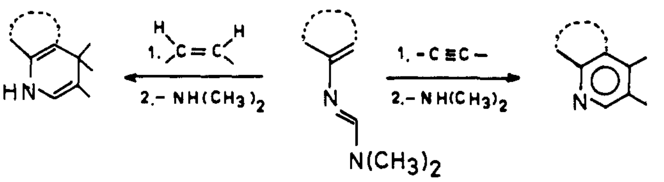
250°) and in higher yields. They are of preparative interest since they provide a simple and efficient route to reactive heterodienes[5] from starting materials **1** and **3**, which are readily available in large quantities from tertiary carboxamides (overall yield, four steps: 60–70%).[1,3a]

The synthetic potential of 1-amino-2-azadienes, **2** and **4**, is illustrated by their facile cycloadditions to electrophilic olefins and acetylenes followed by loss of dimethylamine to yield dihydropyridine or pyridine rings (Table I).

In a typical experiment, 0.654 g (5.84 mmol) of crude **2** directly obtained from the pyrolysis of **1** was slowly introduced into 1.66 g (11.7 mmol) of dimethylacetylene dicarboxylate in 20 ml of CH_3CN at −20°. After 1 hr, the dark brown reaction mixture was concentrated in vacuo. The yield as shown by GLPC analysis was 58%. Bulb to bulb distillation followed by fractional crystallization from benzene–cyclohexane gave pure 2-methyl dimethylcinchomerate (0,572 g, 47%).



Further investigations concerning the synthesis of 1-amino-2-azadienes through rearrangements 2-amino-2*H*-azirines and their use as cycloaddition partners are in progress and will be described in future publications.

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Carbon-13 Magnetic Resonance of Allyl, Pentadienyl, and Arylmethyl Carbanions. Empirical Calculation of π-Electron Densities

Sir:

Proton[1,2] and carbon[1,3-6] chemical shifts have been found to be proportional to π-electron densities in aromatic systems. For proton shifts, the proportionality constant is approximately 10 ppm/electron. This constant has been used to estimate the π-densities at the ortho, meta, and para positions for arylmethyllithiums, and they agree well with the values derived from SCF calculations.[7] For carbon-13 shifts, the proportionality constant is approximately 160 ppm/electron.[1,3,5,6,8] For the cyclic, aromatic systems used in the correlation, the π-electron density at the equivalent carbons is defined as the number of π-electrons divided by the number of π-carbons (e.g., $C_5H_5^-$, $\rho = 1.20$; C_6H_6, $\rho = 1.00$; $C_7H_7^+$, $\rho = 0.86$). It has been implied that this linear shift relationship is applicable only to sp^2 carbons in cyclic, aromatic systems. However, theoretical calculations indicate that it might be more widely applied to sp^2 hybridized carbons in planar, conjugated systems.[10]

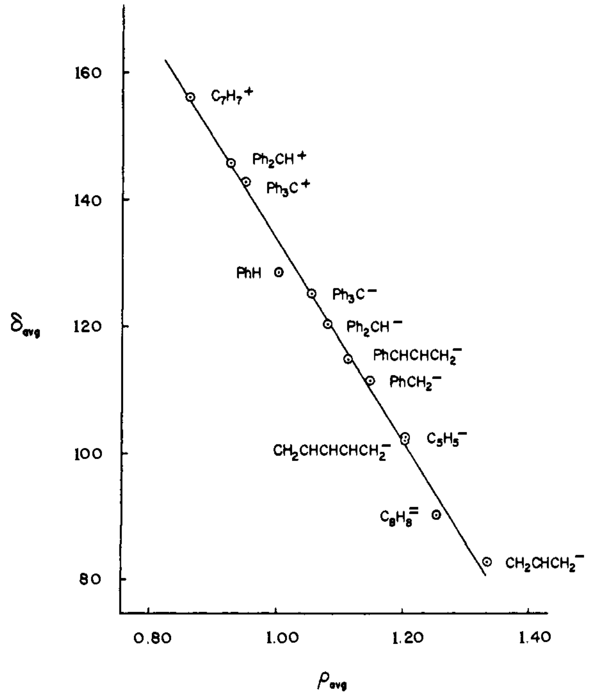
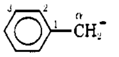


Figure 1. Correlation of average carbon-13 chemical shift with π-electron density.

We wish to report the carbon-13 shift values for allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, benzylpotassium, diphenylmethylpotassium, and triphenylmethylpotassium. Allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, and benzylpotassium were prepared in ~0.5 *M* solutions in tetrahydrofuran (THF) by direct metalation of propene, 1,4-pentadiene, allylbenzene, and toluene with trimethylsilylmethylpotassium as previously described.[11] Diphenylmethylpotassium and triphenylmethylpotassium were prepared by the reaction of the hydrocarbons with potassium sand in THF. The carbon-13 shifts for these carbanions are presented in Table I.

