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Calculated Magnetic Properties of Some Isomers of Pyracylene

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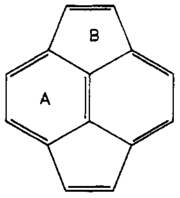
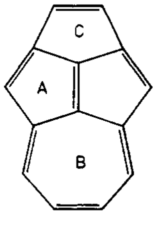
The π-electron magnetic properties of pyracylene (I), two of its isomers (II and III), and the respective dianions of I-III are examined by subjecting them to six different methods of calculation of varying degrees of sophistication. The methods are as follows: (1) London-McWeeny method based on a simple ("topological") HMO, (2) London-McWeeny method based on an iterative ($\beta\omega'\omega''$) HMO, (3) Hall-Hardisson coupled Hartree-Fock method with fixed resonance integrals, (4) the same as method 3 but with resonance integrals iteratively self-consistent with respect to calculated bond orders, (5) Coulson-Gomes-Mallion coupled Hartree-Fock method with fixed resonance integrals, (6) the same as method 5 but with iteratively self-consistent resonance integrals. Relative π-electron "ring currents" and "integrated current densities" are discussed, and, in particular, comment is made on the various values of $\chi_\perp^{\pi(\mathrm{L})}$, the "London" (L) contribution to $\chi_\perp$, the total magnetic susceptibility perpendicular to the molecular plane of the species in question. In the case of methods 5 and 6, the contributions $\chi_\perp^{\pi(\text{non-L})}$ (non-L = non-London) and $\chi_\perp^{\sigma}$ to $\chi_\perp$ are also considered. It is found that the calculated magnetic properties of those species which method 1 predicts to have a paramagnetic $\chi_\perp^{\pi(\mathrm{L})}$ are extremely sensitive to the degree of sophistication of the method (and, especially, of the *wave function*) used to compute them whereas those species predicted to have a strongly diamagnetic $\chi_\perp^{\pi(\mathrm{L})}$ are not so sensitive. I-III are all very different magnetically, though they all have a [12] (i.e., [$4n$], $n = 3$) carbon atom periphery and might, therefore, at least superficially, be regarded as candidates for being "perturbed" [12]annulenes in Trost's model. III appears to serve quite well as a model for a "perturbed" [12]annulene (II and I somewhat less so), as the Trost model has predicted, while the dianions of $4n$-peripheral I-III are all strongly diamagnetic, as also might be expected, at least intuitively, from the Trost model. Consideration of $\chi_\perp^{\pi(\text{non-L})}$ and $\chi_\perp^{\sigma}$ contributions leads to the conclusion that the overall $\chi_\perp$ tensor components for I-III should all be diamagnetic, even though $\chi_\perp^{\pi(\mathrm{L})}$ for III is strongly paramagnetic. Paramagnetic (i.e., "shielding") "ring-current" contributions to intramolecular ^{1}H NMR chemical shifts in I-III are predicted to be in the order III > II > I, while the dianions of I-III are all expected to exhibit "normal" diamagnetic "ring-current" effects, similar to those characteristic of the condensed, benzenoid hydrocarbons.

In their quest for planar, conjugated hydrocarbon systems which may ideally be regarded as "perturbed [12]-annulenes", Trost et al. have synthesised pyracylene[3] (I) and have discussed[4] derivatives of azulenopentalene (II) and dibenzo[*cd,gh*]pentalene (III), two (iso-π-electronic) isomers of pyracylene which also have a 12 carbon atom (i.e., $4n$, $n = 3$) periphery.



(I)



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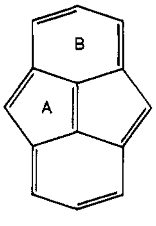

(III)

As a criterion for the success of their peripheral, electronic model, Trost et al. considered the splitting between the highest occupied π molecular orbital (HOMO) and the lowest unoccupied one (LUMO). In an ideal [12]annulene in which no bond alternation is taken into account, a Hückel or SCF calculation predicts degeneracy of π MO's in this region of the energy-level spectrum; Trost et al. therefore postulated that the success of the structures I-III in serving as models for a [12]annulene system can be related to how small a perturbation from the triplet ground state is evident in these molecules. This kind of consideration has led to discussions of "antiaromaticity" and paramagnetic, π-electron "ring currents"—for, in the presence of an external magnetic field with a component perpendicular to their molecular planes, the so-called "antiaromatic", monocyclic [$4n$]annulenes are predicted[5] to sustain what, in the London-McWeeny model,[6] are termed "paramagnetic π-electron ring currents"; these paramagnetic currents are in a direction opposite to the diamagnetic ones which are supposed to occur in benzene and the other [$4n + 2$]annulenes.[5] Coulson and one of the present authors[7a] have since gone into these considerations in some detail for the case of pyracylene (I) while the general question of paramagnetic "ring currents" and "antiaromaticity" has also been discussed by Wilcox et al.,[8] by Benassi et al.,[9] and by one of us.[7d] Meanwhile, Atwood

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et al.[10] have speculated on the existence of paramagnetic "ring currents" in diaza-substituted pyracylene, and Ege and Vogler,[11] and Haddon et al.,[7b,c] have independently confirmed the views of Nakajima and Kohda[12] and of Coulson and Mallion[7a] by observing that SCF calculations on the π-electron magnetic properties of predominantly paramagnetic, conjugated systems have a chance of being qualitatively correct only when realistic carbon–carbon resonance integrals are used. In ref 7a,d and in the present paper, such realistic resonance integrals are arrived at by arranging for carbon–carbon resonance integrals to be made iteratively self-consistent with respect to the corresponding calculated bond lengths. As a referee has kindly emphasized to us, however, self-consistence per se is *not* crucial in the simple methods, and the *realistic* resonance integrals required could equally well be based on experimental bond lengths.

In this paper we present calculations, of varying degrees of sophistication, of the π-electron magnetic properties of the conjugated hydrocarbons I–III and of their dianions in an attempt to assess further the "periphery" model postulated by Trost et al.[3,4]

Methods of Calculation

We shall subject molecules I–III and their dianions to six different types of calculation in order to predict the magnetic properties of their π-electron systems.

Method 1. London–McWeeny Method.[6] This method is based on a simple ("topological"[13]) HMO. As was discussed in ref 7a, this approach has the advantage that its predictions (when expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene) are a function only of the carbon atom σ-bond connectivity of the conjugated system in question and of the areas assumed for its constituent rings. Such ratios do not then depend on any other subjectively chosen parameters. However, although it has been found adequate when applied to diamagnetic, benzenoid hydrocarbons (e.g., ref 14 and 6d), the simple Hückel–McWeeny formalism is not likely to be a satisfactory approach—more because it is a noniterative method than because it is a "Hückel" one[7a]—for the predominantly *para*magnetic π-electron systems dealt with here.[7a,d,11,12] The same assumptions about ring areas were made as in ref 7a.

Method 2. London–McWeeny Method.[6] This method is based on an iterative $\beta\omega'\omega''$[7a,15] HMO. In this approach, Coulomb integrals are iterated with respect to atomic charges (as per the method of Kuhn[16]) while, simultaneously, resonance integrals are made iteratively self-consistent with the corresponding bond orders (via the prescription of Coulson and Golebiewski[15d,17]). While previous experience with pyracylene[7a] appeared to indicate that the $\beta\omega'\omega''$ method simulates an "iterative" SCF calculation[18] much more successfully than does the simple HMO method (see, however, footnote 18), the approach is not one which inspires confidence for several reasons: from a theoretical point of view, iterative procedures which modify both types of integral simultaneously have been the subject of some controversy,[15c,19] for they may, apparently, lead to an incorrect convergence limit, while, on the purely practical level, there are often severe difficulties in achieving convergence at all, to any limit, with the $\beta\omega'\omega''$ method[7a,15c,17] (see Results and Discussion). In the $\beta\omega'\omega''$ calculations reported here, the same assumptions about the ring areas were made as in ref 7a.

