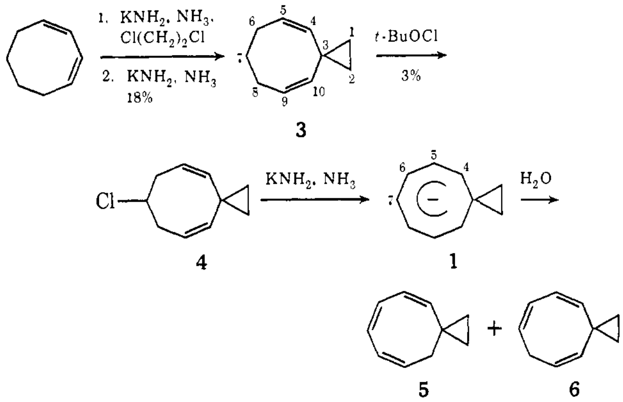
Scheme I



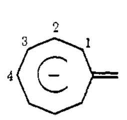
3, 4, 5, and 6 (δ 0.73, 0.82, 0.53, and 0.68, respectively). This indicates a substantial polarization of electron density out of the cyclopropyl ring and into the heptatrienyl anion portion of the molecule,[8] which is opposite to what would be expected on the basis of a greater dispersal of negative charge. Since the heptatrienyl anion portion of **1** has equal π donor and acceptor properties,[6] this polarization firmly establishes the cyclopropane ring as an intrinsically better donor than acceptor group.[9,10]

The chemical shifts for the eight-membered ring protons in **1**, and in the closely related anions **2** and **7**, are given in Table I. The remarkable point which emerges from the comparison of these data is that H$_5$–H$_9$ in **1** are shifted *ca.* 0.6–0.8 ppm *downfield* relative to the corresponding protons (H$_2$–H$_6$) in **2** and **7**, despite the fact that electron density is donated to the eight-membered ring from the cyclopropyl ring of **1**.[11] This is best explained on the basis of a substantial diamagnetic ring current in the π system of **1** (compared with the essentially atropic[6,12] system of **2**) and is the first case in which a ring current has been shown to result from spiro cyclopropyl conjugation. Thus, if aromaticity is defined on the basis of π-electron ring currents,[4] than **1** would be considered to be more "aromatic" than **2**.

Table I. Chemical Shifts for the Olefinic Protons in the Potassium Salts of the Spiro[2.7]decatrienyl (**1**), Methylenecyclooctatrienyl (**2**), and 8,8-Dimethylcyclooctatrienyl (**7**) Anions in Liquid Ammonia

	Chemical shift, ppm[a,b]			
Anion	H$_1$ (H$_4$)	H$_2$ (H$_5$)	H$_3$ (H$_6$)	H$_4$ (H$_7$)
1	4.13	5.97	4.41	5.84
2[c]	4.40	5.35	3.76	5.17
7[d]	4.52	5.42	3.54	5.20

[a] Obtained at −40, −60, and −55° for **1**, **2**, and **7**, respectively; trimethylamine ($\delta_{\mathrm{TMS}}^{\mathrm{NH_3}}$ 2.135) was employed as an internal standard. [b] The numbering of the protons in anion **1** is different from that in **2** and **7** and is given in parentheses. [c] Reference 6. [d] S. W. Staley and N. J. Pearl, *J. Amer. Chem. Soc.*, **95**, 2731 (1973).



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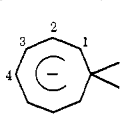

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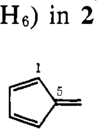

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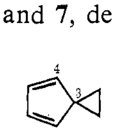

9

On the other hand, aromaticity is often defined in terms of the resonance energy of a π system compared with that of some appropriate model.[5] Interestingly, analysis of the photoelectron spectra of fulvene (**8**) and spiro[2.4]hepta-4,6-diene (**9**) shows a significantly greater C$_1$–C$_5$ π-bond integral in **8** ($\beta_{15} = -2.4$ eV) compared with the corresponding integral in **9** ($\beta_{34} = -1.9$ eV).[13] This, in turn, leads to a greater π-delocalization energy (*cf.* the corresponding π-orbital energies) in **8** than in **9**.[13,14] If the same considerations apply in the case of anions **1** and **2**, the latter species would be considered to be more "aromatic."[15] Thus, the foregoing data provide, for the first time, evidence that the ring current and the resonance energy criteria for the concept of aromaticity may lead to different conclusions.[16]

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation.

