On the Question of Paramagnetic "Ring Currents" in Pyracylene and Related Molecules

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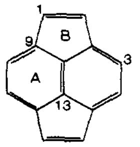
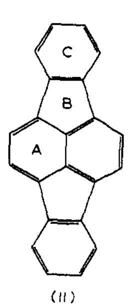
Abstract: Trost et al. have interpreted the proton chemical shifts obtained from the ^{1}H NMR spectra of pyracylene (I) and related molecules in terms of paramagnetic "ring currents"; they claimed that this provides support for the postulate that pyracylene can be regarded as a [12]annulene with an internal vinyl cross-link and that it should, therefore, be a particularly good model for a planar [12]annulene. In order to test this experimental deduction, we present a series of semiempirical MO calculations (of varying degrees of sophistication) of the π-electron ring current intensities (and their contributions to magnetic susceptibilities and anisotropies) of pyracylene and two other molecules, II and III, discussed or studied experimentally by Trost et al.; in addition, we examine the ring currents in acepleiadylene (IV), a nonalternant isomer of pyrene (V) which could formally be considered as a "perturbed" [$4n + 2$]annulene, and in dipleiadiene (VI) which, like pyracylene, has a $4n$ periphery (with, in this case, $n = 4$). Of the three types of calculation performed on pyracylene [(i) London-McWeeny based on a simple ("topological") HMO; (ii) London-McWeeny based on an iterative ($\beta\omega'\omega''$) HMO; (iii) coupled Hartree-Fock based on a PPP-SCF wave function], the best agreement was obtained between the crudest ((i)) and what is, superficially, the most sophisticated ((iii)) calculation. The reasons for this are discussed, and attention is drawn to the apparent importance of using a realistic geometry, rather than an idealized one, when calculating the magnetic properties of conjugated molecules like pyracylene, whose π-electron systems are predominantly paramagnetic. Although they do not appear particularly to favor the "$4n$ periphery" model, these computations do lend support to the postulate of Trost et al. that a paramagnetic ring current exists in pyracylene (at least, in its five-membered rings); however, *no* implications or inferences from this are claimed regarding the "aromaticity", or otherwise, of pyracylene.

In a previous article, Trost et al.,[3] after reporting some elegant synthetic and spectroscopic work on certain systems which they described as "perturbed [12]annulenes," speculated on the possibility of their being paramagnetic π-electron "ring currents" in pyracylene (I).[4] This idea—which was inspired by earlier suggestions[5,6] that cyclic $4n$ π-electron systems should display paramagnetic properties, and by the proposal of Trost et al.[3] that pyracylene can be considered as a perturbed $4n$ annulenic system—seems to lead to a satisfactory rationalization of the experimental proton magnetic resonance (^{1}H NMR) spectra of pyracylene and related molecules, which Trost et al. also reported in their paper.[3]

It was pointed out that one of the major frustrations of trying experimentally to verify theoretical predictions about the properties of $4n$ monocyclic systems is the molecular flexibility and general nonplanarity of such systems larger than cyclobutadiene. In an attempt to rectify this, Trost and his co-workers[3] resolved to introduce molecular rigidity into a basic $4n$ annulenic monocyclic system by incorporating cross-links; in particular, they investigated the perturbation arising as a result of the insertion of an internal π system into a monocyclic periphery, producing, for example, the title molecule, pyracylene (I) (a "perturbed" $4n$ peripheral system in which $n = 3$) (see structure Ia); they also discussed the previously synthesized 1,2:5,6-dibenzopyracylene (II) (systematic name: indeno[1,2,3-*cd*]fluoranthene), which may formally be considered as being derived from a $4n$ periphery (where, in this case, $n = 5$), by the addition of an "internal" π system and two other cross-links.



(I)



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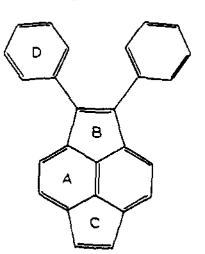
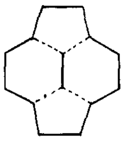


(III)

There is, however, another way to visualize pyracylene—as a "naphthalene" core, plus two "vinyl" bridges (structure Ib). Lo and Whitehead,[7] after calculating the ground-state electronic properties of pyracylene via an SCF ($\pi + \sigma$) method, considered that, on balance, neutral pyracylene is more aptly described by structure Ib than by the peripheral model depicted by structure Ia; Yamaguchi and Nakajima[8] have also concluded that the upfield shift of the ^{1}H NMR spectrum, and the unusually low value of the first half-wave potential of pyracylene, can be well explained in terms of (respectively) the diamagnetic anisotropy and the energy of the lowest vacant SCF-MO, calculated on the basis of the predicted equilibrium configuration which corresponds to the "naphthalene core" model represented by structure Ib.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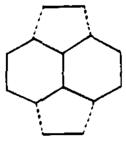
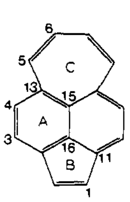

(Ib)

Trost et al.[3] posed the question: "Does a paramagnetic ring current exist in pyracylene?" (i.e., do the magnetically induced circulations of the π-electrons of the system—which, on the Pauling,[9] Lonsdale,[10] London,[5] and Pople[11] models, are supposed to occur when a planar (poly)cyclic, conjugated system is in the presence of an external magnetic field with a component perpendicular to its molecular plane—give rise to a *paramagnetic* (i.e., positive) contribution to the magnetic susceptibility, and, in an ^{1}H NMR experiment, cause a net magnetic *shielding* (i.e., *up*field shift) of the external, peripheral protons situated in the molecular plane?). In addressing themselves to this question, Trost and collaborators considered (among others) molecules I and II, together with the ^{1}H NMR spectra of 1,2-diphenylpyracylene (III), and dihydro and tetrahydro derivatives of it. Since then, Yamaguchi and Nakajima have conjectured[8a] that the periphery of pyracylene may bear a paramagnetic "ring current" characteristic of the $4n$ perimeter but that, on the other hand, the naphthalene core in pyracylene "may exhibit a diamagnetic ring current to the same extent as a free naphthalene molecule".[8a]

