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5-PHENYLTRICYCLO[7.4.1.$0^{3,6}$]- AND 3-PHENYLTRICYCLO-[7.4.1.$0^{2,5}$]TETRADECAHEXAENYL ANION. NOVEL 14π-ELECTRON SYSTEMS

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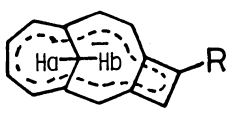
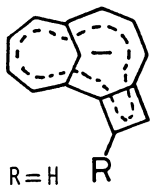
While 5-phenyltricyclo[7.4.1.$0^{3,6}$]tetradecahexaenyl anion, an anionic member of [4n]annuleno[4n]annulene, is moderately diatropic, 3-phenyltricyclo[7.4.1.$0^{2,5}$]tetradecahexaenyl anion appears atropic.

The electronic nature of [4n]annuleno[4n]annulenes represented by butalene, bicyclo[6.2.0]decapentaene and octalene has attracted considerable interest by both experimentalists[1] and theoreticians.[2] We have reported that bicyclo[6.2.0]-decapentaene,[1c] bicyclo[5.2.0]nonatetraenyl anion derivatives,[1d] and a bicyclo-[6.1.0]nonatetraenyl anion derivative[1e] which are isoelectronic 10π-electron systems pertinent to the present interest show induction of moderate diamagnetic ring current (moderate diatropicity) in ^{1}H NMR spectra. However, the observed diatropicity in these molecules is not typical enough to be concluded definitely due to counterbalancing contribution of the total 10π-electron periphery and the local 4nπ-electron peripheries.

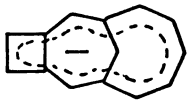
In searching after better conjugated systems for obtaining further insight into the tropicity of [4n]annuleno[4n]annulenes and related compounds, we have chosen tricyclo[7.4.1.$0^{3,6}$]-, tricyclo[7.4.1.$0^{2,5}$]-, and tricyclo[6.5.1.$0^{3,6}$]tetradecahexaenyl anion (1a, 2a, and 3), which are [4]annuleno[11]annulenyl anions and isoelectronic to [4]annuleno[12]annulene, for the following reasons : (i) a good number of methano-bridged annulenes have been synthesized, and there has been accumulated a good deal of ^{1}H NMR data for comparison; (ii) the chemical shifts of the bridge methylene protons are more sensitive to ring current than those of the ring protons providing a better measure for tropicity; (iii) the unfused parent anion, i.e. 1,6-methano[11]annulenyl anion (4),[3] is known to show a distinct paratropicity, which would allow a good assessment of the effects of cyclobutadiene annelation. None of 1 — 3 has been reported. We wish here to report the synthesis and properties of the phenyl derivative of 1a and 2a, i.e. 1b and 2b, where the phenyl group would not perturb severely the electronic nature of 1a and 2a, respectively.



1a: R = H
1b: R = Ph



2a: R = H
2b: R = Ph



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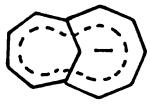

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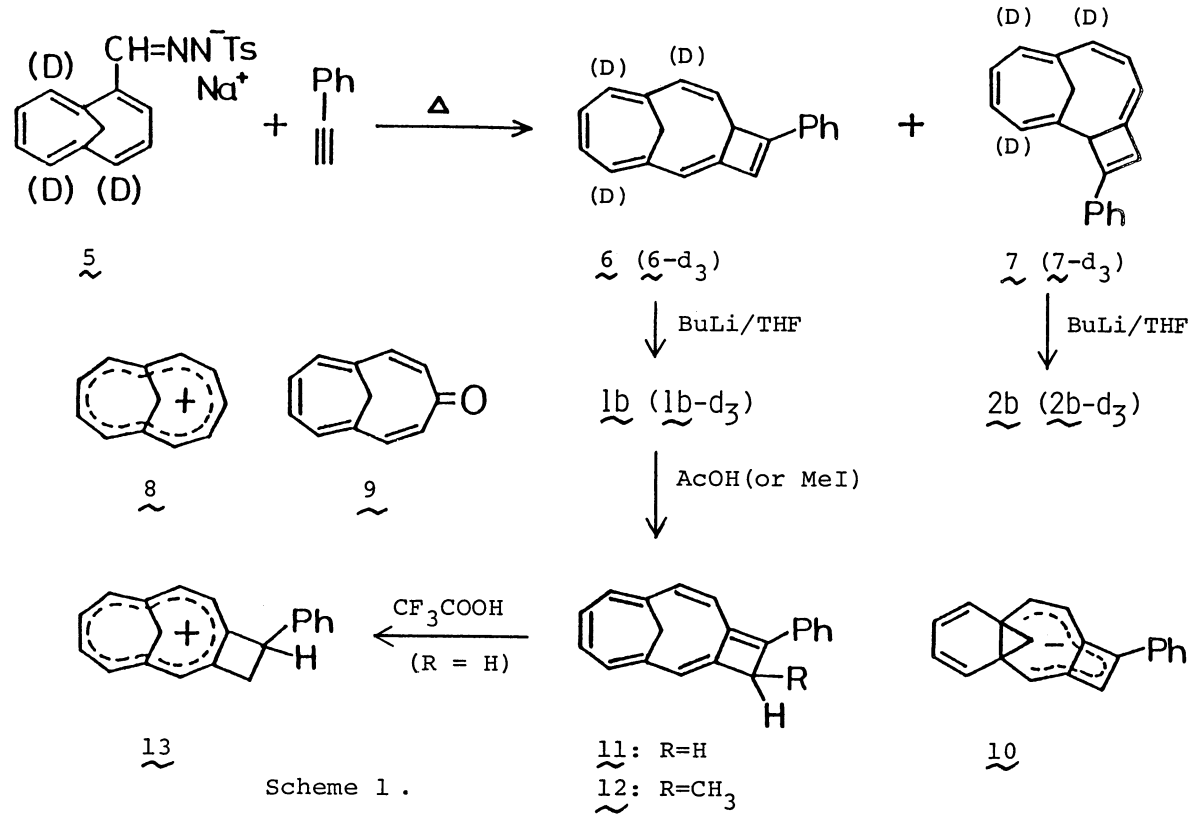
Jones et al. have reported the formation of 5-phenyltricyclo[7.4.1.$0^{3,6}$]tetradeca-2,4,7,9,11,13-hexaene (6) and 3-phenyltricyclo[7.4.1.0.^{2,5}]tetradeca-3,5,7,9-11,13-hexaene (7), which could be suitable precursors for 1b and 2b, by thermal decomposition of 2-formyl-1,6-methano[10]annulene tosylhydrazone sodium salt (5) in the presence of phenylacetylene.[4)]

