Table V. Esr of Substituted Alkyl Radicals in Solution

Radical	T, °C	$\langle g \rangle$	A_{α}, G	A_{β}, G	A_{γ}, G
$\dot{C}H_2CH_2OCH_2CH_3$	−111	2.00257	22.15	33.76	
	−136		22.13	34.68	
$\dot{C}H_2CH_2OSi(CH_3)_3$	− 98	2.00258	22.11	34.01	
	−135		22.12	35.63	
$\dot{C}H_2CH_2CH(CH_3)_2$	− 70	2.00259	22.06	27.59	0.94
	−121		22.07	28.24	0.97
$\dot{C}H_2CH_2C(CH_3)_3$	−105	2.00268	22.06	24.71	0.1[a]
$\dot{C}H(CH_3)CH(CH_3)OAc$	−104	2.00258	22.12	25.53 (CH_3) 15.71 (H)	0.70[b]
$\dot{C}H_2(CH_2)_2C{\equiv}C\text{-}n\text{-}C_4H_9$	−104	2.00266	22.09	29.14[c]	0.74
$\dot{C}H_2(CH_2)_3C{\equiv}C\text{-}n\text{-}C_4H_9$	−103	2.00266	21.97	29.06[c]	0.79

[a] δ protons (decet). [b] Selective broadening of the $M_I = \pm ^1/_2$ lines observed at lower temperatures resulting in reduced amplitude and much poorer resolution compared to the α-methyl quartets. [c] Central line ($M_I = 0$) of the triplet severely broadened.

tion of *tert*-butylbenzene was kindly supplied by Dr. L. F. Friedman. Hydrocinnamoyl peroxide, the β,β-dideuterio compound, and *p*-methoxyhydrocinnamoyl peroxide-α,α-d_2 were described[36] earlier. 9-Bromononyne-5 and 10-bromodecyne-5 were prepared and kindly donated to us by Drs. W. Michaely and J. K. Crandall.

Acknowledgment. We wish to thank the National Science Foundation for generous financial support of this research.

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[36] J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, 90, 4038, 4616 (1968).

Conformations of 7,12-Dihydropleiadene Radical Anions. Electron Spin Resonance and Electron Nuclear Double Resonance Studies

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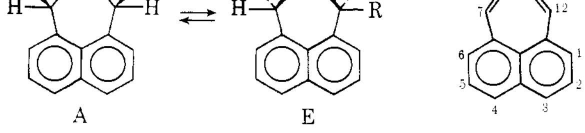
Abstract: The radical anions of 7,12-dihydropleiadene, 1-methyl-7,12-dihydropleiadene, and 7,12-(*o*-phenylene)-7,12-dihydropleiadene have been prepared and their esr spectra interpreted with the aid of endor spectroscopy. The hyperfine coupling constants for the bridge protons in the seven-membered ring have been used to determine the conformation of this ring. Contrary to previous suggestions, the conformation of the methyl-substituted anion is found to be the same as for the unsubstituted radical anion, *i.e.*, two equivalent axial and two equivalent equatorial protons on the seven-membered ring.

The conformationally labile 7,12-dihydropleiadenes (DHPs) have proven to be ideal molecules for studying ring inversion of seven-membered rings[2] (*e.g.*, A $\rightleftarrows$ E (k_r) with R = H) using dynamic nmr techniques.



pleiadene

Since $\Delta G^{\ddagger}$ for inversion is usually *ca.* 13–15 kcal/mol, it was quite easy to measure T_c and $\Delta\nu_{AB}$ for a number of aryl-substituted DHPs (with R = H) and also to "freeze out" diastereomeric conformers A and E (above) when R was a substituent whose steric preference we wished to assess.[3a] From a study of various seven-substituted DHPs (assessing K_{eq} for A $\rightleftarrows$ E with R ≠ H), we found relative steric bulks of "similar" alkyl groups (on cyclohexanes) to change quite drastically[3b] when on the ring. Complementing these stereochemical studies was the discovery of several hydride rearrangements across the seven-membered ring.[4]

When C_1 substituents were present on the DHP nucleus, low-temperature nmr studies in most cases revealed two AB quartets for the C_7 and C_{12} methylene groups,[4] with the C_{12} quartet invariably exhibiting the smaller $\Delta\nu_{AB}$, as in 1-Me-DHP (below). C_8 and/or C_{11} substituents also reduced $\Delta\nu_{AB}$ of the neighboring CH_2

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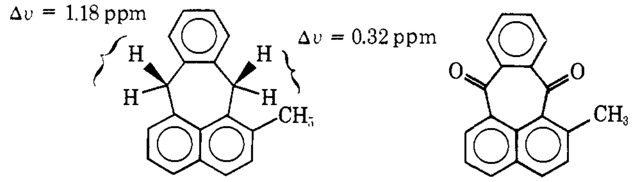
(1) State University of New York at Buffalo, Graduate School Fellow, 1969–1970.