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(8) Evidence for similar polarizations has been reported by (a) R. A. Clark and R. A. Fiato, *J. Amer. Chem. Soc.*, **92**, 4736 (1970); (b) P. Rys, P. Skrabal, and H. Zollinger, *Tetrahedron Lett.*, 1797 (1971).

(9) This is a consequence of the Möbius array of p orbitals around the periphery of the cyclopropane ring in the Walsh model which (unlike a double bond) results in the lowest unoccupied (acceptor) orbital being displaced twice as far from the nonbonding level (in the HMO approximation) as are the highest occupied (donor) orbitals.

(10) For previous indications of the donor–acceptor properties of the cyclopropyl ring, see, *e.g.*, (a) R. H. Eastman and J. C. Selover, *J. Amer. Chem. Soc.*, **76**, 4118 (1954); (b) R. C. Hahn, T. F. Corbin, and H. Shechter, *ibid.*, **90**, 3404 (1968); (c) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *ibid.*, **91**, 6666 (1969).

(11) The signals for the protons at C$_4$ and C$_{10}$ in **1** are shifted upfield relative to H$_1$ and H$_7$ in **2** and **7** primarily due to the shielding by the cyclopropyl ring in **1**; *cf.* C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *ibid.*, **94**, 2291 (1972), and references cited therein. See also ref 4, pp 98–101.

(12) We feel that the terms diatropic, paratropic, and atropic best designate the ability to sustain diamagnetic, paramagnetic, or no ring currents, respectively, in cyclic delocalized π systems; see ref 5 and P. J. Garratt and F. Sondheimer, cited by F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(13) R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim. Acta*, **54**, 1029 (1971).

(14) The nmr spectra for 8 and **9** have not been fully interpreted and ring currents have not been demonstrated for either compound (although these compounds may, in fact, possess ring currents).

(15) Anion **1** is nevertheless probably substantially stabilized by π delocalization between the spiro rings. A similar interaction undoubtedly also influences the results reported in ref 1c.

(16) The resonance energy is a function of the amount of overlap between the p orbitals at C$_1$ and C$_5$ in 8 and at C$_3$ and C$_4$ in **9**. It is important to note in this connection that the C$_1$–C$_5$ bond length in 8 is 1.470 Å (P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, **43**, 401 (1972)) compared with 1.509 Å for the C$_3$–C$_4$ bond length in **9** (J. F. Chiang and C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **95**, 2885 (1973)). On the other hand the ring current is a function of the electron density in the cyclic π system. Since the cyclopropyl group is a poorer acceptor than a double bond,[9] **1** is closer to being a cyclic $4n + 2$ π-electron system than is 2. Similar considerations apply to 8 and **9**.

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A Derivative of 3-Oxahomobiphenylene. A New Antiaromatic System

Sir:

Several stable heterocyclic analogs of biphenylene have been reported.[1,2] In these compounds, one of

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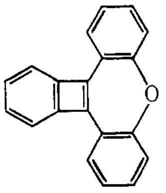
(1) P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 109 (1970).

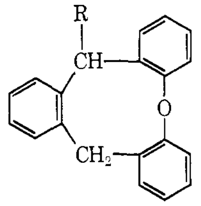
(2) P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **92**, 4492 (1970).

the benzenoid rings of biphenylene has been replaced by a $4n + 2$ five-membered or nine-membered heterocyclic ring. We now report the first example of a biphenylene analog (**1**) in which a benzenoid ring has been replaced by a $4n$ heterocyclic ring, namely an oxepin.

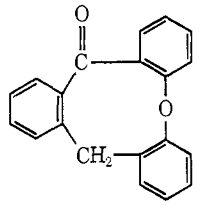
Oxidation of 10*H*,15*H*-tribenzo[*b*,*e*,*h*]oxonin (**2**)[3] by chromic acid in warm acetic acid gave, in 80% yield, the corresponding monoketone **3**, mp 197–199°.[4] Sodium borohydride reduction of **3** gave, in 89% yield, the alcohol **4**, mp 165–166°. Reaction of **4** with thionyl chloride followed by direct treatment of the resulting chloride **5** with a refluxing solution of potassium *tert*-butoxide in *tert*-butyl alcohol afforded, in 32% yield, the condensed benzocyclobutene **6**, mp 131–133°. The cis configuration for compound **6** is assigned on the basis of its benzylic proton signal at δ 5.08, a value close of that (δ 5.20) observed for *cis*-1,2-diphenylbenzocyclobutene.[5] Bromination of **6** by NBS in CCl_4 gave, in 70% yield, the corresponding dibromide **7**, mp 214–216° dec.



