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SOME COMMENTS ON THE USE OF THE "RING-CURRENT" CONCEPT IN DIAGNOSING AND
DEFINING "AROMATICITY"

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Abstract - The use of the "ring-current" concept in diagnosing and defining
"aromaticity" is reviewed, and questions that must be answered before the
"ring-current" criterion can be declared to be a satisfactory one for this
purpose are formulated. The very recent work of Haddon, and of Aihara, has
related 'London' magnetic-susceptibility to resonance energy and this discussion
confirms that the overall 'London'-susceptibility of a polycyclic species,
rather than its individual "ring-current" intensities, is the more appropriate
quantity to consider in this context. It is, however, concluded that the very
systems which are of particular interest to chemists — namely those that are
intuitively felt to be "anti-aromatic" — are just those whose 'London' magnetic-
susceptibilities are the most sensitive to the sophistication of the method
(and, particularly, of the *wave function*) used to calculate them, and that this
constitutes a major drawback to the potential utility of adopting *calculated*
'London'-susceptibility (or exaltation) as a criterion for defining the future
implications of the term "aromaticity".

INTRODUCTION

In 1961, Elvidge and Jackman (1) put forward the very plausible proposal that a
compound should be defined as *aromatic* if it "...will sustain an induced [π-electron] ring-
current" (see Note a) and that the magnitude of this "ring current" may be taken to be a
quantitative measure of "aromaticity". (It was not explicitly stated — though it was
in fact implied — that the induced "ring-current" in question is to be considered as
being *dia*magnetic.) These authors were careful to point out that their treatment was
applicable only to six-membered, monocyclic species (and there has been much subsequent
discussion of these, and other monocycles — see refs. 4-17), though they did express the
hope that ^{1}H-NMR chemical-shifts might lead to a quantitative assessment of "aromaticity"
in a general, arbitrary, conjugated system. In *ca.* 1966, five groups (18-22) independently
gave prominence to the observation that *para*magnetic "ring-currents" are to be expected in
the [4n]-annulenes — though this conclusion was in fact implicit in the much earlier work
of Berthier, Pullman, *et al.* (23-25), and of Wagnière and Gouterman (26). After this, it
became almost common folk-lore in the NMR-Literature that, in some kind of heuristic and
ill-defined way, Elvidge and Jackman's idea could be extended to declare that *any*
conjugated system (whether monocyclic or polycyclic, heterocycle or hydrocarbon) which
appears — either from NMR-measurements or from direct calculations — to support an
overall π-electron *para*magnetism is necessarily "anti-aromatic".

These superficially attractive hypotheses do, however, hide underlying difficulties,
and several authors have commented to this effect in the intervening years. Very early in
the development of this subject, Abraham and Thomas (8) were by no means convinced about
connections between "ring-currents" and resonance energy — though this scepticism is not in
the spirit of some recent quantitative theoretical-work by Haddon (17) and by Aihara (27)
(to which further reference will be made later). Jung (28), in 1969, doubted the value of
extending these ideas to *poly*cyclic hydrocarbons when there exist molecules of this type in
which some rings bear diamagnetic "ring-currents" while others, within the same molecule,

Note a. In this contribution, it will be assumed that the reader is familiar with the "ring-
current" concept, and at least the major papers in the extensive Literature of it.
Accordingly, no historical review will be given here of the "ring-current" effect itself:
specific citations will thus frequently be confined to those papers in which the "ring-current"
idea has been spoken of specifically in connection with the notion of "aromaticity".
Readers not so well versed in the "ring-current" Literature may care to be informed that
Haigh and the present author have recently prepared a very detailed historical and critical
review of the "ring-current" effect, which is due to appear in a forthcoming issue of
Progress in Nuclear-Magnetic-Resonance Spectroscopy (2). See also ref. 3.

sustain paramagnetic "ring-currents" — according to calculations based on the methods of Pople (29) and McWeeny (30) (see Note b).