In this paper, we attempt to throw some light on these speculations by reporting calculations of the π-electron ring current intensities in I–III, in acepleiadylene (IV) (a nonalternant analogue of pyrene (V)), and in dipleiadiene (VI),



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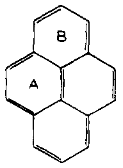

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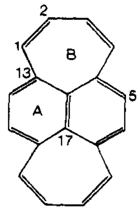

(VI)

which are based on variants of the simple London theory,[5] and on apparently more sophisticated SCF versions of it;[12] these calculations lend support to (one hesitates, perhaps, to say "confirm") the postulate of Trost et al.[3] that a paramagnetic ring current exists in pyracylene—at least in its five-membered rings—but they by no means unambiguously favor the "$4n$-periphery" model for pyracylene which Trost et al. propose.

Methods of Calculation

The original formalism of London[5] allows calculation only of the *overall* "mobile" π-electron contribution to the magnetic susceptibility of a given conjugated molecule, in a direction perpendicular to its molecular plane, but by use of extensions to the theory devised by Pople[13a] and McWeeny,[13b] it is possible to calculate the induced magnetic moment per mole associated with *each ring* of the polycyclic system—that is to say, on the basis of the London approximations, its individual "ring currents". The calculations of ring current intensities reported here were based on a formula recently presented by one of us (eq 25 of ref 13c), with ring- and "circuit" areas[13c] estimated on the assumption of molecular geometries comprising polygons of sides equal in length to the standard carbon-carbon bond length in benzene (as is the custom in these calculations, e.g., ref 13 and 14). Initially, a purely "topological"[15,16] MO was used, and the results, expressed as multiples of the benzene ring current intensity,[17] are presented in Table I (for molecules I–III) and in Table II, which contains the results of similar "topological" calculations on acepleiadylene (IV), a nonalternant analogue of pyrene (V) which could likewise formally be considered as a perturbed annulene (but this time a $[4n + 2]$ one), and dipleiadiene (VI) which, like pyracylene, has a $4n$ periphery, but now with $n = 4$.

Since, at least at the beginning of this work, our main aim was the essentially qualitative one of establishing whether the very simplest London[5] calculation, based on a topological MO,[15,16] leads to the expectation of paramagnetic ring currents (conventionally expressed with a negative sign[17]) or diamagnetic (conventionally positive[17]) ring currents in these molecules, no refinements such as variation of Hückel-Coulomb and resonance integrals were initially entertained. However, in order to ascertain whether the results of such an entirely objective calculation based on a purely topological MO are at least qualitatively reliable, it was considered expedient (particularly since the molecules under investigation are nonalternant hydrocarbons with a certain degree of "bond-fixation"[18,8]) to check some of the predictions of Table I by calculating the London contribution to the magnetic susceptibility of pyracylene (I) by means of two variants (one apparently minor, and the other, on the face of it, more sophisticated) of the original Hückel-London-McWeeny method.

Table I. π-Electron Ring Current Intensities, from a 'Topological' Calculation,[a] in Molecules I–III

	Ring current intensity[a] in rings			
Compd	A	B	C	D
Pyracylene (I)	-0.38_6	-2.31_7		
1,2:5,6-Dibenzopyracylene (II)	$+0.57_1$	-0.63_4	$+0.56_3$	
1,2-Diphenylpyracylene (III)	-0.26_3	-2.16_8	-2.02_8	$+0.87_7$

[a] Calculated from eq 25 of ref 13c (bond orders and imaginary bond-bond polarizabilities having been computed from a simple ('topological') HMO) and expressed as a ratio to the diamagnetic ring current intensity calculated, by the same method (see text), for benzene; a *positive* entry in the table therefore indicates a *diamagnetic* ring current, and a *negative* one, a *paramagnetic* ring current.

Table II. π-Electron Ring Current Intensities from a 'Topological' Calculation[a] in Pyracylene (I), Acepleiadylene (IV), Pyrene (V), and Dipleiadiene (VI)

	Ring current intensity[a] in rings		
Compd	A	B	C
Pyracylene (I)	-0.38_6	-2.31_7	
Acepleiadylene (IV)	$+1.20_7$	$+1.11_5$	$+1.17_0$
Pyrene (V)[b]	$+0.96_4$	$+1.32_7$	
Dipleiadiene (VI)	-0.70_0	-2.86_1	

[a] See footnote to Table I. [b] Results for pyrene from ref 14d.

Table III. Ring Current Intensities in Pyracylene (I) Calculated by Three Methods

	Ring current intensity in	
Type of calculation	Five-membered rings (B)	Six-membered rings (A)
London–McWeeny method based on a simple ('topological') HMO[a]	-2.31_7	-0.38_6
London–McWeeny method based on an iterative ($\beta\omega'$-ω'') HMO[b]	-1.01_3	$+0.30_8$
Coupled Hartree–Fock method based on a PPP–SCF wave function[c]	-2.15_6	-0.20_3

[a] See footnote to Table I. [b] Calculated from eq 25 of ref 13c, the bond orders and imaginary bond-bond polarizabilities required having been computed from an iterative ($\beta\omega'\omega''$) HMO self-consistent with respect to charges and bond orders. [c] By an extension of the Hall–Hardisson[12] method due to Gomes (see text), detailed elsewhere.[32] The quantities listed here are those which, in ref 32, are designated the "relative integrated π-electron current densities" associated with a given ring.