Treatment of 6 with BuLi in THF under nitrogen atmosphere below -30 °C afforded the expected anion 1b in a deep greenish solution. The hydrocarbon 6 was acidic enough to be transformed cleanly to 1b also by treatment with dimsyl sodium in DMSO (pK_a=35[5)]) at room temperature. The anion 1b thus obtained was fairly stable in these solutions under inert gas atmosphere at room temperature.

Figure 1 shows ^{1}H NMR spectra of 1b and 1b-d_3 in DMSO-d_6, the latter being prepared similarly via 6-d_3 starting from 2,5,7,10-tetradeuterio-1,6-methano[10]-annulene[6)] (Scheme 1). The most notable feature in the ^{1}H NMR is the appearance of the bridge methylene protons at considerably high field. Although their averaged chemical shift (δ_{av}=0.61) is 1.4 ppm lower than that of 1,6-methano[11]annulenyl cation (8)[7)] which is typically diatropic (aromatic), it is higher as large as 11.6 ppm than that of 4 (Table 1). As a closely comparable compound, 4,9-methano-[11]annulenone (9)[8)] shows the bridge protons at slightly lower field (δ_{av}=0.86) than 1b does. These comparisons strongly suggest that 1b is diatropic in nature. This is further supported by the considerably low-field chemical shifts of ring protons of 1b (δ_{av}=6.5) which are significantly lower than those of 4 (δ_{av}=2.9[3)]), and are even lower than those of the presursor hydrocarbon 6 (δ_{av}=6.1) despite increase of charge density. Closed "norcaradiene" structure as 10 for 1b can be excluded by the relatively large value of $J_{14a,14b}$ (9.9 Hz).[9)]



Scheme 1.

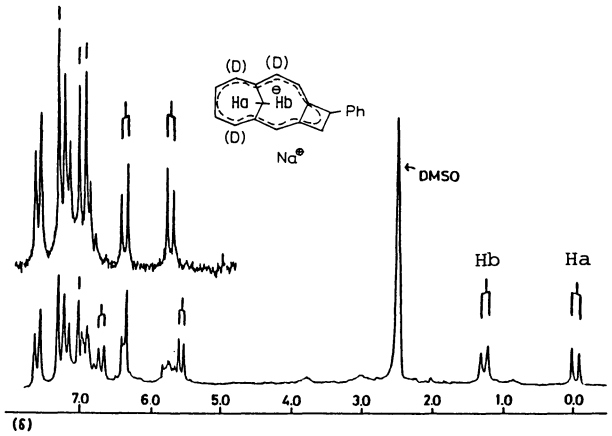


Fig. 1. ^{1}H NMR spectra of 1b (lower) and 1b-d_3 (upper) in CD_3SOCD_3 (100 MHz; CD_2HSOCD_3 as an internal standard, δ 2.49). Assignments are given in Table 2.

Table 1. The chemical shifts of the bridge protons of 1,6-methano[11]annulenes

	δ H_a	δ H_b	δ average
8 [a]	-0.25	-1.74	-1.00
13 [b]	-0.43	-1.50	-0.96
1b [b]	-0.05	1.26	0.61
9 [c]	0.04	1.68	0.86
c)	0.21	3.72	1.97
2b [b]	(0.8-1.8)	4.77	(2.8-3.3)
11 [b]	2.23	4.72	3.48
4 [d]	10.31	14.19	12.25

a) Ref. 7. b) Assignment of H_a and H_b is based on analogy with other methano[11]annulenes. c) Ref. 8. d) Ref. 3.