Method 3. Coupled Hartree–Fock, Hall–Hardisson[20] Method. This method is based on a PPP-SCF wave function with *fixed* resonance integrals (parametrisation scheme as in ref 7a). Although still dependent[5] on the well-known London approximations,[6d,21] this method has enjoyed considerable success when applied to diamagnetic, condensed, benzenoid hydrocarbons (e.g., ref 22 and 11). In view of the discussion in ref 7a,d, 11, and 23, however, even a coupled Hartree–Fock calculation is not likely to be adequate for *para*magnetic, conjugated, π-electron systems if resonance integrals are held constant at the standard benzene value.

Method 4. Coupled Hartree–Fock, Hall–Hardisson[20] Method. This method is based on a PPP-SCF wave function (as in method 3) but with *variable* resonance integrals, iterated so as to be self-consistent with respect to the corresponding calculated bond orders. This is an approach which Ege and Vogler[11] have found useful for paramagnetic systems.

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(12) T. Nakajima and S. Kohda, *Bull. Chem. Soc. Jpn.* **39**, 804 (1966).

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(16) H. Kuhn, *Tetrahedron, Suppl.*, **19**, 437 (1963).

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(18) (a) It was stated in ref 7a that the data of Yamaguchi and Nakajima[18b] listed in the fourth row of Table V of that reference were from an "iterative, coupled-Hartree–Fock procedure (with variation of resonance- and two-center repulsion-integrals at each iteration)". This is, unfortunately, *not* the case, and the above description resulted from a misunderstanding of the 1971 paper[18b] of Yamaguchi and Nakajima which Professor Nakajima has since removed by providing[18c] a more detailed account of the approximations actually used in ref 18b. In fact, Yamaguchi and Nakajima used a Wheland–Mann type of Hückel method to perform the calculations which they reported in ref 18b; the method which they actually adopted therefore corresponds most closely to method 2 of those which we have used in the present paper (i.e., the iterative $\beta\omega'\omega''$ Hückel method). These authors[18b] followed this procedure in order to avoid difficulties of origin dependence of the computed results when they calculated the magnetic susceptibility including electron-repulsion explicitly.[18c] The Nakajima group *has* since reported iterative, coupled Hartree–Fock calculations of magnetic susceptibilities of several conjugated systems in which resonance- and two-center repulsion integrals are varied at each iteration,[18d] although these authors did not study any of the molecules I–III by this method nor any of those dealt with in ref 7a. In the present iterative, coupled Hartree–Fock calculations (methods 4 and 6), resonance integrals *only* were allowed to vary with bond order at each iteration. Professor Nakajima is of the opinion[18c] that for paramagnetic systems such a calculation should be intermediate in "degree of sophistication" between a procedure such as 2 (iterative Hückel) and an iterative, coupled Hartree–Fock one, such as is used in ref 18d, where two-center repulsion integrals are also allowed to vary with calculated bond order at each iteration. Professor Nakajima believes,[18c] however, that this latter refinement does not substantially affect the results, at least qualitatively, and that methods 4 and 6 of the present paper may practically be classified as "iterative coupled Hartree–Fock" in the sense in which this expression is used in ref 18d. (b) H. Yamaguchi and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 682 (1971). (c) T. Nakajima, personal communication to R. B. M., June 18th, 1976. (d) Y. Mikami, S. Miyai, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **46**, 787 (1973).

(19) (a) R. Ettinger, *Tetrahedron*, **20**, 1579 (1964); (b) C. A. Coulson and F. Wille, *ibid.*, **22**, 3549 (1966); (c) G. Doggett, *Mol. Phys.*, **10**, 225 (1966).

(20) (a) G. G. Hall and A. Hardisson, *Proc. R. Soc. London, Ser. A*, **268**, 328 (1962) (note the correction to eq 5.30 and 5.32 of this reference given (on p 1309) by Black et al.[20b]); (b) P. J. Black, R. D. Brown, and M. L. Heffernan, *Aust. J. Chem.*, **20**, 1305 (1967).

(21) (a) A. T. Amos and H. G. Ff. Roberts, *Mol. Phys.*, **20**, 1081 (1971); (b) C. W. Haigh and R. B. Mallion, *ibid.*, **22**, 955 (1971); (c) H. G. Ff. Roberts, *ibid.*, **27**, 843 (1974).

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Method 5. Coulson–Gomes–Mallion Method.[23] This method is based on a PPP–SCF wave function with fixed resonance integrals. All the approaches considered in 1–4 invoke the London integral approximation.[6d,21,23] Coulson and the present authors[23] did, however, derive an exact expression for $\chi_\perp^\pi$, the *total* π-electron contribution to the magnetic susceptibility perpendicular to the molecular plane of a polycyclic, conjugated hydrocarbon. Once given $\mathbf{P}^1$, the first-order correction to the bond order matrix of the molecule in question, this expression makes no further appeal to the London integral approximation. The consequence of this procedure is that the total $\chi_\perp^\pi$ is split into two parts—one, $\chi_\perp^{\pi(\mathrm{L})}$ (due to what we term[23] the "integrated π-electron current densities" around the rings), corresponds to that part of the total $\chi_\perp^\pi$ which would have been calculated anyway, even if the London approximation had been made, and the other, $\chi_\perp^{\pi(\text{non-L})}$ (comprising what we have called the "bond" and "nonbond" moments),[23] corresponds to what might be considered as the "local" π-electron contribution to $\chi_\perp$. In most calculations which lose this latter term by invoking the London approximation, its effect is conveniently incorporated into the empirically determined, "local" σ contributions when comparisons with experiment are to be made.[23]

Another feature of this approach is that it does make provision for breaking down the total $\chi_\perp^\pi$ into contributions associated with each individual ring of a polycyclic, conjugated system. This idea is particularly significant when just $\chi_\perp^{\pi(\mathrm{L})}$ is considered, for it is then possible to calculate integrated π-electron current densities which will be a characteristic of each ring of a polycyclic molecule and which are analogous to what the London–McWeeny method would identify with the "ring-current" intensities in the corresponding rings. The calculation of such quantities is not straightforward in the Hall–Hardisson method as originally presented.[20]

The Coulson–Gomes–Mallion approach has been applied very successfully to predominantly diamagnetic, conjugated molecules, but we have already noted (in ref 23) that our "ring-susceptibility" model is not as reliable when applied to strongly paramagnetic systems. In view of the discussions of ref 7, 11, 18d, and 23, this failure is most likely to be due to the use of carbon–carbon resonance integrals that are *fixed* at the benzene value.

