect 2000 computer with an EPRSC.015 software package.

#### Characterization of Compounds

$^1\text{H}$  NMR spectra were recorded on either a Varian EM 360(A,L) or a Hitachi Perkin-Elmer R-20B Spectrometer. Infrared spectra were recorded on a Beckman Acculab 2 Double Beam Spectrometer. Mass spectra were recorded on an AE<sub>1</sub>-MS-902 Spectrometer.

#### Preparation of Compounds

##### 1,4,5,8-Naphthalenatetrone, 22

This compound was synthesized according to the procedure of S. Yoshino et al. [57]:  $^1\text{H}$  NMR ( $d_6$ -DMSO)  $\delta$  6.9 (s).

##### Naphthazarin, 21

This compound was synthesized according to the method of Fieser [89].

1',2'-Bis(2,5-benzoquinonyl)ethane, 18

This compound was prepared by the method of Wegner et al.

[58]: IR (CDCl<sub>3</sub>) 1660 cm<sup>-1</sup>.

2,3,7,8-tetramethyl-1,4,6,9-Thianthrenetetrone, 19

This compound was synthesized using the procedure of Fickentscher

[59]: <sup>1</sup>H NMR (d<sub>6</sub>-DMSO) δ 2.1 (s); IR (nugol) 1645 cm<sup>-1</sup>.

1,4-(5'-Hydroxy-6'-ketodecamethylene)-benzene, 25a

This compound was prepared by the method of Gram and Daeniker [90]:

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0 (s,4), 0.8-3.0 (broad m,18) ppm; IR (neat)  
1720, 3400-3500 cm<sup>-1</sup>.

1,4-(3',3',8',8'-Tetramethyl-5'-hydroxy-6'-ketodecamethylene)-benzene, 25a

This compound was synthesized by the method of Blomquist and Jaffe

[91]: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (s), 2.6-2.8 (m), 1.0-1.7 (m) ppm; IR  
(neat) 1710, 3300-3600 cm<sup>-1</sup>.

Dodecanoyl dichloride

A mixture of 50.0 g (0.22 mol) of dodecanedioic acid (Aldrich) and 119 g (0.59 mol) of thionyl chloride was stirred at 60°C for 8 h.

The mixture was then rapidly distilled using a short path distillation apparatus (170°C, 0.1 mm) to yield pure diacid dichloride: <sup>1</sup>H

NMR (CDCl<sub>3</sub>) δ 2.8 (t,4), 1.0-2.0 (broad m, 16) ppm; IR (neat) 1800 cm<sup>-1</sup>.

2,2' Dodecanoyldicyclohexanone

To a solution of 31.5 g (0.18 mol) of 1-morpholino-1-cyclohexene (Aldrich) and 19.0 g (0.19 mol) freshly distilled triethylamine in 100 ml dry chloroform was added 25.0 g (0.09 mol) dodecanoyldichloride in 40 ml dry chloroform. The mixture was stirred for 3 h, and then hydrolysed with 100 ml 25% hydrochloric acid by heating to reflux for 5 h. The mixture was then cooled to 25°C, the chloroform layer separated and extracted with two 50 ml portions of water. The washings and the aqueous phase were combined, adjusted to a pH of 5-6 with 25% sodium hydroxide solution, and extracted with two 50 ml portions of chloroform. The chloroform layers were combined, dried with sodium sulphate, and removed at reduced pressure, leaving an oil:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.0-2.5 (broad m); IR (neat) 1580-1620  $\text{cm}^{-1}$ .

Disodium 7,18-diketotetracosanedioate

Forty-two g (0.12 mol) of 2,2'-decanoyldicyclohexanone in 100 methanol was added to a solution of 30 g sodium hydroxide in 400 ml of ethanol. The mixture was then heated to reflux for 1 h, cooled to 25°C, and the off-white crystals collected on a Büchner funnel, after washing with cold ethanol:  $^1\text{H NMR}$  ( $d_6$ -DMSO)  $\delta$  1.0-2.5 (broad m); IR (nugol) 3000-3100, 1700  $\text{cm}^{-1}$ .

Tetracosanedioic acid

Ten g (0.02 mol) disodium 7,18-diketotetracosanedioate and 40 ml of triethanolamine were heated to 180°C until all of the salt dissolved. The mixture was cooled to 80°C, and 25 ml (0.45 mol) of 82% hydrazine

hydrate was added through the reflux condenser, and the mixture heated to reflux for 5 h. Thirty g (0.5 mol) of potassium hydroxide dissolved in 100 ml triethanolamine at 100°C was then added to the reaction mixture, and the temperature maintained at 190°C for 6 h. The reaction mixture was cooled to 100°C, washed out with hot water, and acidified to a pH between 2 and 3 with 12 N hydrochloric acid. The mixture was cooled to 25°C, and the precipitated tetracosanedioic acid collected on a Büchner funnel and subsequently dried under vacuum: IR (nugol) 2900-3000, 1710  $\text{cm}^{-1}$ .

