cussion of this and other questions will be presented in a further report.

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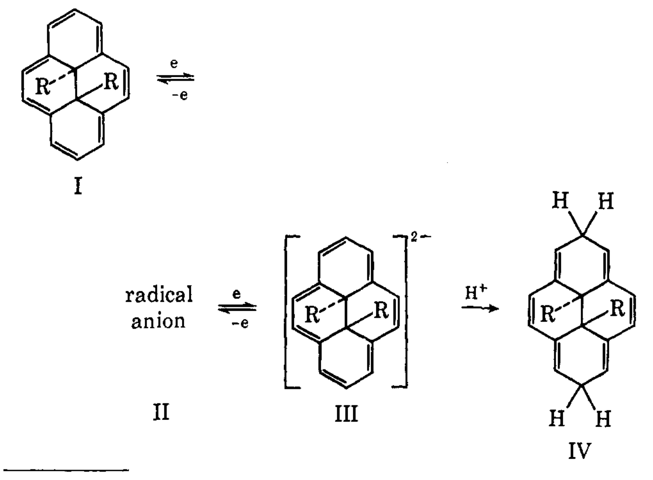
The Dianions of *trans*-15,16-Dialkyldihydropyrenes. Paramagnetic Ring Current Effects

Sir:

Sondheimer and his colleagues have discovered that annulenes having $4n$ π electrons display proton resonance signals in which the chemical shifts of protons internal to the ring are displaced downfield and those peripheral to the ring are displaced toward higher field.[1,2] This has been termed a "paramagnetic ring current effect," and theoretical explanations for it have been provided.[3-5]

It is obvious that, when a neutral hydrocarbon is converted to the corresponding dianion, this corresponds to a change from a $4n$ to a $4n + 2$ system or, alternatively, a $4n + 2$ to a $4n$ system. Thus, it would be predicted that there would be a sharp reversal in ring current effects on interior and exterior protons as a neutral hydrocarbon is converted to its dianion. Oth, Anthoine, and Gilles have recently reported such a result when [16]annulene is converted to its corresponding dianion.[6] We have now studied the conversion of our three *trans*-15,16-dialkyldihydropyrenes to their corresponding dianions. In each case this represents a conversion from a $4n + 2$ π electron system, as in I, to a $4n$ system, as illustrated by III. In contrast to [16]annulene, the dihydropyrenes are fairly rigid molecules and the magnetic properties of the dianions should be informative in defining the nature of the so-called paramagnetic ring current. Also, the availability of dihydropyrenes having differing interior alkyl groups allows partial mapping of the magnetic effects due to the paramagnetic ring current.



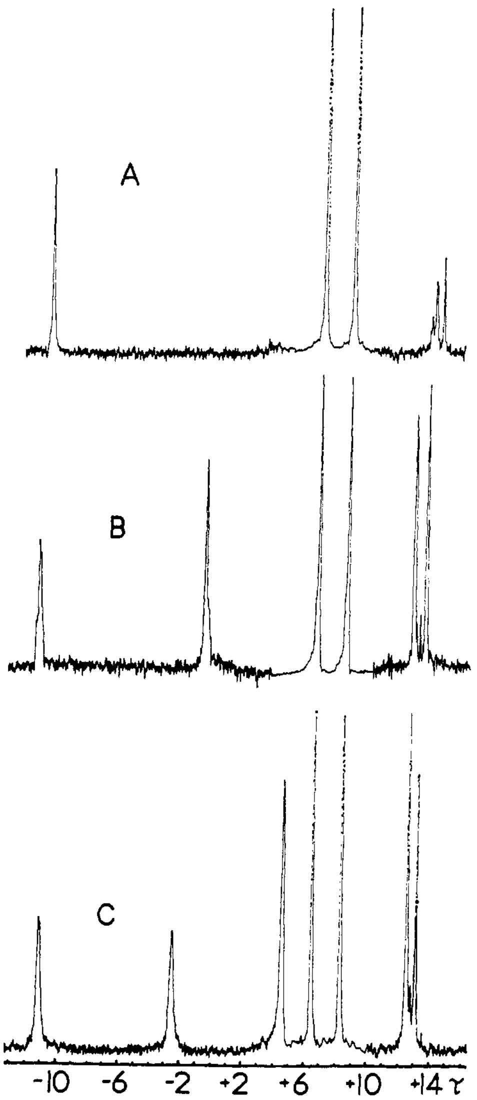


Figure 1. The nmr spectra of the dianions III in tetrahydrofuran-d_8 at −65°. Spectrum A is that of the dianion of *trans*-15,16-dimethyldihydropyrene; B is that of *trans*-15,16-diethyldihydropyrene; and C is that of *trans*-15,16-*n*-propyldihydropyrene. The signals at τ 6.4 and 8.2 are due to the presence of ordinary tetrahydrofuran. Recorded with a Varian HA-100 MHz spectrometer.

