

Measuring Aromaticity by NMR

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I. Introduction

NMR is without doubt the most frequently used experimental tool to decide whether a molecule is aromatic. Deciding *how* aromatic is a more difficult problem, especially if the *how* is to be determined experimentally. Given the contentious nature of *aromaticity*, some may question whether one should bother to try to quantify something one cannot clearly define. In addition, the recent improvements to desk computers make NICS calculations¹ now much easier to do, such that it might appear that further experimental work is unnecessary. As this review will show, experiments can be defined to test whether aromaticity can be measured and the results are not always consistent with expectations from calculations.

Balaban's books^{2a} give an excellent survey of the annulenes and their derivatives, but do not have an extensive section on aromaticity criteria. Several recent papers^{2b} talk about aromaticity and its measurement but do not survey the use of NMR for this purpose. In this review, attempts to measure aromaticity using NMR will be discussed in greater detail and, for convenience, can be divided in to three parts: (i) by comparison of ring currents in different molecules, (ii) by bond localization effects of annulenes on a benzene probe, and (iii) by use of an annulene probe to compare the test molecule to the prototype aromatic, benzene, and hence estimate the delocalization energy of the test molecule under investigation.

II. Comparison of Ring Currents

Consider the five molecules and their chemical shifts shown in Scheme 1. Simple examination of

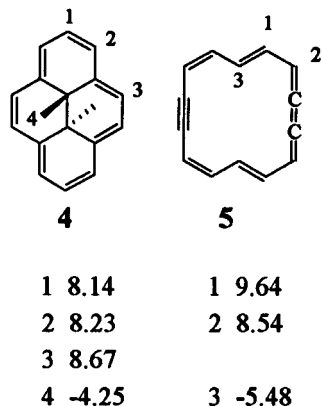
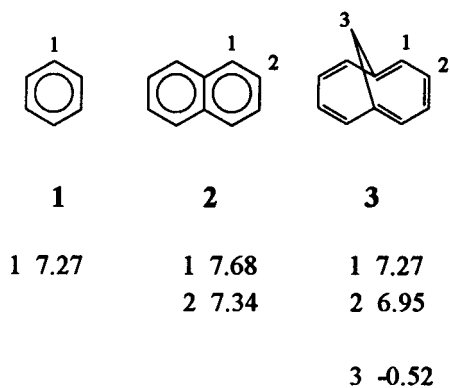


Reg Mitchell went to school in South London, England. There, a chemistry teacher demonstrated the NO-CS₂ reaction, and the bright blue light convinced Reg to study chemistry instead of math. Now, some 40 years later, he does that same experiment and many others as Dr. Zonk in a chemistry show for all ages. Reg studied chemistry at Cambridge, obtaining his Bachelor's degree in 1965 and his Ph.D. degree in 1968 under the direction of Professor Franz Sondheimer. He went to Eugene, OR, for two years as a postdoctoral fellow with Virgil Boekelheide and then returned to the United Kingdom to the plastics industry for two years. In 1972, the pull of the west coast of North America was too strong and he took up his current position at the University of Victoria. He was promoted to Full Professor in 1982. As Dr. Zonk, he has demonstrated the wonders of chemistry to more than 40 000 school children and has organized the regional science fair for 25 years, which together with a monthly radio show "on the chemistry of everyday life" resulted with him being awarded the 2000, BC Science Council "Science Communicator" Award. He has published 130 papers containing interesting aromatic hydrocarbons.

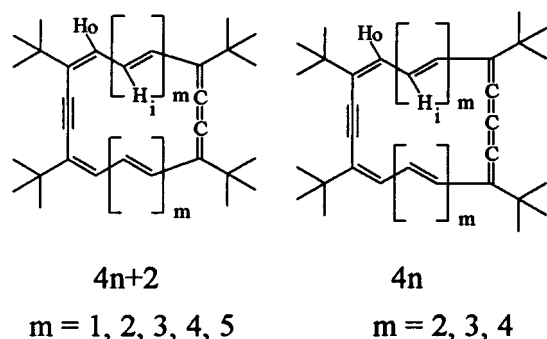
these chemical shifts clearly shows the molecules all to be aromatic, because outside protons are all deshielded and inside protons are shielded. However, the shifts by themselves do not enable one to state which is most aromatic. Haddon³ applied the Biot–Savart Law to a ring current analysis of these and other annulenes and calculated a degree of aromatic character by expressing the fraction of the maximum ring current that each molecule displays and finds the order **1** (1.00) \approx **4** (1.00) > **5** (0.89) > **3** (0.73). Naphthalene (**2**), as do other polycyclic aromatics (note: **3** and **4** are regarded as monocyclic in this context), causes a problem because of the cross-linking of the sp² system. Local anisotropic effects⁴ can also substantially affect proton shieldings in polycyclic aromatics and dehydroannulenes. Thus, although Haddon's paper was extremely significant, it is not a trivial exercise to compare aromaticities in this way, though Boekelheide⁵ was later able to successfully use it on the hexahydrocoronenes. Perhaps the first "simple" comparison of aromaticities

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Scheme 1

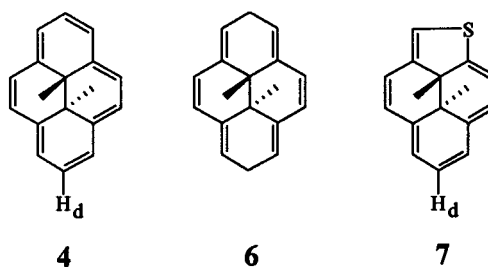


Scheme 2



using ring currents was made by Hess, Schaad, and Nakagawa,⁶ where for the two series of annulenes shown in Scheme 2, they let the difference in chemical shift of the inner and outer protons represent the "ring current" of the molecule. Since both the geometries (shape) and structures (arrangements of atoms) for these series of molecules are similar, the assumption is made that local anisotropies will cancel out or not be that significant. Indeed, they found that the magnitude of the "ring current" fell with the number of π -electrons (N) and was approximately linearly proportional to the resonance energy per electron (REPE), both for examples from the $4n + 2$ series, where $N = 14, 18, 22, 26,$ and 30 , and from the $4n$ series where $N = 16, 20,$ and 24 . This was probably the first demonstration where an easily measured property (chemical shift) was used to represent a theoretical property (ring current) which then might be correlated to a more classically derived theoretical quantity (resonance energy). Haddon⁷ and Aihara⁸ solidified this idea by showing the relationship