Thus, the annelation of a cyclobutadiene to 4 forming 1 causes a striking change of tropicity from the strong paratropicity of 4 to the moderate diatropicity of 1, which supports our previous description that planar or nearly planar [4n]-annuleno[4n]annulenes can be diatropic in nature.[1c-e)]

Quenching the DMSO solution of 1b with acetic acid or methyl iodide gave the deep red, air-sensitive undecafulvene derivative 11 (mp 97-98 °C, 83%) or 12 (oil, 73%).[10)] The fulvene 11 regenerated 1b on treatment with dimsyl anion. The ^{1}H NMR data (Table 2) suggest 11 and 12 to be weakly paratropic. The structure of 11 was further supported by protonation at C-5 with CF_3COOH to give the diatropic cation 13.[10)]

In contrast to fair stability of 1b, the anion 2b was unstable. Treatment of 7 (or 7-d_3) with BuLi in THF at -78 °C gave a deep greenish solution of 2b (or 2b-d_3) which decomposed in a few minutes at -10 °C. The ^{1}H NMR spectra (Table 2) are consistent with the proposed structure except the failure in observing one of the bridge protons, the other one appearing as a doublet (J=9.2 Hz) at δ 4.77. It seems that the missing proton signals are hidden in the intense signals of hexane and butane (δ 0.8-1.8) arising from the use of hexane solution of BuLi. The attempts to generate 2b cleanly using other bases have been so far unsuccessful. The δ_{av} (5.1) of the ring protons of 2b is 1.4 ppm higher than that of 1b and is in the range of chemical shifts that would be expected for atropic anions of this size of conjugated molecules. The apparent decrease of delocalization around the 14π electron periphery in 2b compared to 1b is perhaps ascribed to steric reasons, since molecular models suggest that annelation of a cyclobutadiene next to the bridge-head carbon of 4 decreases coplanarity of the annulene periphery relative to that of 1b owing to increase of strain.

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Table 2. ^{1}H NMR data of some compounds (δ ppm, 100 MHz)

1b	-0.05 (d, J=9.9 Hz, H-14a), 1.26 (d, 9.9 Hz, H-14b), 5.57 (d, 7.3 Hz, H-8), 5.74 (m, H-12), 6.36 (m, H-10, 11), 6.81 (d, 7.7 Hz, H-13), 6.88 (t, para), 6.94 (d, 7.3 Hz, H-7), 7.04 (s, H-2), 7.16 (t, meta), 7.33 (s, H-4), 7.62 (d, ortho) [a]
2b	4.10 (d, J=8.0 Hz, H-8), 4.23 (d, 10.5 Hz, H-6), 4.77 (d, 9.2 Hz, 14b), 4.9-5.3 (m, H-4, 7, 10, 12), 5.9 (m, H-11, 13), 7.1 (m, meta, para), 7.40 (d, ortho) [b]
2b-d_3	4.21 (d, 10.5 Hz, H-6), 4.77 (d, 9.2 Hz, 14b), 5.00 (s, H-4), 5.12 (d, 10.5 Hz, H-7), 5.15 (d, 9.6 Hz, H-13), 5.89 (d, 9.6 Hz, H-11), 7.1 (m, meta, para), 7.40 (d, ortho) [b]
11	^{1}H NMR ($CDCl_3$) δ 2.23 (d, J-11.5 Hz, 1H), 2.74 (d, 15.5 Hz, 1H), 2.90 (d, 15.5 Hz, 1H), 4.72 (dt, 11.5, 1 Hz, 1H), 5.94 (s, 1H), 6.0-6.2 (m, 3H), 6.25 (d, 11.5 Hz, 1H), 6.6 (m, 2H), 7.2-7.6 (m, 5H) [c]
12	1.26 (d, J=6.8 Hz, 3H), 2.22 (d, 11.2 Hz, 1H), 3.09 (q, 6.8 Hz, 1H), 4.66 (dt, 11.2, 1.0 Hz, 1H), 5.91 (s, 1H), 6.1 (m, 2H), 6.15 (d, 11.5 Hz, 1H), 6.31 (d, 11.5 Hz, 1H), 6.6 (m, 2H), 7.2-7.6 (m, 5H) [c]
13	-1.50 (d, J=12.0 Hz, 1H), -0.43 (d, 12.0 Hz, 1H), 3.88 (dd, 16.6, 2.2 Hz, 1H), 4.55 (dd, 16.6, 6.6 Hz, 1H), 5.14 (dd, 6.6, 2.2 Hz, 1H), 7.2-7.6 (m, 5H), 8.32 (d, 9.5 Hz, 1H), 8.5-8.9 (m, 4H), 9.22 (d, 9.5 Hz, 1H), 9.28 (s, 1H) [d]

a) In CD_3SOCD_3. b) In THF-d_8 at -30 °C. c) In $CDCl_3$. d) In CF_3COOH.

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