

Aromaticity and Electron Correlation

S. Kuwajima*† and Z. G. Soos

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received April 7, 1986

Abstract: Aromaticity of conjugated monocyclic systems is studied within the Pariser–Parr–Pople (PPP) π -electron model by taking electron correlation fully into account. Exact PPP energies and ring currents are obtained for neutral and charged systems with up to 14 carbons. Ring currents, which are calculated by the PPP version of the Hückel–London theory, are shown to be higher in charged systems than in neutral systems, in agreement with experiment. This is a correlation effect that cannot be accounted for by Hückel or SCF–MO–PPP theory. Aromatic stabilizations extracted from the exact PPP energies indicate that large neutral $4n$ -electron systems ($4n \geq 16$) become weakly aromatic. Ring currents of these species, however, remain paramagnetic. Charged $4n$ -electron systems are found to be antiaromatic independent of ring size.

Theoretical studies of aromaticity have been principally based on molecular orbital (MO) theory. Although electron correlation has been seriously considered for related problems such as ground-state geometry^{1–4} and spin multiplicity,^{2–5} less attention has been given to correlation effects on aromaticity.^{1,6–8} Theories of the valence-bond (VB) type^{9–12} incorporate some correlations, but possible deviations from MO theory were discussed only in a recent work.¹³ In this paper we study aromaticity of conjugated monocyclic systems beyond MO theory. We adopt the Pariser–Parr–Pople (PPP) π -electron model and perform exact (full CI) calculations.

Ring current, to which special magnetic characters of aromatic molecules are ascribed, is a fundamental notion associated with aromaticity. We obtain exact ring currents within the PPP model for neutral and charged systems. It has been known that charged annulenes often show remarkably high diatropicity (or paratropicity) that seemingly exceeds the diatropicity of neutral annulenes.^{14–17} Müllen et al.'s findings¹⁸ on tetraanionic dehydro[$4n+2$]annulenes ($n = 4–6$) are especially important because the observed high ring currents are difficult to explain by geometrical changes. The origin of those observations has not been recognized. Our PPP calculations, incorporating purely electronic effects, show that ring currents are higher in charged than in neutral annulenes.¹⁹ Such a marked contrast between neutral and charged species is a novel feature in aromaticity. We examine the contrast also in aromatic stability.

An advantage of the PPP model is the flexibility of its parameters; we can follow the evolution of aromaticity with increasing correlation. Such an approach was useful for understanding the nature of low-lying excited states of polyenes.²⁰ Hückel theory corresponds to zero correlation. Increasing correlation, associated with increasing energy of ionic C^- centers, depresses more and more the weight of ionic VB structures. Strong correlation thus leads to the classical VB theory of Pauling,²¹ in which only covalent VB structures are considered. The correlation-dependence study casts a new light on the role of the Hückel and classical VB theories. The classical VB theory is known to be unsuccessful in explaining antiaromaticity: the conventional VB resonance energy predicts that [$4n$] and [$4n+2$]annulenes are equally aromatic.^{21b} Our PPP study, however, shows that large neutral $4n$ -membered rings become weakly aromatic in agreement with the classical VB theory.

PPP Model

We study hypothetical monocyclic systems forming a regular polygon with equal resonance integrals. Although aromaticity of individual molecules is affected by the actual molecular geometry, idealized features of aromaticity are well studied in this manner. A standard set of parameters is used: resonance integral β of -2.40 eV, bond length of 1.397 Å, and one-center electron-repulsion integral V_0 of 11.26 eV. The Ohno formula is used for

intersite electron-repulsion integrals V_{kl} : $V_{kl} = e^2/(r_{kl}^2 + e^4/V_0^2)^{1/2}$ for distance r_{kl} between sites k and l . Correlation dependences are found by varying V_0 , and consequently V_{kl} , without changing the geometry and β . Exact PPP computations were performed by diagrammatic VB methods,²² in which wave functions are represented by a linear combination of all the covalent and ionic diagrams and the resulting eigenvalue equation is solved exactly. Cyclic symmetry adaptation²³ enabled us to calculate systems of up to 14 carbon sites, which involve 2 760 615 singlet VB diagrams and 50 650 symmetry-adapted basis vectors (C_{14c} plus electron-hole symmetry) for the neutral ground state.

We use the PPP version of the Hückel–London theory^{24,25} for ring currents. The resonance integral β is modified by the London factor for an external magnetic field H perpendicular to the molecular plane:

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

- (1) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289, and references therein.
- (2) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.
- (3) Borden, W. T.; Davidson, E. R.; Hart, P. *Ibid.* **1978**, *100*, 388. Jafri, J. A.; Newton, M. D. *Ibid.* **1978**, *100*, 5012.
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- (5) Winkelhofer, G.; Janoschek, R.; Fratev, F.; Spitznagel, G. W.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 332, and references therein.
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- (17) Howes, P. D.; Sondheimer, F. *J. Am. Chem. Soc.* **1972**, *94*, 8261.
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* Present address: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

where S_{kl} is the area of the triangle formed by the gauge origin and sites k and l . Exact analysis on this model has not been reported. Previous PPP studies,²⁶⁻²⁸ using eq 1 or a similar one with McWeeny's test dipoles, were restricted to the Hartree-Fock (SCF-MO) approximation.

The gauge origin is placed at the center of the polygon. With $f = eSH/\hbar cN$ for a system with size N and enclosed area S , the PPP Hamiltonian in second-quantized form is

$$\mathcal{H} = \beta \sum_{k\sigma} [\exp(if)a_{k\sigma}^+ a_{k+1\sigma} + \exp(-if)a_{k+1\sigma}^+ a_{k\sigma}] + \sum_{k,l} V_{kl}(n_k - 1)(n_l - 1)/2 + \sum_k (\alpha n_k + V_0 n_k(n_k - 1)/2) \quad (2)$$

where $a_{k\sigma}$ is the annihilation operator of the electron at site k with spin σ , and $n_k = a_{k\alpha}^+ a_{k\alpha} + a_{k\beta}^+ a_{k\beta}$ is the number operator for site k . Magnetic properties are determined by the second-order contribution in H to the ground-state energy,

$$E = E_0 - (1/2)f^2 E_2 \quad (3)$$

where E_0 is the energy for $H = 0$. The magnetic susceptibility χ is given by $\chi = (eS/\hbar cN)^2 E_2$. Assuming that χ comes from a current flowing along annulene periphery, we obtain the current I as²⁵

$$I/H = (e^2/\hbar^2 c)(S/N^2)E_2 \quad (4)$$

The general eq 3 and 4 are also applicable to the Hückel model with eq 1 and yield²⁵

$$E_2(\text{Hückel}) = -4|\beta| \cos(\pi q/2N) \operatorname{cosec}(\pi/N) \quad (5)$$

Hartree-Fock theory also leads to eq 5 for the present model on account of the cyclic symmetry.