The first of these was what one might regard as the best calculation available within a Hückel framework (that is to say, an iterative one which is self-consistent with respect both to resonance integrals and to the Coulomb integrals). In this approach, the resonance-integral-bond-order relationship used was that previously given by one of us and Golebiewski[19] and, in considering variations of Coulomb integrals with charge distribution within the molecule, not only the charges on nearest neighbor atoms but, in addition, those of *second*-nearest neighbors were also taken into account (as per the model of Kuhn,[20] discussed in detail by one of us and Wille[21] and previously applied to the calculation of the magnetic susceptibilities of conjugated systems by Gayoso and Boucekkine[22]). This whole procedure, iteratively self-consistent with respect to charges and bond orders, has been called[22] the "iterative $\beta\omega'\omega''$ method" and it arguably[23] represents the best available calculation of its type. Such a calculation on pyracylene and dipleiadiene (based on the regular geometries described above and on the parameters of Kuhn[20,22] and of Coulson and Golebiewski[21,22]) required 25 iterations[25] and the results (for pyracylene) are presented in the middle row of Table III.

Finally, as what was initially hoped to be a more unequivocal check on the simple HMO ("topological") calculation, we estimated the π-electron "ring current" magnetic susceptibility of pyracylene, perpendicular to its molecular plane, by means of what is apparently a much more realistic semiempirical method (namely the coupled Hartree-Fock approach of Hall and Hardisson[12,27] which, only recently (with the advent of faster computers), has been applied generally to large, polycyclic molecules).[27a,28c,29c] In this calculation, based on a Pariser-Parr-Pople π-electron wave function, the parametrization used was that of Lazzeretti and Taddei[27a] (i.e., the α core integrals were calculated via the Goeppert-Mayer and Sklar formalism,[30] the γ integrals were estimated by the procedure of Nishimoto and Mataga,[31] 11.08 eV (ca. 1068 kJ mol^{-1} in the units of the *Système International*) was taken as the monocentric repulsion integral for carbon, 11.42 eV (ca. 1101 kJ mol^{-1}) as the ionization potential of carbon, and the β parameter was set at -2.39 eV (ca. -230 kJ mol^{-1}). Twelve iterations were required for the SCF calculation (convergence criterion, 1 in 10^7), and 60 cycles were necessary for convergence of $\mathbf{P}'$, the first-order correction to the bond-order matrix (brought about by the presence of the external magnetic field and calculated by the coupled Hartree-Fock procedure of Hall and Hardisson[12,27a]). The results of this calculation, and certain extensions of it,[32] are presented and discussed in subsection 3 of Results and Discussion.

Apart from some preliminary runs on the Oxford University KDF 9 Computer, all three types of calculations discussed in this section were performed on the University's ICL 1906A Computer.[33]

Results and Discussion

1. The Topological Calculation on Molecules I–VI. It can be seen from Table I that, on the basis of the approximations inherent in the "topological" calculation (which required knowledge only of the carbon-atom connectivity and of the areas of the various constituent rings of each polycyclic system), pyracylene is indeed predicted to sustain paramagnetic ring currents, even in its six-membered rings;[34] the five-membered rings bear a much larger paramagnetic current, however, and so, in spite of their smaller area (ca. 0.66 times that of a standard benzene hexagon), they will still make the major contribution to the overall "London" magnetic susceptibility of pyracylene, perpendicular to its molecular plane; 1,2:5,6-dibenzopyracylene (II), on the other hand, even though it does have a 4*n* periphery, bears a paramagnetic ring current only in its five-membered rings. 1,2-Diphenylpyracylene (III) merely displays the expected ring current behavior of phenyl-substituted polycyclic hydrocarbons, i.e., that the ring current intensities in the moieties joined by the 'single' bond are just slightly modified renditions of those extant in the original, unsubstituted molecules. Thus, because (as far as the ring currents are concerned) phenyl substitution represents a fairly small change in the pyracylene system (or, more precisely, because the imaginary bond-bond polarizabilities (required in the calculation[13c]) between a given bond in one of the phenyl groups and *any* other bond in the conjugated system *outside* the given phenyl ring are zero), the phenyl (diamagnetic) ring currents in III are changed by only about 12% from the benzene value of +1, to ca. 0.88 (cf. biphenyl, with a ring current intensity,[35] from a purely "topological" calculation, of 0.93_5), and those of the pyracylene moiety all remain paramagnetic (see Table I). This pattern of ring current intensities in III is at least qualitatively consistent with the ^{1}H NMR spectra of this molecule (and related ones) reported by Trost et al.[3]

Finally, concerning molecules I–III, we note that, on the basis of the idealized geometries adopted here and the ring currents presented in Table I, the London contribution to magnetic susceptibility in I–III (on the (undoubtedly unjustified) assumption that the latter is planar), expressed as a ratio to that of benzene, and calculated, for example, via eq 9–12 of ref 13c, are: -3.83, $+1.43$, and -1.54, respectively. On the basis of this topological calculation, the 'mobile' π systems of I and III would thus appear to display overall paramagnetism, while that of II would be expected to exhibit a *net* diamagnetism.[36]