Method 6. Coulson–Gomes–Mallion Method.[23] This method is based on a PPP–SCF wave function (as in method 5) but with variable resonance integrals, iterated so as to be self-consistent with respect to the corresponding bond orders. Desirable features of this approach are (a) minimal use of the London integral approximation[24] and (b) iteration of resonance integrals with respect to calculated bond length, as is particularly appropriate for strongly paramagnetic, conjugated systems.[7,11,18d,23]

Results and Discussion

(1) "Ring-Current" Intensities and "Integrated π-Electron Current Densities". (a) Simple Hückel–London–McWeeny Method (1). Table I shows the relative π-electron "ring-current" intensities (benzene diamagnetic "ring current" = 1.000) in I–III and their dianions, calculated according to the simple Hückel–London–McWeeny formalism[6] referred to in Methods of Calculation as method 1. Merely a casual glance at Table I reveals that, on the basis of this very simple calculation, the magnetic behavior of azulenopentalene (II) is expected to differ markedly from that of dibenzo[*cd,gh*]pentalene (III), and that both II and III are quite different in this respect from pyracylene (I), in spite of the fact that I–III all have a 12 (i.e., $4n$, $n = 3$) carbon atom periphery. This observation should perhaps present some misgivings about the "periphery" model of Trost et al.,[3,4] although the model certainly should not be dismissed out-of-hand on the basis of such a naive calculation. We shall, however, discuss this model later in the present section and in section 2 of Results and Discussion in the context of less approximate calculations. For the moment we merely note (Table I) that the five-membered rings of II are predicted to bear a paramagnetic "ring current" of about the same order as that in the five-membered rings of pyracylene (I) while the seven-membered ring in II apparently supports a diamagnetic current of an intensity nearly half that in benzene. In III both five- and six-membered rings are predicted to be only weakly paramagnetic (cf. pyracylene (I)).

Table I. Relative π-Electron "Ring-Current" Intensities (by Method 1 of Methods of Calculation) in Molecules I–III and Their Dianions

species	"ring-current" intensity[a] in rings A	B	C
I[b]	−0.386	−2.317	
II[c]	−2.081	+0.430	−3.113
III	−0.303	−0.110	
I^{2-}	+0.605	+1.165	
II^{2-}	+0.899	−0.123	+1.413
III^{2-}	+0.944	+1.137	

[a] Calculated from eq 25 of ref 6d (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 (1), for benzene; a positive entry in the table therefore indicates a diamagnetic "ring current" and a negative one a paramagnetic "ring current". [b] Results for pyracylene taken from ref 7a. [c] By ostensibly the same calculation, Jung[25] obtained the slightly different values −2.02, +0.45, and −3.03 for the relative "ring current" intensities in rings A, B, and C, respectively, of a azulenopentalene (II). The differences (all <~5%) between the results of Jung's calculations and those reported in this table are most likely to be due to different assumptions about molecular geometry. We have here made the conventional assumption (e.g., ref 6b and 26) that the areas of five-, six-, and seven-membered rings are in the ratio (5 cot (π/5)):(6 cot (π/6)):(7 cot (π/7)) (i.e., ca. 0.662:1.000:1.399).

The dianions of these conjugated systems are often of interest experimentally and, indeed, are sometimes more attainable synthetically.[27] The "ring-current" intensities (via the simple Hückel–London–McWeeny method) in the species I^{2-}, II^{2-}, and III^{2-} are therefore also presented in Table I; with the exception of the weakly paramagnetic ring B of II^{2-}, they are seen to be diamagnetic and of the same order, in fact, as those routinely encountered in the alternant, condensed, benzenoid hydrocarbons (e.g., ref 28).

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(23) C. A. Coulson, J. A. N. F. Gomes, and R. B. Mallion, *Mol. Phys.*, **30**, 713 (1975).

(24) An approximation tantamount to the London integral approximation does, in fact, still have to be invoked in the Hall–Hardisson-coupled Hartree–Fock method[20] for calculation of $\mathbf{P}^1$, the first-order correction to the bond-order matrix of the conjugated system in question (see footnote on p 715 of ref 23). Once given the matrix $\mathbf{P}^1$, however, the Coulson–Gomes–Mallion method[23] makes no further appeal to the London approximation.

(25) D. E. Jung, *Tetrahedron*, **25**, 129 (1969).

(26) R. B. Mallion, *J. Chem. Soc., Perkin Trans. 2*, 235 (1973).

(27) (a) Discussion between Professor B. M. Trost and R.B.M. at Madison, WI, Sept 1975. (b) K. Müllen, personal communication to R.B.M., Apr 21, 1976 and Jan 13, 1977. (c) K. Müllen, *Helv. Chim. Acta*, **61**, 2307 (1978).

Table II. Relative π-Electron "Ring-Current" Intensities Based on an Iterative ($\beta\omega'\omega''$) HMO[a] (Method 2 of Methods of Calculation) in I and III and the Dianion of III

species	"ring-current" intensity in rings A	"ring-current" intensity in rings B
I[b]	+0.308	−1.013
III	−1.051	−0.678
III^{2-}	+0.960	+1.178

[a] Calculated from eq 25 of ref 6d [bond orders and imaginary bond-bond polarizabilities having been computed from an iterative ($\beta\omega'\omega''$) HMO wave function] and expressed as a ratio to the diamagnetic "ring-current" intensity calculated by the same method (2), for benzene; a positive entry in the table therefore indicates a diamagnetic "ring current" and a negative one a paramagnetic "ring current". [b] Results for pyracylene from ref 7a.

This therefore seems to illustrate an analogy, in the context of *poly*cyclic "perturbed [4*n*]annulenes", of Sondheimer's observation[29] that the dianions of genuine, *mono*cyclic ("antiaromatic") [4*n*]annulenes are diamagnetic. The diamagnetic "ring currents" for I^{2-}, II^{2-} and III^{2-} in Table I are certainly consistent with the large HOMO–LUMO separations (1.000, 0.609, and 1.000, respectively) predicted by this calculation.

(b) Hückel–London–McWeeny Formalism Based on an Iterative ($\beta\omega'\omega''$) HMO (2). Table II shows the relative, π-electron "ring-current" intensities (benzene diamagnetic current again = 1.000) in I and in III calculated via the Hückel–London–McWeeny approach based on an iterative ($\beta\omega'\omega''$) HMO (as described in ref 7a and under method 2 of Methods of Calculation). We have referred earlier to the convergence difficulties which sometimes occur with $\beta\omega'\omega''$ wave functions; in fact, in spite of application of some of the techniques described in ref 19a,b, no convergence could be obtained for II. The calculation on III converged within 30 cycles, according to the criteria described in ref 7a, while that on I required 25 iterations.[7a]

Although the use of an iterative rather than a simple HMO reduces the paramagnetic nature of the "ring currents" in pyracylene (that in the six-membered ring actually becoming diamagnetic), the paramagnetic "ring currents" of dibenzo[*cd*,*gh*]pentalene (III) are markedly *increased* by this refinement. There are, in fact, three points worthy of note concerning this calculation on III.

(i) To our knowledge it is the first example of an *increase* in paramagnetism consequent upon making resonance integrals iteratively self-consistent with calculated bond lengths in a conjugated system. Although such self-consistency usually leads to an increase in the HOMO–LUMO separation, there seems to be no a priori reason that it should always do so. In pyracylene, for example, a simple HMO calculation (method 1) gives a HOMO–LUMO separation of 0.414β while the $\beta\omega'\omega''$ calculation (method 2) widens this to 0.672β (in accord with the decreased paramagnetic nature of the pyracylene "ring currents" evident in Table II over those in Table I). In the case of dibenzo[*cd*,*gh*]pentalene (III), however, the HOMO–LUMO separation is predicted to be 0.456β on the basis of the simple HMO scheme, but the $\beta\omega'\omega''$ iterative calculation narrows this down to only 0.034β. Under these circumstances, it is, therefore, not surprising that much-increased paramagnetism is displayed within the "ring-current" intensities of III on going from a simple HMO wave function (Table I) to an iterative $\beta\omega'\omega''$ one (Table II).