To second order in H the PPP Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + if\hat{v}_- - (1/2)f^2 v_+ \quad (6)$$

where \mathcal{H}_0 is the Hamiltonian for $H = 0$. The operators v_{\pm} are given by

$$v_{\pm} = \beta \sum_{k\sigma} (a_{k\sigma}^+ a_{k+1\sigma} \pm a_{k+1\sigma}^+ a_{k\sigma}) \quad (7)$$

Using second-order perturbation theory and noting that $\langle \psi_0 | v_- | \psi_0 \rangle = 0$, we readily obtain

$$E_2(\text{PPP}) = \langle \psi_0 | v_+ | \psi_0 \rangle + 2 \sum_{k \neq 0} |\langle \psi_0 | v_- | \psi_k \rangle|^2 / (E_k - E_0) \quad (8)$$

where E_k and ψ_k denote eigenvalues and eigenvectors of the zeroth-order Hamiltonian, respectively, with ψ_0 being the ground-state eigenvector. Equation 8 is computationally impractical because all the excited states are needed. We instead handle the first-order correction ψ' to the eigenvector:

$$\psi' = \sum_{k \neq 0} (E_k - E_0)^{-1} \langle \psi_k | v_- | \psi_0 \rangle \psi_k \quad (9)$$

Then eq 8 becomes

$$E_2(\text{PPP}) = \langle \psi_0 | v_+ | \psi_0 \rangle - 2 \langle \psi_0 | v_- | \psi' \rangle \quad (10)$$

Operating $\mathcal{H}_0 - E_0$ on eq 9 and using $\langle \psi_0 | v_- | \psi_0 \rangle = 0$, we obtain an equation for ψ' :

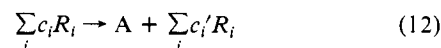
$$(\mathcal{H}_0 - E_0)\psi' = v_- \psi_0 \quad (11)$$

After obtaining the zeroth-order quantities E_0 and ψ_0 by diagrammatic VB methods, solving eq 11 becomes central. The equation is an algebraic linear equation $Ax = b$ with $A = \mathcal{H}_0 - E_0$, $x = \psi'$, and $b = v_- \psi_0$. Since ψ' has different reflection symmetry from ψ_0 , the matrix A represented in the subspace of ψ' does not have a vanishing eigenvalue. In order to take advantage of the extreme sparseness of the matrix \mathcal{H}_0 , we adopted an iteration procedure in which $|Ax - b|^2$ is minimized with respect to each component. Convergence becomes very slow when the

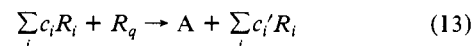
matrix A is large or has an eigenvalue close to zero. In such cases we used a double iteration in which $(A + cI)x_n = b + cx_{n-1}$ was solved for x_n from the $(n-1)$ th solution x_{n-1} at the n th iteration, with c an arbitrary positive number.

Aromatic Stabilization

Total PPP energies, like total Hückel energies and experimental heats of formation, are not immediately suitable for analyzing aromaticity. We need to extract appropriate stabilization energies from total energies. The aromatic stabilization is usually called resonance energy (RE). Experimental measurements of RE for a molecule A have been based on the enthalpy change in the reaction^{29,30}

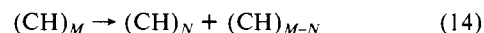


where R_i are reference systems which are assumed to have vanishing RE. While eq 12 is adopted in all-electron ab initio studies,^{1,8} it has not been explicitly used in π -electron theories.³¹⁻³⁵ We adopt eq 12 and derive a method similar to current π -electron theories. In the PPP or Hückel model we have carbon sites (p orbitals), electrons, and resonance integrals, each of which must be conserved in eq 12. The conservation of resonance integrals is essential. The Hückel delocalization energy, now recognized as an unsatisfactory measure of RE,³² can be defined by eq 12 with ethylene references but the conservation of resonance integrals is not satisfied.³⁶ Linear polyenes are the usual references. Within monocyclic systems, infinitely large rings provide a satisfactory reference, a reference used by Aihara³³ and by Haddon³⁷ for Hückel theory. Defining RE for charged systems is not straightforward because appropriate references are not established.^{34a} We devise a new procedure based on an extension of eq 12. We introduce a charged system R_q as a charge source:



R_q may be arbitrarily chosen but must be fixed for all A with a common charge q . A relative scale of stability among equally charged systems is obtained by eq 13, the charge source setting the zero point. Equation 13 itself does not define aromatic stabilization, which we give later on the basis of eq 13.

We define aromatic stabilization E_A of neutral monocycles $(\text{CH})_N$ by the energy change (left minus right)



with $M \rightarrow \infty$. In other words, we cut out the system of interest, say benzene, from an infinite annulene leaving another infinite annulene. E_A is positive for aromatic species. We denote the total π -electron energy of $(\text{CH})_N^q$ with charge q as $E_0(N, q)$. Neglecting terms of order M^{-1} , the ground-state energy of $(\text{CH})_M$ goes as

$$E_0(M, 0) = \epsilon_0 M \quad (15)$$

where ϵ_0 is a constant whose calculation is given in the Appendix. Equation 15 shows energy additivity as required for reference systems. From eq 14 and 15, E_A of neutral $(\text{CH})_N$ is

(29) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

(30) The conventional RE measured with heats of hydrogenation is also defined by eq 12; for benzene, 3 cyclohexene \rightarrow benzene + 2 cyclohexane.

(31) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(32) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305, 2413.

Schaad, L. J.; Hess, B. A., Jr. *Ibid.* **1972**, *94*, 3068.

(33) Aihara, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 517.

(34) (a) Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471.

(b) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.