#### Tetracosanedioic acid, dimethylester

Two g (5.0 mmol) tetracosanedioic acid, 5 drops concentrated sulphuric acid and 50 ml methanol were heated to reflux for 12 h. The reaction mixture was cooled and introduced into a beaker containing 50 g ice. The aqueous layer was extracted with three 50 ml portions of ether which was dried with sodium sulphate and evaporated under reduced pressure to yield the diester. Recrystallization twice from hexane gave pure diester:  $^1\text{H}$  NMR. ( $\text{CDCl}_3$ )  $\delta$  3.5 (s, 3),  $\delta$  1.0-2.3 (broad m, 22) ppm; IR ( $\text{CDCl}_3$ ) 1730  $\text{cm}^{-1}$ .

#### 1-Hydroxy-2-ketocyclotetracosane

Acyloin condensation of the diester was carried out according to the procedure of Allinger [92]. One g (2.5 mmol) tetracosanedioic acid, dimethyl ester in 100 ml dry xylene was added dropwise over a 24-hour period to a 1.0 g (0.034 mol) sodium dispersion in 150 ml xylene. The mixture was cooled to 0°C, and 10 ml glacial acetic acid in 30 ml

xylene was added dropwise. The xylene layer was separated, washed with two 30 ml portions of water, dried with sodium sulphate and distilled at reduced pressure leaving a yellow oil: IR (neat) 1710, 3450  $\text{cm}^{-1}$ .

1,4-(8'-Hydroxy-9'-ketoheptadecamethylene)-benzene, 25b

This compound was made by a method similar to that for 25a: IR (neat) 3500, 1715  $\text{cm}^{-1}$ .

1,4-(12'-Hydroxy-13'-ketotetracosanemethylene)-benzene, 25d

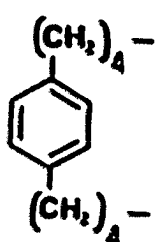
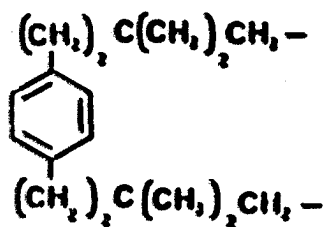
This compound was made by a method similar to that for 25a: IR (neat) 3500, 1715  $\text{cm}^{-1}$ .

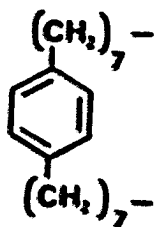
**Structure Proof for Acyloins Employed to Generate Semidiones**

Acyloins 24, 25b, and 5 were used as crude materials while 25a and 25e were Kugelrohr distilled. The observed ESR spectra are taken as proof that the desired acyloin had been formed. Table II describes the physical properties of the purified precursors (diesters) and those properties of the acyloins which were measured. In all cases, IR indicated the presence of the carbonyl and hydroxy functions in the acyloin.



Table II. Physical Properties of Diesters and Acyloins

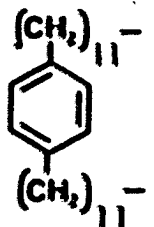
System	System No.	Diester	Acyloin (% yield)
$-(\text{CH}_2)_{12}-$	24	recrystallized twice from hexane and once from methanol; mp 73.5-74.5°C [lit. [93] 74.5-74.8°C] IR, NMR reported in text.	60%, yellow oil; $^1\text{H NMR (CDCl}_3)$ $\delta$ 1.3 (s); IR reported in text.
	25a	bp 160-165°C (0.06 mm) [lit. [90] bp 182-184°C (0.4 mm)]; IR 1740 $\text{cm}^{-1}$ ; $^1\text{H NMR (CDCl}_3)$ $\delta$ 7.1 (s, 4), 3.6 (s, 6), 1.2-2.8 (m, 16).	50%, waxy solid, bp 130-136°C (0.06 mm) [lit. [90] bp 158-161°C (0.4 mm)]; IR (neat) 1720, 3400-3500 $\text{cm}^{-1}$ ; $^1\text{H NMR (CDCl}_3)$ $\delta$ 7.0 (s, 4), 0.8-3.0 (m, 18).
	25e	bp 160-166°C (0.05 mm) [lit. [91] bp 167-177°C (0.08 mm)]; IR (neat) 1745 $\text{cm}^{-1}$ ; $^1\text{H NMR (CDCl}_3)$ $\delta$ 7.1 (s, 4), 3.65 (s, 6), 1.4-2.9 (m, 12), 1.1 (s, 12); mass spectrum, m/e for $\text{H}^+$ = 362.24502; calculated for $\text{C}_{22}\text{H}_{34}\text{O}_4$ , 362.24572.	20%, yellow oil; bp 130-133°C (0.05 mm) [lit. [91] bp 149°C (2 mm)]; material purified by column chromatography with ethyl acetate-hexane (1:1) eluant; $^1\text{H NMR (CDCl}_3)$ $\delta$ 7.1 (s), 2.6-2.8 (m), 10.0-1.7 (m); mass spectrum, m/e for $\text{H}^+$ 302.22398; calculated for $\text{C}_{22}\text{H}_{34}\text{O}_4$ , 302.22459.



