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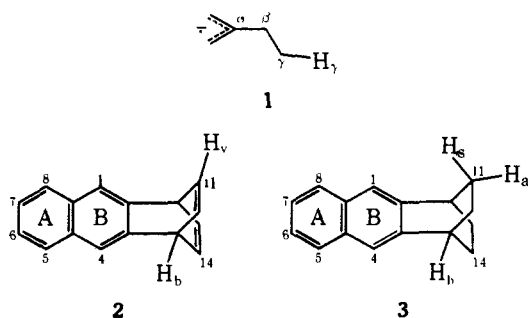
Hyperfine Coupling Patterns in the 2,3-Naphthobarrelene and 2,3-Naphthobarrelane Radical Anions

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Abstract: The radical anions of 2,3-naphthobarrelene (**2**) and 2,3-naphthobarrelane (**3**) were studied by ESR spectroscopy and polarography in order to investigate the importance of long-range coupling, 1,3-π-π interaction, ion pairing phenomena, and steric and strain effects in these species. The magnitudes of the two largest hyperfine splitting constants (hfsc's) of **2·⁻** and **3·⁻** were found to vary appreciably as a function of the solvent and the counterion; these variations are interpreted in terms of ion pairing phenomena. The relative importance of the combined effects of electron repulsion and steric desolvation by the bicyclic moieties versus the effect of strain due to the bicyclic moieties is believed to determine which aromatic protons have the largest hfsc in these species. Analysis of the observed variations in the hfsc's in conjunction with a model for the lowest energy ion pair of **2·⁻** or **3·⁻** was used to assign the two largest hfsc's in both radical anions and to consequently indicate the relative importance of the above effects.

Studies of the hyperfine coupling patterns of complex radical anions as a function of their structure and geometry are a topic of continuing interest.[1] The extent and mechanisms of long-range hyperfine coupling (i.e., coupling at or beyond the γ position relative to the radical center(s), see structure **1**) in radical species in recent years, for example, has received much attention in the literature.[2] Long-range hyperfine couplings (hfsc's) of varying magnitudes have been observed in many rigid polycyclic radical anions, including those containing the semidione,[2a] semiquinone,[2b,c] and semifuraquinone[2d] spin labels.

Few studies[3] of aromatic radical anions containing a fused bicyclic (or higher polycyclic) ring,[4] however, have been reported. In the present paper, we wish to report the results of a study of the hyperfine coupling patterns in the radical anions of 2,3-naphthobarrelene (**2**, 1,4-etheno-1,4-dihydroanthracene) and 2,3-naphthobarrelane (**3**, 1,4-ethano-1,2,3,4-tetrahydroanthracene).

Results

The radical anion of **2** was generated for ESR study by reduction of a dilute solution (1.0×10^{-3} M)[5] of **2** in various ethereal solvents at low temperatures with an alkali metal. Two of the hfsc's of **2·⁻** were found to vary significantly with the solvent and the counterion as illustrated by the data in Table I. The small pentet splitting of $\sim$0.13 G was generally resolved only at lower temperatures. Line width alternation and metal coupling were not observed under any of the conditions studied. Simulations of the experimental ESR spectra (using a computer program which assumes a Lorentzian line shape) were performed using each of the sets of hfsc's shown in Table I. In each case, the simulated ESR spectrum was in excellent agreement with the experimental ESR spectrum.

Similarly the radical anion of **3** was generated for ESR study by reduction of a dilute solution (2.0×10^{-3} M)[6] of **3** in various ethereal solvents with an alkali metal. Appreciable variations of two of the hfsc's of **3·⁻** were also observed upon change of the solvent and counterion, as the data in Table II indicate. Line width alternation and metal coupling were not observed for this radical anion under any of the conditions studied. Each of the experimental ESR spectra corresponding to the sets of hfsc's shown in Table II was

Table I. Hyperfine Splitting Constants[a] of the Naphthobarrelene Radical Anion

Solvent[b]	Metal	Temp, °C	$a_{1,4}$	$a_{5,8}$	$a_{6,7}$	a_{11-14}
MeTHF	K	-50	3.86	5.59	1.77	c
THF	K	-50	4.01	5.41	1.78	
DME	K	-50	4.04	5.40	1.77	
THF	Na	-50	4.09	5.34	1.77	
DME	Na	-50	4.30	5.15	1.75	
DME/10% HMPA	Na	-50	4.30	5.15	1.75	
THF	K	-80	4.01	5.41	1.78	0.13
DME	K	-60	4.03	5.40	1.77	0.12

[a] Hfsc's in gauss; all samples were $1.0 \times 10^{-3} M$. [b] MeTHF = 2-methyltetrahydrofuran, DME = 1,2-dimethoxyethane, THF = tetra-hydrofuran, and HMPA = hexamethylphosphoramide. [c] The smallest hfsc was not resolved under these conditions.

Table II. Hyperfine Splitting Constants[a] of the Naphthobarrelane Radical Anion

Solvent	Metal	Temp, °C	$a_{1,4}$	$a_{5,8}$	$a_{6,7}$	a_{11-14}
MeTHF	K	-50	4.08	5.64	1.78	0.80
THF	K	-50	4.28	5.48	1.78	0.83
DME	K	-50	4.39	5.37	1.77	0.86
DME	Na	-50	4.63	5.11	1.77	0.86
DME/10% HMPA	Na	-50	4.63	5.09	1.76	0.87

[a] Hfsc's in gauss; all samples were $2 \times 10^{-3} M$.