(35) (a) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Gutman, I.; Milun, M.; Trinajstić, N. *Ibid.* **1977**, *99*, 1692.

(36) This conservation is equivalent to the conservation of both single and double bonds, except for non-Kekulé systems; assigning a significant bond energy to single bonds is the essence of the so called Dewar-type RE.

(37) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

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

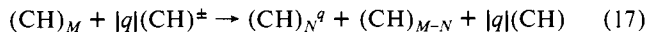
(27) Amos, A. T.; Roberts, H. G. Ef. *J. Chem. Phys.* **1969**, *50*, 2375.

(28) (a) Vogler, H. *J. Am. Chem. Soc.* **1978**, *100*, 7464. (b) Vogler, H. *J. Mol. Struct.* **1979**, *51*, 289; (c) Vogler, H. *Org. Magn. Reson.* **1979**, *12*, 306.

$$E_A(N,0) = \epsilon_0 N - E_0(N,0) \quad (16)$$

This formula is identical with Aihara's A-I resonance energy,^{33,35a} although the analysis is slightly different.

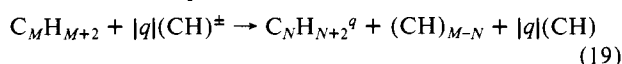
To define aromatic stabilization for charged systems, we first specialize eq 13 to charged monocycles:



Here, $(\text{CH})^+$, $(\text{CH})^-$, and (CH) , which constitute the charge source, are, respectively, isolated single sites with zero, two, and one π electron; the system of interest is again cut out from an infinitely large annulene with simultaneous charge transfer from the charge sources. We denote the resulting stabilization energy as $E_S(N,q)$. The energies of $(\text{CH})^+$, (CH) , and $(\text{CH})^-$ are 0, α , and $2\alpha + V_0$, respectively, with site energy α given in eq 2. Using eq 15 for $M \rightarrow \infty$, we obtain

$$E_S(N,q) = \epsilon_0 N - E_0(N,q) - q(\alpha + \delta_q V_0) \quad (18)$$

where $\delta_q = 0$ and 1 for $q > 0$ and $q < 0$, respectively. $E_S(N,q)$ is only a relative scale, however, and we need an absolute measure of aromatic stabilization. Numerical results of $E_S(N,q)$, presented in the next section, show that the aromatic stabilization is reasonably defined by using charged linear polyenes as a reference.³⁸ The stabilization of linear polyenes $C_N H_{N+2}^q$ is measured by using the same scale as eq 17:



We have used infinitely long linear polyene $C_M H_{M+2}$ as a reference, so that the conservation of the resonance integrals is fulfilled. We denote energies of linear polyenes by the letter F with the same subscripts as for monocycles. The ground-state energy of $C_M H_{M+2}$ is expressed as (see the Appendix)

$$F_0(M,0) = \epsilon_0 M + \epsilon_1 \quad (20)$$

In order to obtain the same ϵ_0 as in eq 15, we used the regular-polygon geometry of monocycles for linear polyenes (Appendix). Using eq 15, 19, and 20, we obtain

$$F_S(N,q) = \epsilon_0 N - F_0(N,q) + \epsilon_1 - q(\alpha + \delta_q V_0) \quad (21)$$

Now, we define the aromatic stabilization $E_A(N,q)$ ($q \neq 0$) by the difference between E_S and F_S :

$$E_A(N,q) = E_S(N,q) - F_S(N,q) \quad (22)$$

Substituting eq 18 and 21 into eq 22 leads to the final formula

$$E_A(N,q) = F_0(N,q) - E_0(N,q) - \epsilon_1 \quad (23)$$

We show the validity of eq 22 in the next section. We note that eq 23 with $q = 0$, which is an aromatic stabilization with linear-polyene reference, yields values in reasonable agreement with eq 16.

Results and Discussion

Energy. Exact PPP energies $E_0(N,q)$ are listed in Table I for $N \leq 14$ and $|q| \leq 2$. The constants $\epsilon_0 = -2.1355$ eV in eq 15 and $\epsilon_1 = 1.17$ eV in eq 20 were obtained by extrapolation, as shown in the Appendix. The aromatic stabilization of neutral species is shown in Figure 1, together with Hückel and Hartree-Fock (HF) results based on eq 14-16. The Hückel results are scaled to fit the exact PPP value of benzene. The broken-symmetry bond-order wave (BOW) state³⁹ was used for the HF solution of the reference and $4n$ -electron species.⁴⁰ Exact PPP results in Figure 1 clearly follow Hückel's $(4n+2)$ rule, but the destabilization of $4n$ -electron species is much smaller in PPP than in

Table I. Total PPP Energies for $|q| \leq 2$ (in eV)

species	$E_0(N,q)^{a,b}$
$[3]^+$, $[3]^-$	-8.569, 7.340 (-0.880)
$[4]^{2+}$, $[4]$	-1.773, -7.225 (0.348)
$[5]^-$, $[5]^+$	-1.969, -10.394 (-0.306)
$[6]$, $[6]^{2+}$	-14.023, -6.932 (-0.349)
$[7]^+$, $[7]^-$	-17.828, -4.552 (-0.162)
$[8]^{2+}$, $[8]$	-15.413, -16.794 (0.451)
$[9]^-$, $[9]^+$	-11.083, -20.787 (-0.101)
$[10]$, $[10]^{2+}$	-22.057, -19.831 (-0.126)
$[11]^+$, $[11]^-$	-26.795, -14.274 (-0.067)
$[12]^{2+}$, $[12]$	-26.608, -25.576 (0.471)
$[13]^-$, $[13]^+$	-19.942, -30.147
$[14]$	-30.350

^aLowest singlet energy. The site energy α (eq 2) is set to be zero. Energy for dianion of an even-membered ring is obtained by adding $2V_0$ to the energy of the dication (electron-hole symmetry). ^bIn parentheses is shown the singlet-triplet gap, $E_T - E_S$, for $4n$ -electron species.

