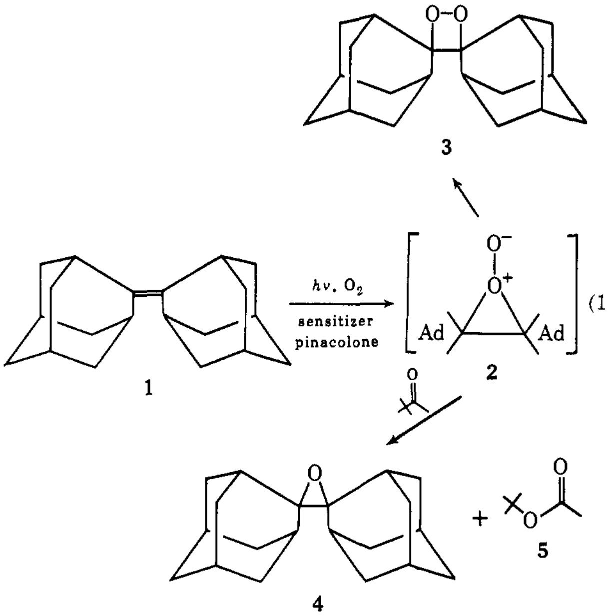
the intermediate perepoxide **2** by the solvent. Concomitant formation of *tert*-butyl acetate (**5**) has been confirmed by gas chromatographic analysis of the reaction solution.

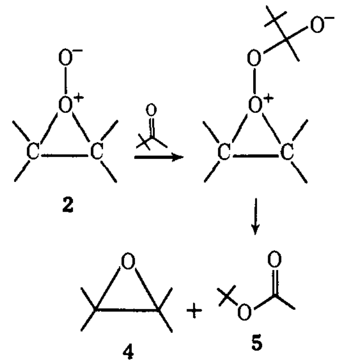
Adamantylideneadamantane (**1**), 15.2 mg, and 2,6-di-*tert*-butyl-*p*-cresol, 2.8 mg, a free radical inhibitor, were dissolved in 10 ml of rigorously purified pinacolone containing 10^{-4} *M* tetraphenylporphine. The solution maintained at ambient temperature and continuously saturated with oxygen was irradiated with a 300-W tungsten filament lamp through a Corning uv-cutoff filter. Quantitative gc analysis indicated complete consumption of the olefin **1** after 2 hr and the production of the dioxetane **3** (81%)[8] and the epoxide **4** (19%). The epoxide **4** has been isolated by column chromatography and preparative gas chromatography and compared to an authentic sample of **4** synthesized by *m*-chloroperbenzoic acid epoxidation of **1**.[9]



(1)

As free radical autoxidations of olefins are known to yield epoxides,[10] several control experiments have been carried out to verify that **4** is an authentic singlet oxygen product. Irradiation of **1** in pinacolone in the absence of the sensitizer yields no detectable dioxetane or epoxide. The free radical inhibitor has no effect on the rate of oxidation of **1** nor on the ratio of the products, **3** and **4**. The photooxidation of **1** in the presence of equimolar 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher,[11] is almost totally inhibited with only trace amounts of **3** and **4** (in the same ratio as observed in uninhibited experiments) formed after 24 hr of irradiation. The conversion of **1** to **3** and **4** is significantly slowed by the addition of the very reactive singlet oxygen acceptor, *cis*-dimethoxyethylene, to the reaction solution. It has been demonstrated that **3** does not yield **4** under the reaction conditions. Irradiation of a degassed solution of **1**, **3**, and tetraphenylporphine in pinacolone yields no epoxide **4**. *tert*-Butyl acetate (**5**) is not produced by photolysis of an oxygen saturated solution of tetraphenylporphine in pinacolone purified by preparative gc. Further, photooxidation of **1** in CH_2Cl_2 with tetraphenylporphine yields **3** quantitatively with $<0.1\%$ of **4**.