Table III. Relative "Integrated π-Electron Current Densities" (by Method 5 of Methods of Calculation) in Molecules I and III and in the Dianions of I-III

species	integrated π-electron current density[a] in rings A	B	C
I[b]	−0.20	−2.16	
III	−1.45	−0.79	
I^{2-}	+0.73	+1.20	
II^{2-}	+1.10	+0.25	+1.60
III^{2-}	+0.91	+1.20	

[a] Calculated via the method described in ref 23 and expressed as a ratio to the diamagnetic "integrated π-electron current density" calculated, by the same method (5), for benzene; a positive entry in the table therefore indicates a diamagnetic integrated current and a negative one a paramagnetic integrated current. [b] Results for pyracylene (I) taken from ref 23.

(ii) In footnote 34 of ref 7a it was observed that the paramagnetic "ring current" calculated for the six-membered (i.e., formally benzenoid) ring in pyracylene (I; Table I) was likely to be an artifact of the noniterative, "topological" calculation. For pyracylene this indeed proved to be true, for the iterative $\beta\omega'\omega''$ calculation turns this current into a diamagnetic one (Table II). In the case of dibenzo[*cd*,*gh*]pentalene (III), however, the iterative $\beta\omega'\omega''$ calculation predicts an even more paramagnetic "ring current" for ring B than does the calculation based on a simple HMO. This therefore appears to be the first paramagnetic "ring current" in a formally benzenoid ring to be encountered in a calculation which has made resonance integrals iteratively self-consistent with respect to calculated bond orders.

(iii) Molecule III also gives rise to the unusual occurrence that, on convergence of the iteration in the $\beta\omega'\omega''$ calculation, all five nonequivalent bonds in the molecule have a bond order less than the benzene value ($^2/_3$).

As an example of the predicted behavior of the dianions via an iterative $\beta\omega'\omega''$ calculation, the "ring-current" intensities obtained from an application of this method to the species III^{2-} are also presented in Table II. They are seen to differ by less than 4% from the corresponding "ring-current" intensities reported in Table I, which are based on a simple ("noniterative") HMO wave function. The diamagnetic "ring currents" for III^{2-} in Table II are once again certainly consistent with the large HOMO–LUMO separation (0.961β) predicted by the $\beta\omega'\omega''$ calculation.

(c) Relative "Integrated π-Electron Current Densities" by the Coulson–Gomes–Mallion Formalism. Table III illustrates the relative "integrated π-electron current densities" (expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene) in I and III, computed via the Coulson–Gomes–Mallion approach based on a "regular" molecular geometry and a PPP wave function with fixed resonance integrals (method 5 of Methods of Calculation). Curiously, as was the case with the $\beta\omega'\omega''$ calculation (see b above), no convergence could be obtained for II when resonance integrals were fixed at the standard benzene value (although this was not the case when resonance integrals were allowed to vary iteratively with bond order; see d below). It is seen that while the integrated π-electron current densities, by method 5, for pyracylene (Table III) compare reasonably well with the McWeeny "ring currents" (Table I) obtained

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(28) (a) J. D. Memory, *J. Chem. Phys.*, **38**, 1241 (1963); (b) C. W. Haigh and R. B. Mallion, *Mol. Phys.*, 18, 767 (1970); (c) R. B. Mallion, *J. Med. Chem.*, **14**, 1824 (1971).

(29) F. Sondheimer, *Acc. Chem. Res.*, **5**, 81 (1972).

from a calculation in which resonance integrals were likewise held constant (method 1), the corresponding quantities for dibenzo[*cd,gh*]pentalene (III) are quite different (cf. Tables I and III). "Ring currents" in the diamagnetic dianions of I and III listed in Table I do, however, compare well with their respective counterparts among the integrated π-electron current densities reported in Table III. Again, this illustrates the observation (previously rationalized in ref 7) that the predicted magnetic properties of overall diamagnetic, π-electron, conjugated systems are much less sensitive to the method used for their calculation than are those of ostensibly similar but paramagnetic π-electron systems. The correspondence between the "ring currents" of Table I and the integrated current densities of Table III is, however, much less marked.

(d) **"Integrated π-Electron Current Densities" by the Coulson–Gomes–Mallion Formalism Based on a PPP Wave Function Iteratively Self-Consistent with Respect to Resonance Integrals.** There are essentially two ways of carrying out a calculation of this sort.

(i) Given a model geometry (equal bond lengths of ca. 1.40 Å, for example), the program of Lazzeretti and Taddei[22,30,31] on which the present computations are based will iterate the *resonance integrals* to self-consistency, but the *geometry* of the molecule is never changed; the second part of the calculation, the computation of the various magnetic moments, is carried out on the assumption of this fixed, model geometry. What in ref 23 we have referred to as the "integrated π-electron current densities" calculated in this way are then proportional to the inverse of the corresponding resonance integrals. Thus, while noniterative calculations (all resonance integrals equal to the standard carbon–carbon resonance integral in benzene, β_0) exhibit a nice "integrated bond current" conservation (see ref 23), this conservation is now only apparent after the individual integrated "bond currents" have been multiplied by a factor $\beta_{\text{iterated}}/\beta_0$ (where β_{iterated} is the resonance integral for the bond in question which is appropriate to a PPP wave function which is self-consistent with respect to bond lengths).

(ii) A "corrected" geometry (with what we might regard as "corrected" bond lengths, R_{ij}[31]) may be obtained from the iterative process described in i and used *throughout* the calculation, including that part which involves computation of the magnetic moments. In this case, it is found by empirical observation that the resulting "integrated bond currents" (for the various bonds i–j) are conserved only when corrected by the multiplicative factor $e^{2.5(R_0-R_{ij})}$ $[1 - 1.262(R_0 - R_{ij})]$ (in which R_0 is the standard carbon-carbon bond length in benzene (1.395 Å)). The exponential term is similar to the one which occurs in resonance-integral bond-length correlations; the second term apparently takes into account the effect of this difference in bond length on the integral $\langle s|\partial/\partial x|t\rangle$ which appears in the expression for these integrated bond current density terms (see ref 23).

In practice, the final numerical results are almost the same whether procedure i or ii is adopted. It should be noted, however, that these "normalization" procedures for obtaining conserved "integrated bond current densities", based variously on the model and "self-consistent" geometries, are essentially empirical, and, although they appear reasonable, their rigorous theoretical justification should not be pressed too far. We apply them here merely for the practical purpose of conveniently discussing the approximate "integrated π-electron bond current densities" as such. These considerations and approximations will *not* be invoked when (in sections 2 and 3 of Results and Discussion) we examine the various net contributions to the overall calculated $\chi_\perp^\pi$, the total π-electron susceptibility perpendicular to the molecular plane of the conjugated system in question.

Table IV. Relative "Integrated π-Electron Current Densities" (by Method 6 of Methods of Calculation) in Molecules I-III and Their Dianions[a]

species	integrated π-electron current density[a,b] in rings A	B	C
I	+0.56	−0.74	
II	−0.63	+0.86	−1.31
III	−1.70	−1.05	
I^{2-}	+0.66	+1.16	
II^{2-}	+1.00	+0.10	+1.34
III^{2-}	+0.95	+1.22	

[a] Via the methods and assumptions based on ref 23 detailed in method 6 of Methods of Calculation and in part d of the Results and Discussion. [b] Expressed as a ratio to the diamagnetic "integrated π-electron current density" calculated, by the same method (6), for benzene; a positive entry in the table therefore indicates a diamagnetic integrated current and a negative one a paramagnetic integrated current.

