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SYNTHESIS AND PROPERTIES OF BICYCLO[5.2.0]NONATETRAENYL ANIONS. A NEW 10 π-ELECTRON SYSTEM[1]

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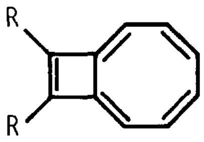
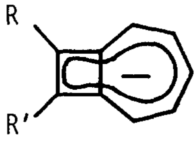
Summary: 8-Phenyl- and 8,9-diphenylbicyclo[5.2.0]nonatetraenyl anion, obtained in fairly stable solutions by base treatment of the corresponding bicyclo[5.2.0]nona-1,3,5,8-tetraenes, display properties characteristic of aromatic systems.

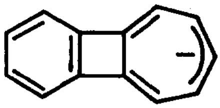
Recently we have reported the synthesis and X-ray crystal structure of bicyclo[6.2.0]decapentaenes (1).[1] The results suggest, in contrast with the transient nature of butalene[3] and the nonplanar, polyolefinic nature of octalene,[4] that the aromatic stabilization of 1 as a peripheral 4n+2 π-electron system prevails over the antiaromatic destabilization of the component 4n π-electron rings, counterbalancing enough the strain energy associated with the (near) planar geometry. In view of less strain energy of planar seven membered ring compared with planar eight-membered ring, bicyclo[5.2.0]nonatetraenyl anion (2), which is isoelectronic to 1, would be expected to be also a resonance stabilized species. As a related compound, Staley et al. reported the synthesis of 8,9-benzo compound 3 which was stated to behave as both a peripheral 4n+2 π-electron system and a local 4n π-electron system.[5] We here describe the synthesis and some properties of 8-phenyl- and 8,9-diphenylbicyclo[5.2.0]nonatetraenyl anion (2a) and (2b).



1: R= H, Ph



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



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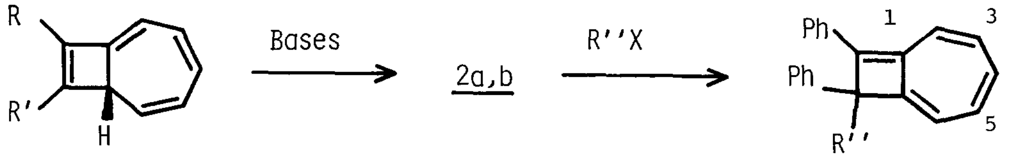
Our approach is based on Jones' findings that cycloheptatrienylidene adds to phenylacetylene giving 8-phenylbicyclo[5.2.0]nona-1,3,5,8-tetraene (4) probably *via* a spiro[2,6]nona-1,4,6,8-tetraene.[6] It was expected that treatment of 4 with bases should produce anion 2a, if this 10 π-electron system is really stabilized by resonance. In order to make NMR analysis easier by introduction of symmetry, it was desirable to prepare 8,9-diphenyl compound 5 that had not been described in the literature. Diphenylacetylene was, however, much less reactive toward the carbene, and after several unsuccessful attempts it was found that 5 was obtainable, albeit low yield, under a condition of high concentration of the acetylene.[7]

When treated with either n-butyl lithium or lithium diisopropylamide (LDA) in tetrahydrofuran (THF) below 0°C, 4 and 5 cleanly yielded anion 2a and 2b, respectively, in deep permanganate-colored solutions. Anion 2b was also formed by action of sodium hydride on 5 in dimethyl sulfoxide (DMSO) at room temperature. These anions were stable in solutions at room temperature under inert gas atmosphere, and heating of a DMSO solution of 2b at 80°C for four hours caused no change in its ^{1}H-NMR spectrum, indicating a high thermal stability.



4: R=H, R'=Ph

5: R=R'=Ph

6: R''=H

7: R''=CH$_3$

The ^{1}H-NMR spectrum of 2b is shown in Fig. 1, which is indicative of the C_{2v} symmetry of the molecule. The parameters deduced are given below.

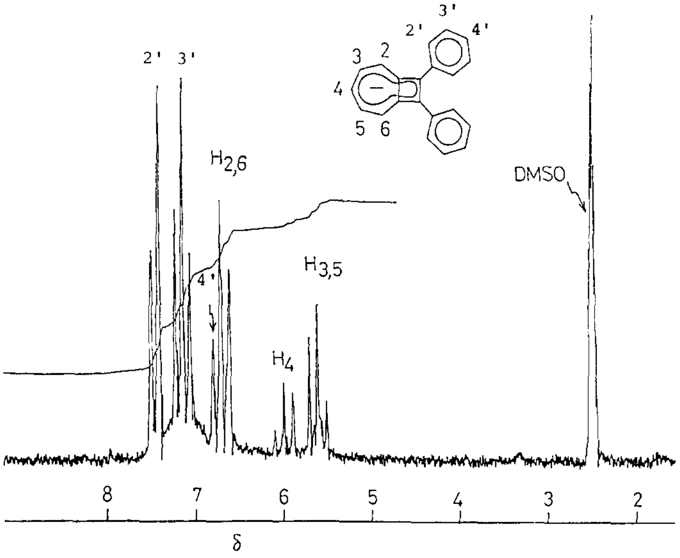


Fig. 1 The ^{1}H-NMR spectrum (90 MHz) of 8,9-diphenylbicyclo[5.2.0]nonatetraenyl anion (as sodium salt) in DMSO-d$_6$

In THF-d$_8$	In DMSO-d$_6$
$\delta_{2,6}=6.64$	6.64
$\delta_{3,5}=5.60$	5.60
$\delta_{4}=5.96$	5.98
$\delta_{2',6'}=7.50$	7.45
$\delta_{3',5'}=7.03$	7.13
$\delta_{4'}=6.60$	6.72

$J_{23}=8.3$

$J_{34}=9.3$

$J_{24}=1.0$

The unsymmetrical anion 2a exhibits the following ^{1}H-NMR signals: δ (THF-d_8) 5.44 (t, H-3 or 5), 5.54 (t, H-3 or 5), 5.96 (t, H-4), 6.2-6.6 (m, H-2,6, 4'), 6.74 (s, H-9), 6.91 (t, H-3', 5'), 7.31 (d, H-2', 6').

