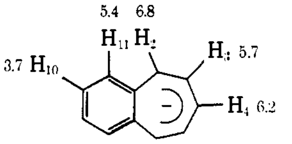

Figure 2. Paratropic shifts ($\Delta\delta_p$) in ppm (see text) for the benzocycloheptatrienyl anion (2).

tive charge (Δq_r) at each position r on going from **2** to **4** by use of the equation $\Delta\delta_q = (10.7\Delta q_r)$ ppm.[21]

The discrepancies between $\Delta\delta_q$ and the observed chemical shift differences for the corresponding protons in **2** and **4** (Figure 1) are termed paratropic shifts ($\Delta\delta_p$) and can be taken as an approximate measure of the shielding by the paramagnetic ring currents in **2** (Figure 2).[22]

It is important to note that (1) all protons are significantly shielded beyond what is expected on the basis of charge-induced shifts alone, (2) $\Delta\delta_p$ is greater for the protons on the seven-membered ring compared with those on the six-membered ring, and (3) the protons adjacent to the ring fusion (particularly H_8 and H_{11}) are shifted more than the other protons on the same ring (*i.e.*, H_9 and H_{10}). These results can be most simply rationalized on the basis of a model employing at least two paramagnetic ring currents, a major one encompassing all 11 carbon atoms, and another about half as strong localized in the seven-membered ring.[23] The extra shift of H_8 and H_{11} relative to H_9 and H_{10} is consistent with the former protons being influenced by both ring currents. Thus, this analysis of the paratropism of **2** is completely in accord with what would be expected on the basis of the π-bond fixation suggested by molecular orbital calculations and by the values of the vicinal coupling constants.

Acknowledgment. We thank the National Science Foundation for support of this work, and Professor H. Günther for permission to cite unpublished data.

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(21) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963).

(22) No correction is necessary for the effect of the diamagnetic ring currents in the π orbitals of **5** since they will also be present in **2** and will not be greatly affected by the bond alternation in the latter compound (see ref 5a). Solvent and counterion effects may contribute but will probably not make a significant difference in the relative values in Figure 2.

(23) A small current may also exist in the six-membered ring.

(24) Gillette Research Foundation Fellow, 1972–1973.

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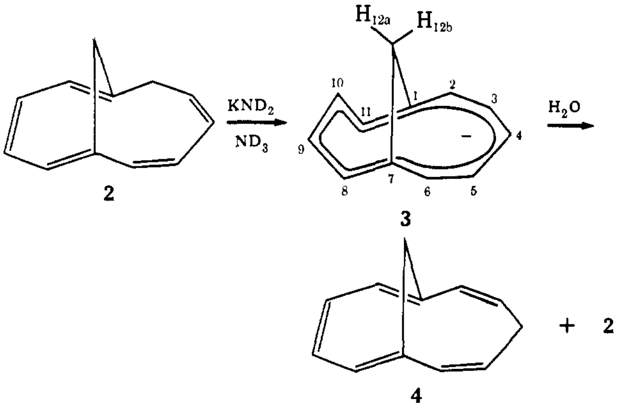
Received February 20, 1973

The Bicyclo[5.4.1]dodecapentaenyl Anion. Factors Affecting Paramagnetic Ring Currents

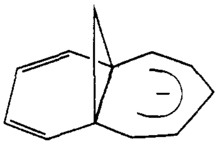
Sir:

The factors which influence paramagnetic ring currents have received some attention from a theoretical standpoint,[1] but there is very little experimental evidence which bears on this problem. We have recently reported the preparation of the benzocycloheptatrienyl anion (**1**) along with an analysis of the ring currents in this paratropic species.[2,3] We now report the preparation of a closely related anion, the bicyclo[5.4.1]dodecapentaenyl anion (**3**) and present an analysis (based on nmr spectral data) which indicates how the paramagnetic ring currents are affected by the distortions in the C_{11} π system of **3** relative to that of **1**.

