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THE APPLICATION OF THE BIOT-SAVART LAW TO THE RING CURRENT ANALYSIS OF PROTON CHEMICAL SHIFTS—I

A COMPREHENSIVE INVESTIGATION OF THE ANNULENES

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Abstract— The Biot-Savart shielding law is applied to a wide variety of annulenes in an effort to delineate the relationship between chemical shift and ring current. The success of the proton chemical shift/ring current analysis of the annulenes is interpreted to provide strong phenomenological evidence for the existence of diamagnetic and paramagnetic ring currents.

NMR spectroscopy is now regarded as the most important, generally applicable technique in the characterization of annulenes.[1] Surprisingly, there has been no attempt to systematically interpret the proton chemical shifts in a quantitative manner. On the other hand the chemical shifts[2] (and diamagnetic susceptibilities) of the benzenoid hydrocarbons have been the subject of an intensive investigation, and the singular magnetic properties of these compounds have been attributed to molecular ring currents.[5,*] A similar response to the presence of an applied magnetic field has successfully been invoked for multi-cyclic hydrocarbons,[6] porphyrins[7] and phthalocyanins.[8] Qualitative interpretations of the proton chemical shifts and diamagnetic susceptibilities of annulenes have been made in terms of the same effect.[9]

In this paper we address ourselves to the following two questions: "Can the proton chemical shifts of annulenes be quantitatively described by the postulation of ring current phenomena?", and if so "What are the magnitudes and signs of the derived ring currents?".

While a number of terms of localized origin contribute to relative proton shielding constants in aromatic molecules (*vide infra*), the ranges of chemical shifts in many annulenes are so large as to make such effects negligible. It is for this reason that *the annulenes provide the best possible test case for the ring current model.** Should the model provide an adequate description of proton chemical shifts in annulenes, we might hope to estimate the ring currents with some accuracy (within 10%). By the same token, those cases for which chemical shifts are small (such that localized contributions may be of comparable magnitude), will be unsuitable for this type of analysis (benzenoid hydrocarbons, etc).

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* The theoretical question as to the existence of ring currents is not explicitly considered in this paper. Rather we seek to test, in a phenomenological manner, the ability of the ring current method to adequately account for proton chemical shifts in annulenes. Nevertheless, the philosophical question of ring current theories will be taken up in a subsequent paper, meanwhile our opinion of their place in chemistry is a matter of record.[1]

Unlike the exaltation in diamagnetic susceptibility which may be associated with a definite ring current effect, the shielding of the protons in a molecule does not bear a simple relationship to the magnitude of the ring current effect. In order to account for the proton chemical shifts, it is necessary to be able to calculate the secondary magnetic field arising from a ring current at any position in a molecule. No *ab initio* quantum-mechanical method has yet emerged and semi-classical procedures must be employed.

The standard semi-classical approach assumes circular symmetry for the ring current, and the secondary magnetic field at the protons is calculated from an equivalent dipole (proposed by Pople)[2a, b] or from current loop(s) (originally proposed by Waugh and Fessenden)[2c, d, k, 5g, k] symmetrically placed with respect to the carbocycle. With very few exceptions,[10] two one-dimensional current distributions have been used and the current loops represented as circular line currents.[2c, d] Within its classical limitations this method is probably quite adequate and surprisingly good results have been obtained considering the geometrical inadequacies of the model. It is this difficulty in correctly treating the geometries of annulenes, most of which are far from circular and in some cases are subject to considerable deviations from planarity, which appears to be responsible for the absence of quantitative treatments in this area.

It does not seem to have been generally recognised that Longuet-Higgins and Salem were able to give a reasonable description of the proton chemical shifts of [18] annulene (**22**) by use of a very simple model based on the Biot-Savart law.[9a, 11] The Biot-Savart law allows the calculation of the magnetic field at any point in space, arising from a linear current flowing between specified points. For our purposes the specified points are related to the atomic positions on the carbocycle. Such an approach is not restricted to 'circular' molecules and obviously may be adapted to three-dimensional systems. As a result, the method has sufficient flexibility to be applied to all annulenes (and indeed all molecules exhibiting a ring current effect), and is well-suited for use in this study.

Unlike the early work[9a, 11] however, we do not constrain the ring current to pass through the atomic centers of the carbocycle. The determination of the optimum current loop placement is based on a least squares minimization of the differences between the observed and calculated ring current chemical shifts[*](summed over all annulenes), for an *arbitrary* ring current in each annulene. Thus our approach is essentially different from previous treatments in that no ring currents are explicitly assumed (or theoretically calculated); rather the ring currents arise from the analysis of the chemical shift data (instead of *vice versa*—see Computation Section).

Scope. In an effort to provide a broad-based test for the method we have endeavoured to include as wide a variety of annulenes[1] as possible. The main obstacle to inclusion for those compounds not considered has been the absence of structural information. All annulenes of known geometry, and those for which reasonable structures could be inferred are included (see Geometries Section).

METHODS OF CALCULATION

Model chemical shifts (*MCS*). In the study of ring current effects on proton shielding

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[*] Ring current chemical shift (RCCS) (ppm) = observed chemical shift (OCS) (τ) − model chemical shift (MCS) (τ).

constants, model compounds are chosen so that the reference protons therein are subject to the same magnetic environment as the protons of interest, with the exception of the magnetic contribution from the ring current. It is rarely possible to exactly duplicate magnetic environments, but with the possible exception of the charged species, the model chemical shifts quoted in Table 1 should be reliable to 0·5 ppm and in most cases the error will be considerably less than this figure.