(2) (a) P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Amer. Chem. Soc.*, 88, 1477 (1966); (b) F. D. Saeva, Ph.D. Dissertation, State University of New York at Buffalo, 1968.

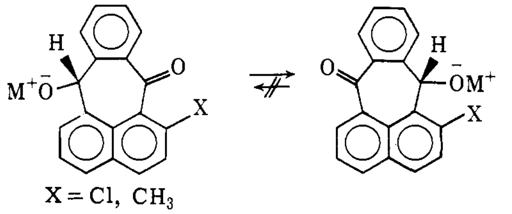
(3) (a) P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *J. Amer. Chem. Soc.*, 88, 1482 (1966); (b) P. T. Lansbury, A. J. Lacher, and F. D. Saeva, *ibid.*, 89, 4361 (1967).

(4) P. T. Lansbury, *Accounts Chem. Res.*, 2, 210 (1969).

but to a lesser extent;[4] in no cases did buttressing groups at positions 1, 6, 8, and 11 cause any significant change in $\Delta G^{\ddagger}$ inversion, implying that their deforming influence was comparable in ground and transition states for inversion or simply too small to noticeably affect the calculated results beyond experimental errors.



Buttressing C_1 groups also affect infrared carbonyl stretching frequencies, as exemplified by 1-methyl-7,12-pleiadione (above) in which the nonequivalent carbonyl groups show $\Delta\nu_{C=O} \cong 16$ cm^{-1} in chloroform solution.[5] The deformation of the C_{12}-carbonyl group[6] is at least in part responsible for the direction of the base-induced hydroxy ketone rearrangement shown below. Here transannular 1,4-hydride shift results in the *product* carbonyl group being more conjugated than the reactant one.[7]



It was desired to establish why buttressing substituents, particularly at C_1, produce substantial differences in $\Delta\nu_{AB}$ for C_7- and C_{12}-methylene groups in the nmr spectra of conformationally "frozen" DHPs. Initial efforts to utilize X-ray crystallography were thwarted by the difficulty of securing appropriate crystals. Therefore, we approached the problem by electron spin resonance spectroscopy, hoping that DHP radical anions would have conformations in solution similar to those of the parent DHPs. Since benzylic hfsc's are angle-dependent,[8] unsymmetrically distorted 1-alkyl-DHP radical anions might conceivably show four different a^H values for the 7 and 12 hydrogens.

Initially the radical anion of DHP itself was studied in order to assign hyperfine coupling constant values for axial and equatorial C_7 (= C_{12}) hydrogens and the naphthyl ring hydrogens and to check for spin density on the *o*-phenylene ring. 7,12-(*o*-Phenylene)-7,12-DHP was also examined, since its benzylic C-H couplings should be minimal ($\theta = 90°$). Finally, 1-Me-DHP and its specifically dideuterated derivatives[9] (7,7-d_2 and 12,12-d_2) were carefully studied, using both esr and endor, in order to determine whether such techniques could tell something about radical anion conformations in solution and, hence, about the parent molecules.