Relative integrated π-electron current densities obtained in this way for I–III and their dianions are listed in Table IV. A comparison between Table III and Table IV (Coulson–Gomes–Mallion integrated bond current densities via *noniterative* and *iterative* PPP wave functions, respectively) reveals the same qualitative trends as a comparison between Tables I and II (London–McWeeny "ring-current" intensities via noniterative and iterative ($\beta\omega'\omega''$) Hückel wave functions, respectively). That is to say, the six-membered ring (A) of pyracylene (I), which, according to the noniterative calculation, was "paratropic",[32] is predicted by the iterative calculation to be "diatropic"[32] (see footnote 34 of ref 7a), while the five-membered ring (B) of I is still paratropic, though much less so, and *both* rings A and B of III are predicted to be *more* paramagnetic by the iterative calculation than by the noniterative one. The rather curious observation noted as point ii near the end of section 1b of the Results and Discussion is thus confirmed by these more sophisticated calculations. Finally, we note the (by now) familiar observation that the currents calculated for the strongly diamagnetic dianions of I–III are qualitatively unchanged (i.e., they all remain diamagnetic) when the calculation is based on a wave function in which resonance integrals have been made iteratively self-consistent with respect to calculated bond lengths instead of on a wave function in which such self-consistency has not been attempted. Having said this, we do note once again in passing, however, that the "integrated π-electron bond currents" in the dianion of II do seem from Tables III and IV to be considerably more sensitive to the wave function used to calculate them than are such currents in the dianions of I and III.

(2) Overall London Contributions to Magnetic Susceptibilities, $\chi_\perp^{\pi(L)}$. The trends in the individual "ring-current" and integrated π-electron current intensities

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(30) P. Lazzeretti, "L'Elaborazione Automatica", Vol. 1, Casalecchio di Reno, Bologna Cineca, Italy, 1973, p 61.

(31) The program of Lazzeretti and Taddei[22,30] uses the relation $R_{ij} = 1.50 - 0.186P_{ij}$, where P_{ij} is the calculated bond order of the bond i–j.

(32) H. W. Vos, Y. W. Bakker, C. MacLean, and N. H. Velthorst, *Chem. Phys. Lett.*, 25, 80 (1974).

Table V. "London" Contributions ($\chi_\perp^{\pi(L)}$ (species)/$\chi_\perp^{\pi(L)}$ (benzene)) to Magnetic Susceptibilities Perpendicular to the Molecular Planes of Molecules I–III and Their Dianions by Various Methods[a]

method of calculation[b]	($\chi_\perp^{\pi(L)}$ (species)/$\chi_\perp^{\pi(L)}$ (benzene)) calcd for I	II	III	I^{2-}	II^{2-}	III^{2-}
simple HMO (McWeeny) (1)	−3.84[c,d]	−4.22	−0.62	+2.75[d]	+1.95	+3.52
"noniterative" coupled Hartree–Fock (Hall–Hardisson) (3)	−3.25[c]		−3.45	+3.04	+2.13	+3.51
"noniterative" coupled Hartree–Fock (Coulson–Gomes–Mallion) (5)	−2.93[e]		−3.23	+2.78	+2.06	+3.29
London–McWeeny method based on an iterative ($\beta\omega'\omega''$) HMO (2)	−0.73[c,e]		−2.75			+3.63
coupled Hartree–Fock (Hall–Hardisson) with variable resonance integrals (4)	+0.15	−0.45	−4.28	+2.85	+2.02	+3.61
coupled Hartree–Fock (Coulson–Gomes–Mallion) with variable resonance integrals (6)	+0.31	−0.40	−3.98	+2.56	+1.90	+3.29

[a] Methods 1–6 of Methods of Calculation. [b] Numbers in parentheses after the description of each method refer to the labeling of this method in the section Methods of Calculation, where further details may be found of the assumptions on which the computation in question is based. [c] Results for pyracylene by methods 1–3 taken from ref 7a,d. [d] A negative value for the ratio ($\chi_\perp^{\pi(L)}$ (species)/$\chi_\perp^{\pi(L)}$ (benzene)) indicates a paramagnetic $\chi_\perp^{\pi(L)}$ (species); a positive value for the ratio indicates that $\chi_\perp^{\pi(L)}$ (species) is diamagnetic. [e] The space between the top and bottom sections of the table divides the results from methods 1, 3, and 5 (which are all based on wave functions which are not iteratively self-consistent with respect to resonance integrals and calculated bond orders) from the results obtained via methods 2, 4, and 6 which *are* based on wave functions which incorporate such "self-consistency".

implicit in Tables I–IV are more clearly and dramatically illustrated when these currents are used to predict their overall contributions to $\chi_\perp^\pi$, the total π-electron contribution to the magnetic susceptibilities perpendicular to the molecular planes of the species in question. We denote these contributions to $\chi_\perp^\pi$ due to "ring currents" or integrated π-electron currents by the symbol, $\chi_\perp^{\pi(L)}$ and refer to them as the London (L) contributions to $\chi_\perp^\pi$. We adopt this nomenclature because the "ring-current" contribution is the only π-electron effect which remains in the McWeeny (methods 1 and 2) and Hall–Hardisson (methods 3 and 4) formalisms once the so-called London approximations have been invoked, while in the calculations based on the Coulson–Gomes–Mallion approach[23] (methods 5 and 6 of Methods of Calculation) the contribution of the "integrated π-electron current" to $\chi_\perp^\pi$ corresponds to that part of $\chi_\perp^\pi$ which would have been retained even if appeal had been made to the London integral approximation. [In fact, in the method of Coulson et al.,[23] the London approximation is *not* applied at this stage, and there are other non-London (non-L; sometimes called local π-electron) contributions to $\chi_\perp^\pi$ which are, in general, nonzero; these are dealt with in section 3.] In the present section we focus attention solely on $\chi_\perp^{\pi(L)}$, the London contribution to $\chi_\perp^\pi$.

In order to make the predictions of the six different methods of calculation we have used directly comparable with each other, we consider the ratio $\chi_\perp^{\pi(L)}$ (molecule)/$\chi_\perp^{\pi(L)}$ (benzene) in all cases, where $\chi_\perp^{\pi(L)}$ (benzene) is the London contribution to $\chi_\perp^\pi$ calculated, by the corresponding method, for benzene. Such ratios as are available for the six different species, I–III, I^{2-}, II^{2-}, and III^{2-}, calculated via the six different methods labeled 1–6 in Methods of Calculation, are reported in Table V. This table illustrates even more unambiguously than did the analogous Table V in ref 7a the extreme sensitivity of the predicted magnetic properties of predominantly paramagnetic, conjugated, π-electron systems to the method used for their calculation and the relative *insensitivity* in this respect of the predicted properties of ostensibly similar but predominantly *diamagnetic*, conjugated species of this type.