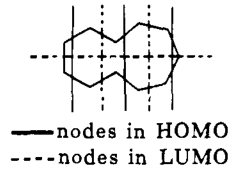
Deep red-brown solutions of anion **3** were prepared by treatment of **2**[4,5] with potassium amide in liquid ammonia. A mixture consisting predominantly of **4**[5] and **2** in a 3:1 ratio was obtained on quenching **3** into hexane–water. The nmr data, obtained at −50° in ammonia-d_3,[6] are given in Figure 1.



The relatively large value of $J_{12a,12b}$ (9.6 Hz) indicates that **3** has an "open" structure rather than a closed "norcaradiene" form as in **5**.[7,8] Of particular interest is the unusually low value of $J_{8,9}$ (4.7 Hz). This appears to be the smallest value of a J_{vic} between "olefinic" protons yet reported for a cycloheptatriene[9] and



5



7

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(1) For theoretical treatments of monocyclic systems, see (a) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); (b) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, No. 21, 109 (1967); (c) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. A*, 22, 103 (1967); (d) R. C. Haddon, *Tetrahedron*, 28, 3613 (1972).

(2) S. W. Staley and A. W. Orvedal, *J. Amer. Chem. Soc.*, **95**, 3382 (1973).

(3) Paratropic (diatropic) substances sustain an induced paramagnetic (diamagnetic) ring current in a magnetic field; P. J. Garratt and F. Sondheimer; cited by F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(4) W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 4, 354 (1965).

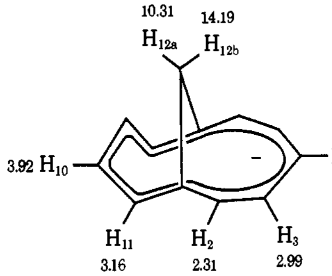
(5) E. Vogel, R. Feldmann, and H. Düwel, *Tetrahedron Lett.*, 1941 (1970).

(6) I. Melczynski, *Angew. Chem.*, 74, 32 (1962). We thank Dr. John Morrison for assistance with this preparation.

(7) A value of *ca.* 4.5 Hz would be expected in **5**; (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 87, 3267 (1965). However, this coupling constant in **3** is slightly smaller than the corresponding values in related bicyclo[5.4.1]dodecyl ring systems; *cf.* ref 4 and 5 and (b) W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *J. Amer. Chem. Soc.*, **92**, 6335 (1970); (c) E. Vogel, R. Feldmann, H. Düwel, H.-D. Cremer, and H. Günther, *Angew. Chem., Int. Ed. Engl.*, 11, 217 (1972); (d) J. Reisdorff and E. Vogel, *ibid.*, 11, 218 (1972).

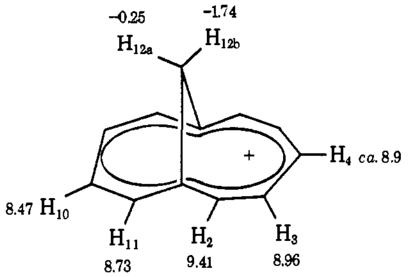
(8) However, there is undoubtedly a substantial interaction between the p orbitals at C_1 and C_7 as suggested by the X-ray structure of the closely related 4,9-methano[11]annulenone; (a) D. W. Hudson and O. S. Mills, *Chem. Commun.*, 153 (1971); (b) see also W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J. P. Weber, *Helv. Chim. Acta*, **51**, 225 (1968).

(9) See ref 7b and 7c and (a) H. Günther and R. Wenzl, *Z. Naturforsch. B*, 22, 389 (1967); (b) E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).