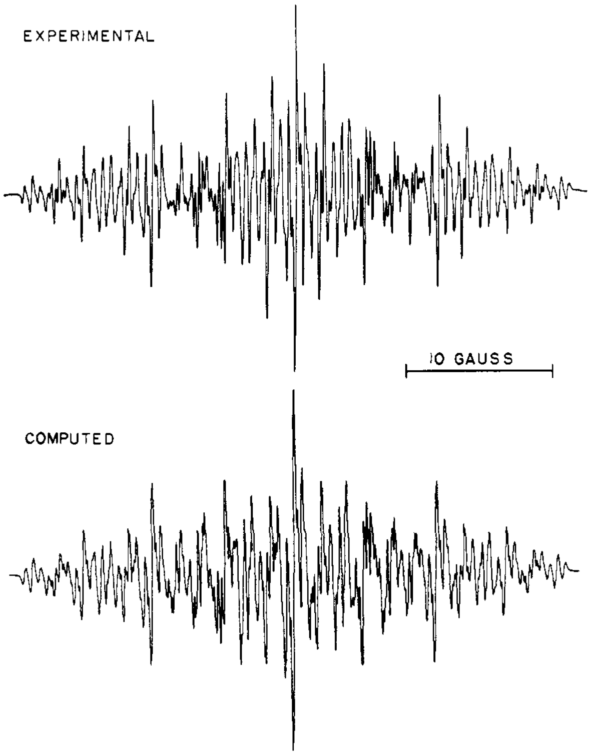


Figure 1. The experimental and computer-simulated esr spectra of 7,12-dihydropleiadene.

Results

Figure 1 shows the experimental and computer-simulated esr spectra obtained from the radical anion of dihydropleiadene (DHP) formed by the reduction of the parent hydrocarbon with potassium metal in 1,2-dimethoxyethane (DME) at −80°. The radical is green when initially formed, much like the naphthalene anion radical which it closely resembles in electronic structure. The radical anion is stable indefinitely at −80° but decays rapidly at room temperature to a red compound which is presumably the carbanion formed by loss of a hydrogen atom from one of the bridges. These carbanions have previously been shown to be red.[10]

One expects seven sets of hyperfine couplings; thus, the analysis of this spectrum is not straightforward and an endor experiment was performed to simplify the interpretation. The central portion of the endor spectrum obtained at −80° is shown in Figure 2. As we have described previously,[11] the endor spectrometer employs a continuous, frequency modulated, radiofrequency magnetic field which normally causes the endor enhancement to be recorded as a first derivative. The spectrum obtained from DHP is, however, apparently a second derivative, a result which is unique to this molecule and the origin of which we do not fully understand. Using the coupling constants obtained from this endor spectrum together with the large couplings readily ob-

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(5) However, in 8-methyl-7,12-pleiadione, only a single carbonyl band is observed, implying reduced 8-CH_3 carbonyl compression.

(6) K. M. S. Islam and G. Ferguson, *J. Chem. Soc. B*, 1135 (1967). These workers have determined the crystal structure of 1-chloro-7,12-pleiadione and found the C_{12}-carbonyl group to be more distorted out of the naphthalene ring plane.

(7) P. T. Lansbury and F. D. Saeva, *J. Amer. Chem. Soc.*, **89**, 1890 (1967).

(8) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(9) J. F. Bieron, Ph.D. Dissertation, State University of New York at Buffalo, 1965.

(10) A. Lacher, PhD. Dissertation, State University of New York at Buffalo, 1967.

(11) R. D. Allendoerfer and D. J. Eustace, *J. Phys. Chem.*, **75**, 2765 (1971).

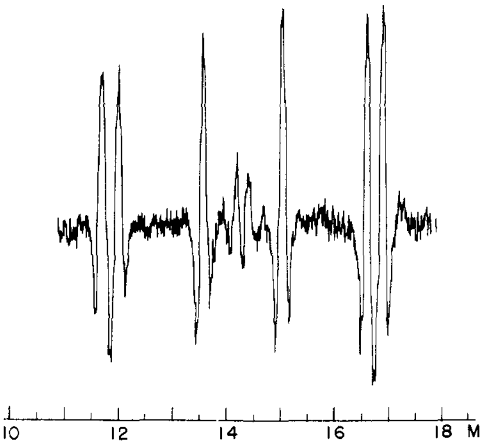

Figure 2. The central portion of the endor spectrum of 7,12-dihydropleiadene, second derivative presentation.

servable in the esr spectrum, the entire esr spectrum can be simulated as is shown in Figure 1.

The coupling constants obtained in this fashion are given in Table I. The 9.66- and 0.52-G couplings were assigned to the methylene bridges by comparison of the DHP esr spectrum with that obtained from 7,12-dihydropleiadene-7,7-d_2. Both the 9.66- and 0.52-G triplets in the undeuterated spectrum become doublets in the deuterated one. The 1.65-, 1.87-, and 4.71-G couplings were assigned to naphthalene ring positions by analogy to 1,8-dimethylnaphthalene.[12] The remaining 0.10-G coupling can then be assigned to either the 8,11 or 9,10 positions on the benzene ring. Assuming the electron spin density distribution in the benzene portion of the molecule is similar to that in the *o*-xylene anion allows this coupling to be assigned to the 8 and 11 positions since all the other observed couplings are accounted for, and the 9 and 10 positions are predicted on this basis to have a coupling constant about $^1/_4$ of that of the 8 and 11 positions. Thus, the couplings for the 9 and 10 positions must be too small to observe.