In particular, let us consider our prototype molecule, pyracylene (I). As we proceed along the series, 1 → 3 → 5 → 2 → 4 → 6 (where the numbers refer to the labelings of a particular computational approach referred to in Methods of Calculation), we are progressing in what we may regard as the direction of increasing sophistication of method, from the McWeeny approach based on a simple HMO (method 1) to the Coulson–Gomes–Mallion formalism based on a coupled Hartree–Fock method with variable resonance integrals (method 6). Methods 1, 3, and 5 are all based on various types of wave functions that are *not* self-consistent with respect to resonance integrals and calculated bond orders, while methods 2, 4, and 6 are based on the corresponding types of wave function which *do* incorporate such "self-consistency". It is quite evident from the column of results on pyracylene (I) in Table V that, so far as *this* molecule is concerned, this latter refinement to the *wave function* is far more important than the choice of actual *method* which, with a given wave function as its basis, is used to calculate the ratio $\chi_\perp^{\pi(L)}$ (molecule)/$\chi_\perp^{\pi(L)}$ (benzene). This ratio for pyracylene via method 1 is large and negative, indicating a strongly paramagnetic $\chi_\perp^{\pi(L)}$ (pyracylene); method 6, however (as well as method 5), predicts the London contribution to $\chi_\perp^\pi$ (pyracylene) to be (marginally) diamagnetic; the other methods, 3, 5, 2, and 4, predict London susceptibility ratios (in increasing order of diamagnetism) intermediate between these two extremes. It is clear, however, that the greatest discontinuity in the sequence occurs between methods 5 and 2 (separated by the extra space in Table V). It is in going from method 5 to method 2 that we change from using a wave function in which individual resonance-integrals are *not* self-consistent with respect to the corresponding calculated bond orders to one in which these two quantities *are* self-consistent.

In the case of azulenopentalene (II), although we have less information (Table V), the trend is the same—method 1 would give the impression that $\chi_\perp^{\pi(L)}$ (azulenopentalene) is strongly paramagnetic, but methods 4 and 6 predict it to be only weakly so. For dibenzo[*cd*,*gh*]pentalene (III) this trend is both reversed and displaced—the simple Hückel–McWeeny method (1) predicts $\chi_\perp^{\pi(L)}$ (dibenzo-

Table VI. $\chi_\perp^{\pi(\text{non-L})}$ and $\chi_\perp^{\pi(\text{L})}$ Contributions to $\chi_\perp^{\pi}$ in I-III and Their Dianions via Methods 5 and 6

	susceptibilities[a] via Coulson–Gomes–Mallion method[23]					
	fixed resonance integrals (method 5)			variable resonance integrals (method 6)		
species	$\chi_\perp^{\pi(\text{non-L})}$	$\chi_\perp^{\pi(\text{L})}$	$\chi_\perp^{\pi\ c}$	$\chi_\perp^{\pi(\text{non-L})}$	$\chi_\perp^{\pi(\text{L})}$	$\chi_\perp^{\pi\ c}$
I	−0.496[b]	+1.076[b]	+0.580	−0.496	−0.112	−0.608
I^{2-}	−0.514	−1.019	−1.533	−0.514	−0.938	−1.452
II				−0.491	+0.147	−0.344
II^{2-}	−0.510	−0.753	−1.263	−0.511	−0.697	−1.208
III	−0.492	+1.183	+0.691	−0.492	+1.461	+0.969
III^{2-}	−0.516	−1.207	−1.723	−0.516	−1.208	−1.724

[a] Tabulated susceptibilities are *absolute* values in SI units (10^{-9} m^3 mol^{-1}). [b] Negative absolute susceptibilities in this table indicate *dia*magnetism (as is conventional); positive absolute susceptibility values denote *para*magnetism. [c] Overall, calculated $\chi_\perp$ tensor components may be obtained by adding the constant $\chi_\perp^{\sigma}$ contribution of −1.278 m^3 mol^{-1} [23] to the tabulated $\chi_\perp^{\pi}$ values for I-III and I^{2-}-III^{2-} listed in these columns (see the Results and Discussion).

[*cd,gh*]pentalene) to be only slightly paramagnetic, but all the other methods are qualitatively agreed that this quantity should be strongly paramagnetic.

As for the dianions of I-III, all six methods are in concordance that all three dianions are strongly and unambiguously diamagnetic. As would be expected from the various currents reported in Tables I-IV, the London susceptibility ratios for I^{2-} and II^{2-} are the ones that are most sensitive to the method used for their calculation (variations, from the data in Table V, of ca. 15% and 12%, respectively) while that for III^{2-} is the least sensitive in this respect (variation of ca. 9%); indeed, among the ratios derived from methods 1-4 (noniterative McWeeny and Hall-Hardisson approaches) there is a variation of $\chi_\perp^{\pi(\text{L})}(III^{2-})/\chi_\perp^{\pi(\text{L})}$ (benzene) of only ca. $^1/_3$%!

By taking the data in the last two rows of Table IV (pertaining to methods 4 and 6) which agree semiqualitatively in all cases, we therefore make the following conclusions about $\chi_\perp^{\pi(\text{L})}$ (species) for the six species considered: pyracylene (I), marginally diamagnetic; azulenopentalene (II), marginally paramagnetic; dibenzo[*cd,gh*]pentalene (III), *strongly* paramagnetic; the dianions of I-III, strongly diamagnetic. The above calculations do quantitatively bear out the contention of Trost et al.[4] that, of the three neutral molecules I-III, dibenzo[*cd,gh*]pentalene (III) is the one which behaves magnetically most like a [12]annulene and is, consequently, the one which would serve best as a model for such a [4*n*]annulene. Furthermore, we also note in passing that the dianions of the [4*n*]periphery polycyclic π systems I-III appear to behave very much like [4*n* + 2]annulenes as far as their $\chi_\perp^{\pi(\text{L})}$ contributions are concerned (i.e., they are diamagnetic). This theoretical deduction is consistent with previous experimental observations[27,29,33] that the dianions of [4*n* + 2]-periphery polycyclic systems such as pyrene and acepleiadylene (molecules V and IV, respectively, of ref 7a) should bear paramagnetic "ring currents".[7a]

(3) Calculation of the Non-London Part of $\chi_\perp^{\pi}$ and Estimation of $\chi_\perp^{\sigma}$. So far in this paper we have discussed only what might be regarded as the London contribution to $\chi_\perp^{\pi}$. However, one of the main virtues claimed for the calculational procedure which we previously devised with Coulson[23] was that it enabled calculation of that part ($\chi_\perp^{\pi(\text{non-L})}$) of the total $\chi_\perp^{\pi}$ which may, in a sense, be thought of as representing the "local" contribution to this total π-electron susceptibility; this contribution (which comprises what in ref 23 we called the "bond moments", "one-center moments", and "nonbond moments") is lost on application of the London integral approximation, but the method described in ref 23 enables it to be calculated.

Until now, we have found it convenient, for purposes of comparison, to express all results as a ratio to the corresponding quantity calculated, by the same method, for benzene;[34] we shall, however, find it more illuminating in the present discussion, when we consider the relative contributions of $\chi_\perp^{\pi(\text{non-L})}$, $\chi_\perp^{\pi(\text{L})}$ and $\chi_\perp^{\sigma}$, to tabulate *absolute* calculated susceptibilities. Accordingly, the susceptibilities reported in Table VI are absolute susceptibilities [they are presented in SI units (10^{-9} m^3 mol^{-1})]. The quantities listed on the left-hand side of Table VI were obtained from the method of Coulson et al.[23] in which all resonance integrals were maintained at the standard benzene value throughout the SCF calculation (i.e., method 5); the data on the right-hand side of Table VI were obtained via the same basic method but with the additional refinement that resonance integrals were allowed to vary iteratively with the corresponding calculated bond orders (method 6).