The aim of this contribution, therefore, is to review the above suggestions and the criticisms that have been made of them, in order to assess their present status and to consider in general the propriety of using what some (34,35) would regard as a rather obscure and somewhat esoteric molecular-orbital index (the "ring current"), concerned with a second-order magnetic-property, in evaluating such a basic and intuitively *global* attribute of a molecule as its "aromaticity".

SOME QUESTIONS THAT MUST BE ANSWERED

A cynic would say that there are actually only two difficulties in discussing the subject of "aromaticity" and "ring currents" — deciding what is meant by "ring current" and assigning a meaning to the term "aromaticity"!   The reader may think that the author is making fun of the question: this is not the case.   The above statement does, however, emphasise, with only a little exaggeration, the problems that inherently beset any assessment such as the one attempted here.   The fact that the present Symposium is just the latest in a long series devoted to an understanding of "aromaticity" shows that this notion is by no means a simple one, while the "ring-current" concept itself has not been exempt from controversy and misunderstanding (2,36-41).   At the heart of the problem lies the undeniable fact that neither "ring currents" nor "aromaticity" are physical observables.

The first hurdle to surmount in a discussion of "ring currents" and "aromaticity" is, however, largely a semantic one.   In asking whether "ring currents" are connected with "aromaticity" we ought to distinguish two interpretations of this suggestion.   (i) *If*, following Elvidge and Jackman (1), we *define* a molecule to be "aromatic" if it will sustain a diamagnetic "ring-current", then, obviously, any molecule which, from subsequent experiment or calculation, is deemed to support such a "ring current" may properly be considered to be "aromatic", in that sense.   (Difficulties to which Jung drew attention in (28) will be discussed later.)   (ii) The crucial point, however, implied by the above question, is whether *every* molecule described as "aromatic" on the basis of such a definition would *also* be declared to be "aromatic" when judged by the several other physical and chemical criteria — a particularly pleasant smell, a predisposition to nitration and sulphonation, a high resonance-stabilisation energy, an approximate equality of bond-length, characteristic ultra-violet absorptions and (in the case of ions and radicals) a strong delocalisation of spin — which a given molecule is often considered to be required to satisfy in order to merit the description "aromatic"; and, conversely, we should require a unanimous verdict from all criteria on which molecules it is appropriate to call "non-aromatic" and which should be termed "anti-aromatic".

This latter point has been emphasised by several authors (9,42,43,17), particularly (in a very eloquent, forceful and — at times — emotional way) by Labarre and Crasnier (42) (see Note c).

Note b. In ref. 28, Jung used the Pople (29) and/or McWeeny (30) LCAO-MO methods for evaluating the individual "ring-current" intensities in a number of conjugated, polycyclic hydrocarbons.   In certain of the cases in which he applied *both* methods to calculate the several "ring-current" intensities in a given molecule, Jung obtained (28) slightly different values (to the two decimal places quoted) *via* the Pople scheme (29) from those obtained by use of the McWeeny formalism (30).   This is perplexing, since the two approaches are entirely equivalent, numerically, for the calculation of relative "ring-current" intensities, provided that they are both based on a simple HMO wave-function and the London approximations, and provided also that each result is expressed as a ratio to the similarly-calculated benzene "ring-current" intensity (2).   These differences must therefore be attributed to rounding errors (albeit surprisingly large ones) in the numerical calculations reported in (28), some of which have been independently verified by the present writer.   In ref. 31, the present author has given an *explicit* expression for a quantity, J_i, proportional to the "ring-current" intensity in the ith ring of any arbitrary, polycyclic, conjugated system. Though in outward appearance very different, this is exactly equivalent to the other formula derived earlier (though for hydrocarbons only) by Pople (29).   It may be noted in passing that the present author's version is particularly amenable to a dissection of the graph-theoretical ideas that specifically underlie "ring-current" calculations (see refs. 32 and 33).