The spectrum of allylpotassium shows two resonances, one at δ 52.8 for the terminal carbons and one at δ 144.0 for the central carbon. The spectrum of benzylpotassium shows upfield shifts for the ortho and para carbons, a downfield shift for the substituted ring carbon, and only slight change for the meta carbons when compared to the corresponding shifts for toluene. Similar chemical shift trends are seen for pentadienylpotassium, 1-phenylallylpotassium, diphenylmethylpotassium, and triphenylmethylpotassium (see Table I). The changes in the aryl carbons indicate a substantial amount of charge delocalization into the ring(s). The benzylic carbon of benzylpotassium is observed at δ 52.7, a 31.2 ppm downfield shift compared to the methyl of toluene. Further, the ortho carbons are nonequivalent for benzylpotassium compounds in which the benzylic substituents are not the same such as 1-phenylallylpotassium, α-methylbenzylpotassium,[13] and α-trimethylsilylbenzylpotassium.[11] These results show that the benzylic and allylic carbons in these carbanions are most probably sp^2 hybridized and that there is considerable double bond character in the benzyl carbon–aryl carbon bond.

Table I. Carbon-13 Chemical Shifts[a]

Carbanion	δ_{C1}	$\delta_{C2,6}$	$\delta_{C3,5}$	δ_{C4}	$\delta_{C\alpha}$	$\delta_{C\beta}$	$\delta_{C\gamma}$
Ph_3C^-	148.6	123.5	128.8	114.2	88.3		
Ph_2CH^-	145.4	116.7	129.4	108.4	78.5		
	152.7	110.7	130.6	95.7	52.7		
$[\mathrm{Ph}\underset{\alpha}{\mathrm{C}}\mathrm{H}\underset{\beta}{\mathrm{C}}\mathrm{H}\underset{\gamma}{\mathrm{C}}\mathrm{H_2}]^-$	147.6	115.9[b]	129.2	108.1	73.0	136.1	79.0
$[\underset{\alpha}{\mathrm{C}}\mathrm{H_2}\underset{\beta}{\mathrm{C}}\mathrm{H}\underset{\gamma}{\mathrm{C}}\mathrm{HCHCH_2}]^-$					79.9	137.6	78.6
$[\underset{\alpha}{\mathrm{C}}\mathrm{H_2}\underset{\beta}{\mathrm{C}}\mathrm{HCH_2}]^-$					52.8	144.0	

[a] Chemical shifts (δ) in ppm downfield from tetramethylsilane (internal); 0.5 *M* potassium salts in THF at 22°. Spectra obtained with JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer using ~1500 average transients. [b] This shift was measured at 45° because ortho resonances were just below coalescence at 22° due to slow rotation about C1–Cα bond, ref 12.

Table II. Average Chemical Shifts and π-Electron Densities

Compound	δ_{av}	ρ_{av}[a]	Notes		δ_{av}	ρ_{av}[a]	Notes
$[CH_2CHCH_2]^-$	83.2	1.333	*b*	Ph_2CH^-	120.7	1.077	*b*
$C_8H_8{}^{2-}$	90.6	1.250	*c, d*	Ph_3C^-	125.8	1.052	*b*
$C_5H_5{}^-$	103.1	1.200	*c. d*	PhH	128.7	1.000	
$[CH_2CHCHCHCH_2]^-$	102.7	1.200	*b*	Ph_3C^+	143.1	0.947	*e*
$PhCH_2{}^-$	112.0	1.143	*b*	Ph_2CH^+	146.1	0.923	*f*
$[PhCHCHCH_2]^-$	114.9	1.111	*b*	$C_7H_7{}^+$	156.4	0.857	*c*

[a] Number of π-electrons/number of π-carbons. [b] This work. [c] Reference 3. [d] Carbon-13 shift measurements were repeated for these carbanions to ensure the same concentration, solvent, and counterion (K^+) [e] Reference 15. [f] Reference 14.

Table III. π-Electron Densities

Carbanion	ρ_{C1}	$\rho_{C2,6}$	$\rho_{C3,5}$	ρ_{C4}	$\rho_{C\alpha}$	$\rho_{C\beta}$
$PhCH_2{}^-$						
Carbon-13	0.88	1.14	1.02	1.24	1.51	
SCF[a]	0.87	1.14	1.07	1.23	1.50	
Proton[b]		1.12	1.10	1.18		
$[CH_2CHCH_2]^-$						
Carbon-13					1.51	0.93
SCF[a]					1.53	0.94

[a] Reference 25. [b] For Benzyllithium, reference 7.