For some time the MCS of an aromatic (annulenic) proton was assumed to be about τ4·2 from a consideration of linearly but not cyclically conjugated polyenes.[2c, 5r] More recently, however, a regression analysis by Figeys[2i, 6c] on a series of benzenoid hydrocarbons led to the somewhat lower figure of τ3·9. This latter value is in agreement with estimates of the differences in shielding experienced by an olefinic and an aromatic proton, in the absence of a ring current effect.[5l, 12, 13] Furthermore, the adoption of the value due to Figeys serves to remove much of the previous dichotomy between chemical shifts and anisotropy of diamagnetic susceptibilities in the benzenoid hydrocarbons as well as improving on the (calculated) relative chemical shifts in these compounds.[2e, i, 5l] Fortunately, however, the ring current chemical shifts (RCCS)* for the annulenes are somewhat larger than those observed in the benzenoid

TABLE 1. MODEL CHEMICAL SHIFTS

Type of proton	Reference compound or source	Model chemical shift (MCS)(τ)	Application (Compounds)	Ref.
Annulenic	Regression analysis on benzenoid hydrocarbons	3·871	All	[a, b]
Exocyclic methylene	2-Methyleneadamantane	5·52	**7**	[c]
Tertiary bridgehead bis-allylic	*trans*-9,10-Dihydronaphthalene	7·14	**13, 17**$^{-}$	[d]
Secondary bis-allylic	*anti*-1,6:8,13-Dimethano-[14]-annulene	7·76[h]	**3**	[e]
Bis-(α-bridgehead) methylene	Adamantane	8·22	**17**	[c]
Methyl (within π-electron framework)	*trans*-15,16-Dimethyl-2,7,15,16-tetrahydropyrene	9·05	**12, 20**	[f]
Charged annulenic	Charged aromatic	± 10 per unit ∓ charge	**10, 20, 21**	[a, g]

[a] See text

[b] Ref 2*i*

[c] R. C. Fort and P. von R. Schleyer, *J. Org. Chem.* **30**, 789 (1965)

[d] S. Masamune and R. T. Seidner, *Chem. Commun.* 542 (1969); S. Masamune, C. G. Chin, K. Hojo and R. T. Seidner, *J. Am. Chem. Soc.* **89**, 4804 (1967)

[e] Ref 53

[f] Ref 58

[g] T. Schaefer and W. G. Schneider, *Canad. J. Chem.* **41**, 966 (1963); B. P. Dailey, A. Gawer and W. C. Neikam, *Discuss. Faraday Soc.* **34**, 18 (1962); H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961); Refs 17, 18 †

[h] Average value

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* Ring current chemical shift (RCCS) (ppm) = observed chemical shift (OCS) (τ) − model chemical shift (MCS) (τ).

† For all compounds in this study to which the MCS charge correction is applied (**10**, **20**, **21**), an improved correspondence between observed and calculated chemical shifts may be obtained by a reduced value for the dependence of chemical shift on charge density (Table I).

hydrocarbons and the choice of an annulenic MCS is less critical in this series (see however, the discussion of dehydroannulenes). This is an important point as the annulenic MCS is unlikely to be a completely invariant property of all annulenes (in contradistinction to the benzenoid hydrocarbons which have relatively constant bond orders[12,14]). Nevertheless, in the interests of a uniform approach, the value derived by Figeys has been used throughout this work.

The difficulties associated with the MCS correction for annulenic protons which are attached to non-neutral carbon atoms have already been pointed out;[15,16] for this reason we have only included those ions in which the RCCS is considerably larger than the necessary charge corrections. The value quoted in Table I seems to be the most generally accepted approximation.[17,18][*]

Geometries. Where atomic coordinates were available from structural investigations, these were used directly, but with all annulenic C—H bond lengths set to 1·10Å.

Thus the crystallographic studies of [16]annulene (**19**)[20][†] and [18]annulene (**22**),[21] which included tabulations of the atomic coordinates referred to the least-squares molecular plane,[22] were suitable for immediate use. The crystallographic studies of naphthalene (**2**),[23] 1,6-methano-[10]annulene (**3**),[‡] *trans*-15,16-dimethyldihydropyrene (**12**),[§] *syn*-1,6;8,13-dioxido-[14]annulene (**14**)[26] and 1,8-didehydro-[14]annulene (**18**)[27] did not give atomic coordinates of all (or any) atoms in the molecular coordinate system, and an appropriate transformation of the unit cell coordinates was necessary.

The atomic coordinates of benzene (**1**) were generated by assuming hexagonal geometry with a C—C bond length of 1·397Å.[28]

The annulenic carbon and hydrogen coordinates of 1,6-oxido-[10]annulene (**4**),[29] 1,6-imino-[10]annulene (**5**),[¶] N-methyl-1,6-imino-[10]annulene (**6**)[¶] and 11-methylene-1,6-methano-[10]annulene (**7**) were taken from the structure of 1,6-methano-[10]annulene (**3**).[‡] Using the 1,6 bridge carbon atoms of **3** as reference points, the coordinates of the etheno fragment of **7** were generated from: 1·46Å (bridge bond length),[‖] 1·33Å (etheno bond length)[31] and bond angles of: 105° (bridge angle),[**] 120° (H—C—H angle).

The perimeter of *trans*-15,16-dihydropyrene (**13**) was taken from *trans*-15,16-dimethydihydropyrene (**12**);[§] the coordinates of $H_{15(16)}$ were obtained on the assumption that the $C_{15(16)}$—$H_{15(16)}$ bonds in **13** would be colinear with the $C_{15(16)}$—$Me_{15(16)}$ bonds in **12**.

[*] For all compounds in this study to which the MCS charge correction is applied **10,20,21**, an improved correspondence between observed and calculated chemical shifts may be obtained by a reduced value for the dependence of chemical shift on charge density (Table 1).

[†] The author thanks Professor Paul for a preprint of this work.[20b]

[‡] Studied as the 2-carboxylic acid derivative.[24] H_2 was assumed to lie along the C_2–COOH bond.

[§] Studied as the 2,7-diacetoxy derivative.[25] H_2 and H_7 were assumed to lie along the C_2–$OCOCH_3$ and C_7–$OCOCH_3$ bonds, respectively.

[¶] For practical reasons certain protons in some molecules were not included in the analysis. This usually stemmed from one or more of the following factors:

(a) Uncertainties in geometry.
(b) An absence of suitable model chemical shifts.
(c) Methyl group undergoing virtually free rotation (six-fold barriers).