Note c. (see next page)

The second question that arises is the following: even *given* the premise that Elvidge and Jackman's definition *is* a constructive starting point for an assessment of "aromaticity", how reliably can any particular molecule be stated to exhibit diamagnetic or paramagnetic "ring-currents"?   For it must be emphasised again that *"ring currents" themselves are not physically observable*, even though they *are* computationally accessible (but see remarks in the next section).   All that one can do, therefore, is to postulate the model of π-electron "ring-currents" and then to calculate, on the basis of such a model, those quantities (such as magnetic susceptibilities (2,20), anisotropies (2,20) and exaltations (2,44), ^{1}H-NMR chemical-shifts (2), and Faraday- and inverse-Faraday effects (9,42,40a)) which *are* experimentally measurable.   Consequently, if a specific molecule is inferred to support "ring currents" of a particular type, this inference must have been gleaned either from direct calculation or by appeal to experimental magnetic-measurements of the kind mentioned in the previous sentence.   If a calculation has been performed, we should want to enquire about its sophistication and about the wave function on which it was based, for the results of calculations on predominantly paramagnetic systems, in particular, are especially sensitive in this respect (35) — see next section; if "ring-current" magnitudes and/or signs have been deduced from some experimental measurement, we should require to know what other effects, besides the "ring current", may intrude upon the property being measured, and whether (and, if so how) such effects have been taken into account and subtracted from the observed measurements in order to leave only the "ring-current" contribution to the magnetic property under consideration.   Finally, it would certainly be relevant to ask whether all types of experimental magnetic-measurements lead to the same conclusions, for a given molecule, about the size — and particularly the sign — of its constituent "ring-current" intensities.

SOME ANSWERS — SOME DIFFICULTIES

Two important advances have been made this year in the quest for answers to the points raised in the previous section.   Haddon (17) has shown that, to a good approximation, there is an analytical relation between resonance energies and "ring-current" intensities in the [4n + 2]-π-electron annulenes, while Aihara (27), in a very elegant paper that nicely invoked Sachs' graph-theoretical theorem (45,46), has demonstrated that diamagnetic-susceptibility exaltation (44) reflects the sign and, to a lesser extent, the magnitude, of the (Dewar (47)) resonance-energy of a general, conjugated hydrocarbon (see Note d). Aihara concludes: "Now we can safely use diamagnetic-susceptibility exaltation as a definite criterion of aromaticity".   In view of the comments in the previous section concerning the unanimity (or otherwise) of the various "aromaticity" criteria, the present author would prefer *either* to reduce this claim to the more-limited and non-committal one of having shown a connection between diamagnetic-susceptibility exaltation and Dewar resonance-energy, *or* to say simply (*cf*. point (i), above) that *if* "aromaticity" were to be *defined* in terms of diamagnetic-susceptibility exaltation, then Aihara's work has shown that application of the resonance-energy criterion would occasion qualitatively the 'correct' verdict concerning the "aromaticity" of any given molecule subsequently under investigation.

One problem which is, however, avoided when overall 'London' magnetic-susceptibility exaltations (or anisotropies), rather than individual "ring-current" intensities, are

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Note c. These philosophical difficulties have been put by Labarre and Crasnier (42) (in a much more striking and poetic fashion than the present author would ever be capable of!), in the following terms (42):

"Chemists and Physicists are at present in the middle of a cavern which Plato would not have disavowed; they observe on the walls of the cavern *certain shadows* resulting from the lighting of an unknown subject (aromaticity) by the different sources of light represented by their various chemical or physical techniques of observation: an agreeable odour, an aptitude to nitration and sulphonation, a ring current, a magneto-optical excess, a diamagnetic anisotropy, a resonance energy, a U.V. bathochromic effect, and even a mathematical term. The question is: Do these shadows all belong to *the same* invisible myth (or reality)? and the answer is: 'Nobody knows at present'."

