

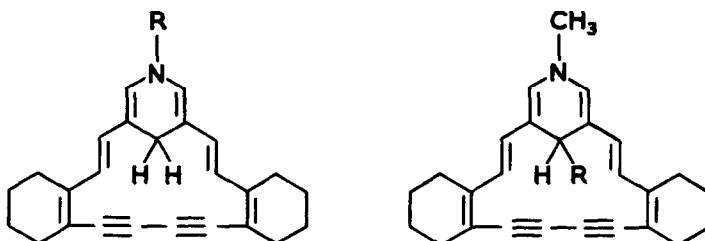
BRIDGED DIDEHYDROAZA[17]ANNULENYL ANIONS, A GROUP OF STRONGLY DIATROPIC HETEROCYCLES ¹

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We have previously reported the synthesis of the methylene-bridged didehydroaza[17]-annulenes 1 - 4.³ As expected, these 18 π -electron systems proved to be diatropic, the



1, R = CH₃

2, R = H

3, R = COOC₂H₅

4, R = COCH₃

5, R = CH₃

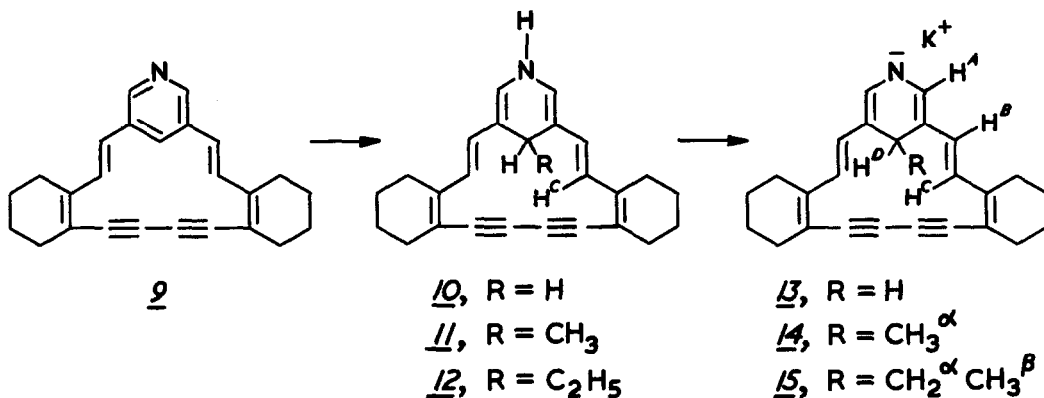
6, R = C₂H₅

7, R = n-C₃H₇

8, R = n-C₄H₉

magnitude of the ring current (1 > 2 > 3 > 4) decreasing with increasing electronegativity of the N-substituent. We have also prepared the bridged N-methyldidehydroaza[17]annulenes 5 - 8⁴ bearing alkyl substituents within the cavity of the π -electron cloud, in which the effect of the diamagnetic ring current on the protons of the alkyl groups could be studied. The anions corresponding to these substances were expected to be considerably more diatropic,⁵ and this has now been established by the observation of the potassium salts 13, 14, and 15.

The dihydropyridines 10, 11, and 12, precursors of the salts, were obtained from the pyridine 9.³ The reduction of 9 with LiAlH₄ to 10 has already been described.³ Treatment of 9 in THF with an excess of CH₃Li in ether at -30° to -5° under N₂ for 20 minutes, followed by quenching with NaHCO₃ solution and chromatography on SiO₂ (Woelm, activity II), gave 70% of 11 as brick-red crystals;⁶ *m/e* 353. Similar treatment of 9 with C₂H₅Li led to



40% of 12 as orange-red crystals;⁶ m/e 367.

The structures of 11 and 12 were confirmed by their ¹H-NMR spectra. Interestingly, these proved to be temperature dependent; *e.g.*, the H^c proton resonances were very broad at room temperature, but became sharper on cooling to -30° or below. This behaviour is presumably due to the conformational mobility of 11 and 12, as has been found for related substances.⁷

The dihydropyridines 10, 11, and 12 were readily converted to the dark violet salts 13, 14, and 15 by reaction with potassium. Dry freshly prepared samples of 10, 11, and 12 (15-20 mg) in THF-d₆ (ca 0.4 ml) and benzene (3 drops, lock signal) were allowed to react with a potassium mirror in a sealed evacuated NMR tube⁸ at room temperature, and the ¹H-NMR spectra of the salts were then recorded. The electronic spectrum of 13, obtained on a sample similarly prepared by reaction of 10 in THF with a potassium mirror in an evacuated cell with a side-arm,⁸ showed λ_{\max} (> 300 nm) 338 (ϵ 18,600),⁹ 353 (19,800), 375 (21,700), 399 (36,000), 420 (20,100), 555 (7000), ca 580sh (9800), and 598 nm (13,100).¹⁰ The sealed solutions of 13, 14, and 15 proved to be fairly stable; no appreciable change was observed after 2 weeks at room temperature, while heating 15 at 80° for 3 days resulted in ca 75% decomposition.