Scheme 3



between resonance energies (RE) and ring currents (RC): $RE = k \cdot RC/A$ where $A =$ ring area and k is a constant. Verbruggen⁹ was then able to take the data for the compounds of Scheme 2 and show that they fit eq 1

$$\Delta\delta/A = k \cdot REPE \quad (1)$$

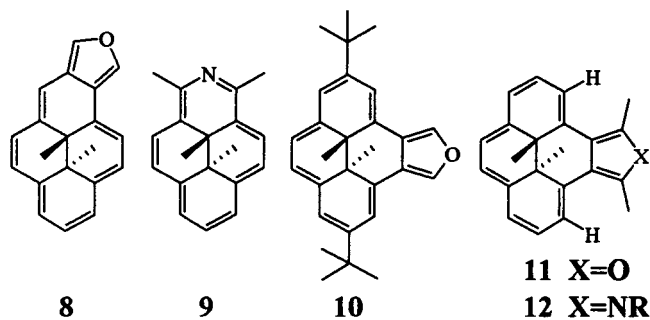
where $k = 2.7$, when REPE is expressed in β units, and $A_{\text{benzene}} = 1$.

To use chemical shifts as a measure of ring currents to comment on aromaticity, systems have to be chosen in which the molecules to be compared have similar geometries and have anisotropic effects which cancel out during the comparison. Unfortunately, there are relatively few such systems. One is *trans*-10b,10c-dimethyldihydropyrene, (**4**). The internal methyl protons of **4** appear at $\delta -4.25$, and this value does not change much (up to 0.3 ppm) for most substituents.¹⁰ Moreover, the shielding due to the ring current is large, ~ 5.2 ppm by comparison to the nonconjugated model **6** (δ 0.97). The molecule is remarkably planar,¹¹ with the internal methyl protons almost above and below the center of the molecule and the π -cloud. These hardly move on annelation or substitution, and so mostly only through-space anisotropy effects have to be considered.¹² Thus, the relative ring currents of the parent [14]-annulene **4** and its thia-analogue **7** shown in Scheme 3 can directly be estimated¹³ from the relative shieldings of the internal methyl protons: In **7**, the internal methyl protons are shielded 2.21 ppm from those in **6**, relative to the 5.22 ppm for those of **4**. The aromaticity of **7** relative to **4** is thus $2.21/5.22 = 0.42$. This ignores any through-space effect of the sulfur atom, which is about 4 Å away from the methyl protons, and the small difference in area of the two molecules.¹³ A second check is given by the most distant protons, H_d . The shifts for **4**, **7**, and model are δ 8.14, 6.85, and 6.13 respectively, which would lead to a relative aromaticity for **7** of 0.36, in reasonable agreement with the value determined from the methyl proton shifts. In a variety of benzannelated analogues of **4**, the relationship

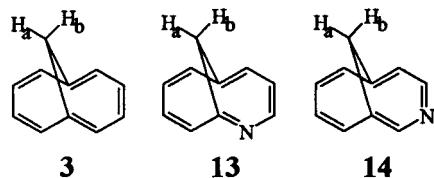
$$\delta(\text{Me}) = 17.515 - 2.685\delta(H_d) \quad (2)$$

was found.¹⁴ For **7**, $\delta(\text{Me})_{\text{calc}} = -0.88$ while $\delta(\text{Me})_{\text{found}} = -1.24$, so it seems likely that the sulfur atom does have a small effect (~ 0.3 ppm) but not much beyond our initial statement for substituents. This 0.3 ppm is only 6% of the total ring current of **4**. Thus, in a relatively simple manner, it can be determined that the thiophene like thia[13]-annulene **7** has about 35–

Scheme 4



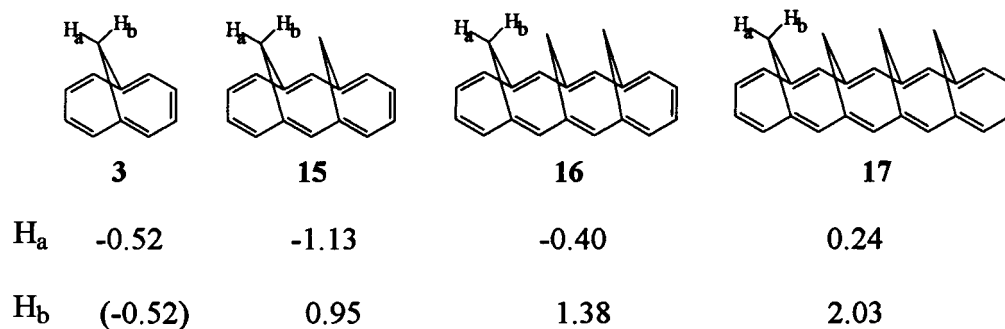
Scheme 5



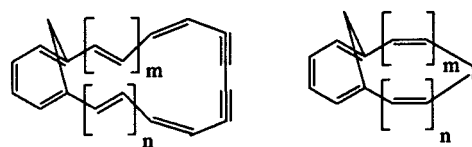
40% of the aromaticity of the [14]-annulene parent **4**. Analogously, the furan-like oxa[17]-annulene (18π) **8**¹⁵ and the pyridine-like aza-annulene **9**¹⁶ have about 13% and 95% of the maximum ring currents, respectively.

