J. Am. Chem. Soc. **1986**, *108*, 1707-1708

Enhanced Ring Current of Charged Annulenes

S. Kuwajima and Z. G. Soos*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received December 9, 1985

Müllen et al.[1] recently reported ^1H NMR shifts of tetraanionic [4*n* + 2]annulenes to be definitely higher than those of corresponding neutral species. The importance of their data has not been recognized. Since significant geometric changes seem unlikely, their findings should have an electronic origin. We show here within the standard Pariser–Parr–Pople (PPP) model that ring currents of charged annulenes are higher than those of neutral annulenes.

The resonance integral β is modified by a magnetic field H through the London factor[2,3]

$$\beta_{kl} = \beta \exp(\pm ieS_{kl}H/\hbar c) \qquad (1)$$

where S_{kl} is the area of the triangle formed by the gauge origin and neighboring sites k and l. Previous PPP studies of ring currents[4-6] were restricted to the SCF–MO approximation. We solve the model exactly. We employed C_{Nv} geometry with bond length of 1.397 Å, $\beta = -2.4$ eV, and the Ohno formula for Coulomb integrals with one-center repulsion of 11.26 eV. To second order in H, the PPP Hamiltonian, with the gauge origin located at the center of the regular polygon, is

$$\mathcal{H} = \mathcal{H}_0 + ifv_- - (1/2)f^2v_+ \qquad (2)$$

with $f = eSH/\hbar cN$ for an annulene of size N and enclosed area S. The operators $v_\pm$ are, respectively

$$v_\pm = \beta\sum_{k\sigma}(a^+_{k\sigma}a_{k+1\sigma} \pm a^+_{k+1\sigma}a_{k\sigma}) \qquad (3)$$

Magnetic properties are determined by the H^2 contribution to the nondegenerate ground-state energy,

$$E = E_0 - f^2E_2/2 \qquad (4)$$

where E_0 is the zeroth-order energy. The ring current I is[3]

$$I/H = (e^2/\hbar^2c)(S/N^2)E_2 \qquad (5)$$

The E_2 term is central for the present discussion,

$$E_2(\mathrm{PPP}) = 2\langle\psi_0|v_-|\psi_1\rangle + \langle\psi_0|v_+|\psi_0\rangle \qquad (6)$$

where ψ_0 is the zeroth-order ground state whose first-order correction $if\psi_1$ satisfies

$$(\mathcal{H}_0 - E_0)\psi_1 = -v_-\psi_0 \qquad (7)$$

We calculated E_0, ψ_0, ψ_1, and E_2 exactly using diagrammatic VB methods[7] up to $N = 14$, which involves about 3×10^6 singlet VB diagrams. Exact results for eq 6, the v_- part in particular, are obtained for the first time. Computational details will be presented separately.

The Hückel solution of eq 1 for a closed-shell annulene with ionicity q yields[3]

$$E_2(\text{Hückel}) = -4|\beta| \cos(\pi q/2N) \operatorname{cosec}(\pi/N) \qquad (8)$$

SCF–MO (or coupled Hartree–Fock) theory also leads to eq 8 for the present PPP model on account of the cyclic symmetry.

E_2(PPP) results are given in Table I for systems with 4*n* + 2 electrons. At $N = 14$ the E_2(PPP) value for $q = -4$ is significantly higher than that of $q = 0$, reproducing Müllen et al.'s findings.

Table I. E_2 Results (eq 4) in Electronvolts

species	$-E_2$(PPP)	species	$-E_2$(PPP)
$[3]^+$	9.43	$[9]^-$	26.08
$[4]^{2\pm}$	9.32	[10]	26.08
$[5]^{3+}$	9.19	$[10]^{4\pm}$	23.79
$[5]^-$	15.02	$[11]^+$	31.49
[6]	17.78	$[11]^{3-}$	29.39
$[6]^{4\pm}$	9.09	$[12]^{2\pm}$	33.80
$[7]^+$	20.58	$[13]^{3+}$	35.45
$[7]^{3-}$	16.51	$[13]^-$	36.78
$[8]^{2\pm}$	22.12	[14]	31.16
$[9]^{3+}$	23.12	$[14]^{4\pm}$	36.71