[‖] Bridge bond lengths seem somewhat shortened in the 1,6-methano-[10]annulenes.[23,30]

[**] A considerable contraction of the normal geminal sp^2 angle[31,32] has been suggested for the bridge angle of this compound.[33] *Cf.* refs 24, 29 and 30.

The annulenic coordinates of *syn*-1,6-methano-8,13-oxido-[14]annulene (**15**),* 1,6:8,13-butano-[14]annulene (**16**)* and 1,6;8,13-propano-[14]annulene (**17**)[34] were taken from the structure of *syn*-1,6;8,13-dioxido-[14]annulene (**14**).[26] The coordinates of the remaining atoms in **17** were generated by using the known geometry of the propano fragment[34] in conjunction with the perimeter coordinates of **14**.

The geometry of the neutral compound **12**† was used for the *trans*-15,16-dimethyldihydropyrene dianion (**20**). The [16]annulene dianion (**21**) was assumed to be a planar bond-equalized structure with exterior bond angles (4) of 120° and interior bond angles (12) of 130°.[20]

Compounds included in this study but not mentioned above had no close congeners from which structural information could be inferred, but were of a composition that permitted a bond-equalized planar structure with undeformed C—C—C angles (neglecting non-bonded interactions). For these compounds: [12]annulene (**8**), 1,5,9-tridehydro-[12]annulene (**9**), cyc[3,3,3]azine (**10**), [14]annulene (**11**),[35] 1,7,13-tridehydro-[18]annulene (**23**),[36] 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro-[18]annulene (**24**), 1,3,7,9,13,15-hexadehydro-[18]annulene (**25**), [24]annulene (**26**) and those compounds mentioned above for which incomplete data were given the following bond lengths were used: C$=$C = 1·40Å, C$\equiv$C = 1·20Å, C—H = 1·10Å.

Computation. Programmed in Fortran IV for use on the IBM 360/67 Computer.

A. *Transformation of unit cell coordinates.* After the usual transformation from unit cell fractional coordinates to an orthogonal cartesian system a transformation to molecular coordinates was made. The molecular coordinate system chosen was based on the centroid and the least-squares molecular plane[22] of the carbocycle in an obvious manner.

B. *Calculation of ring current geometric factors (RCGF).* The Biot–Savart calculation of ring current contributions to chemical shifts has already been developed by Longuet-Higgins and Salem for the two-dimensional case.[9a, 11]

In the general case (Fig 1) the secondary magnetic field arising from *unit* current in the conductor segment *BC*, which is effective in shielding the proton at point A is given by

$$H'_z = \frac{|(\sin\phi_2 - \sin\phi_1)|}{c|DA|}\left(\frac{BC}{|BC|} \times \frac{DA}{|DA|}\right)|\cos\theta|$$

The location of the coordinates of the current loop segments with respect to the carbocycle is best illustrated by a consideration of the position of point C in Fig 1. Point C is taken to lie on the vector passing through C(2) perpendicular to the plane formed by C(1)-C(2)-C(3). This ring current position vector then, represents the locus of points through which the ring current will flow (on the assumption that the above procedure defines the vertical axis of the *p* orbital) for arbitrary current loop separations.

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* For practical reasons certain protons in some molecules were not included in the analysis. This usually stemmed from one or more of the following factors:

(a) Uncertainties in geometry.

(b) An absence of suitable model chemical shifts.

(c) Methyl group undergoing virtually free rotation (six-fold barriers).

† Studied as the 2,7-diacetoxy derivative.[25] H_2 and H_7 were assumed to lie along the C_2–$OCOCH_3$ and C_7–$OCOCH_3$ bonds, respectively.

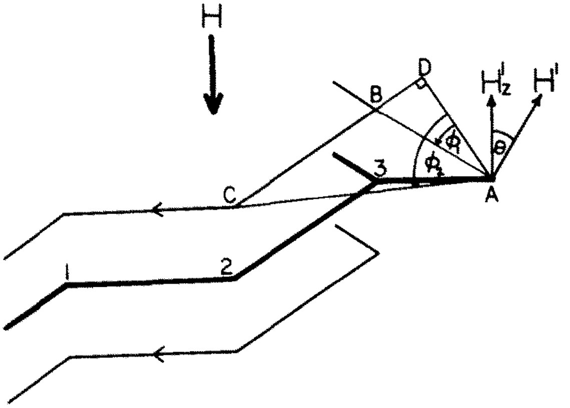

FIG 1. The Biot-Savart calculation of the shielding of proton A due to the ring current in the upper current loop segment BC of the 2-3 bond. H is the applied magnetic field, H' the induced magnetic field at A as a result of the current in BC, and H'_z the component of the induced field effective in shielding proton A.

The total shielding effect of the ring current on a proton is then obtained by summing the contributions from all the current segments in the molecule. The resultant parameter (for unit current) is the ring current geometric factor (RCGF).

C. *Ring current regression analysis.* The ring current (RC)* is calculated from the n observational equations:

$$RCCS_i = RC \times RCGF_i, \quad i = 1, \ldots, n$$

where n is the number of distinct chemical shifts observed for a given molecule. Standard techniques[37] were applied in the analysis although a modified standard deviation was used as a result of the relatively small number of observations generally obtainable for each compound. The sample standard deviation is taken as:

$$SD = \sqrt{\left(\frac{\sum_{i=1}^{n} (RCCS_i^o - RCCS_i^c)^2}{n}\right)}$$

where the superscripts o and c refer to observed and calculated parameters. Thus, the standard deviation of the ring current derived from the analysis (RCSD) becomes:

$$RCSD = \frac{SD}{\sqrt{\left(\sum_{i=1}^{n} RCGF_i^2\right)}}$$

D. *Multivariate regression analysis on ring current and triple bond anisotropy for dehydroannulenes.* The approach was based on the methods described above. Triple bond anisotropy geometric factors (TBAGF) were calculated by use of the double point dipole model.[39–41] The regression analysis (which was treated by standard techniques[42]) is of the form:

$$RCCS_{i,j} = RC_j \times RCGF_{i,j} + TBA \times TBAGF_{i,j}$$

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* The following units have been found convenient and are employed throughout. RCGF: cgs ($cm^{-2}t$) $\times 10^3$; RC: cgs (cm^2t^{-1}) ppt (parts per thousand of the magnetic field); the resultant product, RCCS is then in ppm

where TBA is the molar triple bond anisotropy (which is assumed constant for all triple bonds), and where the subscripts i and j refer to distinct chemical shifts and individual compounds, respectively.