Table III.[a] Temperature Variation of the Hfsc's[b] of the Naphthobarrelene Radical Anion

Solvent	Metal	Temp, °C	$a_{1,4}$	$a_{5,8}$	$a_{6,7}$	a_{11-14}
MeTHF	K	-80	3.83	5.62	1.77	c
MeTHF	K	-50	3.86	5.59	1.77	
MeTHF	K	-30	3.89	5.55	1.77	

[a] Sample was $1.0 \times 10^{-3} M$. [b] Hfsc's in gauss. [c] The smallest hfsc was not resolved under these conditions.

Table IV. Polarographic Data

Compd	$E_{1/2}{}^{a}$	$I_D{}^{b}$	n^c
2	-2.73	2.52	1
3	-2.69	2.39	1

[a] $E_{1/2}$ = half-wave reduction potential in V vs. SCE; measurements were made in DMSO containing 0.1 M Bu$_4$NClO$_4$ as supporting electrolyte and a $10^{-3} M$ concentration of the substrate. [b] I_D = diffusion current constant in μA l. mmol^{-1} mg$^{-2/3}$ sec$^{1/2}$. [c] n = number of electrons associated with the wave.

simulated; in each case, the simulated spectrum was in excellent agreement with the experimental spectrum.

Over the temperature range studied ($\sim$ -80 to -30°),[7] both 2·$^-$ and 3·$^-$ exhibited only a very slight or, under many conditions, a negligible temperature variation of the hfsc's. The greatest temperature variation of the hfsc's for 2·$^-$ was observed in MeTHF with K$^+$ as the counterion; data illustrating this temperature variation are given in Table III. The magnitude of the largest hfsc of 2·$^-$ decreased slightly with increasing temperature, while the magnitude of the second largest hfsc underwent a corresponding slight increase.

Polarographic studies of the electrochemical reduction of 2 and 3 were conducted in anhydrous dimethyl sulfoxide (DMSO). Each of these compounds exhibited a single polarographic wave over the range of negative potentials accessible electrochemically; the polarographic data measured

for these waves are given in Table IV. In each case, the height of the reduction wave was found[8] to be diffusion controlled and the wave was found[8] to be reversible and to correspond to reduction by one electron to the corresponding radical anion.

Discussion

Aromatic Proton Hyperfine Coupling. Since 2·$^-$ and 3·$^-$ are both examples of 2,3-disubstituted naphthalene radical anions, one can assign the $\sim$1.8 G hfsc to protons H$_6$ and H$_7$; a hfsc of similar magnitude has been reported[9] for the corresponding protons in the radical anion of 2,3-dimethyl-naphthalene (4).

4
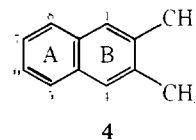
The assignments of the two largest hfsc's in 2·$^-$ and 3·$^-$ are not so straightforward, since in these radical anions there is the a priori possibility of several effects which would necessarily influence the choice of assignment (depending upon which one(s) is dominant). In 4·$^-$, there is a slight polarization of the spin densities away from the electron repelling methyl groups toward ring A, as indicated by the fact that $a_{5,8}$ is somewhat larger in magnitude than $a_{1,4}$ for this species.[9] This same effect is expected in the case of 2·$^-$ and 3·$^-$, since these latter species are also 2,3-dialkylnaphthalene radical anions. In fact, the polarization of spin densities toward ring A might be even greater in the case of 2·$^-$ and 3·$^-$ as a result of a second effect, viz. a solvation effect, which may also be important in the latter two radical anions. The large bulky bicyclic moieties fused to ring B in 2·$^-$ and 3·$^-$ may appreciably interfere with the ability of negative charge present in this ring to be effectively solvated (relative to solvation of charge in ring A). This could result in a further polarization of spin density and hence more negative charge density[10] toward ring A. If one or both of the above effects were dominant, then $a_{5,8}$ would exceed $a_{1,4}$ in magnitude.

On the other hand, Rieke and coworkers[9] have found that the largest hfsc ($\sim$5.4 G) observed for 5·$^-$ is due to protons H$_1$ and H$_4$ in ring B and is a result of a strain effect. The strain effect[9] is believed to result in the C$_1$ and C$_4$

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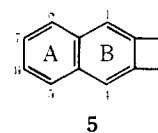
carbon atoms becoming appreciably more electronegative and consequently polarizing spin density more extensively toward ring B. Both 2·$^-$ and 3·$^-$ appear to be strained species,[11] although to a considerably lesser extent than 5·$^-$. Nevertheless the hfsc's of 2·$^-$ and 3·$^-$ which were initially measured in DME and THF were very similar in magnitude to those previously reported[9] for 5·$^-$. This initial result indicated the possibility that a similar strain effect might be present in 2·$^-$ and 3·$^-$, in which case its effect upon the spin density distribution would be surprisingly large in magnitude relative to the degree of angle strain present. If the above strain effect were the dominant factor determining the spin density distribution between rings A and B in 2·$^-$ and 3· $^-$, then the largest hfsc would be $a_{1,4}$.