Note d. Aihara's graph-theoretical formulation (27) of the London theory (2,20) applies specifically to hydrocarbons, but he did remind the reader at the end of ref. 27 of what changes have to be made to the Hückel secular-determinant in order that it may appropriately describe conjugated systems having one or more hetero-atoms.   Veillard long ago (48) modified the London-McWeeny theory (30) to make it applicable to heterocyclic systems and the explicit "ring-current" expression given by the present author in ref. 31 is based upon Veillard's adaptation.   By use of generalised Sachs-theorems that admit consideration of arbitrarily edge- and vertex-weighted graphs (49-51), Aihara's analysis in ref. 27 could thus probably be readily extended to embrace heterocyclic species.

considered in the case of polycyclic systems, is the one pointed out by Jung (28) and referred to in the Introduction — namely the occasional calculation of diamagnetic "ring-current" intensities in some rings and paramagnetic ones in others. In the domain of the monocyclic annulenes (in which context Elvidge and Jackman's (1) original proposal was conceived) this difficulty does not, of course, arise, because the overall 'London'-susceptibility is entirely determined by just the one ring and so has the same sign as the (unique) "ring-current"; for polycyclic molecules, however, although a breakdown of the overall 'London'-susceptibility into contributions from individual rings is often conceptually and aesthetically valuable, for the purposes of establishing a criterion for "aromaticity" the *overall* magnetic-susceptibility anisotropy (or exaltation) would appear to be more useful. (An advantage which the overall 'London'-susceptibility, or exaltation, has for this purpose over calculated "ring-current" chemical-shifts is that the former weight the "ring-current" intensity in each ring by a ring-area factor that has the same order of magnitude for each ring, whereas the latter weights the contribution of each ring by a geometric factor depending approximately on the inverse-cubes of the distances of the carbon- (and/or hetero-) atoms in each ring from the resonating proton under consideration, and such geometric-factors therefore differ markedly from ring to ring (*e.g.* ref. 31)).

There is, however, one very great practical difficulty, of which the present writer has had some considerable experience (3a,35,52), in using calculated-"ring-current" criteria — or any quantity derivable from, or implicit in, the London theory — as a diagnosis for, or a definition of, "aromaticity": this is that calculated "ring-current" intensities are much more sensitive to whether or not the wave function used to compute them is self-consistent with respect to atomic charges and computed bond-orders in the case of π-electron systems observed to have overall paramagnetic (or weakly diamagnetic) 'London'-susceptibilities than in the case of those which calculation predicts to have strongly diamagnetic 'London'-susceptibilities. 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 (18-22,53) and this activity will be particularly favoured 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 is any estimated value of it to be sensitive to the idiosyncracies of the particular method used for the calculation. 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 species. 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 (18-22,53); any (relatively minor) paramagnetic-contribution that 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 the particular method used to calculate it.

The above considerations are dramatically illustrated when six different methods of calculation are used to estimate the overall ratio $\chi_\perp^{London}$ (species)/$\chi_\perp^{London}$ (benzene), where $\chi_\perp^{London}$ (benzene) is the 'London' contribution to $\chi_\perp$ calculated, by the same method, for benzene. The Table lists such calculations for the non-alternant hydrocarbon pyracylene (sometimes considered as a 'perturbed [4n]-annulene' — see (54) and (35)), and for its dianion (which is strongly diamagnetic — to about the same extent, in fact, as a condensed, benzenoid hydrocarbon of approximately the same size — see Note e.) This Table illustrates
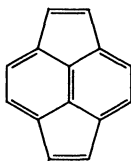
Structural Formula of Pyracylene

Note e. This therefore seems to illustrate an analogy, in the context of polycyclic, 'perturbed [4n]-annulenes', of Sondheimer's observation (55) that the dianions of genuine, monocyclic ("anti-aromatic") [4n]-annulenes are diamagnetic. This is certainly consistent with the large HOMO-LUMO separation (1.000β) for the dianion of pyracylene predicted by a simple HMO-calculation (3a).