The reduction of 15,16-dimethyldihydropyrene (I, R = CH_3) to the corresponding radical anion II (R = CH_3) has been presented previously.[7] Further reduction of the radical-anion II gives the dianion III. As illustrated, the dianion III, on treatment with a proton donor, gives the known bis-triene IV in high yield, providing independent chemical evidence for the formation of the dianion.

The nmr spectra of the three dianions are presented in Figure 1 with the chemical shifts of the relevant protons summarized in Table I. As predicted, there is a very strong paramagnetic ring current effect. The signal for the interior protons at the α carbon, which occurs at τ 13.25–14.25 in the neutral hydrocarbons, now appears in the range of τ −11.0 to −11.24 for the corresponding dianions, a remarkable downfield shift of 25 ppm. Again, in accord with prediction, the signals for the exterior protons, which appear in the range of τ 1.33–2.05

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(1) For a summary, see F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garrat, K. Grohmann, G. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75.

(2) K. G. Untch and D. C. Wysocki, *J. Amer. Chem. Soc.*, **89**, 6386 (1967).

(3) G. Wagniere and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962).

(4) H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109.

(5) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

(6) J. F. M. Oth, G. Anthoine, and J.-M. Gilles, *Tetrahedron Letters*, 6265 (1968).

(7) F. Gerson, E. Heilbronner, and V. Boekelheide, *Helv. Chim. Acta*, **47**, 1123 (1964).

in the neutral hydrocarbon, are observed at τ 12.50–13.96, a shift upfield of about 12 ppm. The signals for the other protons of the interior alkyl groups appear at intermediate field with the protons at the β carbon exhibiting a signal in the range of τ −2.59 to −0.70, and the protons of the γ methyl at τ 4.49. The integrated areas for each of the signals are in accord with these assignments.[8]

Table I

R	Chemical shifts, τ: Protons of the interior alkyl groups α	β	γ	Exterior protons
	Neutral Hydrocarbons (I)[a]			
$\overset{\alpha}{\mathrm{C}}\mathrm{H_3}$	14.25			1.33–2.05
$\overset{\alpha}{\mathrm{C}}\mathrm{H_2}\overset{\beta}{\mathrm{C}}\mathrm{H_3}$	13.96	11.86		1.33–2.05
$\overset{\alpha}{\mathrm{C}}\mathrm{H_2}\overset{\beta}{\mathrm{C}}\mathrm{H_2}\overset{\gamma}{\mathrm{C}}\mathrm{H_3}$	13.95	11.87	10.65	1.33–2.05
	Dianions (III)[b]			
$\overset{\alpha}{\mathrm{C}}\mathrm{H_3}$	−11.00			13.19–13.96
$\overset{\alpha}{\mathrm{C}}\mathrm{H_2}\overset{\beta}{\mathrm{C}}\mathrm{H_3}$	−11.15	−0.70		12.50–13.14
$\overset{\alpha}{\mathrm{C}}\mathrm{H_2}\overset{\beta}{\mathrm{C}}\mathrm{H_2}\overset{\gamma}{\mathrm{C}}\mathrm{H_3}$	−11.24	−2.59	+4.49	12.56–13.14

[a] The synthesis of 15,16-dimethyldihydropyrene has been reported by V. Boekelheide and J. B. Phillips (*J. Amer. Chem. Soc.*, **89**, 1965 (1967)), and that of 15,16-diethyldihydropyrene by V. Boekelheide and T. Miyasaka (*ibid.*, **89**, 1709 (1967)). The preparation of 15,16-di-*n*-propyldihydropyrene was accomplished by Thomas Hylton and will be reported shortly. [b] The dianions were produced using the potassium mirror technique with perdeuteriotetrahydrofuran as solvent. Spectra were recorded at −65° with a Varian HA-100 using HR mode, sweeping through the center band with minimized side bands. For calibration a 400.0-Hz side band was applied and values for the tetrahydrofuran signals relative to tetramethylsilane were assumed. The separation between the tetrahydrofuran signals is in agreement with accepted values. The chemical shift values for the dianions are the average of several spectra whose divergence for any signal was never more than 0.1 ppm.