In such systems, by consideration of both inside and distant external protons, the relative aromaticities can be estimated to about $\pm 3\%$. In the dihydropyrene system, the ring geometry does not seem to be critical. We recently¹⁷ made **10**, the internal methyl protons of which are at δ 0.18; those of the isoelectronic **8** are at δ 0.13 and 0.15! However, for the ring current estimation to be reliable, the molecule must not change planarity much. Lai¹⁸ prepared **11**, the dimethyl derivative of **10**. The relatively severe steric interaction between the external methyl protons and external 14-ring hydrogens, a "bay"-type interaction, reduces the planarity substantially and reduces the ring current of **11** to about 7% of that of **4**, compared to about 16% for the nonmethylated **10**. However, the oxa-**11** can be compared with the aza-**12** ($R = \text{cyclohexyl}$).¹⁸ The latter sustains 27% of the current in **4**, compared to 7% for the former. Clearly pyrrole-like annulenes are more aromatic than furan-like annulenes. Unfortunately, Lai has not yet reported the analogous thia-annulene. In principle, Vogel's¹⁹ 1,6-methano[10]-annulenes should give alternative measurements. However, the positioning of the nitrogen atom relative to the reference internal protons is not insignifi-

Scheme 6

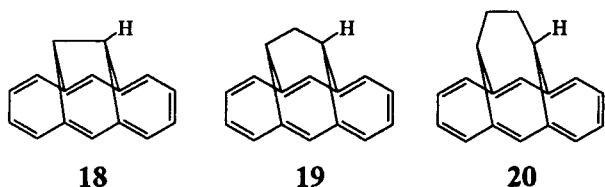


Scheme 7



cant and can affect their chemical shift. For example, in the aza[10]-annulene **13**,²⁰ H_a (δ 0.73) and H_b (δ -0.33) differ in chemical shift by over 1 ppm, while in isomeric **14**,²¹ H_a (δ -0.18) and H_b (δ -0.01) are much closer in chemical shift. Comparison of the latter to the parent annulene **3**²² (δ -0.52) indicates most of the ring current is retained. A more definitive estimate requires a model chemical shift for the bridging methylene protons: assuming³ a value of δ 2.24 would suggest that **14** has about 88% of the ring current of **3**. Vogel²³ reported the proton NMR spectra of the nice homologous series **3**, **15**, **16**, and **17**. The H_a shown in Scheme 6 is always the most shielded of the bridging methylene protons; H_b is much less so, and ring current appears to fall along the series, though no quantitative estimates have been made. Since Haddon⁷ has shown the ring current depends on the ring area (A) and the number of π -electrons, quantitative relative aromaticities are not so easy to obtain. Müllen,²⁴ in discussing the NMR data of the dianions and dication of these and related molecules, suggests that $\Delta\delta(H)/A$ can be used as a rough measure of the ring currents. Using δ 2.24 as the reference model (see above), $\Delta\delta(H_a)/A$ values for **3**, **15**, **16**, and **17** are then 1.38, 1.12, 0.66, and 0.40, which thus support the decay of diatropicity with increasing ring size. Ojima prepared several series of methano-bridged dehydroannulenes²⁵ and heteroannulenes²⁶ (Scheme 7), and both diatropism and paratropism fall with ring size, though quantification was not made. There are literally hundreds of papers which use the chemical shifts of inside or outside protons to indicate whether the molecule is diatropic or paratropic. Very few venture to attempt to quantify this, in part because of the difficulties in comparing different ring skeletons with different numbers of π -electrons and even different charges. For example, Müllen²⁴ compares a series of dianions and dication derived from bridged $[4n+2]$ -annulenes (paratropic systems). Differentiation of the charge and ring current effects is not trivial, especially when the annulenes are not planar. For example, the 16π dianions of **18**, **19**, and **20** (Scheme 8) show downfield shifts of their internal protons of 14.8, 11.5, and 10.9

Scheme 8

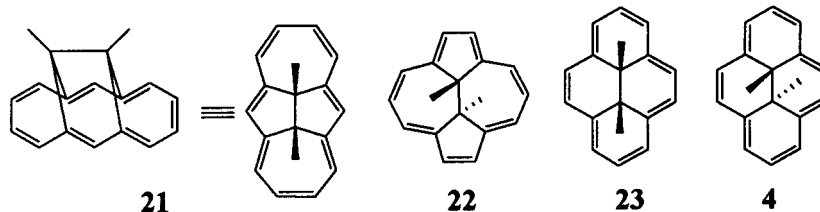


ppm, respectively, from their neutral 14π annulenes ($\delta -1.82$, -1.16 , and -0.96 , respectively). The greater the bending of the perimeter, the less the downfield shift. Paratropic systems evidently seem more sensitive to bending than diatropic ones.

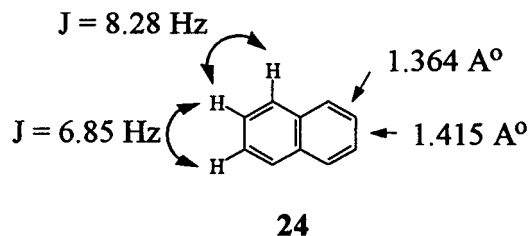
An instructive series of compounds is shown in Scheme 9. All are isomeric 14π systems with the same internal bridge. The protons of this series appear at $\delta -1.82$,²⁵ -4.53 ,²⁶ -2.06 ,²⁷ and -4.25 .²⁸ At first glance, it might appear that **22** and **4** are substantially more diatropic than **21** and **23**. However, whereas the internal methyl protons of **4** are almost over the center of the molecule, those of **23** are not, being further displaced to the side away from the center. This moves them out of the center of the ring current, where it is most shielding. This author believes that this is the principal reason for the large change in chemical shift. Models indicate that **23** is saucer-shaped, with a greater torsion angle between adjacent p orbitals;¹⁰ nevertheless, the outside protons, δ 8.74, 8.24, and 7.50, are not very different from those of the almost planar **4** at δ 8.64, 8.60, and 8.11, indicating that the ring current is not that different. Similar arguments can be used for **21** (δ 8.17, 8.00, 7.82) and **23** (δ 8.77, 8.74, 8.04). The positions of the outside protons would suggest that all four bridged annulenes have strong ring currents. *In comparing internal protons, care must be used that the protons are similarly situated with respect to the center of the ring.* This obviously makes comparisons between different systems quite difficult. Charged annulenes also require much care in comparison. The dianions of **21**, **22**, and **4** have their internal methyl proton signals shifted downfield by 9.6, 16.5, and 25.3 ppm, respectively, from the neutral annulenes, a difference not easily explained.²⁴ Both Müllen and Vogler²⁹ carried out similar studies on the di- and tetraanions of some of the compounds shown in Scheme 2.

In conclusion, "measuring" aromaticity by comparison of chemical shifts as representations of ring current is possible, provided the examples are chosen carefully. The protons to be compared must be located in similar regions³⁰ of the magnetic field; the molecules must have similar planarity and not be subjected to strong anisotropic or charge effects.