3

J_{23} = 10.4 Hz
J_{34} = 10.2
$J_{9,10}$ = 9.0
$J_{10,11}$ = 4.7 Hz
$J_{11,12b}$ = 1.3
$J_{12a,12b}$ = 9.6



6

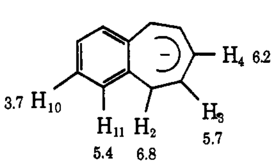
J_{23} = 9.0 Hz
$J_{9,10}$ = $J_{10,11}$ = 9.46
$J_{12a,12b}$ = 10

Figure 1. Nmr spectral data for the (potassium) bicyclo[5.4.1]dodecapentaenyl anion (3) in ammonia-d_3 at −50° (with trimethylamine ($\delta^{NH_3}_{TMS}$ 2.135) as internal standard) and the bicyclo[5.4.1]dodecapentaenyl cation[4] (6) in acetonitrile-d_3 at 32° (with TMS as internal standard); H. Günther, personal communication.

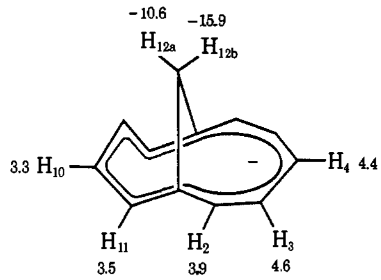
suggests that 3 is twisted about the C_8–C_9 and C_{10}–C_{11} bonds (with the dihedral angle formed by H_8–C_8–C_9–H_9 >40°).[10,11] This high degree of folding in 3 may be viewed as both a mechanism for diminishing "antiaromaticity" and a mode of relieving the angle strain inherent in the more nearly planar cation 6 (in which $J_{8,9} = J_{9,10} = 9.46$ Hz).[12]

It is obvious from the chemical shifts of the protons in 3 that this anion is strongly paratropic. All of the "olefinic" protons absorb substantially upfield from the positions expected on the basis of charge-induced shifts alone, and the C_{12} protons above the ring appear at δ 10.3 and 14.2 ppm, the latter being 15.9 ppm downfield from the position of the corresponding proton in the "aromatic" cation 6![4]

The relative magnitudes of the paramagnetic ring currents at each position in 3 were evaluated by the same approach[2] that was used for anion 1; *i.e.*, the approximate charge-induced chemical shift changes on going from 6 to 3 were calculated[13] and compared with the corresponding observed chemical shift differences. The discrepencies are attributed to the paratropic shift ($\Delta\delta_p$) associated with the highest occupied (and lowest unoccupied) molecular orbital(s) (HOMO and LUMO, respectively) of 3 and are given in Figure 2.[14]



1



3

Figure 2. Paratropic shifts ($\Delta\delta_p$) (see text) for the benzocycloheptatrienyl (1)[2] and bicyclo[5.4.1]dodecapentaenyl (3) anions.

According to theory,[15] paratropism arises from low-lying excited states accessible through allowed magnetic dipole transitions and is therefore inversely related to the energy gap between the HOMO and LUMO. The effect of distortions in the π system of 6 (relative to that of 3) on the energies of the HOMO and LUMO can be evaluated by applying the principle that decreased orbital overlap between two atoms lowers a given MO energy if that MO has a node between these positions and raises the MO energy if there is no node. Evaluation of the two major distortions in 3 relative to 1 (*viz.*, decrease of C_1–C_7 overlap and twisting of the C_8–C_9 and C_{10}–C_{11} bonds) with respect to the nodal properties of the HOMO and LUMO of these anions (see diagram 7) indicates that the first distortion should decrease the HOMO–LUMO energy gap and increase the paratropism whereas the nonplanarity should quench the paratropism.[16]

A decrease in C_1–C_7 overlap is clearly of importance as evidenced by the substantial reduction in $\Delta\delta_p$ for H_2–H_6 in 3 relative to 1 without a corresponding decrease in $\Delta\delta_p$ for H_9 and H_{10}. The latter observation indicates similar *peripheral* ring currents in 1 and 3 which in turn suggests an approximate cancellation of the paratropic effect of C_1–C_7 overlap and the diatropic effect of nonplanarity on this parameter.[17] This analysis raises the intriguing possibility that certain other folded $4n$ π-electron systems having an appropriate MO nodal pattern might exhibit a greater paratropism than analogous planar systems.