The formation of **4** and **5** in the photooxidation of **1** in pinacolone can be accommodated by the Baeyer–Villiger type mechanism shown in eq 2.



(2)

We conclude that epoxide **4** is derived from the perepoxide **2**. It is proposed that **2** is also the key intermediate in the generation of dioxetane **3**. However, we cannot yet exclude the possibility that **3** is formed by an alternate, concurrent reaction of singlet oxygen with **1**. Further experiments in this regard are in progress.

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[8] Under the gc conditions used, the dioxetane is thermally cleaved to 2 mol of adamantanone (**6**). The yield of **3** is based on the yield of **6** obtained. Dioxetane **3** has been isolated from the reaction solution by removal of the pinacolone under vacuum and recrystallization of the residue.

[9] H. Wynberg, E. Boelema, J. H. Wieringa, and J. Strating, *Tetrahedron Lett.*, 3613 (1970).

[10] R. Hiatt in "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., p 113.

[11] C. Ovannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6528 (1968).

The Benzocycloheptatrienyl Anion, a Paratropic Monoanion

Sir:

The horizons of the concept of aromaticity[1] have been expanded considerably in recent years by the preparation and direct observation by nmr spectroscopy of a number of planar or nearly planar compounds possessing cyclic arrays of p orbitals containing $4n$ electrons.[2,3] Some of these compounds show dramatic changes in the proton chemical shifts (compared with analogous cyclic $4n + 2$ systems) which can largely be

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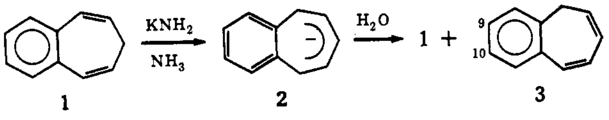
[1] For recent discussions of the definition of aromaticity, see (a) J.-F. Labarre and F. Crasnier, *Fortschr. Chem. Forsch.*, **24**, 33 (1971); (b) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972). For a thermodynamic definition, see (c) M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, No. 21, 207 (1967).

[2] For recent reviews, see (a) F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972); (b) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1971); (c) A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

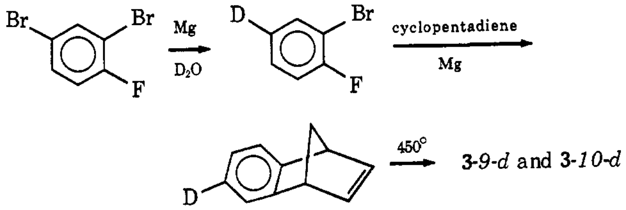
[3] (a) For recent reports, see I. Murata, K. Yamamoto, T. Hirotsu, and M. Morioka, *Tetrahedron Lett.*, 331 (1972); (b) B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, *J. Amer. Chem. Soc.*, **93**, 737 (1971); (c) H. Ogawa, M. Kubo, and H. Saikachi, *Tetrahedron Lett.*, 4859 (1971); (d) R. H. Cox, H. W. Terry, Jr., and L. W. Harrison, *ibid.*, 4815 (1971); (e) H. Neunhoeffer and L. Motitschke, *ibid.*, 655 (1970).

attributed to a net paratropism,[4] in contrast to the net diatropism commonly found in $4n + 2$ systems. The geometric and electronic factors which influence these shifts have not been fully elucidated.[5] In this paper we report the first direct observation (by nmr spectroscopy) of a paratropic anion of unit charge[6] (the benzocycloheptatrienyl anion) and present evidence regarding its molecular structure and the nature of its paramagnetic "ring currents."

Because of the expected instability of cycloheptatrienyl anions,[6d] a strongly basic medium is required in order to produce these species by deprotonation. We have found that treatment of benzocycloheptatriene (**1**[7] or **3**[8]) with potassium amide in liquid ammonia cleanly affords deep red-brown solutions of the benzocycloheptatrienyl anion (**2**) in high yield. These solutions can be quenched into wet ether to produce isomers **1** and **3** in about equal amounts.