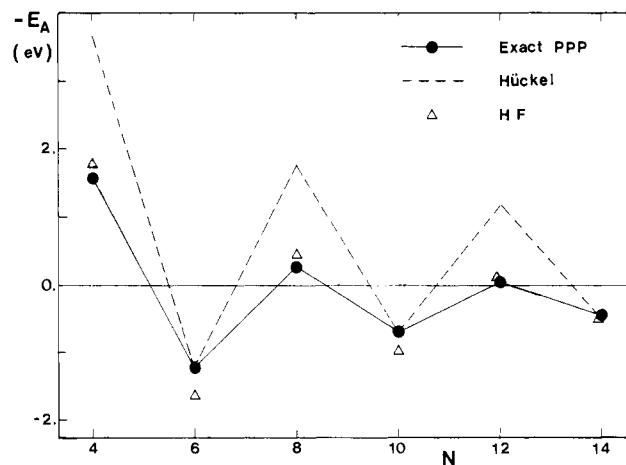
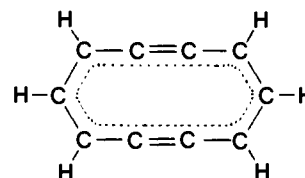


Figure 1. Plot of $-E_A$ from eq 16 vs. N for neutral species. Hückel results are for $\beta = -3.36$ eV to fit the exact PPP value at $N = 6$.

Hückel theory. HF results are in fair agreement with the exact PPP results. A new feature of the exact PPP results is the rapid decrease of antiaromaticity of $4n$ -electron species with increasing N . Indeed, $4n$ -electron species with $4n \geq 16$ appear to become weakly aromatic. We return to this point later.

Before considering charged species, we remark that, as already suggested by Klein and Trinajstić,⁷ all the $4n$ -electron ions turned out to be ground-state triplets (Table I). This is in sharp contrast to the neutral species where $4n$ -electron systems always have a 1B ground state. We further found the lowest singlet state of $4n$ -electron ions to be doubly degenerate. The C_{Nv} symmetry of these states agrees with that of the degenerate lowest states in Hückel theory. The triplet ground state of cyclopentadienyl cation was reported experimentally⁴¹ and studied theoretically.³ Larger species such as dianions of dehydro[$4n+2$]annulenes¹⁸ are certainly ground-state singlets. We underscore the degeneracy of the first singlet state that undergoes energy lowering through the Jahn-Teller effect. Further, the actual shape, which has less than C_{Nv} symmetry, may in most cases suffice for a singlet ground state; for example, the dianion of (unknown) dehydro[10]annulene shown below has singlet ground state even with equal resonance



(41) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017.

(38) We consider that charged linear polyenes are resonance stabilized but not aromatic. For other views, see ref 34a and also: Gund, P. *J. Chem. Educ.* **1972**, *49*, 100. Agranat, I.; Skancke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867.

(39) Fukutome, H.; Sasai, M. *Prog. Theor. Phys.* **1982**, *67*, 41. Cizek, J.; Paldus, J. *J. Chem. Phys.* **1967**, *47*, 3976.

(40) If the restricted HF (RHF) solution with full C_{Nv} and spin symmetry is used for the reference system, the resulting E_A is unreasonably large for large systems. For instance, $E_A(\text{RHF}) = 0.74$ eV at $N = 26$ while $E_A(\text{BOW}) = 0.10$. We did not examine broken-symmetry HF solutions other than the BOW type.

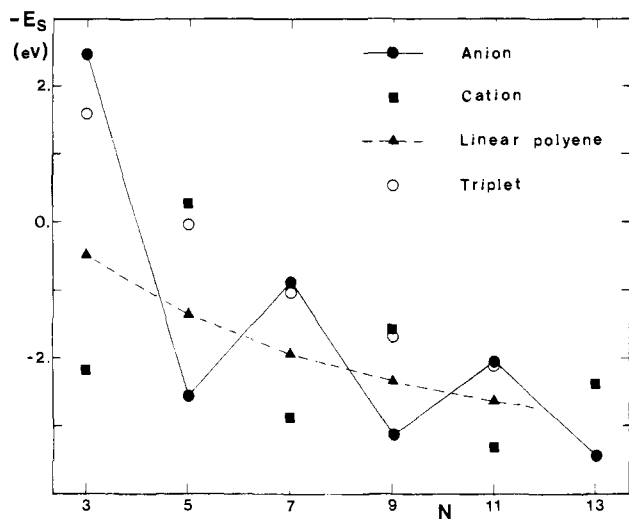


Figure 2. Plot of $-E_S$ from eq 18 ($\alpha = 0$) vs. N for monoionic species; $-F_S(N, \pm 1)$ for linear polyenes are also shown. For $4n$ -electron monocycles, triplet-state results (open circle) are shown along with singlet-state results (closed circle or square).

Table II. Aromatic Stabilizations $E_A(N, q)$ (in eV)

N	$q = 1$	$q = -1$	$q = 3$	$q = -3$
3	1.69	-2.96	<i>a</i>	<i>a</i>
5	-1.64	1.20	0.25	-1.49
7	0.95	-1.07	-1.10	0.53
9	-0.76	0.79	0.58	-0.81
11	0.69	-0.57	-0.61	0.57

N	$q = 0$	$q = \pm 2$	$q = \pm 4$
4	-1.32	0.78	<i>a</i>
6	1.21	-1.29	0.09
8	-0.29	0.77	-0.99
10	0.70	-0.67	0.41
12	-0.05	0.63	-0.58
14	0.45		

^a Fully occupied or vacant state in which $E_A = -\epsilon_1$.

integrals and bond lengths. Such preliminary calculations show the relative order of the singlet and triplet states to be sensitive to the nuclear framework in the PPP model.

Figure 2 shows $E_S(N, q)$, eq 18, for singly charged monocycles. For $4n$ -electron species both the triplet ground state and the lowest singlet state are shown. Also shown are $F_S(N, \pm 1)$ results for linear polyenes. Because of electron-hole (or alternancy) symmetry $F_S(N, q) = F_S(N, -q)$ holds. In Figure 2 oscillation of the stabilization between $4n$ - and $(4n+2)$ -electron species is obvious, supporting the Hückel rule. Then it is natural to regard the amplitude of the oscillation as the aromatic stabilization. This idea is nicely confirmed by the stabilization of linear polyenes, which just falls in the middle of the $4n$ and $4n+2$ oscillation. Thus eq 22 is a reasonable definition for aromatic stabilization.⁴²

Another important feature in Figure 2 is the increasing stability with increasing N , which takes place in both linear and cyclic systems. We regard this effect as charge-delocalization stabilization. Total stability of charged species is determined both by aromatic stabilization and charge delocalization, the latter lacking in neutral species. Available experimental evidence for annulenyl ions, pK_R^+ values^{43,44} and direct equilibrium data,^{16,45} show much

(42) E_S for $|q| > 1$ drastically decreases with increasing N because of Coulomb repulsions between excess charges. Since Coulomb repulsions are strongly affected by the charge distribution, we must reduce as much as possible the difference between the charge distributions of monocycles and reference linear polyenes so that the electrostatic stabilization is canceled in eq 22. This is another reason for our using the regular-polygon geometry for linear polyenes.

