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Calculated "London" π-electron magnetic properties of some "perturbed" annulenes, their dications and dianions*

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Abstract

The "periphery model" for planar polycyclic conjugated systems is tested by applying the method of Coulson et al. for calculating π-electron magnetic properties of such species to a selection of polycyclic neutral molecules, and their respective dianions and dications, all of which appear to have the attributes necessary for them to be considered "perturbed" annulenes. Because some of the species investigated have the potential to be strongly paramagnetic in their calculated π-electron magnetic properties, it was considered appropriate to base this application of the approach of Coulson et al. on a Pariser–Parr–Pople wavefunction that made resonance integrals iteratively self-consistent with respect to calculated bond orders. With one exception (which is discussed) these computations broadly support an analogy, in the context of conjugated systems that may be regarded as "perturbed annulenes", of Sondheimer's observation that the dianions (and, by implication, the dications) of genuine (mono-cyclic) [$4n$]-annulenes are diamagnetic, whereas doubly charged [$4n + 2$]-annulenes are paramagnetic, in their predicted "London" ("ring current") π-electron magnetic properties. These conclusions are not inconsistent with the available experimental data on ^{1}H NMR chemical shifts; it is, however, pointed out that the latter are not necessarily directly comparable with the present calculations because, in the case of the non-alternant and/or multiply-charged species included in this study, other factors such as non-uniform π-electron charge densities are thought likely to make as significant a contribution to the experimentally observed ^{1}H NMR chemical shifts in these systems as the "ring current" effects that are actually being considered here.

INTRODUCTION

The 1960s and 1970s saw great activity directed towards the synthesis of

unusual and exotic conjugated hydrocarbons. The late Professor Coulson himself was particularly taken [1] with the synthetic work of the Hafner school (see, for example, ref. 2). Later, he was excited by the availability of pyracylene [3] and its derivatives [3,4] (a theoretical interest [5] that was continued, after Professor Coulson's death, by two of the present authors [6–8]). This impressive synthetic work was maintained well into the 1980s, with — by way of representative examples (both from 1985) — news of the beautiful cyclo-octa-annelated biphenylenes of Wilcox and Farley [9] and the achievement — albeit "serendipitous" — of dipleiadiene (the subject of our companion paper in this volume [10]) by Vogel et al. [11]. The apotheosis of these synthetic feats concerning conjugated species came at the end of that decade, with the truly remarkable synthesis by Krätschmer et al. [12], in macroscopic quantities, of the perfectly aesthetic, sixty-carbon-atom cluster that is now (unfortunately!) becoming known as Buckminster-fullerene (which we prefer to call by its more appropriate mathematical name of icosahedral C_{60}) — a system in which, the present authors venture to suggest, Charles Coulson would have absolutely delighted, had he lived to see its realisation. Meanwhile, during the 1970s and 1980s, some invaluable banks of experimental data were being accumulated concerning the magnetic properties (and the ^{1}H and ^{13}C NMR chemical shifts especially) of the dianions and dications of many of these molecules — notably by Müllen et al. in Switzerland and Germany, and Rabinowitz et al. in Israel. (Publications by these workers — especially the Müllen school — are legion, and we therefore cite here only refs. 13–22, to which we shall make subsequent reference in this discussion). The main object of these studies was to investigate the validity of so-called periphery models (see, for example, refs. 3,5,7,16,23 and 24), in which these species are regarded as annulenes that are "perturbed" by the presence of central linkages. For example, we referred in the conclusion of our previous paper [10] to the fact that the "London" π-electron magnetic properties of the dianions of two polycyclic "perturbed [4n]-annulenes" studied there are unambiguously diamagnetic. It was re-emphasised [5,10] that this finding seems, on the face of it, to illustrate an analogy (in the context of such perturbed [4n]-annulenes) of Sondheimer's observation [25] that the dianions of genuine, mono-cyclic [4n]-annulenes are diamagnetic. Vogler [26–30] has performed calculations of considerable sophistication on the annulenes themselves, on which there are experimental data [31]. In this paper, we apply our previously described calculational procedure [7,32] (based on a Pariser–Parr–Pople wavefunction [32] that is iteratively self-consistent with respect to bond orders and resonance integrals) in an attempt to establish the "London" π-electron magnetic properties of the neutral molecule, and the respective dianion and dication, associated with each of the six species (**I–VI**) that may be regarded as "perturbed [14]-annulenes", and one (**VII**) that has the attri-

