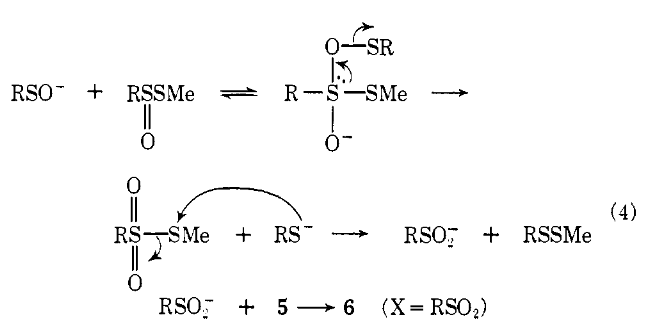
basic reagents, would appear to promote conversion of sulfenic acids (sulfenate) to sulfinic acids (sulfinate), *i.e.*, by a sequence of the type shown in eq. 4.[22]



(4)

It may be anticipated that the unique combination of functional groups in α-sulfinyl and α-sulfonyl disulfides will lead to unusual chemical, physical, and perhaps physiological properties. A study of the chemistry of these novel and now readily available compounds is in progress.

Acknowledgment. We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Air Pollution Control Office, Environmental Protection Agency (AP-1496-01), and the University of Missouri—St. Louis.

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[22] We thank Professor Kice for this suggestion.

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Methylenecyclooctatrienyl Anion, a Cyclic Delocalized Atropic Species

Sir:

The electronic properties of cyclic "4*n* + 1" π-electron systems[1] represent an interesting theoretical problem. Intuitively one might anticipate properties in between those of 4*n* + 2 "aromatic" or diatropic systems and 4*n* "antiaromatic" or paratropic systems,[2,3] but experimental evidence is completely lacking.

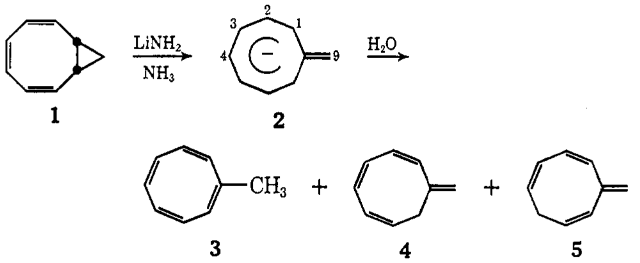
The methylenecyclooctatrienyl anion **2** is of particular interest in this regard since the nonbonding π orbital of the heptatrienyl anion portion of **2** (C_1–C_7) is antisymmetric with respect to the mirror plane through C_4, C_8, and C_9 and consequently does not interact with the orbitals of the exocyclic double bond (which are symmetric with respect to this plane). Thus, even though there is interaction between the symmetric orbitals, the energies of the antibonding levels are expected to balance those of the bonding levels so that there is relatively little transfer of π-electron density into or out of the eight-membered ring.[4] This consideration, along with the greater tendency toward delocalization in an ionic system compared with a polyenic system such as fulvene,[5] suggests that the heretofore unknown anion **2** may be a nearly ideal "4*n* + 1" closed shell π system for study.[6]

We now report that careful treatment of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) with lithium, sodium, or potassium amide in liquid ammonia at *ca.* −60° produces emerald green solutions of the methylenecyclooctatrienyl anion **2**, which have been characterized by nmr spectroscopy (see Table I).[7,8] The lithium salt of **2** is moderately stable up to about 0° in liquid ammonia, at which point it is irreversibly lost, but is stable for at least 1 hr at room temperature in hexamethylphosphoramide (HMPA).[9] In contrast, the sodium and potassium salts of **2** are rapidly lost at −60° in the presence of excess base.

Table I. Chemical-Shift Data for the Methylenecyclooctatrienyl Anion **2** in Liquid Ammonia at *ca.* −60°

	Chemical shift, ppm[a]				
Compd	H_1	H_2	H_3	H_4	H_9
2, Li^+ [b]	4.42	5.38	3.80	5.20	5.00
2, Na^+	4.42	5.37	3.78	5.20	4.99
2, K^+	4.41	5.35	3.76	5.18	4.99
2, Li^+ (HMPA)[c]	4.09	5.09	3.50	4.89	4.54
2 (calcd)[d]	4.0	5.5	3.9	5.4	4.9

[a] Trimethylamine ($\delta_{TMS}^{NH_3} = 2.135$) was used as an internal standard in liquid ammonia and tetramethylsilane (TMS) was employed in hexamethylphosphoramide (HMPA). [b] $J_{12} = 12.5 \pm 0.2$, $J_{23} = 10.2 \pm 0.4$, $J_{34} = 10.8 \pm 0.4$ Hz. [c] In HMPA at 34°. [d] See text.