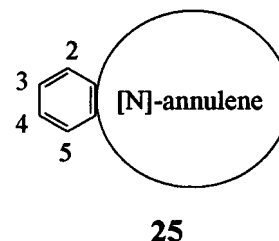
Scheme 9



Scheme 10



Scheme 11



III. Bond Localization Effects

In 1972 Günther³¹ published a "landmark" paper on using the benzene nucleus as a probe for the π -electronic structure of the annulenes. This is based on the fact that whenever two annulenes are fused together, some bond localization occurs in each. This can be seen structurally in Scheme 10 for naphthalene (**24**) and results in unequal bond lengths and coupling constants for adjacent bonds. Günther was able to correlate the degree of bond localization with the nature ($4n + 2$ or $4n$) and the number of π -electrons (N). He initially used HMO calculations and found that the ratio of adjacent bond orders, $P_{2,3}/P_{3,4}$ (Scheme 11), was greater than 1 if $N = 4n + 2$ and less than 1 if $N = 4n$. This ratio of bond orders has become known as the Günther " Q value". In the case of naphthalene (Scheme 10), $P_{2,3} = 0.725$ and $P_{3,4} = 0.603$, so $Q = P_{2,3}/P_{3,4} = 1.202$. Further calculations indicated that cyclic polyenes or even linear olefines gave Q values of 1.04–1.10 and thus from the point of view of testing whether the $[N]$ -annulene was aromatic or not, decided on the following values

If $Q > 1.14$, then the $[N]$ -annulene is aromatic

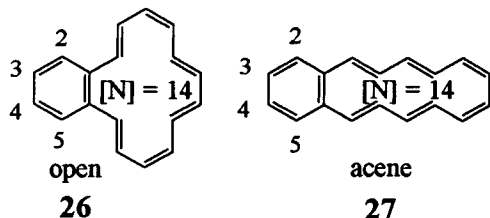
If $Q < 1.03$, then the $[N]$ -annulene is antiaromatic

One should stress that these are calculated values and assume flat structures. Table 1 shows some examples.

He also carried out these calculations using a PPP π -SCF method which allows a differentiation between different geometries of the $[N]$ -annulene (Scheme 12).

Table 1. Günther³¹ HMO Q Values for **25**

N	Q	N	Q
6	1.202	4	0.769
10	1.173	8	0.901
14	1.159	12	0.961
18	1.150	16	0.997

Scheme 12**Table 2.** Günther³¹ π -SCF Q Values for **25** with Geometries **26** and **27**.

N	Q (26)	Q (27)	N	Q (26)	Q (27)
6	1.262		4	0.782	
10	1.196	1.221	8	0.930	
14	1.143	1.195	12	0.984	0.988
18	1.108	1.177	16	1.016	1.018
22	1.082	1.160	20	1.016	1.036

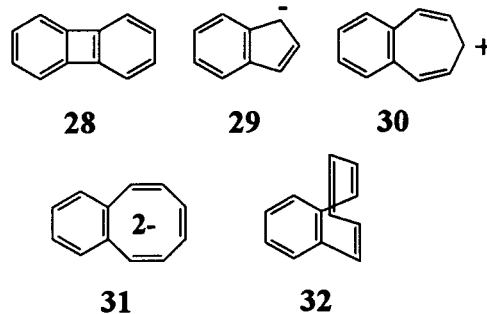
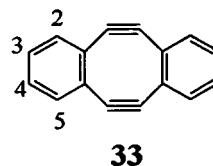
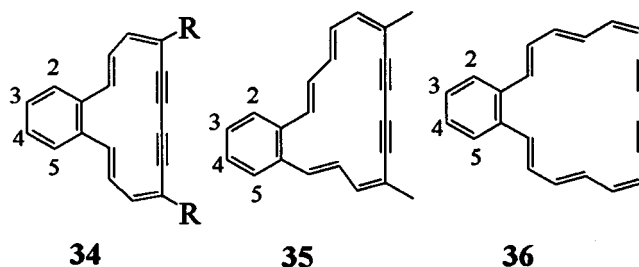
Table 2 shows some of the results for the “open” (pyrene-like) and “acene” (anthracene-like) geometries for several benzo[N]annulenes.

Those with the acene geometry (**27**) appear to have greater localizing power than those of open geometry, type **26**. What are the consequences of this work for “measuring aromaticity by NMR”? Fortunately, bond orders can be estimated from $^3J_{\text{cis}}$ coupling constants, which are fairly easy to measure. Günther³¹ found that on the basis of SCF data and coupling constants for benzene, naphthalene, and anthracene

$$P_{n,m}(\text{SCF}) = 0.104^3 J_{n,m} - 0.120 \quad (3)$$

Thus, by measuring the values for $J_{2,3}$ and $J_{3,4}$ in any benzannulene **25** and use of this equation to calculate bond orders and then Q , a statement as to whether the annulene is aromatic, antiaromatic, or nonaromatic in nature can be made. From a simple viewpoint, if in **25** $J_{2,3} > J_{3,4}$ (see naphthalene, for example, in Scheme 10), then the [N]annulene is aromatic, while if $J_{3,4} > J_{2,3}$ (for example, the values in biphenylene (**28**) are 8.24 and 6.80 Hz, respectively), then the [N]annulene is antiaromatic (in that case the [N]annulene is benzocyclobutadiene). In the subsequent paper,³² this method was used to compare the ions of small benzannulenes, including benzen-related cyclopentadiene (indenyl anion, **29**), benzotropylium ion (**30**), and benzocyclooctatetraene dianion (**31**), which all had Q values indicating strongly aromatic systems. That found for benzocyclooctatetraene itself (**32**) fell in to the nonaromatic range, as might be expected for the tub structure (Scheme 13).