**25b**

purified by column chromatography using ether-hexane (1:1) as eluant; mp 30-31°C; IR 1730 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0 (s, 4), 3.6 (s, 6), 1.0-2.8 (m, 28); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.58, 29.38 (3C), 31.85, 34.56, 36.03, 51.66, 128.68, 140.38, 174.36.

10%, yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.9 (s, 4), 1.0-3.0 (m, 30); IR (neat) 3500, 1715 cm<sup>-1</sup>.



**25d**

purified by column chromatography using ethyl acetate-hexane (1:1) as eluant and recrystallized from methanol; mp 65-67°C; IR (CDCl<sub>3</sub>) 1740 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0 (s, 4), 3.5 (s, 6), 1.0-2.8 (m, 44).

30%, yellow gum; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (m), 1.0-2.5 (m); IR (neat) 3500, 1715 cm<sup>-1</sup>.

Yield information for intermediates in the synthesis of 24.

Dodecanedioyl dichloride, 48 g, 83% yield.

2,2' Dodecanedioyldicyclohexanone, 36 g, 85% yield (run twice).

Disodium 7,18-diketotetracosanedioate, 33 g, 56% yield.

Tetracosanedioic acid, 4 g, 50% yield.

Tetracosanedioic acid, dimethylester, 1.8 g, 84% yield.

Additional information for compounds 21, 22, 25c, and 18.

1,4,5,8-Naphthalenetetrone, 22.

Recrystallized from benzene; mp 222-224°C [lit. [57] mp 224-227°C].

1',1'-bis(2,5-benzoquinoyl)ethane, 18.

Purified by sublimation at 150°C (0.1 mm); mp 192.5-193°C [lit. [58] mp 194°C].

Naphthazarin, 21.

Sublimed at 170°C (0.03 mm); mp 208-213°C [lit. [95] 192-193°C];

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (x, 4), 12.4 (s, 2).

The synthesis of compound 25c is outlined in reference 96.

Grateful acknowledgment is made to the following individuals for generous samples of semidione and semiquinone precursors which greatly facilitated this investigation.

Sources of Samples and Literature References<sup>1</sup>

Triptycene bis(quinone), 3	Prof. H. Iwamura [26]
Triptycene tris(quinone), 7	Dr. O. Webster [94] <sup>1</sup>
Bistriptycene bis(quinone), 8	Prof. A. Docken
[2.2]Metacyclophanequinone, 12	Prof. M. Tashiro [57] <sup>1</sup>
[2.2]Metacyclophanequinhydrone, 14	Prof. M. Tashiro [57]
[2.2]Metacyclophanebishydroquinone, 15	Prof. M. Tashiro [57]
syn-7-Cyanobicyclo[4.1.0]hept-3-ene 2,5-dione, 40	Dr. M. Balci [77] <sup>1</sup>
anti-7-Cyanobicyclo[4.1.0]hept-3-ene-2,5- dione, 41	Dr. M. Balci [77] <sup>1</sup>
syn-7-Cyanomethylbicyclo[4.1.0]hept-3-ene 2,5-dione, 42	Prof. V. Klärner [76] <sup>1</sup>
anti-7-Carbonethoxybicyclo[4.1.0]hept-3- ene-2,5-dione, 43	Dr. M. Balci [77]
Bullvalenedione, 45	Dr. T. Miyashi [85]
1,4-(10'-Hydroxy-11'-ketoicosane- methylene)-benzene, 25c	Dr. Y. Murakami

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<sup>1</sup>The relevant compounds appear in the cited references.

9,10-Dihydro-9,10[1',2']-benzeno-4a,9a-  
[2]butenoanthracena-1,4,17,20-tetrone,

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Dr. K. Kanematsu [57]<sup>1</sup>

1,4-Dihydro-4a,8a-[2]buteno-1,4-methano-  
naphthalene-5,8,9,12-tetrone, 17

Dr. K. Kanematsu [57]<sup>1</sup>

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