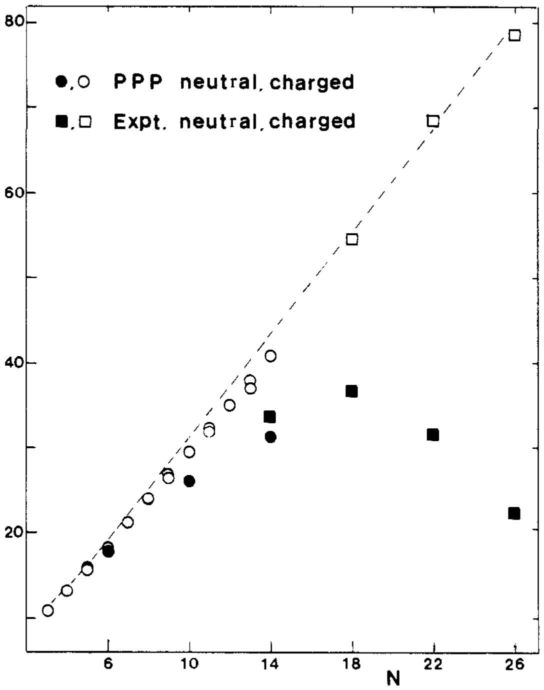


Figure 1. Plot of $-E_2/\cos(\pi q/2N)$ vs. N: PPP, experimental,[1,8] and Hückel (broken line, $\beta = -2.4$) results.

For $N = 6$ and 10, however, the order is reversed because ionicity dominates in small systems: $[6]^{4+}$ has only two electrons contributing to E_2, as is also the case in $[6]^{4-}$ due to cancellation between bonding and antibonding oribitals. The cos ($\pi q/2N$) factor in eq 8 describes the ionicity effect of Hückel theory. We utilize this factor to draw a convincing conclusion. Figure 1 shows E_2(PPP)/cos ($\pi q/2N$), in which the ionicity effect is removed, together with experimental results[8] obtained from Müllen et al.'s data. The charged species, independent of ionicity, now fall almost on a straight line with the neutral species deviating downward. Since the correction factor becomes negligible for large N ($|q| \leq 4$), Figure 1 demonstrates the enhanced ring current of charged annulenes. Although direct comparison with experiments is restricted to $N = 14$ ($q = 0$), where the agreement is good, the PPP results extrapolate very well to experimental values. The above results also agree with the fact that charged annulenes often show remarkably high diatropicity (for example, $\tau_{\text{in}} = 18.0$ ppm for inner protons of [17]annulenyl anion[10] as contrasted to $\tau_{\text{in}} = 12.9$ for [18]annulene[11]).

Another important aspect of the PPP results emerges on comparing to Hückel results, the broken line in Figure 1. Since the

---

(1) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403.

(2) London, F. *J. Phys. Radium* **1937**, *8*, 397.

(3) Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966; Chapter 4.

(4) Hall, G. G.; Hardisson, A. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 328.

(5) Amos, A. T.; Roberts, H. G. Ff. *J. Chem. Phys.* **1969**, *50*, 2375.

(6) Vogler, H. *J. Am. Chem. Soc.* **1978**, *100*, 7464.

(7) Soos, Z. G.; Ramasesha, S. *Phys. Rev. B* **1984**, *29*, 5410; Ramasesha, S.; Soos, Z. G. *J. Chem. Phys.* **1984**, *80*, 3278; *Int. J. Quantum Chem.* **1984**, *25*, 1003.

(8) Haddon's procedure[9] was used with a simplification. ^1H shifts and ring-current geometric factors were averaged for inner and outer protons separately. The differences of the averages were used to estimate I and then E_2 by eq 5. Planar 120° geometry was used with C$\overset{...}{=}$C, C$\overset{..}{-}$C, and C—H bond lengths of 1.2, 1.4, and 1.1 Å, respectively. Current loop separation was 1.2 Å.