The following points are evident from the data presented in Table VI.

(1) The values calculated for $\chi_\perp^{\pi(\text{non-L})}$ are remarkably insensitive both to whether or not resonance integrals are varied and to which of the six species I-III and I^{2-}-III^{2-} is being considered. For the neutral molecules, I-III, the values fall within the range −0.491 to −0.496 for both types of calculation, while the corresponding range for I^{2-}-III^{2-} is −0.510 to −0.516. Previous calculations (e.g., ref 35) have often sought to incorporate $\chi_\perp^{\pi(\text{non-L})}$ contributions into the empirically determined,[36,37] "local" part due to the σ electrons (see below); once again, as was observed in ref 23, this procedure appears to be justified, at least numerically, by the constancy of the $\chi_\perp^{\pi(\text{non-L})}$ terms calcu-

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(33) B. M. Trost, D. Buhner, and G. M. Bright, *Tetrahedron Lett.*, **1973**, 2787.

(34) (a) It is of interest to pursue the question as to who was the first to point out that taking ratios to benzene concealed errors in these sorts of calculations. In ref 7a the comments of Davies[34b] (1961) and of O'Sullivan and Hameka[34c] (1970) were quoted, but we now find that these observations were all anticipated in a much-neglected paper by Brooks[34d] (1940). Brooks states: "The fact that both theories (London's[6a] and Pauling's[34e]) are in such good agreement with experiment, in spite of the many approximations involved, is evidence that the ratios of the anisotropies reduce to purely geometric quantities, which have a significance beyond that of the particular model adopted for specific calculations". Brooks had had correspondence with London himself on the matter, for he marks the above statement in ref 34d with the following footnote: "I am indebted to Professor F. London for this observation". So, the approach we have adopted so far in this paper, of taking ratios to benzene, is indeed very properly attributed to London. (b) D. W. Davies, *Trans. Faraday Soc.*, **57**, 2081 (1961). (c) P. S. O'Sullivan and H. F. Hameka *J. Am. Chem. Soc.*, **92**, 1821 (1970). (d) H. Brooks, *J. Chem. Phys.*, **8**, 939 (1940). (e) L. Pauling, *ibid.*, **4**, 673 (1936).

(35) A. T. Amos and H. G. Ff. Roberts, *J. Chem. Phys.*, **50**, 2379 (1969).

(36) J. Hoarau, *Ann. Chim. (Paris)*, 1 (13), 544 (1956).

(37) M. E. Stockham and H. F. Hameka, *J. Am. Chem. Soc.*, **94**, 4076 (1972).

lated for these several hydrocarbon isomers. Like the $\chi_{\perp}^{\sigma}$ contribution, the $\chi_{\perp}^{\pi(\text{non-L})}$ part of $\chi_{\perp}$ appears to be determined almost entirely by the number of carbon and hydrogen atoms in the molecule.

(2) Because the $\chi^{\pi(\text{non-L})}$ term for the six species I–III and I^{2-}–III^{2-} is practically constant, the (very large) differences in their overall $\chi_{\perp}^{\pi}$ values are essentially due to the $\chi_{\perp}^{\pi(L)}$ part, which we have been discussing in Tables I–V and in the previous sections of this paper. As we have seen, the six species considered differ markedly in that term. When the two contributions $\chi_{\perp}^{\pi(\text{non-L})}$ and $\chi_{\perp}^{\pi(L)}$ are added, therefore, the large variations encountered in the overall $\chi_{\perp}^{\pi}$ values (Table VI) are dominated entirely by the differing $\chi_{\perp}^{\pi(L)}$ terms.

(3) When this essentially constant (and diamagnetic) $\chi_{\perp}^{\pi(\text{non-L})}$ contribution is added to the various $\chi_{\perp}^{\pi(L)}$ terms calculated for I–III and I^{2-}–III^{2-} by method 6, only dibenzo[*cd*,*gh*]pentalene (III) is predicted to have a total $\chi_{\perp}^{\pi}$ which is overall paramagnetic (to the extent of ca. 1×10^{-9} m^3 mol^{-1}).

(4) In ref 23, we estimated the (diamagnetic) σ-electron contribution, $\chi_{\perp}^{\sigma}$, to the total susceptibility component, $\chi_{\perp}$, perpendicular to the molecular plane of pyracylene (I) by means of an empirical Pascal-constant scheme and found it to be -1.278×10^{-9} m^3 mol^{-1}. Since this term is considered to depend only on the total number of C–C and C–H bonds in the conjugated system of interest, $\chi_{\perp}^{\sigma}$ will also assume this value of -1.278 for the isomeric molecules II and III and, in this model, even for the dianions of I–III. On this basis, therefore, $\chi_{\perp}$ ($\equiv \chi_{\perp}^{\pi} + \chi_{\perp}^{\sigma}$) values for *all* species, I, II, I^{2-}–III^{2-}, and even for III, which is predicted in Table VI to have a net $\chi_{\perp}^{\pi}$ which is paramagnetic, would be expected to be diamagnetic overall. This qualitative prediction does, in principle, lend itself to an experimental test. The quantitative extent of this predicted diamagnetism of $\chi_{\perp}$ for the various species considered may be obtained by adding the constant $\chi_{\perp}^{\sigma}$ contribution of -1.278 units to the calculated $\chi_{\perp}^{\pi}$ terms (obtained via method 6) in the right-hand column of Table VI.

Conclusions

We draw the following conclusions from this work.

(1) The calculated π-electron "ring-currents", "integrated current densities", and London contributions to the magnetic susceptibilities of those molecules which a simple, noniterative, Hückel-McWeeny calculation predicts to have an overall *paramagnetic* $\chi_{\perp}^{\pi(L)}$ are extremely sensitive to the degree of sophistication of the method used to predict them. (See Tables I–IV and the left three columns of Table V.)

(2) In order for calculations on such systems to yield realistic results, it is vital that computations be based on realistic resonance integrals; it has been noted that a very convenient way of doing this is to adopt a wave function that is iteratively self-consistent with respect to resonance integrals and calculated bond orders. Incorporation of *this* refinement is much more important than whether the wave function itself is chosen to be either of the Hückel or the SCF-type, at least when the results are expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene. (Witness the results in the top and bottom sections in the left-hand three columns of Table V.)

(3) The calculated magnetic properties of those conjugated systems which are predicted to have a strongly *diamagnetic* $\chi_{\perp}^{\pi(L)}$ are relatively insensitive to the idiosyncracies of the particular method used to calculate them (see Tables I–IV and the right-hand three columns of Table V). When only *ratios* are required of "ring-current" intensities or London contributions to magnetic susceptibilities (relative to the corresponding quantities calculated, by the same method, for benzene), it seems that for these strongly diamagnetic systems a calculation carried out by use of the simple McWeeny method based on an ordinary, noniterative ("topological")[13] HMO (method 1) is as adequate and as quantitative as either of the methods (4 and 6) which involve iterative, coupled Hartree–Fock wave functions. This statement appears to be true for I^{2-}, II^{2-}, and III^{2-} (see Table V) even though these species are not only *charged* but are, in addition, derived from nonalternant hydrocarbons!