Table I

Position	DHP[a]	1-Me-DHP[a]	*o*-Phenylene-DHP[a]
1	1.65	2.17[b]	1.38
2	1.87	2.36	2.15
3	4.71	4.77	4.81
4	4.71	4.77	4.81
5	1.87	1.00	2.15
6	1.65	2.17	1.38
7	9.66, 0.52	9.62, 0.76	0.26
8	0.10	0.10	0.085[c]
9			
10			
11	0.10	0.10	0.085[d]
12	9.66, 0.52	9.62, 0.52	0.26

[a] $T = -80°$, solvent = DME, all couplings are given in gauss. [b] Methyl proton. [c] Two equivalent protons, at positions 8 and 8′. [d] Two equivalent protons, at positions 11 and 11

The appearance of the DHP esr spectrum varies markedly with temperature, but since the endor effect can only be observed near the freezing point of DME for this molecule, we have not attempted to interpret the spectra at other temperatures. The 0.52-G triplet from the equatorial bridge protons is present even at room temperature so the temperature dependence of the esr spectrum cannot be attributed to ring inversion which would exchange the axial and equatorial positions. Temperature-dependent motions of the counterion with respect to the seven-membered ring are also ruled out by the presence of this triplet at all temperatures. Nmr studies on the neutral DHP molecule have also shown that the ring inversion rate of this strained seven-membered ring is too slow to have any effect on the esr spectrum.

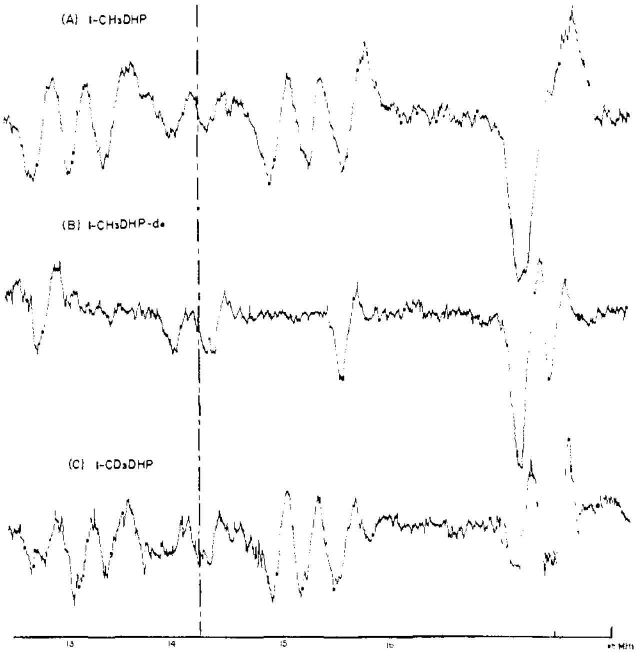

Figure 3. Endor spectra of 1-methyl-7,12-dihydropleiadene and its deuterated derivatives. The dashed line indicates the free proton frequency.

Substitution of a methyl group at the 1 position in DHP destroys what little symmetry the molecule had and makes 14 different hyperfine coupling constants theoretically possible in the esr spectrum of 1-Me-DHP. Figure 3 shows the first derivative endor spectra obtained from 1-Me-DHP (A), 1-Me-DHP-7,7,12,12-d_4 (B), 1-trideuteriomethyl-DHP (C). Comparison of spectra A and C shows that the methyl protons are all equivalent with a coupling constant of 2.17 G and are accidentally equivalent with one other proton. The equatorial bridge protons are readily identified by comparison of spectra A and B. These 0.76- and 0.52-G couplings were assigned to the 7 and 12 positions, respectively, by comparison of the experimental and computer-simulated esr spectra for 1-Me-DHP-7,7-d_2 and 1-Me-DHP-12,12-d_2. The 1:2:1 triplet with a coupling constant of 9.62 G, readily apparent in the esr spectrum of 1-Me-DHP, is assigned to the axial bridge protons by analogy with unsubstituted DHP. These two protons are apparently accidentally equivalent within 0.1 G for we cannot detect any unnatural broadening of the central line of the esr spectrum. The remaining protons were assigned to the naphthalene and benzene ring positions by the analogy with 2-methylnaph-

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(12) R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, 51, 1765 (1969).