A linear shift–π-density relationship is obtained for allylpotassium, pentadienylpotassium, 1-phenylallylpotassium, the arylmethylpotassiums, and the carbenium ions, diphenylmethyl[14] and triphenylmethyl,[15] if the *average* chemical shift of *all* the carbons is plotted against the *average* π-electron density. Average chemical shifts (δ_{av}) and average π-electron densities (ρ_{av}) are presented in Table II and plotted in Figure 1. This linear relationship follows eq 1, including points for the cyclic, aromatic systems, tropylium ion,[3] benzene, cyclopentadienide ion,[3] and cyclooctatetraene dianion[3] with remarkable precision ($r = 0.996$). Equation 1 is very similar to the one proposed recently for a variety of cyclic, aromatic 2, 6, and 10 π-electron systems, including carbenium ions and carbanions ($\delta = 288.5 - 159.5\rho$).[5,6] The excellent correlation obtained with average chemical shifts for species with acyclic carbons in which the π-electron density is *not* the same at each carbon implies that local π-electron density is the dominant effect influencing the carbon-13 chemical shifts.[10]

$$\delta_{av} = 289.5 - 156.3\rho_{av} \qquad (1)$$

However, caution should be exercised not to extend this correlation too broadly. We specifically chose planar, unbridged, all-carbon π-systems containing only hydrogens as substituents. We have found that alkyl substituted allyl, pentadienyl, and benzyl carbanions do not fit well without adjusting the average chemical shift of the π-carbons to account for the effect of the substituent. Olah has found that carbon-13 shifts for α-substituted phenylcarbenium ions, PhC^+R_2 (R = CH_3, cyclopropyl), could not be correlated with charge alone.[16,17] π-Systems containing heteroatoms have been found to give good correlation but with much different slopes.[8,9,18] It is important also to use the same counterion and solvent in order to compare the same type of ion. The potassium salts reported here showed no changes in chemical shifts in different solvents and are most probably all contact ion pairs in THF.[19,20] The carbon-13 shifts of allyllithium,[21] pentadienyllithium,[22] and benzyllithium[21,23,24] differ widely from those of the potassium salts and are very solvent sensitive. This may be due to the presence of solvent separated ion pairs or to a change in the hybridization of the benzylic (allylic) carbon.[21,24]

Equation 1 provides a simple method for the calculation of π-electron densities at *nonequivalent* carbons in delocalized systems by using the chemical shift of the carbon in question rather than the average chemical shift. The results of such calculations for benzyl and allyl carbanions are presented in Table III along with the empirical electron densities for the ortho, meta, and para positions of benzyllithium calculated from proton shifts.[7] π-Electron density values derived from SCF calculations agree extremely well with the carbon-13 values.[25]

Extending this empirical correlation to include planar, conjugated π-systems makes it clear that the π-density scale in Figure 1 encompasses values from zero ($CH_3{}^+$) to two ($CH_3{}^-$). Although these species have remained inaccessible to NMR solution measurements, extrapolation of the linear relationship presented here predicts reasonable values for their carbon-13 chemical shifts. Olah has observed trimethylcarbenium ion and dimethylcarbenium ion at δ 329 and 319, respectively.[26] Removal of two more methyls in going to ($CH_3{}^+$) would be expected to result in a further upfield shift. Equation 1 predicts a value of δ 289.5 for ($CH_3{}^+$). The carbon-13 chemical shift for methyllithium has been found to vary from δ −11 to −15 in triethylamine, diethyl ether, and THF, respectively.[27] This trend suggests an increase in cation solvation with increasing solvent polarity. The carbon-13 shift for ($CH_3{}^-$) predicted by eq 1 is δ −23.1. This is a reasonable value for an sp^2 carbon containing two π-electrons.

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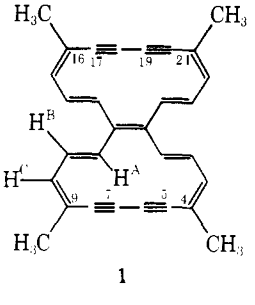
4,9,16,21-Tetramethyl-5,7,17,19-tetrakisdehydro[14]annuleno[14]annulene, a Macrocyclic Analog of Naphthalene[1,2]

Sir:

A little explored aspect of annulene chemistry is the synthesis of fused bicyclic hydrocarbons made up of identical [4*n* + 2]- or of [4*n*]annulene rings. Hitherto, the only well studied example is naphthalene ([6]annuleno[6]annulene), which has been known for a considerable time.[3] It was of interest to make available other representatives of this series, particularly to investigate their "aromaticity" or "antiaromaticity". We now describe the synthesis of 4,9,16,21-tetramethyl-5,7,17,19-tetrakisdehydro[14]annuleno[14]annulene (**1**),[2,4] a simple derivative of the 26π-electron [14]annuleno[14]annulene (e.g., **2**), in which both rings are (4*n* + 2)-membered.