It is instructive, at this stage, to consider the ring current intensities in cyclohepta[*f,g*]acenaphthylene (IV) (or acepleiadylene), calculated by this topological approach. One might perhaps formally regard acepleiadylene as the [4*n* + 2] periphery analogue of pyracylene obtained by replacing one of the five-membered rings of this latter molecule by a seven-membered cycle. Acepleiadylene (IV) is, furthermore, a nonalternant isomer of pyrene (V) which itself might, therefore, also be considered formally as, in some way, a perturbed [4*n* + 2]annulene.[37a] The repercussions of this change on the ring current intensities are quite dramatic (as Table II clearly shows), those in acepleiadylene being large and unambiguously diamagnetic—quite the same order, in fact, as those encountered in the alternant, condensed, benzenoid hydrocarbons (e.g., ref 14a,d,e and 18b) and, in particular, similar in magnitude to the currents[14d] in pyrene (V), its alternant isomer which also has a [4*n* + 2] perimeter (see Table II). On the basis of this 'topological' calculation, therefore, it seems that acepleiadylene, too, might equally be considered (as far as its ring currents are concerned) as a 'perturbed' annulene. This proposition at least seems to be consistent with the experimental ^{1}H NMR data[37b] available for this molecule.

Finally, formal replacement also of the *second* five-membered ring in pyracylene leads to the (hypothetical) molecule dipleiadiene (VI) which, once more, like pyracylene, has a 4*n* periphery (this time with *n* = 4), again, as expected, this 'topological' calculation unambiguously predicts paramagnetic ring currents in all rings, as indicated in the last row of Table II.

2. The $\beta\omega'\omega''$ Iterative Calculation on Pyracylene. The results of the 'topological' calculation on pyracylene were by no means confirmed by the $\beta\omega'\omega''$ calculation (which was iteratively self-consistent with respect to charges and bond orders), as Table III indicates. By the time convergence had been achieved, Coulomb integrals had been corrected by up to ca. $\pm0.055\beta$, while resonance integrals varied from ca. 1.11β for the 'fixed' double bond in the five-membered ring, to ca. 0.85β for the 'single' bond in that ring. This calculation still gave the qualitative result that there is a paramagnetic ring current in the five-membered ring of pyracylene, though of much reduced intensity (-1.01 as compared with the value of -2.32 arising from the topological calculation); however, the iterative calculation predicts that there should be a small but nevertheless *dia*magnetic ring current in the six-membered (benzenoid) ring (at this point, the reader is asked to consider once more ref 34 and the speculations of Yamaguchi and Nakajima[8] mentioned in the introductory section). In a commonly used terminology (e.g., ref 38), the five-membered ring of I would be described as being paratropic and the six-membered ring of pyracylene, on the basis of this iterative calculation, is diatropic. The *overall* 'mobile' π-electron magnetic susceptibility is still predicted to be paramagnetic but because two rings which, from the topological calculation, were thought to be paratropic are now predicted to be diatropic, while the ring current intensity in the two rings which are still expected to be paratropic is more than halved, this overall 'London' (paramagnetic) contribution to the magnetic susceptibility of pyracylene, perpendicular to its molecular plane, is drastically reduced, from −3.83 down to −0.74 (relative to benzene).

3. Various Coupled Hartree–Fock Calculations on Pyracylene. With the parametrization described in Calculations, the coupled Hartree–Fock computation, by the method of Hall and Hardisson,[12] yielded 99.24×10^{-6} cgs emu as the absolute value for the 'mobile' π-electron contribution to the magnetic susceptibility of pyracylene, perpendicular to its molecular plane. Since the corresponding contribution to the magnetic susceptibility of benzene, on the same parametrization, is[27a] -30.53×10^{-6} cgs emu, the 'London' susceptibility of pyracylene, relative to benzene, is −3.25 [that is to say, the ring currents of pyracylene are predicted by this method to exhibit quite definitely an overall *para*magnetism; in fact, the ratio ($\chi_{\perp}{}^{\pi\ \mathrm{London}}$ (pyracylene)/$\chi_{\perp}{}^{\pi\ \mathrm{London}}$ (benzene)) of −3.25 obtained here compares reasonably (to within ca. 15%) with the value of this same ratio (−3.83) arising from the 'topological' calculation (see subsection 1 of the present section)]. This last result appears empirically to confirm an earlier remark of O'Sullivan and Hameka[39] (made, however, with specific reference to predominantly diamagnetic, alternant hydrocarbons) that "... London's calculation is perhaps less accurate than Hall and Hardisson's ..." but that when only the *ratios* of London's result are used, it seems likely that "these ratios are quite accurate". (We emphasize that this statement is quoted in the context of a noniterative calculation in both cases; see subsection 4 of the present section.) It is also possible that the susceptibility ratios obtained from the very crudest HMO calculation, based on the London–McWeeny method, agree (perhaps fortuitously) so well with those from the more sophisticated coupled Hartree–Fock SCF procedure *precisely because* the former calculation takes molecular topology into account in such a rudimentary way.[40] In one respect, the PPP–SCF wave function may also be regarded as being a reflection of molecular topology (though, in fact, a more subjective one, since it requires more semiempirical parameters) in the sense that the core Hamiltonian matrix elements of such a wave function are *nonzero only for bonds* and, on the assumptions made in *this* calculation, have a common value for all bonds (see subsection 4 of the present section).

The Hall–Hardisson calculation, as originally presented,[12] does not make provision for breaking down the total contribution to the overall magnetic susceptibility (perpendicular to the molecular plane) from the 'mobile' π electrons into terms associated with each individual ring of the polycyclic system; however, extensions to the Hall–Hardisson method, by Mr. J. A. N. F. Gomes (of this Department), in which certain invocations of the so-called 'London approximations' are relaxed (full details of this method are being presented elsewhere)[32] give rise to values of −2.16 and −0.20 for quantities[42] (associated with the five-membered and six-membered rings, respectively, of pyracylene) similar to what the London–McWeeny method would identify with the "ring current" intensities (expressed relative to the benzene value) in these rings (Table III). So, once again, predictions based on the most simple-minded topological wave function (−2.32 and −0.39 for the "ring currents" in pyracylene) seem to be confirmed, at least semiquantitatively, by this apparently more sophisticated calculation. In particular, both five-membered *and* six-membered rings are again predicted to be paratropic.