Assignments of the two largest hfsc's in 2·$^-$ and 3·$^-$ are possible on the basis of the observed variations of the hfsc's (Tables I and II) in conjunction with a geometrical model

for the lowest energy ion pair of a radical anion of the class encompassing $2 \cdot^- - 5 \cdot^-$. The variations observed[12] in the hfsc's of $2 \cdot^-$ and $3 \cdot^-$ with the varying conditions of solvent and counterion shown in Tables I and II can be attributed to varying degrees of ion pairing. The fact that only one distinct spectrum was observed and that the measured hfsc's varied in magnitude with changing conditions strongly suggests the presence (under the conditions studied) of a rapid equilibrium[13] between a "free" radical anion and an ion pair(s) or one between two (or more) different ion pairs.

In early conceptions[14] of the geometries of radical anion ion pairs, the counterion was often viewed as being located at positions relatively far apart from the main regions of high negative charge density. More recently, an electrostatic interaction model, in which the counterion is predicted to occupy a preferred position(s) near regions of high electron density, has gained wide support.[15] Upon applying this latter model to predict the geometries of (the lowest energy, most favorable) ion pairs of $2 \cdot^- - 5 \cdot^-$, one might expect the counterion to lie over one of the aromatic rings of the naphthalene moiety. Rieke and Bales[16] have reported evidence that, in case of ion paired $5 \cdot^-$, the preferred position of the counterion is over ring A for steric reasons. The large bulky bicyclic moieties present in $2 \cdot^-$ and $3 \cdot^-$ might be expected to exert an even greater steric influence upon the placement of the counterion in ion pairs of these latter radical anions and result in the counterion preferentially occupying a position over ring A of the naphthalene moiety. Thus we apply Rieke's ion pair model to ion-paired $2 \cdot^-$ and $3 \cdot^-$, a model in which the counterion resides over ring A of the naphthalene moiety.

If perturbation of the spin densities on the aromatic carbon atoms of $2 \cdot^-$ and $3 \cdot^-$ occurs when conditions are varied from those favoring free radical anions to those favoring ion paired radical anions, the perturbation is expected (on the basis of electrostatic considerations[17]) to be in the form of polarization of additional spin density (and hence negative charge density) toward ring A, which is geometrically closer to the counterion than ring B in the above ion pair model. A concomitant polarization of a corresponding amount of spin density away from ring B is likewise expected. Such a perturbation in the spin densities on the aromatic carbon atoms should be directly reflected in the relative magnitudes[18] of the aromatic proton hfsc's according to the McConnell equation.[19] Hence an increased polarization of spin density toward ring A and away from ring B as described above should result in a net increase in the average value of the hfsc's associated with the protons on ring A and a net decrease in the average value of the hfsc's associated with the protons on ring B.

In the case of $2 \cdot^-$ and $3 \cdot^-$, only the two largest hfsc's ($a_{1,4}$ and $a_{5,8}$) were found to vary appreciably in magnitude with varying degrees of ion pairing (see Tables I and II), indicating that the perturbation of the aromatic spin densities in these species due to ion pairing is substantial only[20] at atoms C_1, C_4, C_5, and C_8. Thus, in case of $2 \cdot^-$ and $3 \cdot^-$, an increase in the magnitude of $a_{5,8}$ accompanied by a decrease in the magnitude of $a_{1,4}$ can be taken as being indicative of a net polarization of additional spin density to ring A and away from ring B.

Assignment of the two largest hfsc's in $2 \cdot^-$ and $3 \cdot^-$ is possible from the experimental determination of the direction of variations of these hfsc's with more extensive ion pairing. If the largest hfsc were due to protons H_5 and H_8 (on ring A), an *increase* in the magnitude of the largest hfsc with more extensive ion pairing would be expected on the basis of the McConnell equation,[19] since additional spin density is drawn to ring A and, in particular, mainly to atoms C_5 and C_8 (see above) upon ion pair formation. A concomitant

decrease in the magnitude of the second largest hfsc (which would be $a_{1,4}$ if $a_{5,8}$ were the largest hfsc) with more extensive ion pairing would also be expected, since spin density is drawn away from ring B and, in particular, mainly from atoms C_1 and C_4 (see above) upon ion pair formation. Alternatively, if the largest hfsc were due to H_1 and H_4 (on ring B), exactly the opposite directions of variations in the magnitudes of the two largest hfsc's would be expected, i.e., the largest hfsc ($a_{1,4}$) would be expected to *decrease* in magnitude and the second largest hfsc ($a_{5,8}$) would be expected to *increase* in magnitude upon more extensive ion pair formation.