(43) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984.

(44) Doering, W. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.

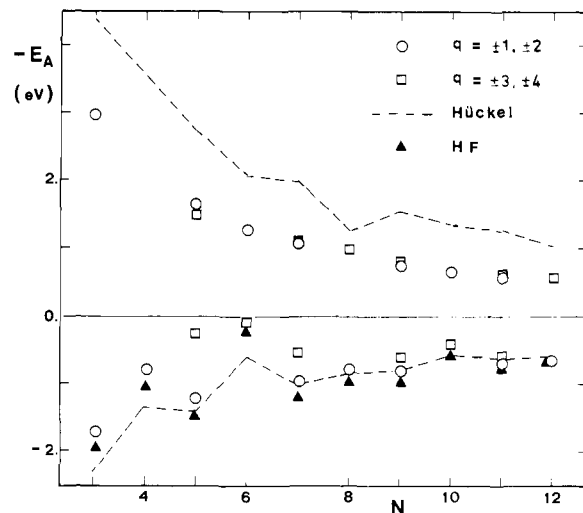


Figure 3. Plot of $-E_A$ from eq 23 vs. N for charged species. $-E_A > 0$ corresponds to $4n$ -electron species while $-E_A < 0$ occurs for $(4n+2)$ -electron species. Hückel ($\beta = -3.36$) and HF results are shown for the smallest $|q|$ when there are two $4n$ - or $(4n+2)$ -electron species.

Table III. Ring Currents: $-E_2(\text{PPP})$ (in eV)

N	$V_0 = 11.26$		$V_0 = 17.00$	
	$q = 0$	$q = \pm 2$	$q = 0$	$q = \pm 2$
4	-88.11	9.32	-22.19	8.84
8	-91.02	22.12	-11.91	19.83
12	-76.74	33.80	-5.22	28.68

N	$q = 0$	$q = \pm 4$	$q = 0$	$q = \pm 4$
	6	17.78	9.09	10.69
10	26.08	23.79	7.01	21.74
14	31.16	36.71	3.19	32.75

N	$q = 1$	$q = -3$	$q = 1$	$q = -3$
	3	9.43	0.0	8.96
7	20.58	16.51	17.68	15.26
11	31.49	29.39	24.01	26.26

N	$q = -1$	$q = 3$	$q = -1$	$q = 3$
	5	15.02	9.19	13.59
9	26.08	23.12	21.16	20.99
13	36.78	35.45	26.26	31.15

higher stability of $(\text{CH})_7^+$ over $(\text{CH})_3^+$ and slightly higher stability of $(\text{CH})_9^-$ and $(\text{CH})_{17}^-$ over $(\text{CH})_5^-$. These results suggest the importance of charge delocalization because aromatic stabilization, on the contrary, decreases with increasing N (see below).

Calculated aromatic stabilizations are listed in Table II. The lowest singlet energies were used in eq 23. Figure 3 shows E_A of charged species for exact PPP and HF theory. For Hückel theory, where eq 23 does not work well, Aihara's A-I resonance energy^{35a} is shown. The exact PPP results show that $(4n+2)$ -electron species are aromatic and $4n$ -electron species are antiaromatic. The magnitude of E_A , which is fairly independent of charge, decreases with increasing N . We see a significant difference between the exact PPP results in Figures 1 and 3; antiaromaticity of $4n$ -electron ions persists for large N in contrast to neutral species. So far as $(4n+2)$ -electron systems are concerned, however, the stability is similar for neutral and charged species. Antiaromaticity of $4n$ -electron ions is considerably higher in Hückel than in PPP theory. The HF results are fairly good for the $(4n+2)$ -electron ions.

Ring Current. Ring current results are shown in Table III in terms of E_2 , which is proportional to ring current if the area S is proportional to N^2 (eq 4). Let us first focus on $(4n+2)$ -electron species with the standard parameter. At $N = 14$, $E_2(\text{PPP})$ for $q = \pm 4$ is significantly higher than for $q = 0$, reproducing Müllen

(45) LaLancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941.

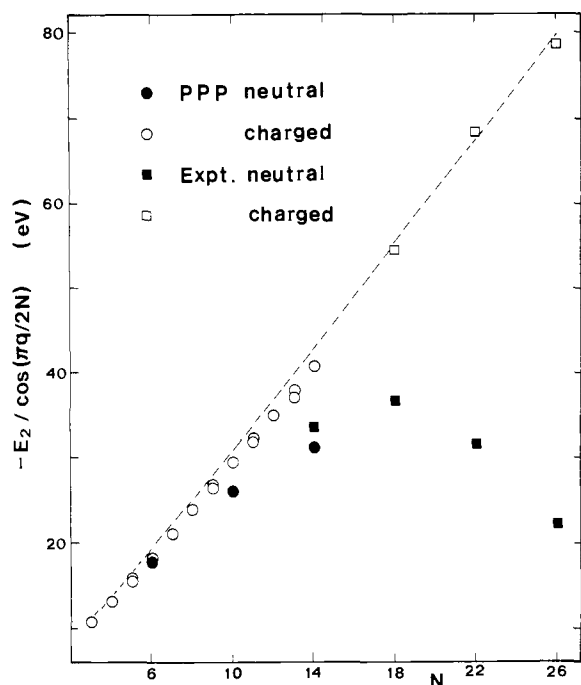


Figure 4. Plot of $-E_2/\cos(\pi q/2N)$ vs. N : PPP, experimental, and Hückel (broken line, $\beta = -2.4$) results.