E. *Analysis of variance as a function of current loop separation.* Two quantities are considered in this analysis:

$$\text{Chemical Shift Variance} = \frac{\sum_{i=1}^{m} \sum_{i=1}^{n} (RCCS^{o}_{i,j} - RCCS^{c}_{i,j})^2}{\sum_{j=1}^{m} n_i}$$

where m is the number of compounds included in the analysis.

$$\text{Average Standard Deviation (by compound)} = \frac{\sum_{j=1}^{m} \sqrt{SD_j}}{m}$$

With two exceptions,* all annulenes considered in this work with two or more different chemical shifts were included in the analysis (Fig 2).

NUMERICAL RESULTS

Preliminary calculations. The analysis of variance as a function of current loop separation is shown in Fig 2. The minima for the chemical shift variance and average standard deviation curves are given in Table 2. It should be noted that the positions of minimum variance are relatively insensitive to the deletion from the analysis of those compounds in which the occurrence of systematic errors might be suspected (Discussion).

The data presented above are construed as strong phenomenological evidence in favour of the line ring current model and indicate that a discrete current loop separation may be used to explain the chemical shifts of all compounds possessing an induced ring current. This evidence is based entirely on the chemical shift data and the Biot-Savart shielding model, and it is stressed that no assumption has been made regarding the magnitude or direction of the ring currents (merely that the ring current for each compound is unique).

It is now appropriate to consider the magnitude of the derived ring currents. Traditionally the benzene chemical shift has been used as a calibrant.[2c, 5r] Ideally, however, one would prefer to test the calculated parameters in an absolute and independent manner. Other evidence may be brought to bear on this problem by a consideration of diamagnetic susceptibilities (to which an induced ring current will make a substantial contribution). The lack of magnetic susceptibility data[5n, 9d] together with the absence of any complete theory[44] of magnetism in the annulenes eliminates most compounds considered here from any comparison of ring currents

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* The ions considered in this work (**20** and **21**) were not included in the analysis of variance as a function of current loop separation, as a result of the uncertainties in MCS values for charged species (see Model Chemical Shifts Section and refs 1, 14 and footnote * on p. 3620)

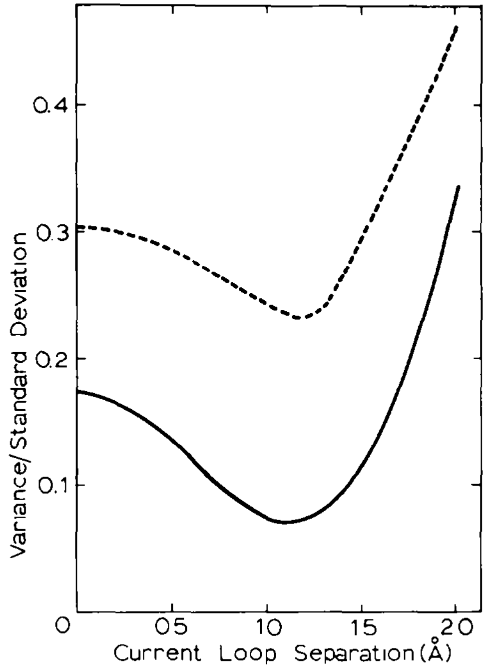

Fig 2. The chemical shift variance (———) (ppm^2) and the average standard deviation (- - - - -) (ppm) as a function of the current loop separation.

derived from chemical shifts and magnetic susceptibilities. However, a complete semi-empirical treatment for the diamagnetism of benzenoid hydrocarbons has been given by O'Sullivan and Hameka[45] which allows a detailed decomposition of the observed diamagnetic susceptibilities into individual contributions. Of this class of compounds only benzene and naphthalene† are considered here, as other members possess multiple ring currents.‡ The ring currents estimated from the regression

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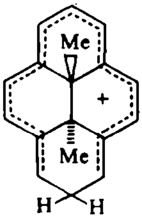
* The internal protons of **20** are very difficult to treat correctly in view of their known sensitivity to charge on the perimeter. Consider for example, the protonation product of **12**, the methyl groups of which



CF_3COO^-/CF_3COOH

absorb at τ9·37 and 9·77.[43] These values may be compared with the methyl chemical shift of *trans*-15,16-dimethyl-2,7,15,16-tetrahydropyrene given in Table 1

†From symmetry considerations naphthalene and cycl[3,3,3]azine (see footnote † p. 3630) possess a single (perimeter) ring current.

‡The Biot-Savart method is obviously not restricted *per se* to those compounds with only one ring current.

TABLE 2. ANALYSIS OF VARIANCE AS A FUNCTION OF CURRENT LOOP SEPARATION[a]

Omitted compounds	Separation with minimum variance (Å) Chemical shift variance	Average standard deviation
None[b]	1·12–1·13	1·18–1·19
1,6–Bridged-[10] annulenes and 1,6; 8,13-Dibridged-[14] annulenes	1·10–1·11	1·21–1·22
Dehydroannulenes	1·22–1·23	1·24–1·25
1,6-Bridged-[10] annulenes, 1,6; 8,13-Dibridged-[14] annulenes and Dehydroannulenes	1·25–1·26	1·27–1·28

[a] For definitions of quantities, see Computation Section

[b] See footnote on p. 3619

analysis on magnetic susceptibilities[45]* are reproduced by the chemical shift data at current loop separations in the range 1·10–1·11Å for benzene and 1·30–1·31Å for naphthalene.†

This dovetails very satisfactorily with the regression analysis on chemical shifts given above. Taken together the data presented here provide strong support for the model with a current loop separation of about 1·2Å. It seems that at this current loop separation we should be able to account for the chemical shifts of all types of annulene protons with ring currents of quantitative significance. It is on this premise that we proceed (Table 3).