Experimentally (see Tables I and II) the largest hfsc of $2 \cdot^-$ and $3 \cdot^-$ was found to increase in magnitude as the solvent was changed from DME to THF to MeTHF (order of increasing degree of ion pairing[21]) while other conditions were kept constant (i.e., counterion, temperature, and concentration). The second largest hfsc in $2 \cdot^-$ and $3 \cdot^-$ decreased in magnitude by an equivalent amount, such that the sum of the two largest hfsc's in these radical anions remained essentially constant (within 0.04 G) under all conditions studied (Tables I and II). Similarly, when the counterion was changed in the order Na^+ to K^+ (order of increasing degree of ion pairing[22]) and other conditions were kept constant, the largest hfsc of $2 \cdot^-$ and $3 \cdot^-$ was found to increase in magnitude and the second largest hfsc was found to decrease in magnitude to such an extent that the sum of these two hfsc's again remained constant. Thus the largest hfsc in $2 \cdot^-$ and $3 \cdot^-$ can be assigned to protons H_5 and H_8 which are located on ring A. This result indicates that in $2 \cdot^-$ and $3 \cdot^-$ the solvation and/or electron-repelling effects (vide supra) of the bicyclic moiety are more important than the strain effect, if present, in determining the spin density distributions on the aromatic carbon atoms in these species.

The temperature dependence observed for the hfsc's (Table III) did not so clearly support only the assignment of $a_{5,8}$ as being the largest hfsc. Instead it could be interpreted as supporting the assignment of the largest hfsc to either H_1 and H_4 or to H_5 and H_8. Ion pair formation is generally more extensive at higher temperatures.[23] If the largest hfsc were due to H_5 and H_8 (on ring A), it should presumably increase in magnitude with increasing temperature, as ion pairing becomes more extensive and results in a polarization of additional spin density to C_5 and C_8 on ring A (vide supra). Under conditions where a temperature dependence was observed for $2 \cdot^-$ and $3 \cdot^-$, however, the largest hfsc was found to decrease in magnitude slightly with increasing temperature, possibly indicating that the opposite assignment of $a_{1,4}$ being the largest hfsc is the correct one. The prediction of the above temperature dependence, however, is based upon the assumption that the observed temperature dependence of the hfsc's is due to shifts in the position of equilibrium between radical anions that are "more extensively" ion paired and radical anions that are "less extensively" ion paired; this assumption is not necessarily a valid one under all conditions.

If a different type of equilibrium is also considered, i.e., one between ion pairs having two different geometries, the observed temperature dependence directly supports the assignment of the largest hfsc to H_5 and H_8. Calculations[24] on the preferred position of the counterion in an ion pair of the naphthalene radical anion indicate that the lowest energy position for location of the counterion is a position over either of the two aromatic rings, when the distance between the counterion and radical anion is within certain ranges.[24] The potential energy diagram for this ion pair as a function of the position of the counterion along the main axis (x axis) of the naphthalene ring thus consists of a well having a double minimum.[24] In the case of a 2,3-dialkyl-

naphthalene radical anion, the potential energies of the two minima are no longer identical and the potential energy minimum corresponding to the counterion being located over ring A is lowest in energy (vide supra). If there is a rapid equilibrium between the two types of ion pairs corresponding to the two minima as illustrated in Scheme I, then

Scheme I

6   7
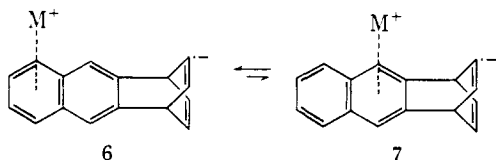
increasing the temperature would tend to increase the population of the higher energy ion pair 7 that is present at equilibrium and hence result in an increase in the magnitude of $a_{1,4}$, since spin density is drawn increasingly toward ring B as ion pair 7 is more heavily weighted in the equilibrium.[25] Thus the small temperature variations of the aromatic proton hfsc's in 2.$^-$ and 3.$^-$ may reflect slight changes with temperature in the relative amounts of the two types of ion pairs 6 and 7 present at equilibrium rather than changes in the relative amounts of two or more types of radical anions differing in the extents to which they are ion paired. Of these two interpretations, we favor the latter since it alone is consistent with $a_{5,8}$ being the largest hfsc, an assignment which all of our other data strongly supports (vide supra).

The direction of the variations of the two largest hfsc's of 5.$^-$ upon more extensive ion pairing, as indicated by the data of Rieke and Bales in ref 16, is exactly opposite to those of 2.$^-$ and 3.$^-$. This is just as expected since the largest hfsc in 5.$^-$ was independently established by deuterium labeling[9] to be due to H_1 and H_4 on ring B rather than due to H_5 and H_8 on ring A as in the case of 2.$^-$ and 3.$^-$. Upon more extensive ion pairing, the largest hfsc of 5.$^-$ decreases[16] in magnitude, since spin density is being drawn from C_1 and C_4 in ring B toward ring A.

The case for the assignment of $a_{5,8}$ as the largest hfsc in 2.$^-$ and 3.$^-$ is strengthened by the fact that the alternative possibility of $a_{1,4}$ being the largest hfsc in these radical anions would pertain only if the perturbations of the aromatic spin densities due to strain were of an unusually large magnitude, considering the modest degree of angle strain present in these species. Furthermore, if one adopts the viewpoint that the largest hfsc in these species can be directly assigned to $a_{5,8}$ for the above reason, then our present experimental results provide evidence that the ion pair model originally proposed for 5.$^-$ by Rieke and Bales[16] is also valid for ion pairs of 2.$^-$ and 3.$^-$. Thus the finding that the largest hfsc ($a_{5,8}$, if assigned directly as discussed above) of 2.$^-$ and 3.$^-$ increases in magnitude upon more extensive ion pairing indicates that, based upon the electrostatic considerations developed earlier, the counterion is closer to ring A than to ring B in ion pairs of these species in direct support of the ion pair model of Rieke and Bales.