(I)   (II)   (III)   (IV)

(V)   (VI)   (VII)
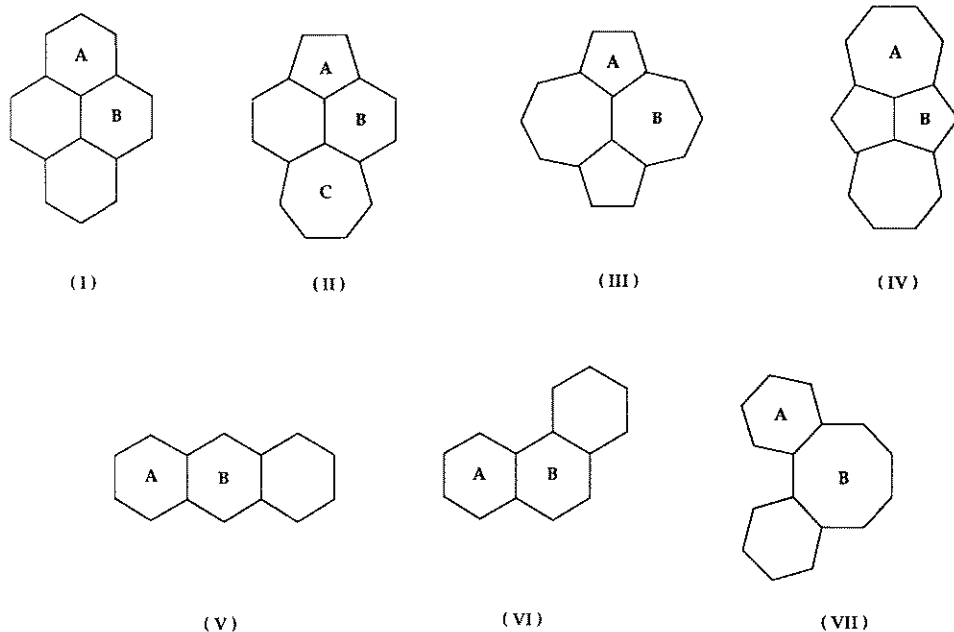
butes to be considered as a perturbed [16]-annulene. (**I–IV** are, in fact, all isomers of pyrene (**I**) [16]). This is being done with the intention of testing the alluringly simple concept of the periphery model [3,5,23] that would allow Sondheimer's [25] conclusions about the dianions and dications of genuine (mono-cyclic) annulenes (confirmed theoretically by Vogler [30]) to be analogously applied to polycyclic systems that may possibly be regarded as "perturbed charged annulenes". Experimental ¹H NMR data on **I–VII**, their dianions, and the dications of most of them, are to be found in the literature (as described in detail in the next section) [13–22, 33–37].

EXPERIMENTAL DATA AND METHODS OF CALCULATION

Experimental ¹H NMR data are available for **I–VII**, their respective dianions, and the dications of some of them, from the following sources: Pyrene (**I**) [16,19,20–22,35]; Acepleiadylene (**II**) [17,34,37]; Bis(cyclo-penta)[*ef,kl*]-heptalene ("Azupyrene") (**III**) [16,37]; Bis(cyclo-hepta)[*cd,gh*]-pentalene (**IV**) [13,16]; Anthracene (**V**) [14,15,19,22,33,35,36]; Phenanthrene (**VI**) [15,22,35] and 1,2:3,4-Dibenzo-cyclo-octatetraene (**VII**) [15,18].