The more interesting case of **33** was dealt with in paper 3,³³ in which $J_{2,3} = 7.61$ Hz, $J_{3,4} = 7.87$ Hz, and hence $Q = 0.961$ —a $4n$ antiaromatic system, consistent with the planar structure for the 8π system (Scheme 14). Interestingly, Vollhardt³⁴ recently computed the NICS value for the eight-

Scheme 13**Scheme 14****Scheme 15**

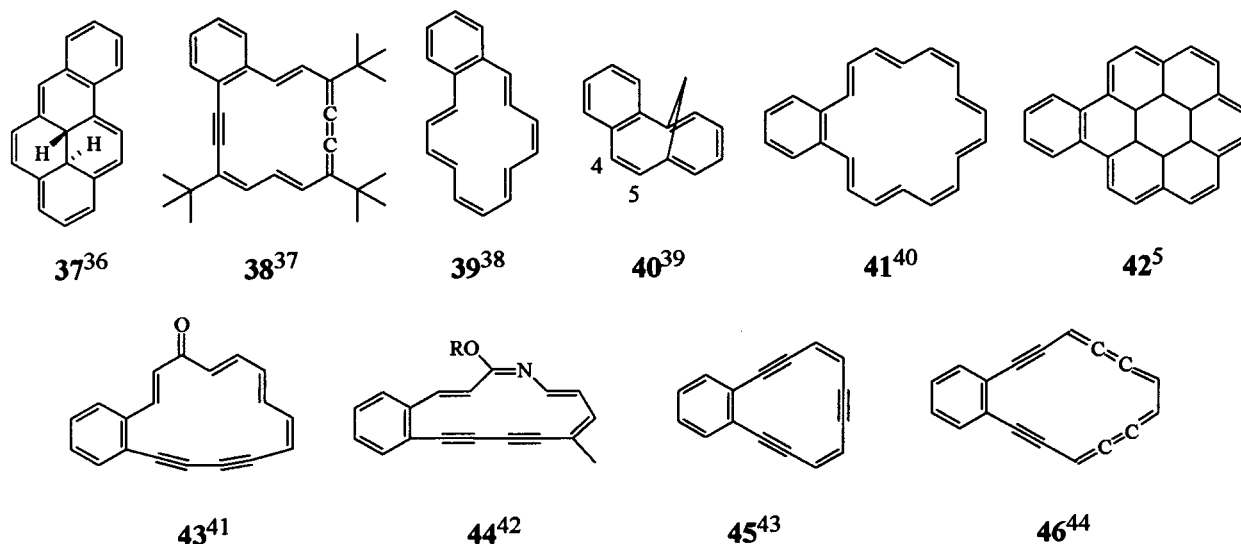
membered ring of **33** as +12, indicating strong paratropism.

Analysis of larger annulenes using the Günther method had to await their synthesis. By 1979, enough was known for Günther to publish paper 4 in the series,³⁵ in which he analyzed data for the benzodehydroannulenes **34** (14π), **35** (16π), and **36** (18π). Proton 2 in each case suffers a phenanthrene-like compression with the annulene proton, and thus $J_{2,3}$ was corrected by 0.3 Hz and then gave Q values of 1.139, 0.986, and 1.108. The difference is relatively clear: the 16π system **35** is paratropic, and the 14π **34** is more diatropic than the 18π **36**. Nevertheless, analysis of the coupling constants in the benzene ring is not always easy, and for many of the benzannulenes made (Scheme 16) it does not appear to have been reported.

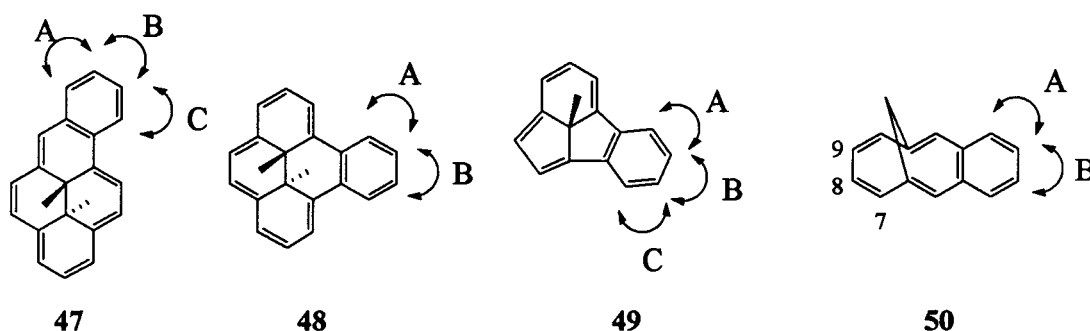
However, four benzannulenes (Scheme 17), **47**,⁴⁵ **48**,⁴⁶ **49**,⁴⁷ and **50**^{39b} have sufficient coupling constant data available to analyze using this method, Table 3.

Corrections⁴⁸ to $J_{\text{C}}(\mathbf{47})$ and $J_{\text{A}}(\mathbf{48}) = 0.3$ Hz (phenanthrene bay) and $J_{\text{A}}(\mathbf{47}) = 0.08$ Hz (naphthalene peri) were applied to obtain the Q values shown. Within experimental error, the Q values are approximately the same, as is the difference of coupling constants, about 1 Hz, which indicates that the 14π rings of **47** and **48** have about the same effect on the benzene ring as do the 10π rings of **49** and **50**. Rees⁴⁷ points out that the resonance energy of a [10]-annulene should be greater than that of a [14]-annulene, and so the Q results suggest that a departure from planarity in **49** (maximum torsion = 39°) reduces its

Scheme 16



Scheme 17

Table 3. Coupling Constants and Q Values for the Molecules of Scheme 17.

	J_A	J_B	J_C	corr J_A	corr J_B	corr J_C	ave (corr J_A , corr J_C)	Q
47	7.96	6.75	8.21	7.88	6.75	7.91	7.90	1.205
48	8.26	6.93		7.96	6.93			1.178
49	8.03	7.05	8.05				8.04	1.168
50	8.13	7.03						1.187

Table 4. Relative Ring Currents of Several Benzannulenes and Annulenes

benzannulene	δ (internal ^1H)	δ (parent)	δ (model)	RC ^{benzannulene} / RC ^{annulene}
47 (14 π)	-1.62	-4.25	0.97	49%
48 (14 π)	-1.85	-4.25	0.97	54%
49 (10 π)	-0.79	-1.67	1.01	67%
50 (10 π)	-0.09	-0.52	2.24	84%
	1.18	-0.52	2.24	38%
40 (10 π)	-0.06	-0.52	2.24	83%
	1.38	-0.52	2.24	31%

resonance energy and ring current. A similar effect may be present in **50**.