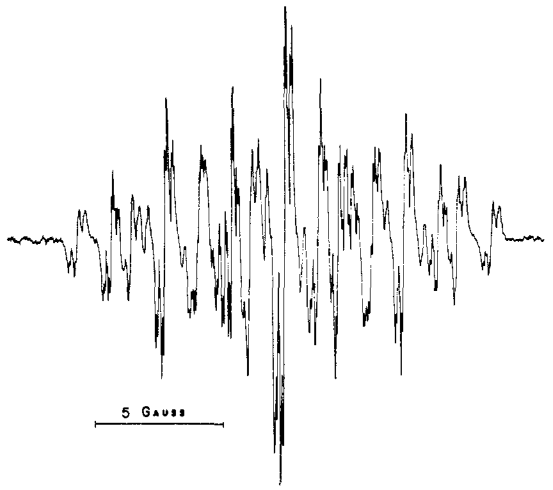
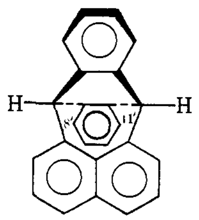


Figure 4. The esr spectrum of 7,12-(*o*-phenylene)-7,12-dihydropleiadene.

thalene and *o*-xylene assuming the substituent effect of the additional methyl groups were strictly additive. Fraenkel, *et al.*,[12] have shown that this is a good approximation for series of polymethyl-substituted naphthalene anions. The hyperfine coupling constants assigned in this fashion are given in Table I.

Figure 4 shows the esr spectrum of the anion radical formed by potassium metal reduction of 7,12-(*o*-phenylene)-DHP. This compound cannot lose a hydrogen atom as readily as DHP since the incipient anion cannot become planar and overlap with the aromatic π system.[13] Therefore, the reduction is complete and quantitative and the anion radical quite stable at room temperature. The resulting esr spectrum is well resolved and readily interpreted directly in terms of the five coupling constants given in Table I. The assignments of coupling constants to molecular positions are by analogy with unsubstituted DHP.



Discussion

Calculation of the conformation of protons attached to carbons β to π systems is normally accomplished by assuming a relation between the hyperfine coupling constant and the dihedral angle θ, defined in Figure 5. Typically this relation has the form[14]

$$a^{\mathrm{H}} = \rho_\alpha(B_0 + B_2 \cos^2 \theta) \tag{1}$$

where B_0 and B_2 are empirical constants and ρ_α is the spin density on the adjacent carbon atom in the π system. For a rapidly rotating methyl group, the average coupling observed for each proton is

$$\bar{a} = \rho_\alpha(\bar{B}_0 + \bar{B}_2/2) \tag{2}$$

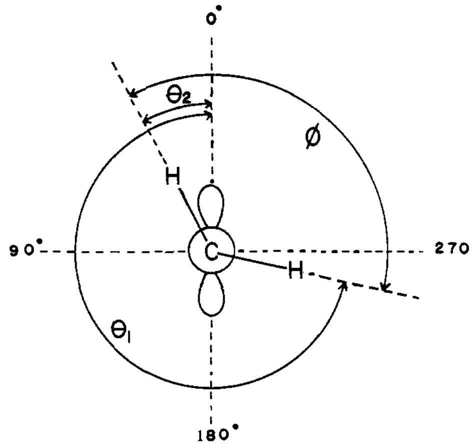


Figure 5. The dihedral angles between β protons and the adjacent carbon p orbital.

Bauld, *et al.*,[14] have recently shown that the parameters B_0 and B_2 are not necessarily the same for sterically hindered rotation as $\bar{B}_0$ and $\bar{B}_2$, the values obtained for freely rotating methyl groups.

When similar systems involving hindered and unhindered β protons are available, the spin density ρ_α may be eliminated by dividing eq 1 by eq 2. Thus

$$\cos 2\theta = \left(\frac{a^{\mathrm{H}} - C_1\bar{a}}{\bar{a}}\right)C_2 \tag{3}$$

where

$$C_1 = \frac{2B_0 + B_2}{2\bar{B}_0 + \bar{B}_2} \text{ and } C_2 = \frac{2\bar{B}_0 + \bar{B}_2}{B_2}$$

If the distinction between B and $\bar{B}$ is invalid or simply ignored, C_1 is exactly 1. Bauld, *et al.*,[14] find that B_2 is slightly greater than $\bar{B}_2$, $\bar{B}_0 > B_0$, and B_2, $\bar{B}_2 \gg B_0$, $\bar{B}_0$ so C_1 is within a few percent of 1.0 in any event. We will assume the value 1.0 is sufficiently accurate for the purpose of calculating the approximate conformation of the methylene bridges in our molecules.