et al.'s finding.¹⁸ Hückel or HF theory, eq 5, always gives higher ring currents to neutral species. This is because fewer electrons contribute to E_2 in cations; in anions cancellation occurs between bonding and antibonding orbitals. A similar effect of charge is seen in the PPP results. At $N = 6$ and 10, $|E_2(\text{PPP})|$ is larger for $q = 0$ than for $q = \pm 4$. We try to eliminate this charge effect to obtain clear contrast between neutral and charged species. In the Hückel theory the charge effect is described by the factor $\cos(\pi q/2N)$. We assume that the same factor applies to the PPP model. Then we can cancel the charge effect by taking $E_2(\text{PPP})/\cos(\pi q/2N)$, which is shown in Figure 4. The PPP results for ions now form a very good straight line; the line is independent of charge, warranting the correction factor. The clear downward deviation of neutral species from the line of ions demonstrates that ring currents of ions are higher than neutral species in large monocycles. (Note that the correction factor becomes negligible for large N .) In Figure 4 we also plot experimental results estimated from Müllen et al.'s data. We converted the experimental ^1H shifts to ring currents by using a procedure originated by Longuet-Higgins and Salem⁴⁶ and extended by Haddon;^{47,48} calculated I/H were then transformed to E_2 by eq 4 using the area S of real annulenes. The PPP results in Figure 4 extrapolate very well to the experimental estimates. Direct comparison is possible at $N = 14$ ($q = 0$) and the agreement is satisfactory.

We stress that the Hückel and HF theories completely fail to explain the enhanced ring current of charged annulenes; eq 5 necessarily leads to higher ring currents in neutral species. As shown in Figure 4, the Hückel value is a good approximation to the exact PPP value for charged species. For neutral species the Hückel value is good at $N = 6$ but becomes poorer and poorer for larger species. Thus electron correlation is very important in large neutral annulenes. Ring current of [18]annulene was a puzzling problem. The original work of Longuet-Higgins and Salem⁴⁶ ascribed the observed ring current, which was about half of the Hückel value, to bond alternation, but X-ray structural study

did not support it. Later, Vogler^{28b} succeeded in obtaining fairly good agreement with experiments by using an elaborate PPP-SCF-MO method in which local anisotropic effects were taken into account. Figure 4, however, clearly shows that electron correlation can be the cause of original failure of the Hückel theory; by extrapolation the exact PPP ring current at $N = 18$ is estimated to be about half of the Hückel value.⁴⁹

The depressed $E_2(\text{PPP})$ of neutral species comes from the v_- part (eq 10), which is always paramagnetic and grows rapidly with increasing N in neutral species. The v_+ or diamagnetic part is simply the bond order p times $2\beta N$, with p remaining almost independent of N .

While Hückel theory gives infinite ring currents (or linear H contribution in eq 3) to neutral $4n$ -electron species with equal β 's, exact PPP theory gives finite paramagnetic ring currents owing to the lifted ground-state degeneracy (Table III). Neutral $4n$ -electron species remain definitely paramagnetic with increasing N in contrast to the behavior of aromatic stability. It has already been pointed out that parallelism between stability and ring current need not hold for polycyclic systems.⁵⁰ The present results indicate that the parallelism is also lost in large neutral $[4n]$ annulenes.

Correlation Dependence. The aromatic stabilization for neutral species with $11.26 \leq V_0 \leq 25.0$ eV are shown in Figure 5. Since the stabilization energy becomes small for large V_0 , we used the unit of an effective exchange integral⁵¹ J that also decreases with increasing V_0 . In Figure 5 larger V_0 depresses more and more the antiaromaticity of $4n$ -electron species, making them eventually aromatic. This is expected because all the systems become aromatic under strong correlation, the conclusion from the classical VB theory (or the Heisenberg model,^{52,53} which is equivalent to classical VB theory). Aromatic stabilization of the classical VB theory (based on eq 14-16) is also shown in the figure. The PPP results oscillate around the classical VB line with decreasing amplitude with increasing N . For large V_0 the PPP results almost coincide with the classical VB line beyond some N . We conclude that PPP results will eventually fall on the classical VB line even in the realistic parameter region. In other words, neutral $4n$ -electron systems become weakly aromatic for large N , probably for $4n \geq 16$ as suggested in Figure 1.

We note that the oscillation of the PPP results around the classical VB line is in full agreement with a recent VB theory of aromaticity,¹³ which also concluded depressed ring currents in large neutral annulenes. We remark that the decreasing antiaromaticity in the HF results of Figure 1 never suggests possible aromatic character for large $4n$ -electron species because the BOW state, the state with bond-order alternation for equal bond lengths, cannot represent aromatic species.

The aromatic stabilization for $4n$ -electron ions with $V_0 = 17.0$ eV is shown in Figure 6 to behave quite differently from neutral species. While the latter are aromatic for $4n \geq 8$, all the $4n$ -electron ions remain antiaromatic. Also, $(4n + 2)$ -electron ions have larger aromatic stabilization than neutral species. This again illustrates the different behavior in aromatic stability of neutral and charged species. The ring current results for $V_0 = 17.0$ in Table III also give further support for the enhanced ring current of ions. While $|E_2|$ of both neutral and charged species decreases from the value at $V_0 = 11.26$, the decrease is drastic in neutral species. Consequently, we see exaggerated contrast between neutral and charged species. The higher ring current of charged species is clear for $N > 6$ without using the $\cos(\pi q/2N)$ factor. The paramagnetic nature of neutral $4n$ -electron species is un-

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

(48) ^1H shifts τ and ring current geometric factors⁴⁷ F were averaged for inner and outer protons separately to obtain τ_i , τ_o , F_i and F_o . Ring currents were obtained by $I/H = 3(\tau_i - \tau_o)/(F_i - F_o)$. A merit of the procedure is that detailed assignment of NMR signals is not needed. Planar 120° geometry was used with $\text{C}=\text{C}$, $\text{C}-\text{C}$, and $\text{C}-\text{H}$ bond lengths of 1.2, 1.4, and 1.1 Å, respectively. Current loop separation was 1.2 Å.⁴⁷

(49) Vogler's SCF-MO-PPP method^{28b} has been successfully applied to neutral molecules. His success in annulenes, however, seems to owe much to the inclusion of local anisotropic effects, which veil the too rapid increase of the MO ring current with increasing N . We still perceive the fallacious increase in his results: calculated ^1H shifts are too low in dehydro[14]annulene but too high in dehydro[18]annulene.^{28c}

(50) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 5704; **1985**, *107*, 298.