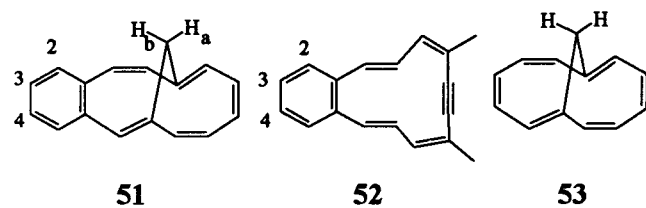
In the same way in which the annulene partially bond localizes the benzene ring, the benzene ring partially localizes the annulene and reduces its ring current. This can be very clearly seen for the molecules **47**–**50** by comparison of the chemical shift of the internal (methyl) protons with those of the parent annulenes, Table 4. The benzene does reduce the ring current of the [14]-annulene by a greater percentage than for the [10]-annulene, as it should, since as

stated above ring currents are proportional to resonance energies. For **47**–**49**, the through-space anisotropic effect of the benzene ring on the methyl protons should be <0.1 ppm.⁴⁵ Clearly, this is not the case for **40** or **50**, where the internal methylene protons differ in chemical shift by >1.2 ppm. If the more distant proton is used, these benzo[10]-annulenes (**40**, **50**) have about 83% of the ring current of the parent **3**. However, the relatively large $^3J_{4,5}$ of 11.05 Hz found for **40** and the quite different values for the adjacent coupling constants of **50** of 10.76 Hz ($^3J_{7,8}$) and 8.05 Hz ($^3J_{8,9}$) suggest that there is substantial bond alternation; the ring currents then are probably not that high.

How can Günther's Q values be used to measure relative aromaticity? For any [N]-annulene, the effect on the benzene ring is proportional (though not linearly)³¹ to the resonance energy of the annulene. If the perimeter of the annulene is distorted, the effective resonance energy decreases, and so the effect on the benzene ring will be less. Thus, Q values should measure "real" aromaticities rather than just maximum calculated values. Comparisons between [N]-annulenes for the same N and same geometry are thus valid. Although for $4n + 2$ annulenes Q decreases as n increases, the decrease is not linear, so comparisons between annulenes of different N or different geometry require care. Table 5 has some examples.

Table 5. Q Value Comparisons for Various Annulenes ($\geq 10\pi$)

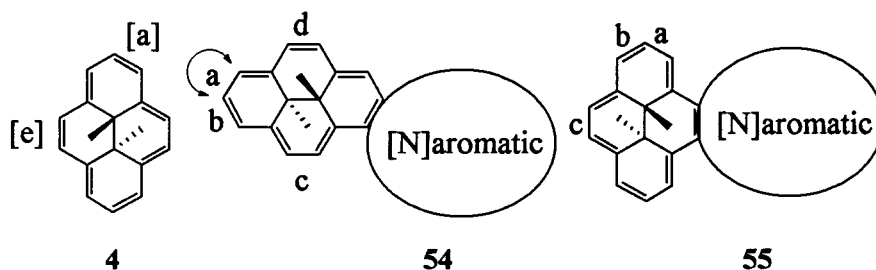
$4n + 2$	Q	$4n$	Q
10π-calcd	1.196 (26)	12π-calcd	0.984 (26)
49	1.221 (27)		0.988 (27)
50	1.168	51	1.048
14π-calcd	1.143 (26)	16π-calcd	1.016 (26)
34	1.195 (27)		1.018 (27)
47	1.139	35	0.986
48	1.205		
18π-calcd	1.178		
	1.108 (26)		
	1.177 (27)		
36	1.108		

Scheme 18

From these data it is probably safe to conclude that **48** is more “aromatic” than **34** and **49** and that **35** is more “antiaromatic” than **51**. This latter molecule is interesting to compare to **52** (Scheme 18).

In **51**, the bridge protons resonate at δ 4.52 and 4.43,⁴⁹ while in the parent **53** they are at δ 6.1;⁵⁰ the model shift is δ 2.24.³ Thus, **51** sustains about 58% of the paramagnetic ring current of **53**. The Q value analysis and the strongly alternating values found for the 12-ring 3J coupling constants (4.9, 12.3, 7.3, and 13.1 Hz)⁴⁹ question this however (see also the comments on **40**, **49**, and **50** above). Note that since **51** contains a 12 π paratropic ring, H^2 is expected to be³ and is (δ 6.78) more shielded than H^3 (δ 7.12). Likewise, in **52**, H^2 is at δ 7.08 relative to the model at δ 7.53 and the 14 π **34** at δ 8.25. Unfortunately, in **52**, H^2 and H^3 are reported⁵¹ as a singlet. Possibly, their chemical shifts are very similar, which decreases the intensity of the outside lines, making a Q analysis not possible.

The problem with using benzene as the probe is that it is sometimes quite difficult to analyze the AA'BB' set of coupling constants, which is required to obtain and then correlate the bond orders with chemical shift data. When this fails, one can normally resort to the fact that if the [N]-annulene is strongly diatropic, then H^2 of **25** is more deshielded than H^3 and vice-versa if the annulene is paratropic. To some

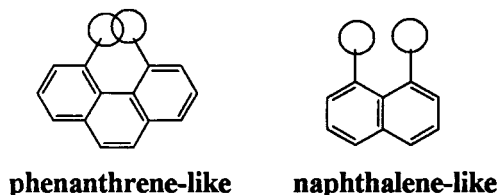
Scheme 19

extent these difficulties are overcome if a suitable bridged annulene is used as the probe.

IV. Use of Bridged Annulene Probes

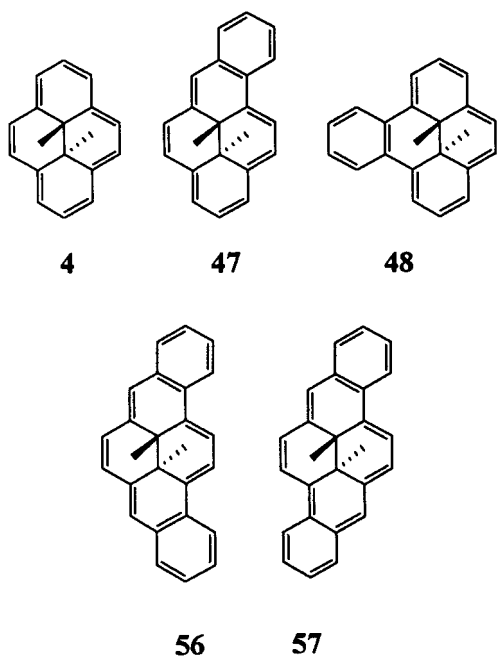
In our opinion, bridged [14]-annulene **4** makes an ideal probe of aromaticity (Scheme 19).