Errors. The absolute errors quoted in Table 3 are the larger of the following two estimates: (1) random error—calculated by doubling the ring current standard deviation,‡ (2) systematic error§—taken as the maximum difference in derived ring current (from the value at 1·2Å) on allowing the current loop separation to vary from 1·0 to 1·4Å. For compounds with a single proton resonance (**1**, **9**, **25**) where no statistical error estimate is available, the range 0·9 to 1·5Å is used.

The errors are probably realistic for compounds which possess only external annulenic protons; for compounds with protons of more than one type the errors may be too large. Relative errors (particularly among structurally related compounds) will be considerably less than the absolute errors.

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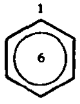
* The value obtained in ref 45 for the ring current contribution to the anisotropy of benzene is in good agreement with calculation. There is a vast literature on such calculations; for discussions and references see refs 1, 5*l*, *n*, *o*, *q*, *r*, 12, and 45. The most sophisticated calculation[5k,m] gives a slightly smaller value for the ring current diamagnetism, which if applied as outlined above would decrease the magnetically derived current loop separations by about 0·1Å, which is considered to be within the experimental error of the comparison and is not regarded as significant (*viz.* the differences observed for benzene and naphthalene).

† Unfortunately the precision of this estimate is rather low (see Discussion). Nevertheless, at least semi-quantitative agreement with this line of data is indicated.

‡ Note that we have used a modified standard deviation (Computation Section). For a normal distribution, the standard deviation (defined in the usual way) is 1·4826 times the probable error.

§ The main source of systematic error in this study is the approximation of a quantum mechanical current distribution by line currents. An objective estimate of the systematic error is difficult; the procedure used represents a doubling of the range of minimum variance of current loop separations shown in Table 2.



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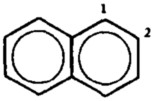

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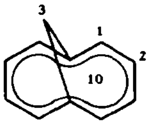

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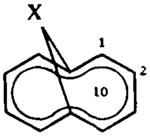
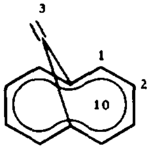


4: X = O
5: X = NH
6: X = NMe



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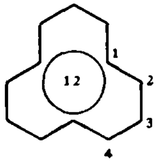

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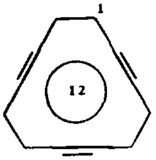

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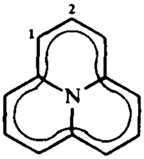

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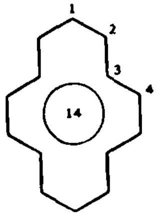

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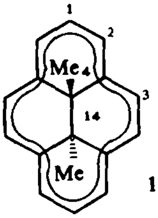

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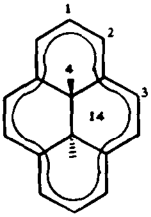

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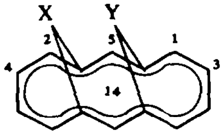

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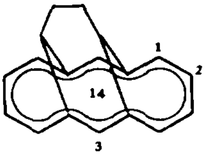
15: X = O; Y = CH_2



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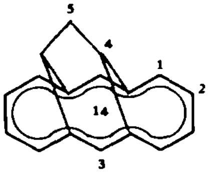

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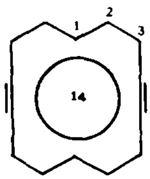

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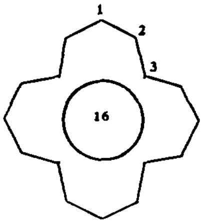

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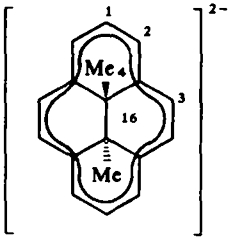

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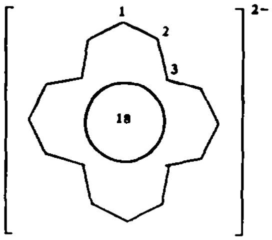

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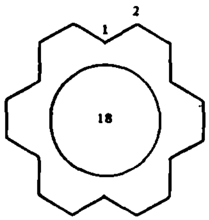

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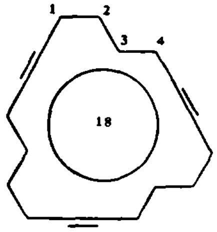

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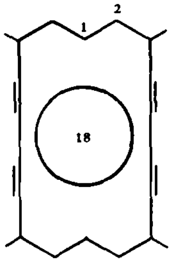

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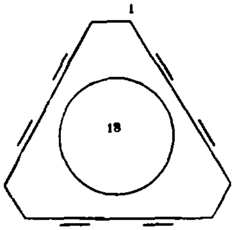

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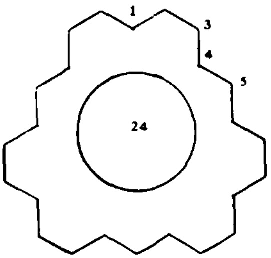

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TABLE 3. CALCULATED RING CURRENTS