(51) Bulaevskii's exchange integral J was used:⁵² $J = (\beta^2 + U^2)^{1/2} - U$ with $U = (V_0 - V_{12})/4$.

(52) Bulaevskii, L. N. *Zh. Eksp. Teor. Fiz.* **1966**, *51*, 230 (*Sov. Phys. JETP* **1967**, *24*, 154).

(53) Linderberg, J.; Öhrn, Y. *J. Chem. Phys.* **1968**, *49*, 716.

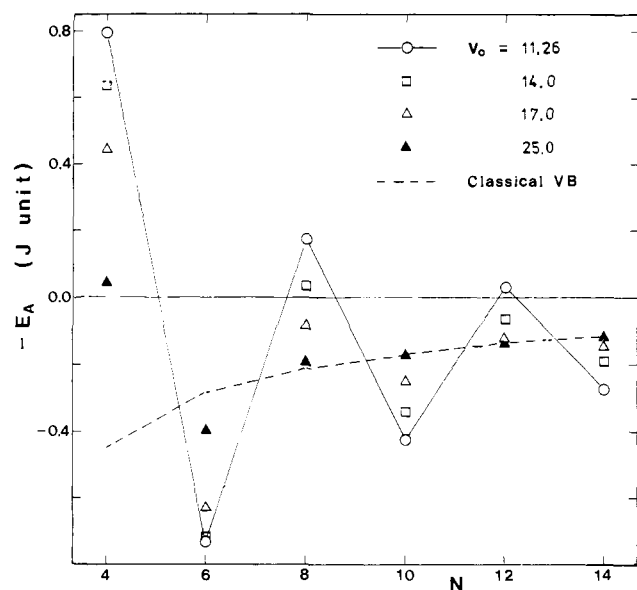


Figure 5. Plot of $-E_A$ vs. N for neutral species with varying V_0 . The energy unit J is an effective exchange integral.⁵¹

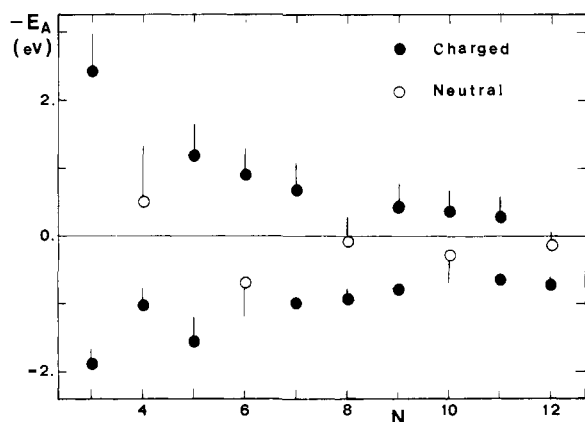


Figure 6. Plot of $-E_A$ vs. N for $V_0 = 17.0$ with $|q| \leq 2$. Short lines show the shift from $-E_A$ for $V_0 = 11.26$.

changed at $V_0 = 17.0$, suggesting unchanged paratropicity of large $4n$ -electron species at $V_0 = 11.26$.

Conclusion

We have found new features of aromaticity in monocyclic systems by studying the PPP model exactly. The outstanding finding is the enhanced ring current of charged annulenes. So far as the PPP model is concerned, this is a correlation effect which cannot be accounted for within MO theory. Another new result is the weakly aromatic nature of large neutral $4n$ -electron systems. We consider this to be another correlation effect because it is a characteristic feature of the classical VB theory. In contrast to neutral systems, charged $4n$ -electron species remain antiaromatic independent of ring size. We also find finite paramagnetic ring currents in neutral $4n$ -electron systems without bond alternation; their magnitude becomes smaller for large N but they remain paramagnetic. Investigation of stronger correlations supports these conclusions by showing similar features with much exaggeration. Stronger correlation generally shifts features which appear in large systems to smaller systems.

The enhanced ring current of charged annulenes has ample experimental support.¹⁴⁻¹⁸ This effect, indeed, appears to be beyond annulenes since similar observations have been reported for porphyrins⁵⁴ and a novel conjugated molecule.⁵⁵ On the other hand, experimental support for the weakly aromatic nature of large

neutral $4n$ -electron rings is not available. A basic problem here is the competition with bond-alternation effects that may overwhelm weak aromatic stabilization of large annulenes. As a preliminary survey, we investigated the possibility of vanishing bond alternation in large $[4n]$ annulenes but the result was negative. Therefore, it is not likely that the effect has sharp experimental evidence. Nevertheless, we still stress its theoretical importance in that the effect reflects turnover from Hückel theory to VB theory in aromaticity of large monocycles.

A general feature emerging from the present study is different behavior in aromaticity of neutral and charged species, especially for large species. While MO theory does not give any explanation, it is not unexpected in VB theory. Within qualitative VB theory in which only lowest energy VB structures are considered, interactions between VB structures are exchange interactions in neutral systems. In charged systems a different type of interaction, electron transfer between adjacent carbon sites, appears.⁵⁶ Aromaticity of charged systems arises from interference of the exchange and electron-transfer interactions, thus resulting in basic difference from aromaticity of neutral systems.⁵⁷ In any case, contrasting neutral and charged species is an interesting new viewpoint in the study of aromaticity. Extending the investigation to polycyclic systems will be an interesting next step.

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Appendix

To obtain the constants in eq 15 and 20, we have to extrapolate energies of finite systems to infinity. Since cyclic systems do not give good extrapolation because of $4n-(4n+2)$ oscillations, linear polyenes were used to obtain ϵ_0 of cyclic systems. We consider two types of linear polyenes, with regular-polygon shape and with straight-line shape. We use the term linear polyene with respect to resonance integrals, regardless of the shape. The quantity ϵ_0 in eq 20 for the regular-polygon linear polyene should be equal to ϵ_0 for the monocycle. The difference between the Hamiltonians of the two systems is only the resonance integral connecting the terminal sites of the linear polyene. We may regard the difference as a perturbation. Then, the perturbation energy is certainly of the order of β , yielding eq 20 with ϵ_0 of the monocycle. A similar argument is possible between the regular-polygon and straight-line linear polyenes. The difference in the Hamiltonian then is the intersite Coulomb interactions. Since a local part of the regular polygon reduces to a straight line for $N \rightarrow \infty$, local interactions are essentially the same between the two Hamiltonians. Further, long-range interactions will be effectively shielded for neutral systems. Thus the difference in the Hamiltonian will occur only around the ends, which leads to the equality of ϵ_0 's. Since usual 120° -angle linear polyenes have a local shape different from monocycles, their ϵ_0 value is different.²² We tried both the regular-polygon shape and straight-line shape for extrapolation. The equality of ϵ_0 's was verified within the error of the extrapolations. Since the estimated error was smaller for the straight-line shape, we adopted this extrapolation. Our extrapolation formula is