The parameter C_2 is thus the only unknown quantity required to calculate θ_1 and θ_2 in dihydropleiadene if one assumes $\bar{a}$ is given sufficiently accurately by the methyl coupling constant in 1,8-dimethylnaphthalene. C_2 may be evaluated by noting that in the conformationally rigid *o*-phenylene-DHP, the methine protons are constrained to lie exactly in the plane of the naphthalene π system. Thus, $\theta = 270°$ and eq 3 becomes

$$C_2 = \bar{a}/(\bar{a} - a^{\mathrm{H}})$$

Hence, for dehydropleiadenes $C_2 = 0.958$ or 1.045 depending on the sign of a^{H} which cannot be determined experimentally. This 9% uncertainty in C_2 makes relatively little difference to the conformational angles computed below, but, if one ignores the distinction between B and $\bar{B}$, the quantity $(C_2 - 1)/2$ becomes B_0/B_2. The sign and magnitude of this quantity have been discussed at great length in the literature.[15]

The sign of B_0/B_2 in *peri*-alkylnaphthalenes can be found as follows. For a molecular system with two β protons on the same carbon atom in a stable conformation, the angles θ_1 and θ_2 (Figure 5) can be obtained from the experimental coupling constants without

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[13] A. Streitwieser, *et al., J. Amer. Chem. Soc.*, **86**, 3578 (1964), have noted that triphenylmethane-α-*t* exchanges its tritium with lithium cyclohexylamide in cyclohexylamine *ca.* 10^6 times more rapidly than tryptycene-1-*t*.

[14] C. E. Hudson and N. L. Bauld, *ibid.*, **94**, 1158 (1972), and references contained therein.

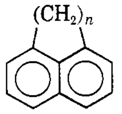
[15] N. L. Bauld, C. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, **54**, 1834 (1971), and references contained therein.

knowledge of C_2 if the difference in the two dihedral angles, $\phi = \theta_2 - \theta_1$, can be estimated. Combining two equations with the form of eq 3 and assuming $C_1 = 1$ for protons 1 and 2 give

$$\tan 2\theta_2 = \frac{a_1 - \bar{a}}{a_2 - \bar{a}} \csc 2\phi - \cot 2\phi \qquad (4)$$

Thus, having determined θ_2 without reference to empirical parameters, C_2, and therefore B_0/B_2, can be calculated. Table II shows the results of such a calculation for three well-known systems related to the one being considered here. The angle ϕ was estimated from molecular models of the compounds. The calculated values for θ_1 and θ_2 agree remarkably well (to better than ±10°) with the values obtained from the molecular models used to estimate ϕ indicating eq 4 is at least a consistent way of interpreting the esr data. In each case, the value of B_0/B is found to be positive and no reasonable variation of ϕ will cause it to become negative. It seems reasonable, therefore, to assume that B_0/B is positive for the dihydropleiadene systems and thus $C_2 = 1.045$.

Table II



n	Estd ϕ, deg	θ_2, deg	θ_1, deg	B_0/B
2[a]	135	337.5	202.5	0.042
3[b]	120	1.4	241.4	0.048
4[b]	120	24.2	264.2	0.169

[a] Coupling constants taken from J. P. Colpa and E. deBoer, *Mol. Phys.*, **7**, 333 (1964). [b] Coupling constants taken from R. F. C. Claridge and B. M. Peake, *J. Magn. Resonance*, **6**, 29 (1972).

For the *peri*-alkylnaphthalenes in Table II, the value of $\bar{a}$ used in the calculation was that for the methyl coupling in 1,8-dimethylnaphthalene and judging by the similarity of the ring proton coupling constants this value should be accurate within a few per cent. However, when the methylene protons are bridged between two π systems, $\bar{a}$ must be calculated in a more complicated way as Bolton, *et al.*,[16] have discussed for the 9,10-dihydroanthracene system. The simple HMO approach to calculation of $\bar{a}$ from eq 2 gives

$$\bar{a} = (B_0 + B_2/2)(X_A\rho_{\alpha A} + X_B\rho_{\alpha B}) = X_A\bar{a}_A + X_B\bar{a}_B \qquad (5)$$

for a system coupled to two π systems. X_A and X_B are the fractions of the total spin density associated with each of the π systems A and B. $\rho_{\alpha A}$ and $\rho_{\alpha B}$ are the spin densities associated with the methyl-substituted position in the model methyl-substituted hydrocarbon.