Other aromatics can be fused to **4** in the [a]-position to give **54** or in the [e]-position to give **55**. In either case, the magnetic through-space effect of the [N]-aromatic on the internal methyl protons is small (<0.2 ppm) because they are above and below the center of the dihydropyrene part of the molecule and are 5–6 Å away from the center of the [N]-aromatic when it is benzene. Indeed, even though the two methyl groups of **54** are formally different, they are often very similar in chemical shift (e.g., -1.618 and -1.626 for **47**, [N]-aromatic = benzene).¹⁴ Any change in the chemical shift of these internal methyl protons can thus be mainly attributed to a change in the ring current caused by a change in delocalization in the dihydropyrene ring. A change in delocalization results in a change in coupling constants. In **54**, there are four sets (a–d) of annulene coupling constants which are relatively easy to analyze; in **55** there are three sets. In principle, a and c should be similar, as should b and d. In reality, however, there are several steric compressions which can increase the observed J values by about 0.3 Hz for “phenanthrene-like” and 0.08 Hz for “naphthalene-like” (Scheme 20) interactions.⁴⁸

Scheme 20

As discussed in the Introduction, Hess and Schaad⁶ were the first to show in 1977 that there was a linear relationship between RE per electron and chemical shift differences in Nakagawa's annulenes of Scheme 2. In that year, at ISNA-III (The International Symposium of Novel Aromatics), they suggested that the chemical shifts of the internal methyl protons in our annulenes should correlate with the average deviation of the bond orders from that of the parent **4**. An initial analysis using HMO bond orders and selected bonds showed this to be the case.⁵² We then set out to demonstrate that using the π -SCF bond

Scheme 21



orders of Günther (above) (which take into account the geometry of the annulene), a correlation exists and it had predictive value. This was achieved in 1982.⁵³ For the five compounds shown in Scheme 21, the average deviation of bond order, Δp , from that of a perfect [14]-annulene (0.642) was calculated (excluding the bond(s) between the fused rings) and plotted against the chemical shift shielding of the internal methyl protons (see above)

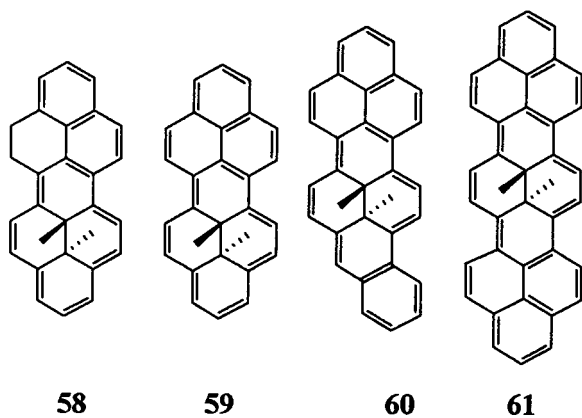
$$\Delta\delta = 0.97 - \delta(\text{Me}) \quad (4)$$

and gave a reasonable straight line with fit

$$\Delta\delta = 5.533 - 27.52\Delta p \quad (\rho = 0.9902) \quad (5)$$

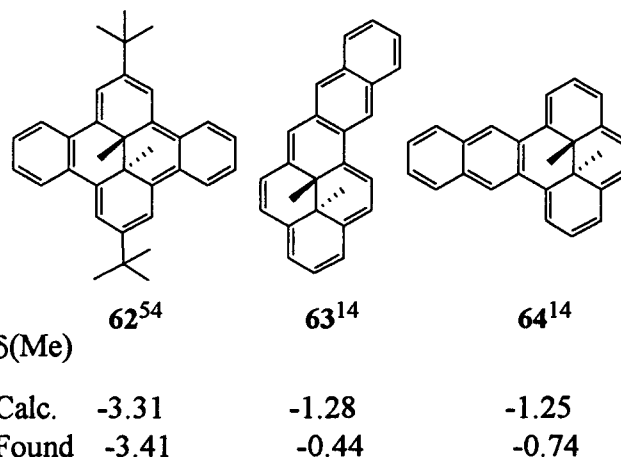
for values of $\Delta\delta$ from 1 to 5 ppm and Δp from 0.005 to 0.167. Although there was no derived theoretical

Scheme 22

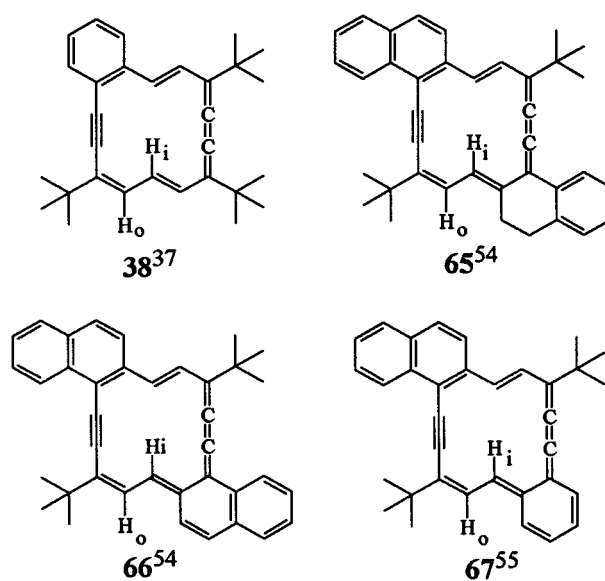


$\delta(\text{Me})$				
Calc.	-2.75	-3.97	-1.73	-2.99
Found	-2.78	-4.19	-1.35	-3.20
		-4.28	-1.41	

Scheme 23



Scheme 24



relationship between these quantities, the equation was put to the test for the molecules shown in Scheme 22. As can be seen, the results were remarkably good and *clearly* indicated that the internal methyl protons were reasonably good markers for the ring current and that this mainly depended upon the degree of delocalization around the macrocyclic ring. Many other predictions were made for then unknown annulenes, some of which are now known, and these are shown in Scheme 23. In principle, that type of analysis should hold for any annulene where the chemical shift measurements are mainly dependent upon ring current and not by anisotropy factors. Indeed, for Nakagawa's annulenes, using **38**, **65**, and **66** as calibrants, two relationships may be derived.⁵³ If the shielding, $\Delta\delta_i$, of the internal proton H_i (Scheme 24) from a model at δ 5.60 is used, then

$$\Delta\delta_i = 11.070 - 59.11\Delta p \quad (\rho = 0.9982) \quad (6)$$

was found, and if the difference in chemical shift of the inner and outer protons, $\delta_o - \delta_i$ was used, then

$$\delta_o - \delta_i = 16.552 - 86.01\Delta p \quad (\rho = 0.9997) \quad (7)$$

was found. Application of these to the benzonaphtho

analogue **67** gave calculated values for $\delta_i = -2.22$ and $\delta_o = 9.60$, in amazing agreement with the found values of -2.05 and 9.50 , respectively.