The hfsc's of 2.$^-$ and 3.$^-$ with Na^+ as the counterion were virtually identical in DME and in DME containing added HMPA. These hfsc's for 2.$^-$ and 3.$^-$ are believed to be characteristic of the "free" radical anions in which perturbations due to ion pairing are minimized. The difference between the two largest hfsc's ($a_{5,8}-a_{1,4}$) of the "free" radical anions of 2 and 3 (0.85 and 0.46 G, respectively) is greater in each case than the corresponding difference (0.3 G) previously reported[9] for "free" 4.$^-$, indicating an even greater polarization of spin density toward ring A in 2.$^-$ and 3.$^-$ relative to that of 4.$^-$. This greater polarization of spin density toward ring A in 2.$^-$ and 3.$^-$ most likely is due

to one or both of the following factors: (1) the bicyclic moieties in 2 and 3 may be more electron repelling than methyl groups; (2) the bulky bicyclic moieties in 2.$^-$ and 3.$^-$ may appreciably interfere with solvation of negative charge in ring B and result in an increased polarization of spin density toward ring A.

It does not appear possible to dissect the relative importance of the above two factors except in a very qualitative manner. It can be argued though that the second factor is probably important to some degree. To a first approximation, the electron releasing or electron repelling ability of the bicyclic moiety in either 2.$^-$ or 3.$^-$ can be considered approximately equivalent to that of two isopropyl groups. The total electron releasing ability of an isopropyl group, however, is essentially identical[26] with that of a methyl group; the polarization of spin density in 2.$^-$ and 3.$^-$ consequently might be expected to be approximately the same as that in 4.$^-$, if only the first of the above factors were important. The fact that there is a greater polarization of spin density toward ring A in 2.$^-$ and 3.$^-$ in comparison to 4.$^-$ thus suggests that the second factor is also of importance. The inability (see ref 4) of the corresponding benzo-fused bicyclic molecules to undergo radical anion formation is also suggestive of the interference by the bicyclic moiety in the solvation of charge on the aromatic ring fused to the bicyclic moiety. It thus appears that this second factor, which one might term steric desolvation, is of some importance in these radical anions.

Nonaromatic Proton Hyperfine Coupling. The small pentet splitting of 0.13 G observed for 2.$^-$ can be attributed to the four equivalent vinyl protons $H_{11}-H_{14}$. Similarly the pentet splitting of ~ 0.8 G observed for 3.$^-$ indicates interaction of the odd electron with four equivalent protons; the latter hfsc is assigned to the four equivalent anti protons H_a of 3.$^-$, since these protons are in a good w-plan arrangement[27] with the $2p_z$ orbitals of C_2 and C_3 and would be expected[27] to exhibit a significantly larger hfsc than the corresponding syn protons H_s, which are not in a w-plan arrangement.

The magnitude (0.13 G) of the vinyl proton coupling in 2.$^-$ indicates that only a small amount of spin density appears on the two ethylenic moieties of this species. This small coupling could result from: (1) a mechanism[2b] involving spin transfer without electron transfer to the ethylenic bond, e.g., a spin polarization mechanism; (2) a mechanism[2b] involving spin transfer with electron transfer to the ethylenic bond, e.g., a mechanism involving direct 1,3-π-π conjugation of the two weakly overlapping π moieties; or (3) a combination of both of these mechanisms.

A simple Hückel calculation indicates that there is very little weighting[28] of the vinyl carbon atoms in the lowest antibonding MO of 2.$^-$. Alternatively, orbital symmetry analysis can be used to arrive at this same prediction. Kosman and Stock[2b] have shown that long-range hyperfine coupling via direct 1,3-π-π conjugation of two π systems is unimportant if the symmetries of the orbitals involved on the two π systems differ. In 2.$^-$, the lowest antibonding MO ψ_6 of the naphthalene moiety containing the odd electron is symmetric with respect to the plane of symmetry present in this species whereas the antibonding MO's of the ethylenic moieties of 2.$^-$ are antisymmetric with respect to this symmetry element. Thus a mechanism of spin transfer of type 2 (see above) involving donation of electron density from the naphthalene moiety to the unoccupied antibonding MO's of the ethylenic moieties in 2.$^-$ can be ruled out on the basis of the molecular orbital calculations and the different symmetries of the pertinent MO's.

The results of the polarographic study of the reduction of 2 and 3 indicate the lack of an appreciable lowering of the

energy of the lowest antibonding MO of **2**·⁻ as a result of 1,3-π-π conjugation (relative to the energy of ψ_6 of the naphthalene moiety). Thus compounds **2** and **3** were both found to undergo reversible one-electron reductions to their respective radical anions, but the $E_{1,2}$ for **2** was found to be 0.04 V more cathodic than the $E_{1/2}$ for **3**. Just the opposite result would be expected[29] if 1,3-π-π conjugation were important in **2**·⁻ and if it consequently afforded a lowering of the energy of the lowest antibonding MO in **2**·⁻. Thus the polarographic results are also suggestive of a mechanism for the vinyl proton hfs other than 1,3-π-π conjugation.