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(10) See the discussion in ref 9a.

(11) Also *cf.* the value for the analogous coupling constant in 4,9-methano[11]annulenone (6.74 Hz; ref 7b) for which the X-ray structure shows a dihedral angle of 29° (ref 8a).

(12) K. Mullen, H. Günther, and E. Vogel, cited in ref 7b, footnote 13.

(13) The ω technique (A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 4) was employed using bond integrals (β) suggested by the structure of 4,9-methano[11]annulenone (ref 7a) and by the coupling constants in Figure 1.

(14) For approximations involved in this calculation, see ref 2, footnote 22. The nonplanarity of 3 compared with 1 adds an additional approximation.

(15) (a) J. H. Van Vleck, "Electric and Magnetic Susceptibilities,', Oxford University Press, New York, N. Y., 1932; (b) see B. M. Trost G. M. Bright, C. Frihart, and D. Britelli, *J. Amer. Chem. Soc.*, **93**, 737, (1971), for additional references.

(16) Less important distortions include a probable twisting at C_1–C_2 and C_6–C_7 and at C_7–C_8 and C_1–C_{11} (see ref 8a), the effects of which should largely cancel, and a possible slight twisting at C_2–C_3 and C_5–C_6.

(17) A similar conclusion recently published by F. Gerson, K. Mullen, and E. Vogel (*Angew. Chem., Int. Ed. Engl.* **10**, 920 (1971)) is rendered problematical due to the lack of interpretation of the nmr spectra of the dianions studied. *Cf.* W. G. Schneider in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 63; R. G. Lawler and C. V. Ristagno, *J. Amer. Chem. Soc.*, **91** 1534 (1969).

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation. We also thank Professor H. Günther for permission to cite unpublished data.

[18] Gillette Research Foundation Fellow, 1972–1973

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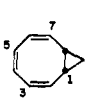
Received February 20, 1973

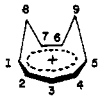
Protonation of *cis*-Bicyclo[6.1.0]nona-2,4,6-trienes in Superacidic Media. Carbon-13 Nuclear Magnetic Resonance Study of the Mono- and 1,3-Bishomotropylium Ions under Long Life Conditions

Sir:

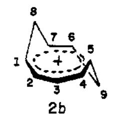
The facility with which *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) undergoes protonation to yield the parent monocyclic 1,3-bishomotropylium ion was reported in 1971.[1] At that time, several factors were considered to mitigate against the possibility that the resulting cation was transoid (**2b**), and its cis conformation (**2a**) was favored. More recently, however, chlorosulfonyl isocyanate[2] and tetracyanoethylene additions[3] to **1** have been found to occur in a manner which suggests the possible transient involvement of **2b** or the structurally related noninteracting cation **2c**. It was noted that the double-Mobius nature[4] of **2b** could possibly allow for homoaromatic delocalization, thereby rationalizing the observed charge distribution in **2**. Additionally, kinetically controlled electrophilic attack from the exo direction on the folded (rather than extended) conformation of **1** was established.[2,3]



1

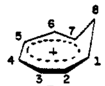


2a



2b

2c



3

A more detailed study of the protonation of **1** and its derivatives appeared highly desirable, and we therefore undertook to assess the behavior of these polyenes in superacids under conditions of long life. The high symmetry of **2** was clearly evident in its off-resonance decoupled cmr spectrum obtained in FSO_3H-SO_2ClF solution at −95°. The chemical shifts of the constituent carbon atoms are summarized in Table I where direct comparison with monohomotropylium ion (**3**) (generated under comparable conditions at −60°) is made. Although the ring current effect in **2** is clearly weaker than in **3**,[1,5] the two spectra are seen to compare favorably.