1 **2**

3 **4** **5**

Addition of **2** in ammonia to pentane–water produced a mixture of 1% **3**,[8a,10] 24.5% **4**,[11] and 74.5% **5**.[12] A

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[1] We define these as cyclic delocalized systems in which the atoms of the ring possess essentially 4*n* + 1 π electrons in a closed shell configuration.

[2] We use the terms aromatic and antiaromatic advisedly. For recent discussions of the concept of aromaticity, see (a) J.-F. Labarre and F. Crasnier, *Top. Current Chem.*, 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).

[3] Atropic molecules possess no net (nmr) ring currents. The terms diatropic and paratropic (possessing diamagnetic and paramagnetic ring currents, respectively) have been defined by P. J. Garratt and F. Sondheimer; see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

[4] Note that this contrasts with the benzyl π system, in which the nonbonding orbital is symmetrical.

[5] P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, 43, 401 (1972), and references cited.

[6] G. Boche and D. Martens (*Angew. Chem., Int. Ed. Engl.*, **11**, 724 (1972)) briefly mentioned several related anions but our evidence suggests that these compounds are nonplanar.

[7] Portions of this work were presented at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, Abstracts, p O-C-7.

[8] For previous reports of the behavior of **1** in strongly basic media, see (a) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Amer. Chem. Soc.*, **87**, 3158 (1965); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

[9] Prepared by the treatment of **1** with lithium dimethylamide in hexamethylphosphoramide.

[10] A. C. Cope and H. C. Campbell, *J. Amer. Chem. Soc.*, **74**, 179 (1952).

[11] We thank Professor P. D. Gardner for ir and nmr spectra of **4** (see ref 8a).

[12] Nmr (CCl_4) complex multiplet at δ 6.3–5.4 (6 H, olefinic), singlet, at 4.88 (2 H, H_9), and a complex triplet at 2.99 (2 H, H_5, $J_{45} = J_{56} = 7$ Hz); uv (hexane) λ_{max} 267 nm (ε 9240).

similar mixture (<1% **3**, 34% **4**, and 66% **5**) was obtained upon quenching **2** in HMPA in the same manner. That these mixtures primarily represent a *kinetic quench* was established by the observation that a markedly different mixture of isomers (67% **3**, 31% **4**, and 2% **5**) was obtained on equilibration of either **3** or **4** in 0.5 *M* potassium *tert*-butoxide in dimethyl sulfoxide at 25°.[13]

The coupling constants in **2** are all relatively large (>10 Hz) and are indicative of a more or less planar delocalized structure.[14] Of particular interest is the observation that the chemical shifts of all protons in **2** move significantly upfield on changing the solvent from ammonia to hexamethylphosphoramide (see Table I). The nearly identical upfield shifts for H_1–H_7 (0.3 ppm) coupled with the somewhat larger shift for H_9 (0.46 ppm) can perhaps be explained by a change from contact to solvent-separated ion pairing and/or to free ions[15] The detection of this phenomenon by nmr spectroscopy seems to have been reported previously only in the case of simple "aromatic" anions.[16]

Interestingly, if one employs "model" chemical shifts of δ 6.1 and 5.0 for the ring[17] and exocyclic methylene[18] protons, respectively, and corrects for charge-induced chemical shifts ($\Delta\delta_q$) by us of the equation $\Delta\delta_q = kq_r$ where $k = \pm$ 10.7 ppm per ± charge,[19] then it is seen that the chemical shifts for H_2–H_6 in **2** in liquid ammonia[20] are in good agreement with calculated chemical shifts based on self-consistent HMO charge densities (see Table I).[21] The observed chemical shifts for H_1 and H_7 are, as expected, lower than the calculated value due to deshielding by the exocyclic double bond.

The above analysis points to several important conclusions. First, both the nmr data and the quenching data suggest that there is not a significant amount of negative charge at C_9 in **2** and that structure **2** is the major valence bond contributing structure.[22] Second, *there is no evidence for substantial diamagnetic or paramagnetic ring currents in this anion, thereby indicating that "4n + 1" π systems are atropic.*[3] Interestingly, this behavior is dramatically altered by the presence of donor and acceptor groups conjugated with the eight-membered ring, as will be reported in subsequent publications.

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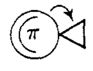
Contrasting Reactivities of the Spiro[2.5]octadienyl and Spiro[2.7]decatrienyl Anions

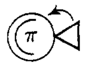
Sir:

The title anions exemplify classes of compounds in which cyclopropyl rings are spiro fused with cyclic π systems containing 4*n* + 2 and 4*n* π electrons (**1** and **2**, respectively).