Although other possible mechanisms[2b] for this coupling cannot be completely ruled out, a mechanism involving spin polarization of the electrons of the vinyl C–H bonds could certainly give a hfsc of the observed magnitude and in our view is the most attractive possibility. Such a spin polarization of the vinyl C–H electrons could conceivably occur via a direct through-space mechanism[27] or, as a second possibility, via an indirect mechanism[27] involving transmission of the spin polarization through the σ bonds. Of these two possibilities, the direct through-space spin polarization is more likely in the case of **2**·⁻; a mechanism for the vinyl proton coupling involving transmission of spin polarization through the σ bonds might be expected[30] to also result in detectable coupling of the bridgehead protons in **2**·⁻ which was not observed.

No hyperfine coupling assignable to the bridgehead protons was observed for either **2**·⁻ or **3**·⁻, as might be anticipated since the bridgehead C–H bonds in these species are located at angles of essentially 90° with respect to the $2p_z$ atomic orbital on the respective adjacent π carbon atoms. Since the dominant term in the β proton coupling equation[27] contains a $\cos^2 \theta$ relationship, where θ is the dihedral angle between the $2p_z$ orbital and the C–H bond, one would expect the coupling in these cases where θ is ~90° to be zero or very small. Other radical anions containing the bicyclo [2.2.2] moiety have also failed to exhibit any detectable bridgehead proton coupling, including a semidione[2a] and a semiquinone.[2b]

In conclusion, the finding that the largest hfsc in **2**·⁻ and **3**·⁻ is due to protons H₅ and H₈ on ring A indicates that the combined effects of steric desolvation and electron repulsion by the bicyclic moieties of these species are more important than the strain effect, if present, due to the bicyclic moiety in determining which hfsc is the largest in these species. This study is to our knowledge the first one in which analysis of the variations of hfsc's under changing conditions is used in conjunction with an ion pair model to assign hfsc's in specific radical anions.

Experimental Section

2,3-Naphthobarrelene (2). This material was prepared according to the method of Zimmerman and Bender.[31] Upon recrystallization from 75% aqueous ethanol, the white crystals melted at 131–132° (lit.[31] 130–132°).

2,3-Naphthobarrelane (3). To a solution of 250 mg (1.22 mmol) of 2,3-naphthobarrelene (**2**) in 10 ml of 95% ethanol and 5 ml of ether was added 10.0 mg of 5% Pd/C. The resulting mixture was hydrogenated at 40 psi for 1 hr on a Parr apparatus. The reaction mixture was filtered through celite and concentrated in vacuo. Vacuum sublimation (2 mm) of the crude product at 113° afforded 179 mg (72%) of a white solid: mp 121–123.5°; NMR (CCl₄, 100 MHz) δ 1.34–2.04 (A₂B₂ m, 8, methylene), 3.08 (broad s, 2, naphthalylic), and 7.26–8.02 and 7.56 (A₂B₂ m and s, 6, arom); ir (KBr) 3.43 (s), 3.51 (s), 6.24, 6.70, 6.92, 7.55, 8.99, 9.88, 10.57 (s), 11.29 (s), 11.68 (s), and 13.45 (s); uv (cyclohexane) 249 (2822), 258 (4164), 268 (5616), 278 (6085), 289 (3971), 303 (553), 313 (299), and 317 (464) nm.

Anal. Calcd for C₁₆H₁₂: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.76.

ESR Samples. All samples for ESR were prepared on a high vacuum line using techniques that have been previously described.[32] Samples having a known concentration of the reducible substrate were prepared by adding a measured volume of a standard hexane solution of the substrate to the ESR sample tube and then slowly evacuating the sample tube to remove the hexane. After briefly drying the deposited substrate in vacuo, the solvent(s) was distilled into the sample tube and then degassed by means of several freeze–thaw cycles. The alkali metal was then distilled to the top of the sample tube to afford a mirror. The tube was sealed in vacuo at <0.1 μ. The samples were developed in the standard manner in a hexane slush just prior to use and then quickly transferred to the precooled ESR cavity. The ESR spectra were recorded on a Varian V-4500 ESR spectrometer equipped with a Varian variable temperature accessory.

Polarography. The polarographic studies were conducted using a Sargent Model XVI polarograph equipped with a Sargent Model A IR compensator. The DMSO that was used for the polarographic samples had been distilled from calcium hydride under reduced pressure and was stored over molecular sieves. The (n-Bu)₄NClO₄ used was reagent grade and had been dried at 80° overnight on a high vacuum line (<1 μ) prior to use. All of the polarographic samples were 0.1 M in the supporting electrolyte and 1 × 10⁻³ M in the substrate. All polarographic measurements were conducted at ambient temperature in a three-electrode polarographic cell equipped with a saturated calomel electrode as the reference electrode. The m and t values characteristic of the capillary of the DME were measured with the capillary immersed in a 0.1 M solution of (n-Bu)₄NClO₄ in DMSO with the circuit closed and with the potential set at the $E_{1/2}$ of the polarographic wave being studied.