$$F_0(N,0) = \epsilon_0 N + \epsilon_1 + \epsilon_2/N \quad (\text{A1})$$

The PPP energies of straight-line linear polyenes are, in eV and with vanishing site energy α : -7.46887 , -11.69754 , -15.94665 , -20.20448 , and -24.46671 for $N = 4, 6, 8, 10$, and 12 , respectively. Using $N = 8-12$ or $N = 6-12$ (least-squares fit) along with eq A1, we obtain $\epsilon_0 = -2.1355 \pm 0.001$. A plot of $F_0(N+2, 0) - F_0(N, 0)$ vs. $1/N(N+2)$ yields a very good straight line, showing the quality of the extrapolation based on eq A1. We applied the above procedure to the exactly solvable Hubbard model with $|t|/U = 0.25$, obtaining the extrapolation of $\epsilon_0 = -0.5736$

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$|t|$ for the exact value of $\epsilon_0 = -0.57373 |t|$. In the text we used regular-polygon linear polyenes for eq 20. We obtained its ϵ_1 by fixing ϵ_0 of eq A1 to -2.1355 and by using a least-squares fit with $N = 8-12$. The estimated value is $\epsilon_1 = 1.17 \pm 0.01$. The PPP

energies of the regular-polygon linear polyenes are -7.66142 , -11.88706 , -16.11224 , -20.34785 , and -24.59242 for $N = 4-12$, respectively. Extrapolations for the HF theory and different V_0 are made by the same procedure.

Mediated Electrochemical Reduction of CO₂. Preparation and Comparison of an Isoelectronic Series of Complexes

Daniel L. DuBois* and Alex Miedaner

Contribution from the Solar Energy Research Institute, Golden, Colorado 80401.

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Abstract: The preparation and characterization of complexes of the type $[M(\text{triphos})L](\text{BF}_4)_2$ are described (for $M = \text{Ni}$, L is $\text{P}(\text{OME})_3$ and PEt_3 ; for $M = \text{Pd}$, L is CH_3CN , $\text{P}(\text{OME})_3$, PEt_3 , $\text{P}(\text{CH}_2\text{OH})_3$, and PPh_3 ; for $M = \text{Pt}$, L is PEt_3 ; triphos is $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$). On the basis of cyclic voltammetry and bulk electrolysis experiments, the Pd complexes are shown to catalyze the electrochemical reduction of CO₂ to CO in acidic acetonitrile solutions. The analogous Ni and Pt complexes are not catalysts for CO₂ reduction under the same conditions. Kinetic studies have been carried out on $[\text{Pd}(\text{triphos})(\text{PEt}_3)](\text{BF}_4)_2$ and a mechanism for the reduction of CO₂ is proposed.

The chemistry of CO₂ is receiving increasing attention for a variety of reasons including its potential as a C₁ feedstock,¹ the increase in atmospheric CO₂ concentration,² and its possible use as a substrate for storing solar energy.³ However, the electrochemical reduction of CO₂ at most metal electrodes is accompanied by an overvoltage of 1–1.5 V and results in a variety of products.⁴ This high overvoltage has prompted the search for more suitable electrodes and catalysts capable of mediating the electrochemical reduction of CO₂. The use of indium electrodes,⁵ electrodes modified with polymers containing Pd,⁶ and carbon electrodes modified with cobalt phthalocyanine complexes⁷ have all resulted in significant lowering of the overpotential for heterogeneous CO₂ reductions. Homogeneous catalysts including porphyrins and tetraaza macrocyclic complexes,^{8,9} $\text{Rd}(\text{dppe})_2\text{Cl}$,¹⁰ iron sulfur clusters,¹¹ bipyridine complexes,^{12,13} and formate dehydrogenase¹⁴

also significantly lower the overpotential.

In this paper, we report the synthesis and characterization of a new series of isoelectronic complexes, some of which are capable of mediating the electrochemical reduction of CO₂ to CO. The ability of these complexes to mediate the electrochemical reduction of CO₂ is dependent on the metal and on ligand structure. These catalysts appear to have mechanistic features different from other homogeneous catalysts that mediate the electrochemical reduction of CO₂, and operate at potentials approximately 0.6 V positive of other homogeneous catalysts, excluding formate dehydrogenase.

Experimental Section

Physical Measurements. Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer 599B spectrophotometer. All of the BF₄ salts show a broad strong infrared absorption between 900 and 1150 cm⁻¹. A Varian E109 spectrometer was used for obtaining EPR spectra. EPR spectra were recorded on 1×10^{-3} M dichloromethane solutions. A JEOL FX90Q FT NMR spectrometer equipped with a tunable, variable-temperature probe was used to collect ¹H, ³¹P, and ¹³C NMR spectra. Me₄Si was used as an internal reference for ¹H and ¹³C spectra. A capillary filled with phosphoric acid was used as an external reference for ³¹P NMR spectra. All ³¹P NMR spectra were proton decoupled.

Electrochemical measurements were carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. A Houston Instruments Model 2000 x-y recorder was used for plotting cyclic voltammograms. A silver wire was dipped in concentrated nitric acid, then dipped in concentrated hydrochloric acid, and rinsed with distilled water. After drying, this wire was used as a pseudo-reference electrode. This reference electrode was separated from the working and counter electrode compartments by a Vycor frit. Ferrocene was used as an internal standard. The potential of ferrocene vs. aqueous SCE in 0.2 N LiClO₄ solution of acetonitrile is reported to be +0.307 V.¹⁵ All of our measurements were carried out in 0.2 N NEt₄BF₄ solutions of acetonitrile. In this solution, we found the potential of ferrocene to be +0.40 V vs. aqueous SCE. For cyclic voltammetry, a glassy carbon disk electrode

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