The nmr spectral data for anion **2**, recorded at −50° in ammonia-d_3,[9] are given in Figure 1. The assignments for the benzo protons in the AA'XX' multiplets at δ 3.82 and 2.06 were made on the basis of deuterium labeling at H_9 in anion **2** prepared *via* **3** as follows.[8,10,11]



The coupling constants in the six-membered ring of **2**, obtained by calculation of the AA'XX' multiplets,[12] are of particular interest. The value of $J_{9,10}$ in cation **4** is 1.5 Hz less than $J_{10,11}$,[13] indicating a first-order bond fixation[14] (as indicated in Figure 1) which maximizes the C_1–C_7 bond order and hence the "aromaticity" of the seven-membered ring. In contrast, $J_{9,10}$ is 1.6 Hz greater than $J_{10,11}$ in anion **2**, indicating bond fixation in the direction which minimizes the C_1–C_7 interaction (see Figure 1); this decreases the "antiaromaticity" of the seven-membered ring and increases the π-bond order of the 11 carbon periphery.[15–17]

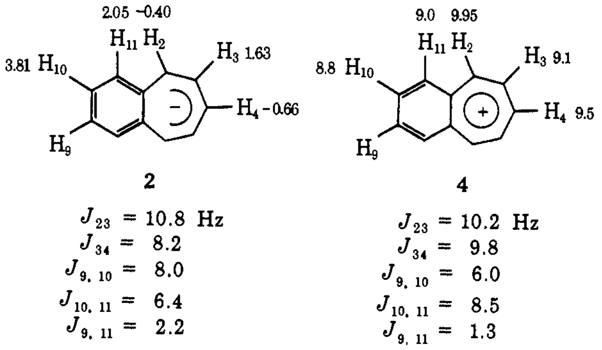


Figure 1. Nmr spectral data for the (potassium) benzocycloheptatrienyl anion (**2**) in ammonia-d_3 at −50° (with trimethylamine ($\delta_{\mathrm{TMS}}^{\mathrm{NH_3}}$ 2.135) as internal standard) and the benzocycloheptatrienyl cation[13] (**4**) in acetonitrile-d_3 at 32° (with TMS as internal standard).[13a]

It is clear from the proton chemical shifts that anion **2** is strongly paratropic. The signals for H_2–H_6 appear 3.5–4 ppm upfield from the corresponding protons in a number of cycloheptadienyl anions,[18] despite the fact that the carbon atoms in the latter anions are calculated to have larger negative charges.

According to theory,[5b,19] paramagnetic ring currents arise from the contributions of low-lying excited states accessible through magnetic dipole transitions. To a first approximation the paratropism in **2** may be attributed to the paratropism associated with the highest occupied (and lowest unoccupied) molecular orbital(s) (ψ_6 and ψ_7).[5c] This latter factor is derivable by comparison of the π system of **2** with the corresponding π system in which ψ_6 is empty, *viz.*, the benzocycloheptatrienyl cation (**4**). This comparison was made by first calculating the charge distributions in **2** and **4** by an iterative HMO method[20] and by then calculating the charge-induced shift ($\Delta\delta_q$) due to the increase in nega-

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(4) Paratropism (diatropism) is the ability to sustain an induced paramagnetic (diamagnetic) ring current in a magnetic field; *cf.* the terminology of P. J. Garratt and F. Sondheimer, ref 2a.

(5) 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).

(6) For previous studies of cycloheptatrienyl anions, see (a) H. J. Dauben, Jr., and M. R. Rifi, *J. Amer. Chem. Soc.*, **85**, 3041 (1963); (b) W. v. E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963); (c) R. Breslow and H. W. Chang, *ibid.*, **87**, 2200 (1965); (d) R. Breslow and W. Chu, *ibid.*, **95**, 411 (1973); (e) M. J. S. Dewar and N. Trinajstić, *Tetrahedron*, **26**, 4269 (1970).

(7) G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).