Table IV. Relative π-Electron Ring Current Intensities, Based on an Iterative ($\beta\omega'\omega''$) HMO,[a] in Molecules I, IV, and VI

Compd	Ring current intensity[a] in rings A	B	C
Pyracylene (I)	$+0.30_8$	-1.01_3	
Acepleiadylene (IV)	$+1.19_8$	$+0.81_8$	$+0.83_7$
Dipleiadiene (VI)	$+0.34_4$	-0.91_8	

[a] See footnote *b*, Table III.

4. The Importance of Iteration with Respect to Bond Length. In the preceding two subsections we have noted the superficially somewhat surprising result that the SCF calculation on pyracylene which was *not* iterative with respect to bond lengths was in better agreement with the simple HMO calculation than with the iterative $\beta\omega'\omega''$ one. In Table IV are listed ring current intensities, based on a $\beta\omega'\omega''$ HMO calculation, for pyracylene (I) (transcribed from Table III), as well as for acepleiadylene (IV) and dipleiadiene (VI). From this table, it can be seen that $4n$-peripheral dipleiadiene ($n = 4$) follows much the same pattern as $4n$-peripheral pyracylene ($n = 3$) in that all its rings are expected to be paratropic, on the basis of a simple, noniterative, 'topological' HMO calculation (Table II), and yet diatropism is predicted for its six-membered rings when an iterative $\beta\omega'\omega''$ wave function is used. In fact, on the basis of such an iterative calculation, the *dia*magnetic ring current intensities in the six-membered rings of pyracylene (I) and dipleiadiene (VI) are very nearly equal at ca. ⅓ of the benzene value, while the five-membered rings of I, and the seven-membered rings of VI, bear a *para*magnetic ring current of approximately the same order of magnitude as the *dia*magnetic one in benzene. The $[4n + 2]$-peripheral hydrocarbon, acepleiadylene (IV), however, which was unambiguously diamagnetic according to the topological calculation (Table II), is still predicted to be strongly diamagnetic, even by this iterative calculation; in fact, the ring current intensity computed for its six-membered rings (ca. 1.20, on the basis of the $\beta\omega'\omega''$ wave function) is almost the same as that (ca. 1.21) obtained via the topological calculation, although the diamagnetic ring current intensities in the five- and seven-membered rings of IV are predicted by the iterative calculation to be some 25% less than the corresponding 'topological' values.

Hence, it is seen that calculated ring currents are much more sensitive to whether or not the wave function used to compute them is self-consistent with respect to atomic charges and bond orders in the case of overall paramagnetic, conjugated, π-electron systems than in the case of strongly diamagnetic ones. This is in fact not surprising, for paramagnetic contributions will be largest when magnetic dipole transitions can take place between the ground-state (occupied) and excited-state (unoccupied) orbitals,[6,43] and this activity will be particularly favored when the separation between the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals is small. The smaller this separation turns out to be, however, the more likely it is to be sensitive to the idiosyncracies of the particular method used to calculate it. Hence, the predicted magnetic properties of predominantly paramagnetic systems should be much more dependent upon the method used for their calculation than those of diamagnetic systems. In the latter cases, the diamagnetic contribution to the net current is the major one and this is a function only of the electron density in the ground state;[6,43] any (relatively minor) paramagnetic contribution which might possibly obtain is determined once again by the HOMO–LUMO separation which, in the case of diamagnetic systems, is much larger and estimates of it are therefore much less dependent on the peculiarities of

Table V. 'London' Contributions ($\chi_\perp^{\pi \mathrm{London}}/\chi_\perp^{\pi \mathrm{London}}$(benzene)) to Magnetic Susceptibilities Perpendicular to the Molecular Planes of Molecules I, IV, and VI, by Various Methods

	($\chi_\perp^{\pi \mathrm{London}}/\chi_\perp^{\pi \mathrm{London}}$(benzene)) calculated for		
Method of calculation	Pyracylene (I)	Acepleiadylene (IV)	Dipleiadiene (VI)
London–McWeeny method based on a simple ('topological') HMO[a]	−3.83	4.79	−5.40
'Non-iterative' coupled Hartree–Fock (Hall–Hardisson)	−3.25		
London–McWeeny method based on an iterative ($\beta\omega'$-ω'') HMO[b]	−0.74	4.11	−1.88
Iterative coupled Hartree–Fock (with variation of resonance and two-center repulsion integrals at each iteration)[c]	−0.40	3.92	−0.34

[a] Calculated from the relative ring current intensities of Table II, and idealized molecular geometries, via eq 9–12 of ref 13c. [b] Calculated from the relative ring current intensities of Table IV, and idealized geometries, via eq 9–12 of ref 13c. [c] Taken from ref 8a (Yamaguchi and Nakajima).

the particular method used to calculate it.

The above considerations are dramatically illustrated when the variously calculated "ring current" intensities discussed in this paper are used to estimate (Table V) the total π-electron ring current contribution to the magnetic susceptibilities of molecules I, IV, and VI, in a direction perpendicular to their respective molecular planes ($\chi_\perp^{\pi \mathrm{London}}$). Also included for comparison in Table V are the overall $\chi_\perp^{\pi \mathrm{London}}$ contributions (expressed as a ratio to the similarly calculated benzene value) for I, IV, and VI from the iterative, coupled Hartree–Fock calculations of Yamaguchi and Nakajima,[8a] in which C–C bond lengths and, consequently, the resonance and two-center repulsion integrals, were allowed to vary with bond order at each iteration until self-consistency was reached. Even at these fairly crude, semiempirical levels of calculation, it is quite clear from Table V that, as was anticipated and rationalized in the preceding paragraph, the predicted magnetic properties of predominantly paramagnetic systems, such as pyracylene (I) and dipleiadiene (VI), are much more sensitive to the type of wave function used to calculate them than are those of strongly diamagnetic systems such as acepleiadylene (IV). In particular, an iterative, Hückel calculation appears to give a much more realistic result than an SCF one which is not self-consistent with respect to bond lengths.