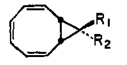
Table I. Cmr Data for **2** and **3**[a]

C atom in **2**	Chem shift,[b] δ	C atom in **3**	Chem shift,[b] δ
C_1, C_5	56.7[c]	C_1, C_7	71.5
C_2, C_4	25.8	C_2, C_6	40.0
C_3	10.3	C_3, C_5	48.5
C_6, C_7	52.6[c]	C_4	49.0
C_8, C_9	162.2	C_8	150.0

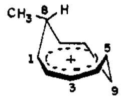
[a] A Varian HA-100 instrument was employed and the Fast Fourier Transform (FFT) method was employed. [b] The carbon shifts are cited relative to external CS_2. [c] Interchangeable values.

When the deuteration of **1** in FSO_3D-SO_2ClF at *ca.* −125° was reexamined, distribution of the isotope between the inner and outer positions of C_8 or C_9 was found to be 50:50 within our limits of analysis. Therefore, little if any stereoselectivity obtains in the incorporation of deuterium while proceeding from **1** to **2**.

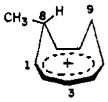
syn-9-Methyl derivative **4a**, which cannot attain a folded conformation and consequently lacks the ability to achieve good initial overlap of the internal cyclopropane bond with the developing charge center at C_2, gave only broad polymeric-type absorptions upon protonation at −78 to −150°. In contrast, anti isomer **4b** readily gave an nmr spectrum (Figure 1) comparable to that of **2** which, after decoupling clarified all assignments, was consistent only with **5a** or **5b** (Table II).



4a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = Cl$
d, $R_1 = Cl$; $R_2 = H$
e, $R_1 = R_2 = CH_3$



5a



5b

Table II. 100-MHz Pmr Data for Protonated *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**5**) (FSO_3H-SO_2ClF, 1:4 (v/v), *ca.* −130°)

Proton	Chem shift,[a] τ	Coupling constants, Hz
H_3	0.98	$J_{2,3} \equiv J_{3,4} = 6.0 \pm 0.5$
H_2	2.05	$J_{1,2} = 9.5 \pm 0.5$
H_4	2.19	$J_{4,5} = 9.0 \pm 0.5$
H_5	2.92	$J_{5,9o} = 9.5 \pm 0.5$, $J_{5,9i} = 11.0 \pm 0.5$
H_6	2.95	$J_{6,9o} = 10.0 \pm 0.5$, $J_{6,9i} =$ *ca.* 0
H_1	3.02	$J_{1,8i} = 11.0 \pm 0.5$
H_7	3.53	$J_{6,7} = 8.0 \pm 0.5$, $J_{7,8i} =$ *ca.* 0
H_{9o}	6.06	$J_{9o,9i} = 12.0 \pm 0.5$
H_{8i}	7.86	
H_{9i}	8.30	
CH_3	8.46	

[a] Chemical shifts measured relative to internal $CHDCl_2$ (τ 4.70).

The remarkable dichotomy in behavior between **4a** and **4b** points again to the fact that protonation of this ring system at C_3 must necessarily occur from the folded conformation to arrive at a homoaromatic species.[2,3]

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[1] P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971).

[2] L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972); L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972).

[3] J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2904 (1972).

[4] This term is employed to emphasize the unusual three-dimensional orbital construct of **2b** and refers simply to the π orbital directionality inherent in this cation.

[5] This diminished interaction is also revealed in carbon shift differences. For example, $\Delta\delta^{13}C = \delta C_1 + \delta C_3$ in ion **2** is about +46 ppm. a much larger value than that for the comparable difference in ion **3**, $\Delta\delta^{13}C = \delta C_1 - \delta C_4 = 22.5$ ppm. Equally revealing is the fact that the $\Delta\delta^{13}C$ values of such homotropylium ions are generally smaller than those in monocyclic pentadienyl cations (54.4–89 ppm).