TABLE   'London' contributions $(\chi_{\perp}^{\pi London}(\text{species})/\chi_{\perp}^{\pi London}(\text{benzene}))$
to magnetic susceptibilities perpendicular to the molecular
planes of pyracylene and its dianion, by various methods[§]

| Method of Calculation	$(\chi_{\perp}^{\pi London}(\text{species})/\chi_{\perp}^{\pi London}(\text{benzene})$	
	—— Calculated for ——	
	Pracylene	Pyracylene Dianion
Simple Hückel-McWeeny (30,35) (Method (I))	− 3.84*	+ 2.75*
'Non-iterative' coupled Hartree-Fock (Hall-Hardisson (56)) (35) (Method (II))	− 3.25	+ 3.04
'Non-iterative' coupled Hartree-Fock (Coulson *et al.* (57)) (Method (III))	− 2.93	+ 2.78 [†]
London-McWeeny method based on an iterative $(\beta\omega'\omega'')$ HMO (35) (Method (IV))	− 0.73	−
Coupled Hartree-Fock (Hall-Hardisson (56)) with variable resonance-integrals (Method (V))	+ 0.15	+ 2.85
Coupled Hartree-Fock (Coulson *et al.* (57)) with variable resonance-integrals (Method (VI))	+ 0.31	+ 2.56

[§]From refs. 3a and 52.

* A *negative* value for the ratio $(\chi_{\perp}^{\pi London}(\text{species})/\chi_{\perp}^{\pi London}(\text{benzene}))$
indicates a *paramagnetic* $\chi_{\perp}^{\pi London}(\text{species})$; a *positive* value for the
ratio indicates that $\chi_{\perp}^{\pi London}(\text{species})$ is *diamagnetic*.

[†]The dotted line divides the results from methods (I), (II) and (III)
(which are all based on wave functions that are *not* iteratively self-
consistent with respect to resonance integrals and calculated bond-orders)
from the results obtained *via* methods (IV), (V) and (VI) which *are* based
on wave functions that incorporate such 'self-consistency'.

sensitivity of the predicted magnetic-properties of predominantly paramagnetic, conjugated, π-electron systems to the method used for their calculation and the relative *in*sensitivity in this respect of the predicted properties of ostensibly similar but predominantly *dia*magnetic conjugated-species of this type.

Let us concentrate on pyracylene; as we proceed along the series

$$(I) \longrightarrow (II) \longrightarrow (III) \longrightarrow (IV) \longrightarrow (V) \longrightarrow (VI)$$
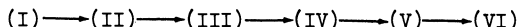
(where the Roman numerals in brackets refer to the labellings of a particular computational approach referred to in the Table), we are progressing in what may be regarded as the direction of increasing sophistication of method, from the McWeeny approach (30) based on a simple HMO (method (I)) to the formalism of Coulson *et al.* (57) in the context of a coupled-Hartree-Fock method with variable resonance-integrals (method (VI)). Methods (I) - (III) 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 (IV) - (VI) are founded on the corresponding types of wave function which *do* incorporate such 'self-consistency'. It is clear, therefore, that the question of whether or not the wave function employed possess such self-consistency is much more important, for the calculation of magnetic properties, then 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 'London' magnetic-susceptibility) calculated, by the same method, for benzene. The ratio ($\chi_\perp^{\pi London}$ (pyracylene)/$\chi_\perp^{\pi London}$ (benzene)) obtained *via* method (I) is large and negative, indicating a strongly paramagnetic $\chi^{\pi London}$ (pyracylene); method (VI), however, as well as method (V), predicts the London contribution to $\chi_\perp^\pi$ (pyracylene) to be (marginally) diamagnetic; the other methods, (II)-(IV), predict 'London' susceptibility-ratios (in increasing order of diamagnetism) intermediate between these two extremes. It is evident, however, that the greatest discontinuity in the series occurs between methods (III) and (IV) (separated by the dotted line in the Table). It is in going from method (III) to method (IV) 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.