1



2, R = H
4, R = OH
5, R = Cl



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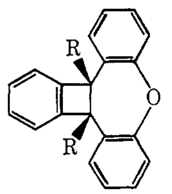
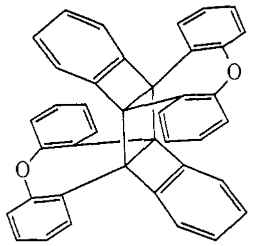


6, R = H
7, R = Br

Reaction of dibromide **7** with zinc–silver couple[6] in warm tetrahydrofuran afforded an orange-red solution (λ_{max} 496 nm) of the oxahomobiphenylene **1**. Solutions of **1** could be preserved unchanged for several hours at −78°; at room temperature, however, the red color vanished within 1 min with the formation of a colorless dimer **8**, mp 347–349° dec (80% based upon **7**). When **1** was generated in the presence of 1,3-diphenylisobenzofuran, it was trapped efficiently to give, in 76% yield, the Diels–Alder adduct **9**, mp 264–266°.[7] Attempts to effect a cycloaddition of **1** to 4-phenyltriazoline-3,5-dione were unsuccessful, but these reactions afforded (~12% yield) the oxidation product of **1**, 10*H*,15*H*-tribenzo[*b*,*e*,*h*]oxonin-10,15-dione (**10**), mp 179–181°, identical with material prepared by an independent synthesis.[8]



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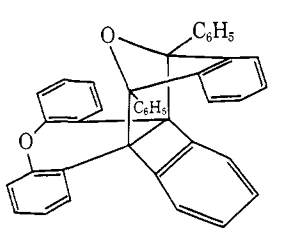

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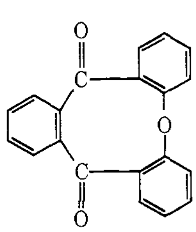

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Red solutions of **1** gave no esr signal at −195°, indicating a singlet ground state for **1**. The observed high reactivity of **1**, however, is indicative of an antiaromatic ring system. A comparison of the stability of **1** with that of related compounds in which the oxygen of **1** has been replaced by other atoms would be of considerable interest; the synthesis of such compounds is under active investigation in our laboratory.

Acknowledgment. We thank the National Science Foundation for a grant (GP 24057X) in support of this research.

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[3] T. Sato, K. Uno and M. Kainosho, *J. Chem. Soc., Chem. Commun.*, 579 (1972).

[4] Satisfactory analyses and spectral data were obtained for all new compounds.

[5] L. A. Carpino, *J. Amer. Chem. Soc.*, 84, 2196 (1962).

[6] J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 540 (1972). We thank Professor B. M. Trost for suggesting this reagent.

[7] Compounds **8** and **9** are assigned the most likely stereochemistry. A head-to-head structure for **8** and an endo structure for **9** cannot, however, be excluded on current experimental evidence.

[8] M. Schaaf, Ph.D. Dissertation, Wayne State University, 1969. Addition of the Grignard reagent from 2-iodophenyl phenyl ether to phthalic anhydride and acid-catalyzed cyclization of the product gave **10** in good yield.

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Received May 24, 1973

Mass Spectrometry in Structural and Stereochemical Problems. CCXXXIII.[1] On the Stereochemical Dependence of the Retro-Diels–Alder Reaction

Sir:

Recent investigations in this laboratory have shown that the retro-Diels–Alder (RDA) reaction in the mass spectral decomposition of some Δ^7 steroidal olefins exhibits a high degree of stereospecificity with A/B cis compounds decomposing significantly more readily by this route than the corresponding trans compounds.[2] This observation is *a priori* surprising, since RDA processes have frequently been observed in trans-fused polycyclic hydrocarbons.[3] A comparison of the relative importance of the RDA reaction in cis–trans isomeric polycyclic hydrocarbons has, however, not been made so far. To study this problem more fully we have

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[1] For paper CCXXXII in this series, see P. J. Derrick, A. M. Falick, A. L. Burlingame, and C. Djerassi, submitted to *J. Amer. Chem. Soc.* for publication.

[2] I. Midgley and C. Djerassi, unpublished results.

[3] For examples of RDA reactions in A/B trans Δ^2 steroids and B/C trans Δ^{12} triterpenes see: (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day, San Francisco, Calif., 1964; (b) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, 21, 1855 (1965).