	Chemical Shift (ppm)[a]									
	Observed (OCS)			Model (MCS)				Ring Current	Ring Current	
Compound	H	(τ)	Ref	(τ)	RCCS[b]	RCGF[c] (cgs × 10³)[d]	Deviation[e] (ppm)	Standard Deviation[e]	RC[c](cgs ppt)[d]	Absolute Error[f]
1	1	2·734	[j]	3.871	−1·137	0·95858	—	—	−1·1861	0·3513
2	1	2·315	[k]	3·871	−1·556	1·34720	−0·041	0·0258	−1·1247	0·1693
	2	2·662		3·871	−1·209	1·11872	0·049			
3	1	2·727	[l]	3·871	−1·144	1·18447	−0·241	0·0407	−0·7622	0·0814
	2	3·051		3·871	−0·820	1·27250	0·150			
	3	10·519		7·76	2·759	−3·65383	−0·026			
4	1	2·541	[l]	3·871	−1·330	1·18447	−0·151	0·0837	−0·9958	0·1673
	2	2·744		3·871	−1·127	1·27250	0·140			
5[g]	1	2·592	[m]	3·871	−1·279	1·18447	−0·196	0·1087	−0·9147	0·2173
	2	2·889		3·871	−0·982	1·27250	0·182			
6[g]	1	2·734	[m]	3·871	−1·137	1·18447	−0·173	0·0963	−0·8136	0·1926
	2	2·997		3·871	−0·874	1·27250	0·161			
7	1	2·585	[m]	3·871	−1·286	1·18447	−0·221	0·0891	−0·8991	0·1781
	2	2·984		3·871	−0·887	1·27250	0·257			
	3	6·808		5·52	1·288	−1·37970	0·047			
8	1	1·98	[n]	3·871	−1·891	−8·92697	0·017	0·0105	0·2137	0·0211
	2	4·35		3·871	0·479	1·51431	0·155			
	3,4[h]	4·11		3·871	0·239	1·39533	−0·059			
9	1	5·55	[o]	3·871	1·679	1·42154	—	—	1·1811	0·2482
10	1	7·93	[p]	3·871	4·059	1·51431	0·464	0·2572	2·3738	0·5144
	2	6·35		3·871	2·479	1·27635	−0·551			
11	1,2,4[i]	2·4	[q]	3·871	−1·471	1·57500	−0·297	0·0253	−0·7451	0·0507
	3	10·0		3·871	6·129	−8·30142	−0·056			

TABLE 3— *continued*

12	1	1·86	r	3·871	−2·011	1·38742	0·139	0·0209	−1·5495	0·0515
	2	1·37		3·871	−2·501	1·58857	−0·040			
	3	1·33		3·871	−2·541	1·68689	0·073			
	4	14·25		9·05	5·20	−3·30666	0·076			
13	1	2·03	s	3·871	−1·841	1·38742	0·258	0·0245	−1·5128	0·0491
	2	1·50		3·871	−2·371	1·58857	0·032			
	3	1·42		3·871	−2·451	1·68689	0·101			
	4	15·49		7·14	8·35	−5·44916	0·106			
14	1,2	2·25	t	3·871	−1·621	1·33421	−0·024	0·0373	−1·1969	0·1835
	3,4	2·40		3·871	−1·471	1·33044	0·121			
	5	2·06		3·871	−1·811	1·43782	−0·090			
15	1	2·346	u	3·871	−1·525	1·33421	−0·111	0·0428	−1·0596	0·1606
	2	2·358		3·871	−1·513	1·33421	−0·099			
	3	2·664		3·871	−1·207	1·33044	0·203			
	4	2·571		3·871	−1·300	1·33044	0·110			
	5	2·254		3·871	−1·617	1·43782	−0·094			
16	1	2·43	v	3·871	−1·441	1·33421	−0·080	0·1117	−1·0200	0·2234
	2	2·88		3·871	−0·991	1·33044	0·366			
	3	2·14		3·871	−1·731	1·43782	−0·264			
17	1	2·264	w	3·871	−1·607	1·33421	−0·086	0·0184	−1·1402	0·0368
	2	2·446		3·871	−1·425	1·33044	0·092			
	3	2·115		3·871	−1·756	1·43782	−0·117			
	4	11·157		7·14	4·017	−3·59028	−0·077			
	5	10·611		8·22	2·391	−2·04756	0·056			
18	1	15·48	x	3·871	11·609	−7·80909	−0·207	0·0663	−1·5131	0·1327
	2	0·36		3·871	−3·511	1·71740	−0·912			
	3	1·46		3·871	−2·411	1·57189	−0·033			
19	1,2[i]	4·80	y	3·871	0·929	1·53987	−0·039	0·0042	0·6288	0·0182
	3	−0·32		3·871	−4·191	−6·65021	−0·009			

TABLE 3. CALCULATED RING CURRENTS—*continued*

	Chemical Shift (ppm)[a]							Ring Current	Ring Current	
	Observed (OCS)			Model (MCS)						
Compound	H	(τ)	Ref	(τ)	RCCS[b]	RCGF[c] (cgs × 10^3)[d]	Deviation[e] (ppm)	Standard Deviation[c]	RC[c](cgs ppt)[d]	Absolute Error[f]
20	1	13·30	z	5·30	8·00	1·38742	0·018	0·2103	5·7534	0·4207
	2	13·40		5·30	8·10	1·58857	−1·040			
	3	13·96		5·30	8·66	1·68689	−1·045			
	4	−11·0		9·05	−20·05	−3·30666	−1·025			
21	1	2·55	aa	5·12	−2·57	1·64873	0·375	0·0458	−1·7861	0·0916
	2	1·17		5·12	−3·95	1·93912	−0·487			
	3	18·17		5·12	13·05	−7·33118	−0·044			
22	1	12·26	bb	3·871	8·389	−7·09849	−0·160	0·0589	−1·2043	0·1178
	2	0·97		3·871	−2·901	1·91776	−0·591			
23	1	2·98	cc	3·871	−0·891	1·65510	0·180	0·0531	−0·6470	0·1062
	2	1·90		3·871	−1·971	1·85023	−0·774			
	3	8·26		3·871	4·389	−7·08202	−0·193			
	4	2·44		3·871	−1·431	2·03270	−0·116			
24[j]	1	15·24	dd	3·871	11·369	−7·43542	−0·183	0·0728	−1·5537	0·1457
	2	0·34		3·871	−3·531	1·77965	−0·766			
25	1	2·98	ee	3·871	−0·891	1·60265	—	—	−0·5560	0·1030
26	1,4[i]	−2·05	ff	3·871	−5·921	−6·50447	−0·157	0·0522	0·8862	0·1045
	2,3,5[i]	5·27		3·871	1·399	2·12083	−0·481			