The ¹H-NMR parameters of the salts 13, 14, and 15 are given in Table 1, as well as the chemical shift differences for the various signals on passing from the diatropic N-methyl compounds 1, 5, and 6¹¹ to the corresponding salts.¹² The anions are clearly much more diatropic than the N-methyl derivatives, all the outer proton signals having moved to lower field, and the inner proton signals to higher field. The shifts in each direction are

Table 1. $^1\text{H-NMR}$ parameters of compounds 13, 14, and 15 in THF-d_6 at 100 MHz
 [τ values, internal standard benzene (τ 2.73)]

	Outer H				Inner H			
	H ^A	H ^B	Allylic H	Nonallylic H	H ^C	H ^D	H ^a	H ^B
<u>13</u>	1.03s	1.19d ^a	6.3-6.9m	7.7-8.1m	11.51d ^a	14.24s	-	-
<u>14</u>	1.37s	1.29d ^a	6.4-6.9m	7.7-8.2m	11.17d ^a	13.47q ^b	12.41d ^b	-
<u>15</u>	1.36s	1.22d ^a	6.4-6.9m	7.7-8.2m	11.06d ^a	13.28t ^c	11.83dq ^d	11.24t ^e
Δ (<u>13-1</u>)	-1.63	-1.11	<u>ca</u> -0.5	<u>ca</u> -0.3	+4.15	+3.35	-	-
Δ (<u>14-5</u>)	-1.42	-1.19	<u>ca</u> -0.5	<u>ca</u> -0.3	+4.57	+3.96	+1.78	-
Δ (<u>15-6</u>)	-1.38	-1.22	<u>ca</u> -0.5	<u>ca</u> -0.3	+4.48	+3.80	+1.66	+1.07

^a $\underline{J} = 15\text{Hz}$. ^b $\underline{J} = 6\text{Hz}$. ^c $\underline{J} = 5\text{Hz}$. ^d $\underline{J} = 5$ and 7Hz . ^e $\underline{J} = 7\text{Hz}$.

of the same order as those found for passing from suitable atropic models to the N-methyl derivatives 1, 5, and 6.^{3,4} It is noteworthy that the difference in ring current between the anions and the corresponding N-methyl compounds is greater in the C-alkyl salts 14 and 15 than in 13, as judged by the inner H^C and H^D resonances. This is probably due to the fact that the C-alkyl groups cause less deviation from planarity in the anions than in the N-methyl derivatives.⁴

The negative charge of the anions does not significantly affect the preceding discussion, the expected effect of this charge, if it were equally distributed between seventeen atoms, being an upfield shift of ca 0.6 p.p.m. for the H^A, H^B, and H^C signals. This is in accord with the observation that the upfield shifts of the H^C resonances in the anions (as compared to those of the corresponding N-methyl compounds) are 0.6 - 0.8 p.p.m. greater than those of the H^D resonances (Table 1), since little negative charge would be expected to reside on the bridge carbon atom. It is of interest that the differences in chemical shift between the outer and inner olefinic proton signals of the bridged didehydroaza[17]annulenyl anions are smaller than those of the isoelectronic [17]annulenyl¹³ and methoxytridehydro-[17]annulenyl¹⁴ anions.

REFERENCES AND NOTES

1. Unsaturated Macrocyclic Compounds 106. For part 105, see R.T. Weavers and F. Sondheimer, Angew. Chem. in press.

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6. The substance decomposed on attempted melting point determination.
7. R.T. Weavers and F. Sondheimer, Angew. Chem. in press (Unsaturated Macrocyclic Compounds 104).
8. For the apparatus used, see W.H. Okamura and T.J. Katz, Tetrahedron 23, 2941 (1967).
9. The ϵ values are minimum ones, quantitative conversion of 10 to 13 being assumed.
10. By comparison, 10 in THF exhibited λ_{\max} (> 300 nm) 342 (ϵ 38,100), 355 (43,000), 373 (27,200), 426 (7700), ca. 455sh (4300), 491 (2600), and 527 nm (870).
11. The $^1\text{H-NMR}$ spectra of these compounds 3,⁴ were redetermined in THF-d₆.
12. The N-methyl derivatives 1, 2, and 6 were chosen for comparison, since they are more diatropic than the corresponding N-H compounds 10, 11, and 12, and their $^1\text{H-NMR}$ spectra are not temperature dependent in the observed temperature range (unlike those of 11 and 12).
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