It appears, therefore, that the question of whether or not the wave function employed possesses such self-consistency is much more important, for the calculation of magnetic properties, than the question of whether that wave function is of the Hückel or SCF type—at least when the results are expressed as a ratio to the corresponding quantities (ring current intensity or magnetic susceptibility) calculated, by the same method, for benzene.

Conclusions

In their paper,[3] Trost et al. maintained that any treatment of the pyracylene system must take into account the upfield ^{1}H NMR shift of pyracylene relative to its dihydro isomers; they argued that, in any given molecule, the net ring current effect on a particular proton chemical shift may be a combination of both a paramagnetic and a diamagnetic contribution. Dihydropyracylenes should not show (and indeed they do not show) any unusual proton NMR shifts; thus, these workers concluded that the upfield shifts of the pyracylenes relative to the corresponding dihydro systems are due to a net paramagnetic current or, at least, a greatly diminished diamagnetic one. Of the three computational approaches employed in this paper, two predict a paratropism for all rings of pyracylene, one predicts a paratropism for the five-membered rings only, and all predict a net 'London' π-electron paratropism for the molecule. To this extent, therefore, the present calculations can be said to be in accord with the postulate of Trost et al.[3] that pyracylene (I) (and certain other polycyclic molecules, such as II and VI, which might formally be regarded as perturbed $4n$-peripheral systems) bears what, on the theoretically naïve but conceptually useful model due to London, are termed "paramagnetic π-electron ring currents" —in at least *some* of their rings.

However, the main lesson to be learned from these computations is that ring current intensities calculated from wave functions (whether they be simple Hückel or even SCF) which are *not* self-consistent with respect to charge and bond length may be not merely quantitatively, but even qualitatively, very different from those estimated on the basis of the corresponding iterative calculations. For example, of the present calculations, the 'topological' and 'noniterative' SCF ones favor the 'perturbed [$4n$]annulene model' for pyracylene (Ia) while the iterative ones point more to the 'naphthalene core' model (Ib). These observations evidently make the a priori prediction of the overall diamagnetic or paramagnetic nature of *poly*cyclic hydrocarbons, *merely by inspection, on the basis of their carbon-atom connectivity*, a somewhat hazardous undertaking. It should be borne in mind, however, that the $\beta\omega'\omega''$ method, on which some emphasis has been placed in this discussion, has been criticized, for it relies for self-consistency only on resonance-integral-bond order and Coulomb integral-charge relationships, ignoring effects on the σ framework. Quite possibly, then, there is no reason to trust this approach more than the others and probably one can at best conclude only that, for paratropic molecules, the calculated ring currents are much more dependent on the approach employed than for diatropic systems.

Finally, even though certain planar, *mono*cyclic $4n$ systems (which, incidentally, can be shown,[6] in the context of the London method,[5] to support paramagnetic ring currents) have been dubbed "anti-aromatic", we are not claiming that the calculations reported here necessarily imply anything about the "aromaticity" (or otherwise) of the polycyclic molecules I–VI, or, indeed, that there is bound to be any *direct* connection[44] between the all-embracing, traditionally chemical, concept of aromaticity and the postulate of ring currents —entities which are, after all, only very specialized and esoteric indices relating to part of the π-electron contribution to the second-order magnetic properties of (poly)cyclic, conjugated systems.[46]

Acknowledgments. The coupled Hartree–Fock calculations on pyracylene reported in this paper were performed by means of a program which was kindly provided by Dr. P. Lazzeretti and Professor F. Taddei of the University of Modena, Italy, and adapted for the Oxford University ICL 1906A Computer by Mr. J. A. N. F. Gomes (Linacre College). One of us (R.B.M.) is grateful to the Dean, Canons, and Students of Christ Church for support in the form of a Research Lecturership of the House. The present account of this work was not seen by C.A.C., for he died before the manuscript (and, indeed, before some of the calculations reported in it) had been completed. Thanks are, therefore, due from the surviving author (R.B.M.) to Dr. S. L. altmann (Brasenose College), Mr. C. W. Haigh (University

College, Swansea, University of Wales) and Professor R. McWeeny (University of Sheffield) for kindly commenting on the content of an earlier draft of the paper. Professor B. M. Trost (University of Wisconsin, U.S.A.), a referee who declined the privilege of anonymity, also made helpful suggestions for which I (R.B.M.) am very grateful. Any errors which remain are, of course, entirely the responsibility of R.B.M., and are certainly not due to C.A.C.