ESR Simulations. The ESR simulations were performed using a Digital Equipment Corp. PDP-10 computer and a Calcomp plotter. The ESR simulation program that was used is one that was written by Professor J. Harriman of the University of Wisconsin and was modified for use on a PDP-10 computer. A Lorentzian line shape for the spectral lines is assumed in this program.

References and Notes

(1) Cf. E. G. Janzen, *Anal. Chem.*, **46**, 478R (1974).
(2) Some leading papers are: (a) G. A. Russell, G. W. Holland, and K. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967); (b) D. Kosman and L. M. Stock, *ibid.*, **91**, 2011 (1969); (c) S. F. Nelsen and B. M. Trost, *Tetrahedron Lett.*, 5737 (1966); (d) S. F. Nelsen and E. D. Seppanen, *J. Am. Chem. Soc.*, **89**, 5740 (1967).
(3) Two recently reported examples are: (a) S. F. Nelsen and J. P. Gillespie, *J. Am. Chem. Soc.*, **95**, 2940 (1973); (b) J. R. Dodd, R. F. Winton, R. M. Pagni, C. R. Watson, Jr., and J. Bloor, *ibid.*, **96**, 7846 (1974).
(4) Attempts to prepare the radical anions of 2,3-benzobicyclo[2.2.2]oct-2-ene, 2,3-benzobicyclo[2.2.1]hept-2-ene, and related compounds were all unsuccessful; in each case, either no ESR signal or only a very weak poorly resolved one could be obtained. The unreactivity toward radical anion formation in these compounds contrasts markedly with that of the related xylenes, which yield their corresponding radical anions relatively easily under similar conditions. We believe that the low reactivity of the former compounds toward radical anion formation is due to the bulky bicyclic moiety in these molecules interfering with their ability to be solvated upon radical anion formation. Consequently, the equilibrium in these cases for reduction lies heavily on the side of unreduced hydrocarbon and metal rather than on the side of radical anion.
(5) This concentration of **2** was the lowest value that resulted in a sufficiently intense ESR spectrum of **2**·⁻ upon reduction. The relatively high concentration of **2** required in this case suggests the presence of an equilibrium in this system in which much of the substrate remains on the side of unreduced hydrocarbon and alkali metal rather than on the side of radical anion.
(6) A somewhat higher concentration of **3** relative to **2** was required to give a sufficiently intense ESR spectrum of **3**·⁻.
(7) Loss of signal intensity and appreciable line broadening of the hyperfine lines prevented measurements of the hfsc's above −30°.
(8) The polarographic waves for the reduction of **2** and **3** were shown to be diffusion controlled waves from measurements of the diffusion current i_D as a function of $h^{1/2}$, the height of the DME. The reversible one-electron character of these waves was demonstrated from the fact that plots of $-E$ vs. log $i/(i_d - i)$ were linear with slopes of 62 mV. For details of these plots, see L. Meites, "Polarographic Techniques," 2nd ed,

Interscience, New York, N.Y., 1965.

(9) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).

(10) The spin densities and negative charge densities on the aromatic carbon atoms in $2\cdot^-$ and $3\cdot^-$ are of the same magnitude at least according to simple theory in these species since the naphthalene moieties present are alternant π systems.

(11) In **2** (and presumably also $2\cdot^-$), consideration of a molecular model suggests that this molecule has a $C_2C_3C_b$ (C_b = bridgehead carbon atom) angle of approximately 110° rather than the strain free value of 120° for sp^2-hybridized carbon atoms. A similar model of **3** suggests that the $C_2C_3C_b$ angle in this molecule is approximately 116°.

(12) The magnitudes of the hfsc's of a "free" radical anion can vary with solvent due to perturbations of the spin densities by different solvent interactions. Such variations, at least for aromatic hydrocarbon radical anions, are usually quite small ($<\sim 0.1$ G). The appreciable variations (up to ~ 0.5 G) found in the present study are best viewed as resulting from shifts in the position of a rapid equilibrium of ion pairs and/or a free ion.

(13) See N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967), for a discussion of such equilibria.

(14) Cf. E. DeBoer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).

(15) M. Iwaizumi and J. R. Bolton, *J. Magn. Reson.*, **2**, 278 (1970), and references cited therein.

(16) R. D. Rieke and S. E. Bales, *Tetrahedron Lett.*, 2439 (1972).

(17) Polarization of spin density and hence negative charge density toward ring A, which is closer to the counterion, would result in a decrease in the distance between the positive counterion and the average center of negative charge. Some polarization of spin density in this direction may give a more favorable electrostatic arrangement of the charges, and, to the extent that it is more favorable, would occur. Polarization in the opposite direction toward ring B on the other hand would always represent a less favorable electrostatic arrangement of the charges (since the distance between the positive counterion and the average center of negative charge would be increased) and hence should not occur.

(18) The theoretical basis for the direction of variations of the hfsc's is developed in the discussion in terms of the changes expected in the hfsc's of $2\cdot^-$ and $3\cdot^-$ in going from a free radical anion to an ion paired radical anion. The hfsc's actually measured for $2\cdot^-$ and $3\cdot^-$, however, are believed to be average hfsc's resulting from a rapid equilibrium(a) between two or more types of ions differing in the extent to which they are ion paired. This does not matter for present purposes, however, since the experimentally measured changes in the hfsc's as a result of shifts in the above equilibrium(a) are in the same direction and reflect the changes expected in the hfsc's of $2\cdot^-$ and $3\cdot^-$ in going from a free radical anion to an ion paired radical anion.