There now seems to be general agreement [5–10,38–42] that when "London" contributions to π-electron magnetic effects are to be calculated in conjugated systems (especially those species for which such contributions are likely to be strongly paramagnetic), self-consistency of resonance integrals with respect to bond lengths is vital in order to obtain even qualitatively reasonable results [9]. It has been pointed out [7,9] that

experimental bond lengths could function perfectly satisfactorily in this capacity, if they were available — but that, whatever the device used to achieve this end, "realistic" [5–10,38–42] resonance integrals (however obtained) must be used. Accordingly, in view of the exhaustive investigations concerning application of the six different methods reported in our earlier work [6,7], and in our companion paper in this volume [10], we adopt here only the most sophisticated of these procedures: what has been referred to in refs. 6, 7 and 10 as "Method 6". This is the approach, based on a Pariser–Parr–Pople wavefunction, that two of us (J.A.N.F.G. and R.B.M.) devised in collaboration with Professor Coulson [32]. However, in contrast to its original version, we adopt here such a wavefunction with *variable* resonance-integrals, iterated so as to be self-consistent with respect to the corresponding bond orders. Desirable features of this formalism are [7]: (a) minimal use of the London integral-approximation [32]; (b) iteration of resonance integrals with respect to calculated bond length, which, as has just been pointed out, is particularly appropriate for any system that may potentially have strongly paramagnetic "London" contributions to its π-electron magnetic properties [5–10, 38–42]. The parametrisation adopted and the molecular geometries assumed were as in ref. 32, and the wavefunction was as described in Method 6 of ref. 7. The calculations were performed on a Silicon Graphics Personal Iris Computer in the University of Porto.

RESULTS AND DISCUSSION

The results of our calculations are presented in Tables 1–3. Tables 1 and 2 display relative "integrated π-electron current densities" [32] for the several individual rings in the neutral molecules **I–VII** (Table 1), and the corresponding doubly charged species (Table 2). The data shown in Tables 1 and 2 are expressed as a *ratio* to the corresponding quantity ("integrated π-electron current density") [32] calculated (by the same method) for benzene, so the numbers reported in this way in Tables 1 and 2 are dimensionless. These "integrated π-electron current densities", which arise from our formalism detailed in ref. 32, may be thought of as being analogous to π-electron "ring current" intensities calculated by other more standard methods (such as, for example, the now classic approaches of Pople [43], McWeeny [44]; see also refs. 45 and 46). However, it should be borne in mind that, when not expressed as ratios, "integrated π-electron current densities" are dimensionally different from "ring currents". Finally, Table 3 lists the overall "London" contribution [7,32] ($\chi_{\perp}^{\pi(L)}$ (species)) to the magnetic susceptibility perpendicular to the respective molecular planes of the various species; as in previous publications [7,10,32], we consider the

TABLE 1

Relative "integrated π-electron current density" in neutral molecules I–VII[a]

Molecule	Ring		
	A	B	C
I	1.27	0.76	
II[b]	0.43[b]	1.12[b]	0.46[b]
III	1.49	0.88	
IV	1.32	0.88	
V	0.89	1.26	
VI	1.07	0.82	
VII	0.67	− 0.60	

[a] Calculated by Method 6 of refs. 6, 7 and 10. A positive value indicates a diamagnetic "integrated π-electron current density"; a negative value denotes a paramagnetic "integrated π-electron current density".

[b] Results for acepleiadylene (II) are taken from our companion paper [10] in which we have found it convenient to adopt a lettering nomenclature for the three symmetrically distinct non-equivalent rings of II different from the one used here.

TABLE 2

Relative "integrated π-electron current densities" in the dications and dianions of I–VII[ab]

Species	Ring		
	A	B	C
I[2−] [b]	− 1.02	− 0.29	
II[2+]	− 4.77	− 1.04	− 0.17
II[2−]	− 1.63	− 2.55	− 10.72
III[2+]	− 3.41	− 0.83	
III[2−]	0.34	0.80	
IV[2−]	− 0.35	− 1.05	
IV[2−]	− 7.17	− 4.38	
V[2−] [b]	− 0.60	− 1.15	
VI[2+] [b]	− 1.20	− 1.33	
VII[2+] [b]	1.07	1.05	

[a] Calculated by Method 6 of refs. 6, 7 and 10. A positive value indicates a diamagnetic "integrated π-electron current density"; a negative value denotes a paramagnetic "integrated π-electron current density".