Supplementary Material Available: final geometries, free valences, and charge densities for the molecules pyracylene (I), acepleiadylene (IV), and dipleiadiene (VI), contained in Tables AI to AVII (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Deceased, January 7, 1974.
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(16) By a 'topological' MO is meant one which depends solely on the *adjacencies* of the atoms comprising the conjugated system—that is to say, which, of such atoms, are bonded to each other. The topological wave function is then simply the set of (normalized) eigenvectors of the vertex adjacency matrix of the graph[15] representing the σ-bond connectivity of the atoms which constitute the given conjugated system (the corresponding energy levels being related to the eigenvalues of this matrix[15]). The Hückel matrix, with all α's the same and all β's equal, is isomorphic with this topological adjacency matrix. An attractive feature of the use of such an MO is that once given the *areas* of the various rings, *no* subjective or arbitrary parameters whatever are involved in the ring current *ratios* (expressed relative to the benzene value) given in Tables I and II; all are immediately and automatically determined (via, for example, eq 25 of ref 13c) once the carbon-atom connectivity and ring areas have been specified (see also ref 15h).
(17) Benzene, therefore, has a diamagnetic ring current intensity of +1, on this scale. The reader is alerted to the possibility of some confusion which could arise as a result of this (nevertheless quite usual) method of expressing relative ring current intensities since diamagnetism is conventionally negative and yet diamagnetic ring currents will be written with a *positive* sign; similarly, paramagnetism is conventionally considered as positive, but paramagnetic ring currents are here expressed with a *negative* sign.
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(22) (a) J. Gayoso and A. Boucekkine, *C. R. Acad. Sci., Ser. C*, **272**, 184 (1971); (b) *ibid.*, **274**, 358 (1972); (c) J. Gayoso, Thèse, Docteur Ès Sciences, Université de Paris, 1973 (R.B.M. thanks M. le Dr. Gayoso for kindly providing a copy of this Thesis).
(23) Iterative procedures which modify both types of integral simultaneously have been criticized by Doggett[24] on the grounds that they could lead to an incorrect convergence limit; however, exhaustive investigation by Gayoso[22c] on some small test molecules, via a technique similar to the one being described, has given rise to results which are what he describes[22c] as "*rigoureusement identiques*" to those obtained by use of Doggett's procedure.
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(25) The several devices for obtaining more rapid convergence in such calculations, suggested by Ettinger,[26] and by one of us and Wille,[21] were *not* actually used during the iterative calculations on pyracylene and dipleiadiene; uninterrupted iteration for 25 cycles, as described in the text, produced a satisfactory convergence (i.e., charges, bond orders, resonance integrals, and corrections to Coulomb integrals all unchanged, in the last cycle, to six decimal places); this is, in any case, many more than the four iterations which, Gayoso claims,[22c] furnish for most purposes results which are 'sufficiently' near self-consistency. The procedures described in ref 21 were, however, used to speed convergence in the case of the iterative calculations on acepleiadylene (IV) (see subsection 4 of Results and Discussion).
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(27) (a) P. Lazzeretti and F. Taddei, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1825 (1972). (b) It is true that the original Hall and Hardisson approach[12] (as programmed by Lazzeretti and Taddei[27a]) does use the recently criticized[13c,28] London approximation: (R.B.M. is grateful to Messrs. J. A. N. F. Gomes, C. W. Haigh, and H. G. Ff. Roberts for discussion on this point); however, it does have the advantage, over other recently proposed methods, that it uses the more rigorous coupled Hartree–Fock procedure, rather than what has become known as the uncoupled method, with Feenberg–Goldhammer correction[29] (although the error due to this 'geometric' approximation has recently been shown to be very small[29c]). Furthermore, it would appear that use of the London approximation in order to obtain "ring current" contributions to magnetic susceptibilities is a less drastic procedure than its application in the calculation of "ring current" chemical shifts.[28a,c]
(28) (a) C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **22**, 955 (1971); (b) A. T. Amos and H. G. Ff. Roberts, *ibid.*, **20**, 1081 (1971); (c) H. G. Ff. Roberts, *ibid.*, **27**, 843 (1974).
(29) (a) A. T. Amos, *J. Chem. Phys.*, **52**, 603 (1970); (b) A. T. Amos and H. G. Ff. Roberts, *Mol. Phys.*, **20**, 1073 (1971); (c) H. G. Ff. Roberts, *Theor. Chim. Acta*, **33**, 269 (1974).
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(33) A referee has suggested that the final geometries, free valences, and charge densities resulting from these calculations should be tabulated in order to enable the reader to evaluate, in a more concrete way, the results presented in the next section; accordingly, these data for the principal molecules pyracylene (I), acepleiadylene (IV), and dipleiadiene (VI) will appear in the microfilm edition of this volume of the journal. See paragraph at the end of this paper concerning Supplementary Material.
(34) To our knowledge, this is the first paramagnetic ring current in a six-membered (i.e., formally benzenoid) ring to be reported and is, it must be admitted, very surprising; it is very likely, however, that this apparently paramagnetic ring current is actually just an artifact of the noniterative, 'topological' calculation (see discussion in the text).
(35) (a) R. McWeeny, *J. Chem. Phys.*, **17**, 1341 (1949); (b) *Proc. Phys. Soc., London, Sect. A*, **64**, 261 (1951); (c) R. B. Mallion, unpublished calculation, 1969, all correcting the wrong value of London.[4b,c]
(36) (a) A referee has (quite correctly) pointed out that the 'London' or 'mobile π-electron' contribution to magnetic susceptibility, unscrambled from σ- and what could be described[32] as 'localized' π-electron contributions, is not a physical observable; he suggests, therefore, that total molecular susceptibilities should also be tabulated in this paper, by including σ-electron contributions to susceptibilities, calculated by means of previously proposed parameters (e.g., ref 36b). However, what particular empirical parameters are appropriate for calculation of these σ-electron contributions depends sensitively on the sophistication of the method used to compute the π-electron contribution, and on whether the *total* π-electron contribution [i.e., both "nonlocal" (London) and "local" has been calculated (as was the case, for example, in ref 32) or—if the London approximation has been invoked[5,32]—only that due to the mobile π electrons. This *caveat* has been entered at some length in ref 32 and is not, therefore, discussed further in this paper. In any case, there do not appear, at present, to be any available experimental data on total susceptibilities of pyracylene and most of the molecules dealt with here. (b) M. E. Stockham and H. F. Hameka, *J. Am. Chem. Soc.*, **94**, 4076 (1972).
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(40) (a) Davies[41] has stated the opinion that "... the comparative success of London's method for aromatic hydrocarbons may be attributed to the dependence of the theoretical anisotropy on the square of the area of the rings in a molecule" and that "... any method that takes this into account is likely to give reasonable results for the ratio ..." of a given calculated anisotropy to that calculated, by the same method, for benzene. We might also add that, at least for paramagnetic systems of the type considered here, another important requirement for obtaining 'reasonable' ratios is the use of a π-electron wave function which is iteratively self-consistent with respect to atomic charges and bond orders. (see subsection 4 of this section).