To our knowledge the signal at τ −11 for the interior α-methylene protons of these dianions is the lowest downfield value yet recorded for hydrogen bonded to carbon. From the theories proposed,[2–4] it is clear that the magnitude of the paramagnetic ring current effect is dependent on rather different considerations than diamagnetic ring current effects. The paramagnetic ring current effect should be particularly sensitive to the energy difference between the lowest singlet and triplet states for the compound.[2] Presumably, this energy difference is smaller in the case of the rigid dihydropyrene dianion than for the floppy isoelectronic [16]annulene, and so it is reasonable that the paramagnetic ring current effect is much larger for the dihydropyrene dianion. Aside from rigidity, other factors such as peripheral substitution should play a role in the magnitude of the paramagnetic ring current effect, and experiments designed to test whether or not there are such correlations are under way.

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(8) The downfield signals in Figure 1 are broad and not sufficiently resolved to allow an interpretation of the coupling pattern. The condensation necessary to present these spectra in a reasonable space is a contributing factor. However, the lack of resolution is apparently more fundamental. One probable explanation is the presence of low concentrations of the radical anion in equilibrium with the dianion, thus leading to broadening of the signals by electron exchange.

(9) We thank the National Science Foundation for their support of this investigation.

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Mechanisms of Indole Alkaloid Biosynthesis. The *Corynanthe–Strychnos* Relationship

Sir:

As a result of our previous study[1] of the sequential appearance of various alkaloidal types in germinating *Vinca rosea*, strong circumstantial evidence was adduced for the order *Corynanthe* → *Aspidosperma* → *Iboga* and experimental proof was provided by the incorporation of multiply labeled stemmadenine (VI) and of [Ar-^{3}H]corynantheine aldehyde (IIa) into the appropriate *Aspidosperma* and *Iboga* representatives. Further definition of the important role of the *Corynanthe* system as a progenitor of both *Strychnos* and *Iboga* types is now provided by two methods.

In the first of these, a more detailed examination of the alkaloidal fractions of *V. rosea* seedlings has uncovered several alkaloids hitherto undescribed in this species. The latest sequence is shown in Table I. Of particular interest are the new isolates geissoschizine (III), which has previously been described as a degradation product of geissospermine,[2] and preakuammicine[3] (IV). The circumstantial evidence for the parallel of sequence and intermediacy depicted in Chart I is compelling, the precursor activity of I, IIa, VI, and VII for the "later" alkaloids having already been demonstrated.[1,4]

Table I. Isolation of Alkaloids from *V. rosea* Seedlings

Germination time, hr	Alkaloid isolated[a]	Type
0	None	
26	Vincoside (I)	"Corynanthe"
	Corynantheine (II)	Corynanthe
28–40	Corynantheine aldehyde (IIa)	
	Geissoschizine (III)	
	"Preakuammicine" (IV)[a,b]	"*Corynanthe–Strychnos*"
42–48	Akuammicine (V)	*Strychnos*
50	Stemmadenine (VI)	"*Corynanthe–Strychnos*"
72	Tabersonine (VII)	*Aspidosperma*
	11-Methoxytabersonine (VIII)	
100–160	Catharanthine (IX)	*Iboga*
	Coronaridine (X)	

[a] Identified by comparison with authentic samples. We thank Professors J. Le Men, R. Goutarel, and A. R. Battersby and Drs. G. F. Smith and D. Stauffacher for gifts of alkaloids. [b] A. I. Scott and A. A. Qureshi, submitted for publication.

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(1) A. A. Qureshi and A. I. Scott, *Chem. Commun.*, 945, 947, 948 (1968).

(2) M. M. Janot, *Tetrahedron*, **14**, 113 (1961), and references cited therein.

(3) See Table I, footnote *b*.

(4) A. R. Battersby, A. R. Burnett, and P. G. Parsons, *Chem. Commun.*, 1282 (1968).