The center of gravity of the seven-membered ring protons of 2a and 2b are δ ca 6.0 and 6.09, respectively, which are about 0.6 ppm lower than that of 8,9-benzo compound 3 ($\delta_{av.}$=5.43)[5] and close to the center of gravity of the ring protons of 1,6-methanocyclononatetraenyl anion ($\delta_{av.}$=ca 6.0), a 10 π-electron aromatic ion.[8] The four-membered ring proton of 2a (δ=6.74) is observed down-shifted about 0.2 ppm compared to that of the precursor 4 (δ=6.51) in spite of increased charge density. It is also noteworthy that the difference between the coupling constants, J_{23} and J_{34}, of 2b (ΔJ=1.0 Hz) is smaller than that of 3 (ΔJ=2.3 Hz)[5] and only slightly larger than heptalene dianion (ΔJ= 0.55 Hz),[9] suggesting a rather small bond alternation, if any, in C-2 to C-6.

These observations point to an appreciable degree of delocalization of the negative charge and of induction of diamagnetic ring current around the 10 π-electron periphery of 2.

The ^{13}C-NMR spectrum of 2b shows signals at δ (from TMS) 109.6 (d, J_{C-H}= 148 Hz, C-2), 110.4 (d, 148 Hz, C-3), 116.2 (s, C-8), 119.0 (d, 144 Hz, C-4), 120.2 (d, 160 Hz, C-4'), 125.5 (d, 158 Hz, C-3'), 128.2 (d, 156 Hz, C-2'), 131.6 (s, C-1), 139.8 (s, C-1'),[10] further supporting delocalization of the negative charge.

Quenching of 2b with water gave an air-sensitive, wine-colored, crystalline hydrocarbon 6 : 35% yield; mp 132°C; δ (CCl_4) 3.85 (1H, s), 5.07 (1H, d, J=6.2 Hz), 5.2-6.0 (3H, m), 6.28 (1H, d, 11.6 Hz), 7.2 (10H, m); λ_{max} (cyclohexane) 244 (log ε 4.26), 252 (sh, 4.21), 348 (4.35), 361 (4.54), 382 (4.57), 464 (2.74), 496 (2.79), 537 nm (2.73).[11] Treatment of 6 with LDA regenerated 2b. These data are in accord with the heptafulvene structure depicted in which the ^{1}H-NMR signals at δ 3.85, 5.07, and 6.28 can be reasonablly assigned to H-8, H-6, and H-2, respectively. Reaction of 2b with methyl iodide yielded a similar compound 7 : 33% yield; oil; δ (CCl_4) 1.72 (3H, s), 5.01 (1H, d, J= 6.0 Hz), 5.2-6.0 (3H, m), 6.28 (1H, d, 11.6 Hz), 7.2 (10H, m).

In conclusion, anions 2a and 2b behave as compounds of an aromatic 10 π-electron system. Since the phenyl group(s) in these anions would not severely perturb the π-electron system, the parent anion would be expected to show similar properties.

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References and Notes

1) Part of this work was performed at Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan during M. O.'s faculty membership there until April, 1981.

2) (a) M. Oda, H. Oikawa, N. Fukazawa, and Y. Kitahara, Tetrahedron Lett., 4409 (1977); (b) C. Kabuto and M. Oda, ibid., 21, 103 (1980); (c) M. Oda and H. Oikawa, ibid., 21, 107 (1980); (d) A. Tajiri, M. Hatano, and M. Oda, Chem. Phys. Lett., 78, 112 (1981).

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7) A mixture of the isolated potassium salt of tropone tosylhydrazone (3.2 mmol), obtained by the reaction of tropone tosylhydrazone and potassium t-butoxide in THF followed by collection of the separated salt by filtration and drying, diphenylacetylene (20 mmol), dioxane (4 ml), and 18-crown-6 (100 mg) was heated under an efficient stirring at 100°C for 80-120 min. Extraction (n-hexane) and chromatographic separation (silica gel, eluted with n-hexane-CH_2Cl_2 (98:2)) gave adduct 5 in 5-8% yields as yellow crystals; mp 112-113°C; δ (THF-d_8) 4.80 (1H, s), 5.7-6.4 (5H, m), 7.1-7.8 (10H, m); λ_{max} (cyclohexane) 245 (log ε 4.48), 251 (4.47), 291 (4.28), 385 nm (3.98).

8) (a) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, Angew. Chem. Int. Ed. Engl., 5, 604 (1966); (b) P. Radlick and W. Rosen, J. Am. Chem. Soc., 88, 3462 (1966).

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10) The assignments are based on the long range couplings observed in the non-decoupled spectrum. These long range couplings are, however, omitted for clarity in the data described.

11) In addition to 6, a small amount of an yellow hydrocarbon was obtained, of which structure has been yet uncertain because of instability and scarcity of the material.

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