[a] No account is taken of solvent effects. All MCS and most OCS values have been obtained in one of the standard nmr solvents (CCl_4, $CHCl_3$, or alkanes). Where chemical shift discrepancies exist in the literature those values given in ref 1 were used in the analysis. Where a temperature dependence of the chemical shifts has been reported, the values obtained from the non-mobile spectrum nearest to 25° were used. Annulenes **8**, **11**, **19**, **22** and **26** all exhibit mobile nmr spectra at 25°, and the non-mobile nmr data quoted were obtained at considerably lower temperatures. The conformational behaviour and nmr spectra of these molecules are fully discussed in ref 1

[b] Observed Ring Current Chemical Shift (see footnote on p. 3614)

[c] For definitions see Computation Section

[d] For units see footnote on p. 3618

[e] Observed RCCS—Calculated RCCS

[f] See text

[g] See footnote * on p. 3617

[h] Incomplete assignment. Average value used

[i] Incompletely resolved. Average value used

[j] F. A. Bovey, *NMR Data Tables for Organic Compounds*, Vol. 1, New York, N.Y., Interscience (1967)

[k] See footnote * on p. 3628

[l] Ref 51

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[dd] J. Ojima, T. Katakami, G. Nakaminami and M. Nakagawa, *Tetrahedron Letters* 1115 (1968)

[ee] Ref 57

[ff] I. C. Calder and F. Sondheimer, *Chem. Commun.* 904 (1966)

DISCUSSION

In general the method appears to give an adequate description of the chemical shifts of the large variety of annulenes included in the study. Due to the absence of previous data, no discussion of the derived ring currents can be entertained.[14] The agreement between observed and calculated chemical shifts of difficult cases is considered below, but in the main discussion centers on the structures employed and additional contributions to the chemical shift.

Benzene and naphthalene. We have already remarked on the disagreement between benzene and naphthalene; their great sensitivity to current loop separation makes them rather unsuitable for this type of study and indicates that it would be impractical to attempt the calculation of ring currents from the chemical shifts of benzenoid hydrocarbons.

Although the annulenic MCS is taken to be invariant for this class of compounds the small variation that probably does occur becomes very significant and would have to be taken into account for a complete description of the chemical shifts of these compounds. The recent re-analyses of the naphthalene spectrum* make it unlikely that the relative benzene, naphthalene chemical shifts can be completely reconciled using an identical MCS. The differences are very small however, for an error of 0·1 ppm (of the expected sign[12]) in the benzene MCS would remove most of the disagreement between these compounds.†

1,6-Bridged-[10]*Annulenes* (**3**, **4**, **5**, **6**, **7**) *and* 1,6;8,13-*dibridged-*[14]*annulenes* (**14**, **15**, **16**, **17**). The RCGF values obtained for the ring protons of the 1,6-bridged-[10]annulenes probably represent the most serious failure of the method (as constituted). This reversal in magnitude of the RCGF values persists at all current loop separations and the disagreement is a maximum in the plane of the ring. The ring chemical shifts in these compounds are not therefore analogous to the naphthalene values.[51] The differences arise from the non-planarity and unique geometry of the 1,6-bridged-[10]annulenes.[24, 29, 30]

A partial understanding may be obtained, however, by a consideration of the positioning of the current loops in these molecules as defined by the ring current position vectors (Computation Section). Due to the unnatural angles in these compounds the current loops derived from our procedure are far from being directly above and below the carbocycle (as they are in a planar molecule). If the current loops are forced to lie directly over the carbocycle, the ring RCGF values converge as the current loop separation is increased, become equal at about 0·7Å, and at 1·2Å give a reasonable description of the observed chemical shifts (the ring current standard deviations are considerably reduced). It is difficult to assess the validity of this procedure. On the assumption that the line current should flow through the locus of maximum cross-sectional electron density of the carbon *p* orbitals, the evidence would indicate that the *p* orbitals deviate considerably from their expected orientation. Fortunately, however, the ring currents derived from this procedure are virtually unchanged (slightly reduced) and still lie well within the quoted errors. This, together

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* The chemical shift values for naphthalene are taken from the most recent analysis, in which CS_2 was used as a solvent.[48] Earlier determinations[2c, 50] lead to somewhat better correspondence between benzene and naphthalene, and slightly reduce the optimum current loop separation for naphthalene (to 1·2–1·3Å).

† It has been suggested that gas phase chemical shifts may be necessary in order to completely reconcile the relative ring currents in this series (Prof. L. M. Jackman, personal communication, 1971).

with the fact that the bridge groups are in good agreement indicates that the errors in the ring RCGF values are self-cancelling.

The geometry of the 1,6;8,13-dibridged-[14]annulene perimeter is more natural, and in contrast to the 1,6-bridged-[10]annulenes, these compounds are reasonably well described by the method (as applied); re-positioning the current loops in the manner described above does not improve the agreement. Furthermore, that the *p* orbitals are not vertical follows from a consideration of the *syn*-bridged and *anti*-bridged homologues which would be expected to have very similar π-electron properties if the *p* orbitals were upright (irrespective of the ring geometry). The only *anti*-1,6;8,13-dibridged-[14]annulene which has been isolated is olefinic, in contrast to the *syn*-bridged isomers all of which appear to be aromatic.[52]

1,6;8,13-Butano-[14]annulene (**16**) shows the largest chemical shift deviations, which is probably because the internal butano group cannot be accommodated without a deformation of the ring. This is in constrast to 1,6;8,13-propano-[14]annulene (**17**) where the presence of the internal bridge does not disturb the overall geometry of the molecule, which is very similar to *syn*-1,6;8,13-dioxido-[14]annulene (**14**).[26,34]

Annulenes (**8**, **11**, **19**, **22**, **26**). Due to the non-bonded interactions of the internal hydrogens, [12]annulene (**8**) and [14]annulene (**11**) are expected to deviate considerably from the planar geometry used in the calculation. Distortions from planarity somewhat reduce the calculated RCGF values, and as a result the ring currents in these two molecules may be slightly underestimated.