(19) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

(20) A perturbation of the spin densities at atoms C_9 and C_{10} cannot be detected directly since these carbon atoms do not bear protons. However,

the observation that $a_{5,8}$ increases in magnitude to the same extent that $a_{1,4}$ decreases (see later discussion) while all of the other hfsc's remain essentially the same upon more extensive ion pairing strongly indicates that any perturbation of the spin densities at these atoms is at most a small one.

(21) Ion pairing is generally much more extensive in MeTHF than in either THF or DME, since MeTHF has a considerably lower dielectric constant than either THF or DME. Ion pairing is generally less extensive in DME than in THF, which is usually attributed to the fact that DME can act as a bidentate ligand and coordinate more effectively with the counterion than can THF. Both DME and THF have very similar dielectric constants. See A. C. Aten, J. Dieleman, and G. J. Hoijtink, *Discuss. Faraday Soc.*, **29**, 182 (1960).

(22) As a general rule, the extent of ion pairing increases with increasing size of the counterion. Thus the smaller Na^+ is less likely to form an ion pair with a radical anion than is the larger K^+. See reference cited in ref 21.

(23) See reference cited in ref 21.

(24) I. B. Goldberg and J. R. Bolton, *J. Phys. Chem.*, **74**, 1965 (1970).

(25) The fact that only slight changes in the hfsc's were observed suggests that the shift in the position of this equilibrium with temperature is also very slight and ion pair **7** is always present to only a very small degree. If substantial amounts of **7** were present at equilibrium, one might expect to observe nonequivalence of the vinyl proton hfsc's and/or line width alternation in this radical anion.

(26) This is indicated by the fact that the substituent constants for Me and *i*-Pr are virtually the same. For Me, $\sigma_m = -0.069$ and $\sigma_p = -0.17$. For *i*-Pr, $\sigma_m = -0.068$ and $\sigma_p = -0.15$.

(27) Cf., for example, ref 2b.

(28) For example, a simple Hückel calculation in which $\beta_{2,11}$ (and other resonance integrals for equivalent 1,3-transannular interactions) = 0.25 and in which other resonance integrals were assigned their standard values (i.e., $\beta = 1$ for adjacent interacting AO's and $\beta = 0$ otherwise) afforded a coefficient of -0.049 at each vinyl carbon atom in the LAMO. Smaller (more realistic) values for $\beta_{2,11}$, etc., in this calculation afford even smaller coefficients at these positions for the LAMO.

(29) This expectation follows from the well-known fact that there is an approximate linear correlation between the half-wave reduction potential of a compound and the energy of its lowest antibonding MO, which the odd electron occupies in most radical anions. See the discussion in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N.Y., 1961, Chapter 7.

(30) This expectation follows from the fact that a spin polarization mechanism of spin transfer should not be dependent upon any dihedral angle as is a hyperconjugation mechanism.

(31) H. E. Zimmerman and C. O. Bender, *J. Am. Chem. Soc.*, **92**, 4366 (1970).

(32) Cf., for example, H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.*, **92**, 6507 (1970).

Activation Parameters for the Ring Inversion of 1,4-Oxathiane. The Use of Complex Spectral Patterns for Obtaining Reliable Thermodynamic Parameters

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Abstract: The activation parameters for the ring inversion process (chair to twist) of 1,4-oxathiane were found to be $\Delta H^\ddagger = 8.78 \pm 0.7$ kcal/mol, $\Delta S^\ddagger = 0.45 \pm 0.35$ eu, and $\Delta G^\ddagger = 8.69 \pm 0.3$ at 177.2°K by variable temperature NMR. These results are discussed in relation to the use of new methods of computer analysis and more accurate temperature measurement and control. Predictions of entropies of activation, and hence calculation of enthalpies of activation, for ring inversion processes based on reaction path degeneracies are discussed.

Measurement of enthalpies and entropies of activation for the ring inversion process in six-membered rings by NMR methods has not always produced satisfactory results. This arises from difficulties inherent in the NMR methods of determining rate constants. Results reported for the cyclohexane ring inversion (Table I) illustrate the problem. The original results[1a] for this compound ($\Delta G^\ddagger = 10.1$ kcal/mol, determined; $\Delta S^\ddagger = 3.6$ eu,[2] estimated; $\Delta H^\ddagger = 10.8$ kcal/mol,[2] estimated from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$) are in excellent agreement with the most recent results from experimentally derived data[1g] ($\Delta G^\ddagger = 10.22$ kcal/mol, $\Delta S^\ddagger = 2.8$ eu, and $\Delta H^\ddagger = 10.8$ kcal/mol). In the years between these two reports a wide range of enthalpies and entropies of activation ($\Delta H^\ddagger = 9.0$ to 11.5 kcal/mol, $\Delta S^\ddagger = -6.5$ to 4.9 eu) were reported. In contrast, the $\Delta G^\ddagger$ values are relatively invariant. The difficulties in determining accurate enthalpies of activation, even though accurate free energies of activation can be determined, have been discussed elsewhere.[3]

Inaccuracies in the NMR method can be separated into