For 9,10-dihydroanthracene, both systems A and B are the *o*-xylene radical anion and, thus, $X_A = X_B = {}^1/_2$ which gives $\bar{a} = \bar{a}_{\text{xylene}}$, a result which is approximately a factor of 2 too small when compared with the experimental result.

Bolton, *et al.*,[16] have shown that a hyperconjugative model gives a more accurate estimation of $\bar{a}$. The appropriate equation here is

$$\bar{a} = [(X_A\bar{a}_A)^{1/2} + (X_B\bar{a}_B)^{1/2}]^2 \qquad (6)$$

which gives $\bar{a} = 2\bar{a}_{\text{xylene}}$ for 9,10-dihydroanthracene, in excellent agreement with the experimental result.

In the dihydropleiadene systems the model compounds are 1,8-dimethylnaphthalene ($a = 4.54$)[12] and xylene ($\bar{a} = 2.00$),[17] and the fractional spin density in each system can be estimated by comparing the ring proton couplings with those of the model compounds. Table III lists the values obtained for our dihydropleiadenes.

Table III

Compound	$\bar{a}$, *G*
Dihydropleiadene	5.31
1-Me-DHP[a]	5.41,[b] 5.21[c]
o-Phenylene-DHP	5.98

[a] Includes the inductive effect of a 1-CH_3 group calculated as in ref 12. [b] Position 7. [c] Position 12.

If the effect of spin density in the benzene portion of the molecules had been neglected entirely, the same conformations as those calculated below could be obtained from eq 3 by allowing C_1 to deviate from 1. Thus, while our method of evaluating the various empirical parameters is substantially different from that of Bauld, *et al.*,[14] the final form of eq 3 is the same and the quality of any fit to experimental data should be substantially the same. Table IV gives the conformations of the methylene protons in the substituted dihydropleiadenes studied.

Table IV

Compound	θ_1, deg	θ_2, deg
Dihydropleiadene	260.3	15.6
1-Me-DHP	257.0[b]	17.8[b]
	260.1[c]	13.9[c]
o-Phenylene-DHP	270[a]	

[a] Angle required by symmetry. [b] Position 7. [c] Position 12.

Thus, the conformation of the seven-membered ring in the dihydropleiadene anion radical is similar to that proposed by Lansbury, *et al.*,[18] for the neutral hydrocarbon. That is, one methylene proton from each of the 7 and 12 bridges is essentially axial, being tilted only 16° from vertical toward the center of the ring and the other proton is essentially equatorial, lying 10° below the plane of the naphthalene portion of the molecule. As is shown in Table IV, methyl substitution at the 1 position in DHP·⁻ has no measurable effect on the conformation of the seven-membered ring. This result is contrary to the original suggestion by Lansbury *et al.*,[18] based on low-temperature nmr data, that methyl substitution at the 1 position produces distortion at the 12 position of the seven-membered ring and, hence, causes the observed reduction of $\Delta\nu_{AB}$ for the C_{12} protons. It seems unlikely that the difference in electronic structure between DHP and its anion

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(16) M. Iwaizumi and J. R. Bolton, *J. Magn. Resonance*, **2**, 278 (1970).

(17) J. R. Bolton, *J. Chem. Phys.*, **41**, 2455 (1964).

(18) P. T. Lansbury and F. Saeva, *Tetrahedron Lett.*, **48**, 5991 (1966).

radical can account for this discrepancy. The absolute values of the angles in DHP agree well with those predicted by molecular models and so one would expect any difference predicted between positions 7 and 12 to be accurate to a few degrees, and thus a different explanation of the nmr data must be sought.

Experimental Section

Infrared spectra were measured on a Beckman IR-5A spectrometer. Electron spin resonance spectra were recorded with a Varian 4502 X-band spectrometer which was modified for the endor experiments as described in ref 11. Melting points are uncorrected.