(4) Pyracylene (I), azulenopentalene (II), and dibenzo[*cd*,*gh*]pentalene (III) are very different magnetically, even though they all have a 12 ($4n$, $n = 3$) carbon atom periphery and might, therefore, on the basis of the model of Trost et al.,[3,4] be thought to have at least one of the attributes necessary for being considered as "perturbed" [12]annulenes. $\chi_{\perp}^{\pi(L)}$ for III is very paramagnetic while the corresponding quantities for I and II are marginally diamagnetic and marginally paramagnetic, respectively. The Trost model does not, however, claim that compounds I–III should be essentially identical in their properties.[4,27] All that the model can say is that, on the scale from diamagnetism to paramagnetism, III stands to the right (i.e., toward paramagnetism) and I less so. To this extent, therefore, the present calculations may possibly be interpreted as giving some semiquantitative support to the Trost "periphery" model,[3,4] for the molecule which would apparently serve best as a perturbed [12]annulene is indeed III, with I being most displaced from the "ideal" case, as Trost et al. originally suggested.[4] (We have very recently investigated a slightly more refined model than that of Trost which is based on a VB formalism and which involves consideration of circuits other than just the peripheral one.[38])

(5) The present calculations are consistent with what may be considered as an intuitive extension of the Trost model in that they do seem to suggest unambiguously that the $\chi_{\perp}^{\pi(L)}$ contributions for the dianions of $4n$-periphery systems are strongly diamagnetic—to about the same extent, in fact, as the "well-behaved", neutral, condensed, benzenoid hydrocarbons (e.g., Table V and ref 28 and 23). The dianions of I–III are, in fact, very interesting for they do, of course, have the same carbon atom connectivities and approximately the same ring areas (this is not quite true but is assumed to be so in the present calculations) as the corresponding neutral molecule. To this level of approximation, therefore, the vast difference in magnetic behavior between individual members of I–III and their respective dianions is a function mainly of electron configuration. Once the assumption about invariance of molecular geometry between a given neutral molecule and its dianion has been made in the context of the topological HMO calculation (method 1) and of those PPP-SCF calculations (methods 3 and 5) which are *not* iteratively self-consistent with respect to resonance integrals and calculated bond orders, such differences in magnetic behavior are due *only* to electronic configuration. Since, in these three cases, the wave function depends only on the carbon atom connectivity of the system (see, for example, ref 13 and 39 and footnote 16 of ref 7a), the π-electron energy-level family and the set of LCAO coefficients of the

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(39) R. B. Mallion and D. H. Rouvray, *Mol. Phys.*, **36**, 125 (1978).

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various π MO's are *identical* in the neutral molecule and in the dianion. Under these circumstances, the difference in calculated $\chi_{\perp}{}^{\pi(L)}$ values between a given neutral molecule and its dianion is attributable solely to the fact that the dianion has one more doubly occupied orbital than the neutral molecule. There are thus consequential (and dramatic) changes in the HOMO-LUMO separation on which, according to Van Vleck's expression,[40] the diamagnetic/paramagnetic nature of the species in question sensitively depends.[7d] This is certainly borne out by the figures presented in Table V.

(6) When the non-London π contributions, $\chi_{\perp}{}^{\pi(\text{non-L})}$, and the σ contributions, $\chi_{\perp}{}^{\sigma}$, to $\chi_{\perp}$ are taken into account, the overall quantities $\chi_{\perp}$ ($\equiv \chi_{\perp}{}^{\pi(L)} + \chi_{\perp}{}^{\pi(\text{non-L})} + \chi_{\perp}{}^{\sigma}$) for I-III are all expected to be diamagnetic. This is true even of III, the $\chi_{\perp}{}^{\pi(L)}$ of which is predicted by methods 4 and 6 to be strongly paramagnetic. If, therefore, crystals of I-III could be obtained and the components of the susceptibility tensors perpendicular to their respective planes could be measured experimentally, the present calculations anticipate that these would all turn out to be diamagnetic. In practice, however, it is unlikely that this experimental feat will be easily achieved in the near future, and it seems most likely that I-III, as they are synthesised, will be studied by means of solution ^{1}H NMR spectroscopy.[25] In the context of this technique, it is the London (or "ring current") contribution which dominates the appearance of the resulting ^{1}H NMR spectra, via its influence on relative ^{1}H NMR chemical shifts (although it should be borne in mind that the nonuniform π-electron charge density extant in these nonalternant systems, and particularly in their dianions, can have an equally important effect on relative ^{1}H NMR shielding).[41] By considering the results of the two "best" methods of calculation (4 and 6) presented in Tables IV and V, we would predict the *paramagnetic* (i.e., shielding) "ring-current" contributions to intramolecular ^{1}H NMR chemical shifts[42] in I-III to be in the order III > II > I. The dianions of I-III are all expected to exhibit "normal" diamagnetic "ring-current" effects similar to those characteristic of the condensed, benzenoid hydrocarbons.

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Registry No. I, 187-78-0; I dianion, 12564-35-1; II, 22719-10-4; II dianion, 75718-00-2; III, 13357-45-4; III dianion, 75718-01-3.

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[42] (a) More recent work by the Trost group[42b] has extended NMR studies on pyracylene to consider the influence of "ring currents" on ^{13}C chemical shifts.[42c] (b) B. M. Trost and W. B. Herdle, *J. Am. Chem. Soc.*, **98**, 4080 (1976). (c) For some comments by one of the present authors on "ring-current" effects in ^{13}C NMR, see R. B. Mallion, *Nucl. Magn. Reson.*, **4**, 1-66 (1975).

Thermolysis of *n*-Butylsilver(I) Ate Complexes

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Lithium di-*n*-butyl(tri-*n*-butylphosphine)silver(I) (**2**) and other organosilver(I) ate complexes have been prepared and their mechanism of thermal decomposition studied. Chemical characterization of **2** by reaction first with dibromoethane and then iodine yielded only 1-iodobutane, showing that **2** was formed and that **2** was not in equilibrium with *n*-butyllithium. ^{13}C and ^{31}P NMR spectra of lithium dimethyl(tri-*n*-butylphosphine)silver(I) are described which support this conclusion. Dilithium trimethyl(tri-*n*-butylphosphine)silver(I) was also identified by ^{13}C NMR. Analysis of the products of thermal decomposition of **2** suggests that the observed thermal stabilization of **2** with respect to the rapid thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) (**1**) is the result of an altered mechanism for carbon-silver bond cleavage. Lithium di-*n*-butyl(tri-*n*-butylphosphine)silver(I) is proposed to decompose to give products derived from *n*-butyl radicals and *n*-butyllithium. The principal thermal decomposition products from **2** were octane (26%), butane (71%), and 1-butene (3%). Crossover experiments in which mixed lithium *n*-butyl(*n*-pentyl)silver(I) was thermally decomposed yielded a statistical distribution of coupled products. Substitution of magnesium bromide for lithium had no effect on the product mixture from these thermal decomposition reactions. Kinetics of decomposition of **2** were first order in **2**. Other possible pathways for decomposition of organosilver(I) ate complexes are discussed and the suggested mechanism for this thermal decomposition reaction is compared to similar organocopper(I) and organogold(I) chemistry.

The facility with which carbon-metal bond cleavage reactions occur and their mode of scission are a central feature of organometallic chemistry. In the case of organo transition metal compounds, facile thermal cleavage of carbon-metal bonds is often observed and can occur through a variety of mechanistic pathways.[1] Stabilization of organo transition metal compounds with respect to such thermal decomposition has been accomplished by a variety of means.[2,3] Modification of the alkyl ligand of an organo

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