[b] The Coulson–Rushbrooke pairing theorem [47–49] leads us to expect the same predicted π-electron magnetic properties for both the dications *and* the dianions of the alternant [47–49] systems included in our list (I, V–VII); accordingly, only data for one type of doubly charged species (namely, the dication) are explicitly recorded.

TABLE 3

Relative "London" contributions $(\chi_\perp^{\pi(L)}(\text{species})/\chi_\perp^{\pi(L)}(\text{benzene}))^a$ to magnetic susceptibilities perpendicular to the molecular planes of molecules **I–VII** and their dications and dianions[b]

Molecule	$\chi_\perp^{\pi(L)}(\text{species})/\chi_\perp^{\pi(L)}(\text{benzene})$		
	Neutral species	Dication	Dianion
I	4.04	− 2.51	CR[b]
II	3.02[c]	− 5.59	− 18.07
III	4.30	− 7.16	2.97
IV	4.85	− 2.38	− 24.46
V	3.06	− 2.31	CR[b]
VI	2.93	− 3.73	CR[b]
VII	0.12	4.08	CR[b]

[a] Calculated by Method 6 of refs. 6, 7 and 10. A positive value for this ratio indicates a diamagnetic "London" contribution to the magnetic susceptibility perpendicular to the molecular plane of the species in question; when this value is negative, the same "London" contribution should be understood to be paramagnetic.
[b] "CR" refers to the fact that the Coulson–Rushbrooke pairing theorem [47–49] leads us to expect the same predicted π-electron magnetic properties for both the dications *and* the dianions of the alternant [47–49] systems included in our list (**I, V–VII**); accordingly, only data for one type of doubly charged species (namely, the dication) are explicitly recorded.
[c] The result for neutral acepleiadylene (**II**) is taken from our companion paper in this volume [10].

ratio

$$\frac{\chi_\perp^{\pi(L)}\ (\text{species})}{\chi_\perp^{\pi(L)}\ (\text{benzene})}$$

where $\chi_\perp^{\pi(L)}$ (benzene) is the "London" contribution to the magnetic susceptibility perpendicular to the molecular plane calculated, by the same method (Method 6 of refs. 6, 7 and 10), for benzene. The reader will find it convenient to bear in mind that, throughout Tables 1–3, a positive entry denotes diamagnetism, and a negative entry indicates paramagnetism.

The Coulson–Rushbrooke pairing theorem leads us to expect the same predicted π-electron magnetic properties — "integrated π-electron current densities" (Table 2) and "London" contributions to magnetic susceptibilities (Table 3) — for both dianions and dications of the alternant [47–49] systems included in our list (**I, V, VI, VII**): Accordingly, only data for one type of doubly charged species (the dication) associated with these systems are explicitly recorded in Tables 2 and 3.

It may be seen immediately from Table 1 that — as would, perhaps, have been anticipated — the "integrated π-electon current densities" for those molecules we investigated that are neutral alternant condensed benzenoid hydrocarbons (**I, V and VI**) are quite unexceptional, being of the same sign

and order of magnitude as similar quantities and "ring current" intensities calculated by various methods — iterative and non-iterative — and reported previously on numerous occasions elsewhere (representative examples are to be found in refs. 35, 44, 46 and 50–55). The non-alternant neutral species in our list (**II–IV**), which, like the alternant benzenoid hydrocarbons just referred to (**I, V** and **VI**), have a 14- (i.e. [$4n + 2$]-) carbon-atom periphery, also show diamagnetic "integrated π-electron current densities" of unremarkable size. The non-benzenoid 1,2;3,4-dibenzo-cyclo-octatetraene (**VII**), with its 16- (i.e. [$4n$]-) carbon-atom perimeter is, however, seen to be fundamentally different as regards its "integrated π-electron current densities", in that its eight-membered ring is paramagnetic, whereas its six-membered ring is diamagnetic (to about the same extent).