The synthesis of the following compounds have been reported previously: 7,12-dihydropleiadene,[19] 1-chloro-7,12-dihydropleiadene,[19] 1-methyl-7,12-dihydropleiadene,[9] 7,12-*o*-phenylene-7,12-dihydropleiadene,[20] 7,12-dihydropleiadene-7,7-d_2,[2a] 1-methyl-7,12-dihydropleiadene-7,7-d_2,[9] and 1-methyl-7,12-dihydropleiadene-12,12-d_2.[9]

To obtain 1-trideuteriomethyl-7,12-dihydropleiadene, the following sequence was followed. Using the procedure of Newman and Boden,[21] 1-chloro-7,12-dihydropleiadene was treated with cuprous cyanide in *N*-methylpyrrolidone to give 1-cyano-7,12-dihydropleiadene: mp 177.5–178.5°; $\nu_{C\equiv N}$ (Nujol) 4.51 μ; M$^+$ *m/e* 255.

Anal. Calcd for $C_{19}H_{13}N$: C, 89.39; H, 5.13; N, 5.48. Found: C, 89.42; H, 5.14; N, 5.45.

The nitrile was hydrolyzed with basic peroxide using the method of Noller[22] to give 1-carboxamido-7,12-dihydropleiadene: mp 250° dec; ir (Nujol) 2.99, 3.15, and 6.08 μ; M$^+$ *m/e* 273. The amide was hydrolyzed by the method of Sperber, *et al.*,[23] using *n*-butyl nitrite to yield 1-carboxy-7,12-dihydropleiadene: mp 236–240°; ν_{OH} 3.6–3.9 μ (b); $\nu_{C=O}$ 5.92 μ; M$^+$ *m/e* 274. The acid was treated with diazomethane to give the methyl ester which was reduced with aluminum chloride and lithium aluminum deuteride. This yielded after sublimation 1-trideuteriomethyl-7,12-dihydropleiadene which contained some alcohol ($-CD_2OH$) as shown by mass spectrometry. The mixture was used to obtain the endor spectrum of 1-trideuteriomethyl-7,12-dihydropleiadene since any remaining alcohol would form a diamagnetic alkoxide salt on reduction with potassium rather than a radical anion and, thus, would not interfere with the experiment.

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Radical Intermediates in the Oxygenation of Phenylmagnesium Bromide. Evidence from Aromatic Phenylation

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Abstract: In a mixture of bromobenzene and diethyl ether, the oxygenation of phenylmagnesium bromide gives bromobiphenyls. The isomer distributions are similar to those obtained when bromobenzene reacts with phenylazotriphenylmethane or benzoyl peroxide, well-recognized sources of phenyl radicals. Thus, phenyl radicals are implicated as intermediates in the oxygenations. This is consistent with reaction mechanisms involving electron-transfer steps such as $PhMgBr + O_2 \rightarrow Ph\cdot + MgO_2Br$, or $PhMgBr + ROO\cdot \rightarrow Ph\cdot + ROOMgBr$, where R could be H.

Oxygenations of aliphatic Grignard reagents are believed to proceed through a two-stage reaction sequence (eq 1 and 2).[2] There is strong evidence that

$$RMgX + O_2 \longrightarrow ROOMgX \quad \text{oxidation stage} \qquad (1)$$

$$ROOMgX + RMgX \longrightarrow 2ROMgX \quad \text{metathesis stage} \qquad (2)$$

the oxidation stage involves free alkyl radical intermediates.[3–5] For this stage, a chain sequence of a type suggested by Russell is the most likely mechanism (eq 3 and 4).[6] The initiation step could be an electron-transfer reaction of the Grignard reagent with oxygen (eq 5). Apparently the metathesis stage does not proceed through free alkyl radicals.[5]

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (3)$$

$$ROO\cdot + RMgX \longrightarrow ROOMgX + R\cdot \qquad (4)$$

$$RMgX + O_2 \longrightarrow R\cdot + MgO_2X \qquad (5)$$

The oxygenation behavior of aryl Grignard reagents contrasts with that of alkyl Grignards. While high yields of alcohols (60–90%) are obtained from alkyl Grignard reagents, from phenylmagnesium bromide in diethyl ether phenol yields are poor (10–20%).[3] Benzene, biphenyl, 1-phenylethanol, and ethanol are major products (10–25% yields), while small quantities of such products as quinone, *p,p'*-terphenyl, diphenyl ether, and *p,p'*-biphenol have been reported.

Some of these products suggest that radicals are intermediates in the reactions. Thus, biphenol suggests phenoxy radicals. The ethanol and 1-phenylethanol are clearly derived from the solvent. This has been the basis of suggestions that phenyl radicals are intermediates in the oxygenations and that they attack the solvent.[7]

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