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(42) These are the quantities which, in ref 32, are called the "integrated π-electron current densities" associated with the various rings of a given polycyclic, conjugated system.

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(44) Such a connection has been suggested[45a] and the proposal has been much taken up, the latest instance being in a recent study[45b] of the "aromatic character" of certain five-membered heterocyclic systems. For a vehement criticism of the idea, see ref 45c and 45d and, for a less forceful (though equally cogent) one, based on calculations of the type presented here, see ref 14b. In a very recent paper[45e] Benassi et al. address themselves to the whole question of magnetic criteria for aromaticity. (See also ref 6f and 45f,g.)

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(46) NOTE ADDED IN PROOF (by R.B.M., December, 1975). (a) In a very recent article in this journal, Wilcox et al.[46b] have given a discussion (very similar to that in section 4 of the present Results and Discussion, and in Conclusions) concerning the occurrence of paramagnetic "ring currents" in the polycyclic hydrocarbon, cycloocta[*def*]biphenylene. They have also examined the inferences which may, or may not, properly be drawn on this basis about the "aromaticity", or otherwise, of that conjugated system. (b) C. F. Wilcox, J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *J. Am. Chem. Soc.*, **97**, 1914, (1975). (c) In order to test the predictions made in the present paper about the π-electron magnetic properties of the (as yet hypothetical) molecule, dipleiadiene (VI), my colleagues I. P. Fleid, D. Franks, and M. C. Grossel (Christ Church, Oxford) are currently engaged on a synthesis of this molecule. It is hoped that their findings will be published in a future issue of the journal.

The Electronic Origin of Geometrical Deformations in Cyclohexadienyl and Cyclobutenyl Transition Metal Complexes

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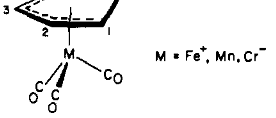
Abstract: A case is presented for an electronic factor in the out-of-plane bending of the saturated carbon in cyclohexadienyl-$M(CO)_3$ complexes, M = Fe^+, Mn, Cr^-. In the cyclohexadienyl ligand hyperconjugation extends the nonbonding MO wave function to the methylene hydrogens. The phase of the CH_2 hydrogen contributions to that MO is such that when the C_6H_7 ligand is bound to the $M(CO)_3$ group there arises a secondary M–CH_2 interaction which is destabilizing. In cyclobutenyl and cyclooctatrienyl complexes this interaction is lacking and thus these should be less bent than cyclohexadienyl complexes. A similar analysis rationalizes the bending away from the metal in cyclopentadiene–$Fe(CO)_3$ complexes, its lessening in cyclopentadienone complexes, and the bending toward the metal in fulvene or cyclopentadienyl–carbonium ion complexes. The charge distribution and substituent effects in $C_6H_7M(CO)_3$ complexes are examined, as well as a case of hypothetical isomerism in benzyl-$M(CO)_3$.

There exists a substantial chemistry of transition metal complexes of cyclohexadienyl and cyclobutenyl ligands, exemplified by structure **1**. Examples exist for M = Fe^+, Mn, Cr^-, and their lower transition series analogues. The assignment of a formal charge to the metal is, of course, arbitrary. Nevertheless it focuses on the basic electronic similarity of these complexes, an aspect that might be obscured by an argument over the cationic or anionic nature of the coordinated cyclohexadienyl ligand.



1

In all known structures of type **1** the six-membered organic ring is highly nonplanar, and distorted in the same way—atoms 1 through 5 remain in an approximate plane, but the saturated carbon 6 moves out of that plane and away from the metal. The dihedral angle between planes 165 and 12345 takes on values of 43° in $C_6H_7Mn(CO)_3$,[1] 39° in dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron,[2] 50° in $C_6(CH_3)_6HRe(CO)_3$,[3] 40° in (2-methoxycyclohexadienyl)$Fe(CO)_3^+$,[4] 41° in tricarbonyl(bis(ethoxycarbonyl)methyl)cyclohexadienylmanganese,[5] 43° in a complex of a somewhat different but related type, bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyliron),[6] and angles of approximately 45° in structures of three substituted 1,2-dihydropyridinechromium tricarbonyl complexes.[7,8]

It should be noted that the free organic ligand is either planar or only moderately distorted. In the crystal structure of the tetrachloroaluminate salt of the heptamethylbenzenonium cation, **2**, the six-membered ring is essentially planar.[9] However, in three recent structures of stabilized σ complexes, **3**,[10] dihedral angles up to 17° have been found.[11] Stabilized anionic σ complexes, that is Meisenheimer complexes, have been known for some time.[12] Several crystal structures of such highly substituted cyclohexadienyl anions are available,[13] and in all the six-membered ring is approximately planar. The problem of potential nonplanarity of cyclohexadienyl radicals has been discussed recently.[14]

At any rate it is clear that upon formation of a transition metal complex there is a significant enhancement of the