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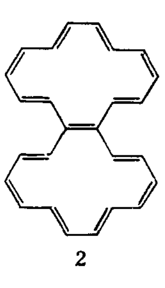
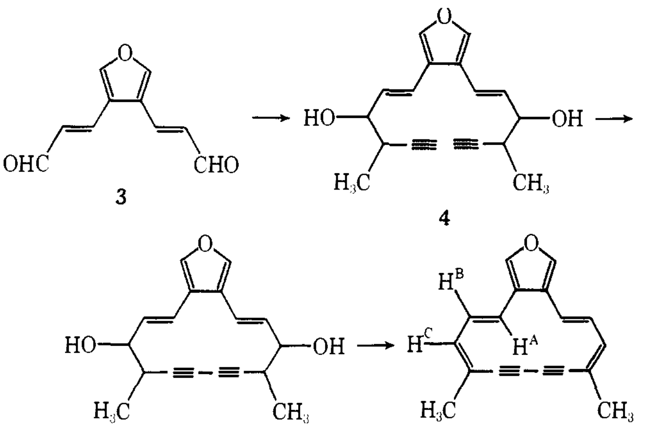


2

A potential intermediate for the synthesis of **1** was the dialdehyde **14**, a suitable precursor of which appeared to be the previously described dimethylbisdehydro[14]annuleno[*c*]furan, **6**.[5] Since **6** was required in quantity, an improved synthesis was developed. 3,4-Furandicarboxaldehyde[6] was converted to the bisvinylog **3**, mp 158–160° [7a,8,9] in 77% yield by the method of Cresp et al.[10] Reaction of **3** with an excess of the Mg derivative of 3-bromo-1-butyne[11] in ether at −30° for 15 min gave the pale yellow diol **4**[9] as a stereoisomeric mixture, which was coupled to the macrocyclic diol **5** with O_2, CuCl, NH_4Cl, and HCl in aqueous C_2H_5OH and benzene. It was unnecessary to purify or separate the stereoisomers of the noncrystalline **4** and **5**. Treatment of crude **5** with mesyl chloride and $N(C_2H_5)_3$[12] in dimethoxyethane (0°, 1.5 hr, N_2) and subsequent elimination with 1,5-diazabicyclo[4.3.0]non-5-ene at 20° for 3.5 hr then led to **6**[7b] in ~30% yield (based on **3**).[13,14]



3 **4** **5** **6**

After considerable experimentation it was found that suitable modification of the furan ring of **6** could be effected by treatment with $Pb(OAc)_4$ in CH_3COOH[15] (20°, 30 min, N_2), which led to the diacetate **7** (red gum;[9] λ_{max} (ether) 307 sh (ϵ 62,500), 319 (91,500), 371 (9800), 393 (9300), 458 sh (330), 504 sh (280), 552 sh nm (190)). Hydrolysis of **7** with oxalic acid in aqueous THF (20°, 12 hr, N_2), gave the corresponding diol **8** (orange solid; *m/e* 262 ($M^+ - H_2O$)) instead of the dialdehyde **14**, as evidenced by the ^1H NMR and ir spectra. The ^1H NMR spectra of **7** and **8** indicated them to be ca. 1:1 mixtures of the cis and trans isomers,[15] which were not separated. Substance **8** proved to be base-sensitive, but could be condensed with carbethoxymethylenetriphenylphosphorane[16] in benzene (80°, 16 hr, N_2). The reaction led to ~50% (based on **6**) of the trans, trans diester **9**[7a,17] as red needles: mp 141–142°:[9] λ_{max} (ether) 343 (ϵ 62,500), 405 sh (14,800), 418 nm (15,600). Reduction of **9** with *i*-Bu_2AlH in benzene (6°, 15 min, N_2) gave the diol **10** as red needles:[9,18] λ_{max} (ether) 336 (ϵ 56,400), 384 sh (9900), 396 sh (10,700), 413 (13,400), 476 (4900), 520 (540), 569 nm (400). Oxidation of **10** with MnO_2 in CH_2Cl_2 (20°, 1 hr, N_2) yielded 74% (based on **9**) of the dialdehyde **11** as orange needles:[9,18] λ_{max} (ether) 265 (ϵ 10,000), 347 (51,900), 420 nm (15,900), with absorption to 600 nm (Scheme I).

Treatment of **11** with an excess of the Mg derivative of 3-bromo-1-butyne,[11] as previously, gave the diol **12** which was coupled to **13** with $Cu(OAc)_2 \cdot H_2O$ in DMF at 65° for ~4 hr. The red noncrystalline diols **12** and **13** are mixtures of stereoisomers, which were not separated. Dehydration of crude **13** via the dimesylate, essentially as before, then yielded 5% (based on **11**) of the tetrakisdehydro[14]annuleno[14]annulene **1** as dark red-brown prisms: *m/e* 384.1871 (calcd 384.1878);[7a,18] λ_{max} (ether) 258 (ϵ 14,400), 278 sh