(8) S. J. Cristol and R. Caple, *J. Org. Chem.*, 31, 585 (1966). We thank Professor Martin Pomerantz for a sample of **3**.

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

(10) The favored position of metalation in 2,4-dibromofluorobenzene (deuteration occurs in 55% yield) appears to contrast with the results for 2,5-dibromoiodobenzene; H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc., Jap.*, 37, 40 (1964). See also R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 33.

(11) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

(12) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 166. These values were confirmed by computer simulation.

(13) (a) H. Günther, personal communication. See also (b) D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, 90, 107 (1968); (c) D. J. Bertelli and P. Crews, *Tetrahedron*, **26**, 4717 (1970).

(14) G. Binsch in "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," E. D. Bergmann and B. Pullman, Ed., Academic Press, New York, N. Y., 1971, p 25, and references cited.

(15) Antiaromatic destabilization should decrease with increasing size of the $4n$ π-electron ring; H. P. Figeys, *Tetrahedron*, **26**, 5225 (1970), and references cited.

(16) The Q value of **2** (where $Q = P_{8,9}/P_{9,10}$, the ratio of SCF bond orders in the benzo ring) is remarkably low (0.77); see D. Cremer and H. Günther, *Justus Liebigs Ann. Chem.*, **763**, 87 (1972).

(17) The somewhat low value of J_{34} in **2** (8.2 Hz) may indicate a slight twisting of the C_3–C_4 and C_4–C_5 bonds. For comparative values of J_{vic} in seven-membered rings, see ref 13b and 13c and P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

(18) (a) F. L. Wiseman, Jr., Ph.D. Thesis, University of Maryland, 1970; (b) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, 91, 4608 (1969); (c) H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1084, 1471 (1969); (d) H. Kloosterziel and E. Zwanenburg, *ibid.*, **88**, 1373 (1969); (e) S. W. Staley, A. W. Orvedal, and N. J. Pearl, unpublished results.

(19) (a) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932; (b) see ref 3b for a discussion and additional references.

(20) The values of both the Coulomb integral (α) and the bond integral (β) were varied until self-consistent charge distributions were obtained; see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 4.

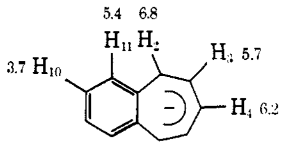

Figure 2. Paratropic shifts ($\Delta\delta_p$) in ppm (see text) for the benzocycloheptatrienyl anion (**2**).

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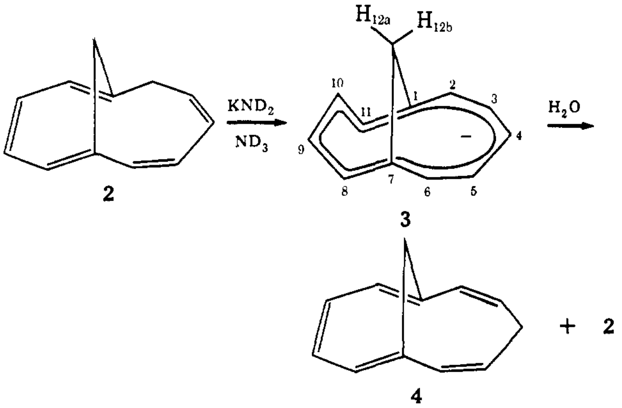
The Bicyclo[5.4.1]dodecapentaenyl Anion. Factors Affecting Paramagnetic Ring Currents

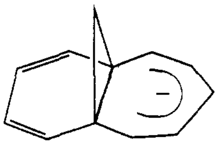
Sir:

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



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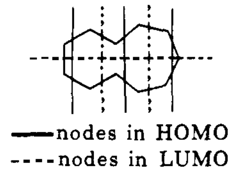

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[1] For theoretical treatments of monocyclic systems, see (a) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); (b) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, No. 21, 109 (1967); (c) F. Baer, H. Kuhn, and W. Regel, *Z. 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).