(9) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613.

(10) Schröder, G.; Plinke, G.; Smith, D. M.; Oth, J. F. M. *Angew. Chem.* **1973**, *85*, 350.

(11) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

0002-7863/86/1508-1707$01.50/0

Hückel line is common to the neutral and charged species (eq 8), it is close to the PPP results for the latter but too high for the former. Hückel theory has long been known to overestimate the ring current in [18]annulene. The assumption of bond alternation[12] to explain the reduced ^{1}H NMR shifts is not supported by X-ray structural data.[13] Vogler[14] obtained much improved, but still too high, ^{1}H shifts for the observed geometry by an elaborate SCF-MO-PPP method that includes local anisotropic contributions. We emphasize here the role of electron correlation in selectively depressing the ring current of neutral species. The enhanced ring current of charged vs. neutral annulenes requires going beyond MO theory.

Acknowledgment. We gratefully acknowledge NSF support for this work under DMR-8403819.

---

(12) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445.

(13) Bregman, J.; Hirshfeld, F. L.; Rabinovich, D.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *19*, 227. Hirshfeld, F. L.; Rabinovich, D. *Ibid.* **1965**, *19*, 235.

(14) Vogler, H. *J. Mol. Struct.* **1979**, *51*, 289.

Stereochemical Control of Transannular Radical Cyclizations. A New Approach to the Synthesis of Linearly Fused Cyclopentanoids[1]

Jeffrey D. Winkler* and V. Sridar

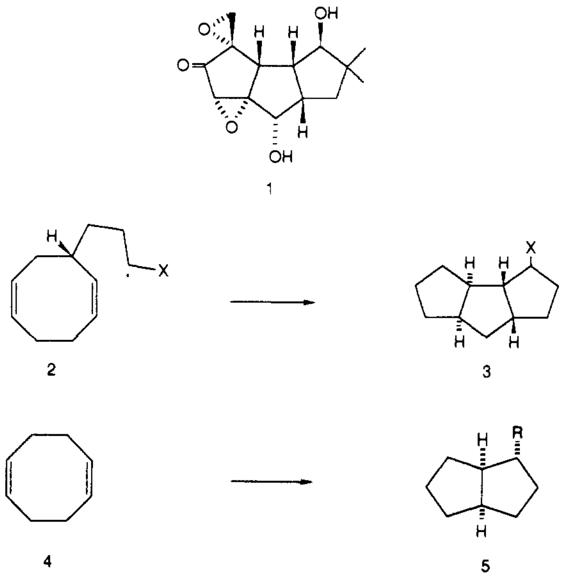
Searle Chemical Laboratories, Department of Chemistry
University of Chicago, Chicago, Illinois 60637

Received November 19, 1985

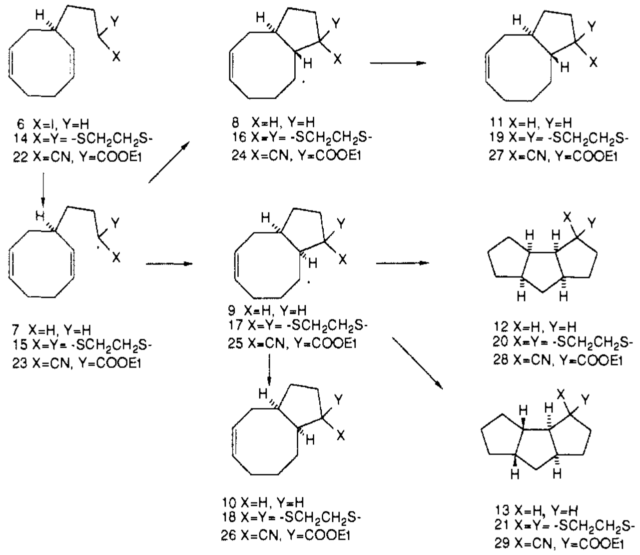
Most of the existing strategies for the synthesis of linearly condensed cyclopentanoids, such as the hirsutane sesquiterpenes, i.e., coriolin (**1**), sequentially construct each ring in the tricyclic system, with some notable exceptions.[2] We report herein our preliminary results with a conceptually novel approach to this problem—the application of transannular radical cyclizations to the control of stereochemistry in the formation of carbocyclic ring systems.[3] By judicious choice of X (Scheme I) the cyclization of **2** leads to the formation of **3**, in which three five-membered rings and four contiguous centers of asymmetry are produced in a single chemical step.