As for the dianion of pyracylene, five methods are unanimous that it should be strongly and unambiguously diamagnetic; all predict 'London'-susceptibiltiy ratios that agree to within 15%. The dianion of pyracylene is, in fact, of some considerable interest for it does, of course, have the same carbon-atom connectivity and approximately the same ring-areas (the latter is not quite true but it is assumed to be so in the present calculations) as the neutral molecule. To this level of approximation, therefore, the vast difference in magnetic behaviour between pyracylene and its dianion is a function mainly of electronic configuration (see, for example, ref. 58). Once the assumption about invariance of molecular geometry between pyracylene and its dianion has been made in the context of the 'topological' (32,35,46) HMO-calculation (method (I)) and of those PPP-SCF calculations (methods (II) and (III)) that are *not* iteratively self-consistent with respect to resonance integrals and calculated bond-orders, such differences in magnetic behaviour are due *only* to electronic configuration; this is so because the wave function depends only on the carbon-atom connectivity of the system (32,35,46), with the result that the π-electron energy-level family and the set of LCAO-coefficients of the various π-MO's are *identical*, according to the approximations made in *this* calculation, in the neutral molecule and in the dianion. Under these circumstances, the difference in calculated $\chi_\perp^{\pi London}$ 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 (53), the diamagnetic/paramagnetic nature of the species in question sensitively depends. This is entirely borne out by the numbers presented in the Table.

As a final emphasis of the message that is becoming clear from these calculations, let us consider the results of the crudest (method (I)) and the most-refined (method (VI)) approaches considered in this investigation (*i.e.*, the first row and the last row of the Table). It is manifestly evident from these data that the relative 'London'-susceptibility of the dianion is hardly changed when an SCF-method based on a wave function with iteratively variable resonance-integrals, and making minimal appeal to the London integral-approximation (2,3,57) (method (VI)), is replaced by the McWeeny formalism (30) founded on a simple Hückel-MO with fixed resonance-integrals (method (I)). This is certainly not so for pyracylene itself, predicted by the simple Hückel-McWeeny method (30) (method (I)) to be strongly paramagnetic. The results obtained by the more-refined calculation (method (VI)) (52,57) are even *qualitatively* different from those of the crudest (method (I)) (30,35) (see Note f).

Note f. (see next page)

CONCLUSIONS

By no means all the questions about the concept of "aromaticity" raised in the second section of this paper have been answered: indeed, consistent with the title of this contribution, magnetic criteria of "aromaticity" are the only ones that have been considered in any detail here.   The following points have, however, emerged from the preceding discussion:

1)   The very recent work of Haddon (17) and Aihara (27) has related 'London' susceptibility to Dewar resonance-energy — almost quantitatively in the case of $[4n + 2]$-π-electron annulenes, and at least qualitatively for polycyclic *molecules*.

2)   The overall 'London'-susceptibility of a polycyclic system, rather than its individual "ring-current" intensities, *is* the more appropriate quantity to consider in this context.   It must, of course, be continually borne in mind in discussions of this sort that 'London' diamagnetism or paramagnetism, unscrambled from σ- and other ('localised') π-electron contributions to magnetic susceptibilities, is *not* an experimental observable; (see ref. 57 for a very detailed appraisal of this important point.)

3)   It is, however, an unfortunate fact that the very systems which are of particular interest to chemists — namely those which we intuitively feel should be the "anti-aromatic" ones — are just those whose 'London' magnetic-susceptibilities are the most extremely sensitive to the sophistication of the method (and, particularly, of the *wave function*) used to calculate them!   This is vividly illustrated by the data given in the Table.

In the opinion of the present author, this latter point constitutes a major drawback to the potential utility of adopting *calculated* 'London'-susceptibility (or exaltation) as a criterion for defining what we should in future agree to understand by the term "aromaticity".

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Note f. In particular, the apparently paramagnetic "ring-current" noted in (35) as being borne by the six-membered ring in pyracylene has been shown (52) to be no more than an artifact of the simple 'topological' (32,35) HMO-calculation based on fixed resonance-integrals.   Had this paramagnetic "ring-current" in the six membered ring of pyracylene been genuine it would (to the author's knowledge) have been the first paramagnetic "ring-current" to be reported in a six-membered (*i.e.*, formally 'benzenoid') ring.   More-recent calculations by Gomes and the present author (52) *have*, however, confirmed (by means of a calculation by method (VI) of the Table) the notion of their being a paramagnetic "ring-current" in a six-membered ring in one of the *isomers* of pyracylene (dibenzo [*cd,gh*] pentalene) discussed by Trost and Kinson in ref. 59.

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