It is equally evident from Table 2 that the situation just described for the neutral species is, for the most part, exactly reversed in the case of the corresponding dications and dianions. The alternant benzenoid species (**I, V** and **VI**) with [$4n + 2$]- perimeters have, on transformation to the respective dications (and, by implication, dianions), become paramagnetic. The non-benzenoid (though alternant) species (**VII**), with its [$4n$]- periphery, has, by virtue of the same (imagined) oxidation (and reduction) processes, become unambiguously diamagnetic — both rings of it, in fact, now exhibiting precisely the same sort of "integrated π-electron current density" values as are normally and routinely encountered for these quantities (and for "ring current" intensities) among the rings of the neutral alternant condensed benzenoid hydrocarbons [35,44,46,50–55]. The situation as far as the non-alternant species **II–IV** are concerned is less clear-cut. With the intuition that we have developed over the years for these types of quantities, we consider the "integrated π-electron current densities" calculated for ring A in **IV**$^{2-}$ and ring C of **II**$^{2-}$ as well as those of ring A of **II**$^{2+}$, ring B of **IV**$^{2-}$, and ring A of **III**$^{2+}$, to be uncomfortably large. The numbers quoted here have, however, been checked several times and we therefore report them — but not without some misgivings. With that quantitative reservation, however, we can conclude from Table 2 that (except for the case of **III**$^{2-}$, referred to below) the dications and dianions associated with the [$4n + 2$]- peripheral systems **I–VI** are predicted to display *para*magnetic "integrated π-electron current densities", whereas those of the [$4n$]- peripheral system **VII** are calculated to bear such integrated currents that are *dia*magnetic. The one exception, mentioned above, is the dianion of **III**: this is still predicted to bear diamagnetic "π-electron current densities", though the transformation **III** $\rightarrow$ **III**$^{2-}$ does result in a diminution of those diamagnetic currents, causing a shift in the direction of paramagnetism, without the currents' themselves actually becoming paramagnetic.

These conclusions are also largely borne out by an examination of the *overall* "London" contributions [7,32] ($\chi_{\perp}^{\pi(L)}$(species)) to the magnetic susceptibilities perpendicular to the respective molecular planes of these conjugated systems, as the ratios [7,32] ($\chi_{\perp}^{\pi(L)}$(species)$/\chi_{\perp}^{\pi(L)}$(benzene)) shown in Table 3 indicate. It is clear from Table 3 that for the neutral molecules corresponding to each of the $[4n + 2]$-periphery systems **I–VII**, such "London" contributions are all unambiguously *dia*magnetic, whereas for the respective dications and dianions (again with the tantalising exception of **III**$^{2-}$) they are equally definitely *para*magnetic — though we again draw attention to our unease (referred to earlier) about the unexpectedly large values calculated for **II**$^{2-}$ and **IV**$^{2-}$. The $[4n]$-periphery system **VII** has calculated "London" contributions associated with it that are (just) weakly diamagnetic for the case of the neutral molecule; such contributions for both types of doubly charged species are, by contrast, predicted to be *strongly* diamagnetic — once again, of the same order of magnitude as those values routinely encountered for the neutral alternant condensed benzenoid hydrocarbons [35,44,46,50–55].

CONCLUDING REMARKS

These observations do not contradict the available experimental data on ^{1}H NMR chemical shifts of the molecules, and their doubly charged anions and cations, investigated here [13–22,33–37]. However, these experimental data [13–22,33–37] are not necessarily directly comparable with the present calculations, because — as was emphasised in our companion paper in this volume, [10] — in the case of the non-alternant and/or multiply-charged species included in this study, other factors, such as non-uniform π-electron charge densities, are likely to make as significant a contribution to the experimentally observed ^{1}H NMR chemical shifts in these systems as the "ring current" effects themselves, that have been the subject of consideration in this paper.

Nevertheless, it may be qualitatively concluded that our computations broadly support the suggestion of an analogy, in the context of those polycyclic systems that might be regarded as "perturbed annulenes", of Sondheimer's observation [25] that the dianions (and, by implication, the dications) of genuine (mono-cyclic) $[4n]$- annulenes are diamagnetic, whereas doubly charged $[4n + 2]$- annulenes are paramagnetic, in their predicted "London" ("ring current") π-electron magnetic properties. Despite, however, the possibly reassuring tone of this general conclusion, the exception exemplified by the dianion of **III** does once again emphasise the warning, given by the late Charles Coulson and one of the present authors [5], that ". . . 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, [is] a somewhat hazardous undertaking."

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