The correspondence between the crystallographic and solution structures of [16]annulene (**19**) and [18]annulene (**22**) is probably not quite so close as might be expected for the more rigid internally bridged molecules.[54] Nevertheless, while solution geometries would be preferable, the crystallographic structures provide a sufficiently good model for our present purposes.

The uncertainty in the conformation of [24]annulene (**26**) together with the poor nmr data dictate a rather low confidence level for the derived parameters of this compound.

It is interesting to note the decrease in magnitude of the RCGF values for internal protons as the ring size increases, whereas an opposite trend is evident for the outer protons. Apparently the chemical shifts of the internal protons of very large annulenes will not be quite so sensitive to the presence of ring currents.

Dehydroannulenes (**9**, **18**, **23**, **24**, **25**). An attempt to include the effects of molar triple bond anisotropy (TBA) on chemical shifts in the dehydroannulenes[39-41] was not successful (Computation Section). The value derived from the ring current and triple bond anisotropy analysis on all the dehydroannulenes indicated a TBA of +5·26 cgs ppm. On the assumption that TBA values might vary among different compounds, we also subjected **18** and **23** to individual analyses (only these two dehydroannulenes have more than two distinct chemical shifts), and again the derived values were positive (2·63 and 3·11 cgs ppm, respectively). While recent determinations have indicated that the diamagnetism may have previously been overestimated,[40] and while conjugation would be expected to reduce the anisotropy of the triple bond by quenching the induced electronic circulations, there is certainly no evidence for a positive triple bond anisotropy.[40,39–41,55]

Furthermore, in none of the above analyses were the deviations significantly reduced, and from a purely statistical point of view there was no justification for the inclusion of this extra variable in the analysis of the chemical shifts. However, the triple bonds almost certainly make a contribution to proton shielding constants, and the best approach may be to allow for their presence by selecting model chemical shifts from structurally analogous compounds.[56] The chemical shifts of protons attached to double bonds in linear conjugation with acetylenic units are quite sensitive to their immediate environment (generally falling in the range τ3·0–4·5),[56,57] but in no obvious geometric manner. Recourse to simple models has not clarified the matter,[41] but the development of structurally related iso-conjugate model compounds does appear to offer a partial solution.[56] In the interests of a unified and straightforward approach we have retained the annulenic MCS in this study but exploratory calculations with iso-structural models indicate that the chemical shift deviations are considerably reduced by this scheme. The chemical shift disagreement for proton H-2 of compounds **18**, **23** and **24**, which appears to be the main source of error in the analysis, is completely removed by this approach. With the exception of **9** and **25** the derived ring currents are virtually unchanged. Our confidence in the analysis of these two compounds is lessened accordingly. However, at such time as model chemical shifts for specific dehydroannulene environments have been reliably established, this would become the preferred approach.

Cycl[3,3,3]*azine*. The large chemical shift deviations observed for cycl[3,3,3]azine (**10**) are somewhat perplexing at first sight. The answer apparently lies in the large peripheral charge densities which are expected to be developed in this molecule.[47] While the bridging N atom does not interfere with the application of the method,*† it does allow a perturbation of the perimeter which could not occur in an unbridged [12]annulene. If the calculated charge densities[47] in conjunction with the MCS charge correction‡ (Table 1) are applied to **10** the standard deviation falls to 0·0582, although the ring current is only changed to 2·2684 cgs ppt.

Trans-15,16-*Dihydropyrenes* (**12**, **13**). The small difference in ring current calculated for *trans*-15,16-dimethyldihydropyrene (**12**) and *trans*-15,16-dihydropyrene (**13**) may not be significant, as different solvents were used for the two nmr determinations.[58,59]

Dianions (**20**, **21**). There are a number of difficulties in correctly treating charged annulenes:[15] apart from the problems of model chemical shift ‡ and geometry, the change distribution in the *trans*-15,16-dimethyldihydropyrene dianion (**20**) and the [16]annulene dianion (**21**) are not symmetry dictated (unlike the smaller regular polygonal systems[14]). Nevertheless these compounds are too important to be omitted from any treatment of ring currents in annulenes. While **20** and **21** were not included in the analysis of variance as a function of current loop separation §, the minima are quite reasonable (1·3–1·4 and 1·0–1·1Å, respectively).

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* From symmetry considerations naphthalene and cycl[3,3,3]azine† possess a single (perimeter) ring current.

† Although a bond equalized geometry (D_{3h} symmetry) is assumed for cycl[3,3,3]azine (dynamic rather than static Jahn–Teller effect[46]), even in the presence of a permanent distortion (C_{3h} symmetry)[47] no current will flow through the cross links.

‡ For all compounds in this study to which the MCS charge correction is applied (**10**, **20**, **21**), an improved correspondence between observed and calculated chemical shifts may be obtained by a reduced value for the dependence of chemical shift on charge density (Table 1).

§ See footnote * on page 3619

SUMMARY AND CONCLUSIONS

A general treatment of ring currents in annulenes based on a split loop Biot-Savart model has been shown to give a consistent description of chemical shifts in annulenes. The sign of the ring current contribution to the proton chemical shifts is correctly predicted in all cases. The relative magnitudes of the chemical shifts are also correctly described with the exception of compounds **3**–**7** and **23**, for which the discrepancies are minor and subject to reasonable explanation. It is therefore concluded that ring currents may be reliably estimated, at least for those annulenes which give rise to a broad range of proton chemical shifts.

The success of the ring current model in reproducing the chemical shifts of these systems strengthens the feeling that this property is an appropriate quantity to consider in relation to the magneto-electric characteristics of annulenes.[14]

The analysis of the remaining* annulenes, dehydroannulenes and bridged annulenes is attendant only on the availability of geometries (and model chemical shifts in some cases). The application of the model to homoannulenes will provide a further interesting extension.

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