4*n* + 2 π electrons

1



4*n* π electrons

2

The elucidation of the properties of such systems is of interest since, on the basis of simple perturbation theory, type **1** compounds are expected to experience electron donation from the π system into the cyclopropyl ring whereas type **2** compounds should display somewhat greater polarizations in the opposite direction.[1] The latter point has been verified for several compounds,[2] including the spiro[2.7]decatrienyl anion **3**,[3] but evidence concerning this point has yet to be obtained for type **1** compounds.[4] In addition, the spiro[2.5]octadienyl anion **4** has been of continuing interest as a possible intermediate or transition state in the 1,2 carbon to carbon migration of the phenyl group in carbanions.[5] In this paper we report data which demonstrate remarkably different reactivities for anions **3** and **4**.

Spirodienes **5**[6] and **6**[7] were obtained in 7 and 1% yields, respectively, by careful application of the alkyla-

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[13] Uncertainties are <1%; material balances were >85%.

[14] For the (dilithium) isopropenylcyclooctatetraene dianion J_{23} = 11.5 Hz and $J_{34} = J_{45}$ = 9.9 Hz. We greatly appreciate the assistance of Dr. Jeffrey Seeman with these measurements.

[15] That this shift is real and is not due to a referencing problem is demonstrated by the observation of a similar shift for the ring protons of the 9-*tert*-butyl derivative of **2** but not for the *tert*-butyl protons, which are essentially unshifted. We thank Professor A. G. Anastassiou and Dr. R. C. Griffith for a sample of the *anti*-9-*tert*-butyl derivative of **1**.

[16] J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Amer. Chem. Soc.*, **94**, 2306 (1972), and references cited therein.

[17] R. C. Haddon, *Tetrahedron*, **28**, 3613 (1972), and references cited therein.

[18] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

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

[20] Comparison is made with the liquid ammonia data since the value of *k* in this equation is based on chemical shifts obtained from what are probably contact ion pairs.[19]

[21] The ω technique was employed with all $\beta = \beta_0$; A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 115–116. Calculated charge densities are −0.197 (C_1), −0.056 (C_2), −0.201 (C_3), −0.063 (C_4), and −0.013 (C_9).

[22] Calculations based on the CNDO/2 approximation (J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965); P. A. Dobosh, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind., Program 141) appear to overestimate the amount of negative charge on C_9.

[1] This result obtains regardless of the charge in the π system and is a consequence of the fact that the highest occupied molecular orbitals (HOMO's) of the 4*n* π-electron systems are antisymmetric with respect to the plane of the cyclopropyl ring and therefore do not interact with the (Walsh) cyclopropyl orbitals, whereas the symmetric lowest unoccupied molecular orbitals do. The reverse situation (*i.e.*, symmetric HOMO's and antisymmetric LUMO's) is found in the 4*n* + 2 π-electron systems.

[2] (a) Spiro[2.5]octadienyl cation: G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971); (b) spiro[2.4]hepta-4,6-diene: R. A. Clark and R. A. Fiato, *ibid.*, **92**, 4736 (1970).

[3] S. W. Staley and W. G. Kingsley, *ibid.*, in press.

[4] Spiro[2.6]nona-4,6,8-triene is probably folded and shows no evidence of significant interaction; (a) C. J. Rostek and W. M. Jones, Jr., *Tetrahedron Lett.*, 3957 (1969); (b) see also M. Jones, Jr., and E. W. Petrillo, Jr., *ibid.*, 3953 (1969).

[5] (a) Review: H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 6; see also (b) E. Grovenstein, Jr., and Y.-M. Cheng, *J. Amer. Chem. Soc.*, **94**, 4971 (1972), and references cited therein; (c) G. Fraenkel and J. W. Cooper, *ibid.*, **93**, 7228 (1971), and references cited therein; (d) J. J. Eisch and C. A. Kovacs, *J. Organometal. Chem.*, **25**, C33 (1970).

[6] Nmr (CCl_4): complex d of t at δ 5.55 (H_5 and H_7, J_{45} = 10.5 Hz, J_{56} = 3.4 Hz), d of t at 4.97 (H_4 and H_8, J_{46} = 1.9 Hz), a seven-line multiplet (t of t) at 2.77 (H_6), and a singlet at 0.62 (4 H, cyclopropyl); uv (hexane) end absorption only ($\epsilon_{220\text{ nm}}$ 3470).

[7] A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **9**, 899 (1970). We thank Professor de Meijere for a copy of the nmr spectrum of this compound.