Several years ago, Dowbenko[4] and Friedman[5] independently reported that the addition of exogenous radicals to 1,5-cyclooctadiene (**4**) produces exo-substituted bicyclo[3.3.0]octanes, i.e., **5**, in which three contiguous stereocenters are produced in a single synthetic operation from achiral precursors. To examine the intramolecular version of this reaction, we prepared **6** (Scheme II) and submitted it to the usual radical cyclization conditions. Irradiation (150-W lamp) of **6** in the presence of 1.1 equiv of tri-*n*-butyltin hydride in benzene (0.02 M) containing a catalytic amount of azoisobutyronitrile (AIBN) for 4 h led to the formation of four new products, **10–13**, in a ratio of 11:73:5:11, respectively (61% yield).[6]

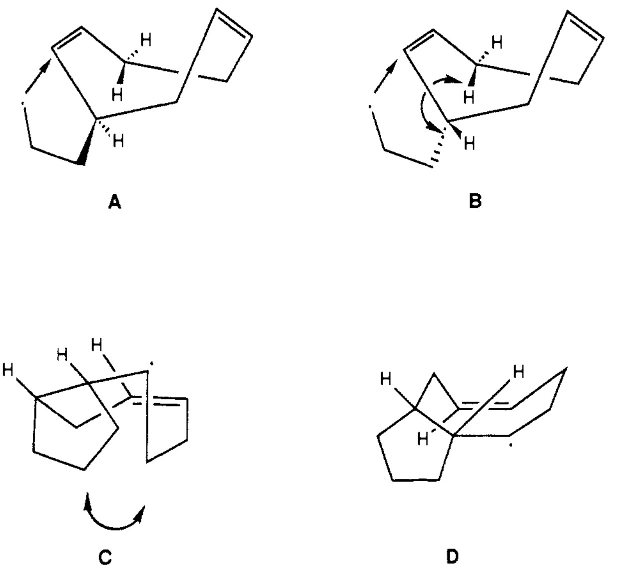
Scheme I



Scheme II



Scheme III



The kinetic preference for trans-fused products (73:27 ratio of trans-/cis-fused products) in the intial cyclization reaction can be understood by examination of the twist boat cyclooctadiene conformations shown below (Scheme III).[7] The preferred con-

---

(1) Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 8–13, 1985; paper ORGN 142.

(2) (a) Curran, D.; Rakiewicz, D. *J. Am. Chem. Soc.* **1985**, *107*, 1448. (b) Little, R.; Muller, G.; Venegas, M.; Carroll, G.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371. (c) Wender, P.; Howbert, J. *Tetrahedron Lett.* **1983**, 5325. (d) Beckwith, A.; Roberts, D.; Schiesser, C.; Wallner, A. *Tetrahedron Lett.* **1985**, 3349.

(3) (a) Sutherland, J.; Sam, T. *J. Chem. Soc., Chem. Commun.* **1971**, 970. (b) van der Line, L.; van der Weerdt, A. *Tetrahedron Lett.* **1984**, 1201. (c) Paquette, L.; Colapret, J.; Andres, D. *J. Org. Chem.* **1985**, *50*, 201.

(4) Dowbenko, R. *Tetrahedron* **1964**, *20*, 1843.

(5) Friedman, L. *J. Am. Chem. Soc.* **1964**, *86*, 1885.

(6) The identities of **10–13** were unambiguously established by correlation with independently prepared authentic samples (see supplementary materials for experimental details).

0002-7863/86/1508-1708$01.50/0