Clearly as the amount of bond fixation (calculated) in the annulene increased, the shielding caused by the ring current decreases. Could this be correlated with a physical measurement of the bond fixation? Our early work^{45,46} did show that the observed coupling constants were consistent with the calculated bond orders; however, it was not until our more encompassing paper¹⁴ of 1995, with far more examples known, that we were able to set up the correlations between the internal methyl protons, $\delta(\text{Me})$, and the most distant protons, δH_d (see Scheme 3) for **54** (Scheme 19) as

$$\delta(\text{Me}) = 17.515 - 2.685\delta(\text{H}_d) \quad (r^2 = 0.998) \quad (2)$$

and between $\delta(\text{Me})$ and the ratio of the coupling constants J_b/J_a for **54** (Scheme 19) as

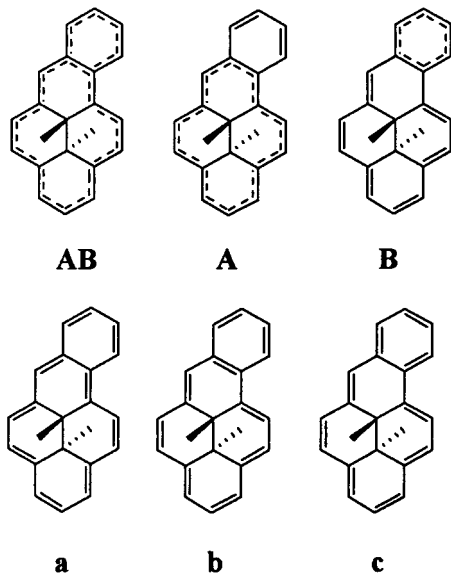
$$\delta(\text{Me}) = 7.99(J_b/J_a) - 12.29 \quad (r^2 = 0.996) \quad (8)$$

Thus, as the ratio of adjacent coupling constants increases (more bond fixation), the chemical shift becomes less negative, i.e., less shielded, less ring current. The other pair of coupling constants in **54** must be corrected for the large steric (bay) compression in J_c but are related by the equation

$$J_b/J_a = 1.769(J_d/J_c) - 1.023 \quad (r^2 = 0.9994) \quad (9)$$

Even though we showed that we can measure the strength of the ring current by its effect on the internal methyl protons and that this correlates with the calculated degree of bond fixation and with the ratio of measured coupling constants, we still did not have a way to express the results so that they could be easily seen as a measurement of aromaticity. This was rectified in 1990⁵⁶ and published more fully in 1995.¹⁴ We based our approach on the Hess, Schaad, and Agranat paper⁵⁷ on the resonance energies of annulenoannulenes and the conjugated circuit theory

Scheme 25



of Randić.⁵⁸ The benzannulene **AB** (Scheme 25) has three Kekulé structures **a**, **b**, and **c**. Delocalization of the 14π circuit **A** utilizes **a** and **b** and fixes the bonds in the 6π circuit **B**, while delocalization of the 6π circuit **B** utilizes **b** and **c** and fixes the bonds in the 14π circuit **A**. The periphery circuit only localizes the fused bond and is a minor perturbation.^{57,58} Thus, for practical purposes, **AB** can be thought of as two circuits **A** and **B**, the importance or contribution of which depends on their relative resonance energies. Thus, the delocalization of the **A** fragment depends on the resonance energy of the **B** fragment. In a comparison of two annelated annulenes, the degree of delocalization in the **A** fragment depends on the relative resonance energies of the **B** fragments; the larger the resonance energy of **B**, the less the delocalization in **A**, the smaller will be the ring current in **A**. Now a simple comparison of resonance energies ("aromaticities") is possible by comparing the ring current change in the 14π fragment **A**, when it is annelated with benzene, i.e., when **AB** = **47** with that when it is annelated with any other annulene, i.e., **54** (Scheme 19). Thus

$$\frac{\text{RE of } [N]\text{-annulene in } \mathbf{54}}{\text{RE of benzene}} = \frac{\text{change in chemical shift of Me in } \mathbf{54} \text{ from } \mathbf{4}}{\text{change in chemical shift of Me in } \mathbf{47} \text{ from } \mathbf{4}} = \frac{\Delta\delta(\text{Ar})}{\Delta\delta(\text{Bz})} \quad (10)$$

Thus, for the naphthoannulene **63** (Scheme 23), where $\delta(\text{Me}) = -0.44$, $\Delta\delta(\text{Ar}) = -(4.25 - 0.44) = -3.81$ ppm; for the benzannulene **47** (Table 4), where $\delta(\text{Me}) = -1.62$, $\Delta\delta(\text{Bz}) = -(4.25 - 1.62) = -2.63$ ppm. Thus, $\text{RE}_{\text{naph}}/\text{RE}_{\text{benz}} = -3.81/-2.63 = 1.45$, in quite good agreement with the Dewar value⁵⁹ of 1.52.

To make this relationship more general (for polycyclic systems), the bond localization energy (BLE) must be used in place of the resonance energy (RE).¹⁴ Consideration of the Kekulé structures shown for the two naphthoannulenes **63** and **68** in Scheme 26 indicates that for **63**, allowing the 2,3-bond of naphthalene to delocalize over the 14π -system causes a total loss of resonance energy of the naphthalene; for 2,3-fusion, $\text{BLE} = \text{RE}$; for fusion at the 1,2-bond of naphthalene as in **68**, participation of the 1,2-bond in the 14π -system still permits a benzene subunit in the naphthalene; for 1,2-fusion $\text{BLE} = \text{RE}(\text{naphthalene-benzene})$. For the phenanthroannulenes **69** and **70**, again a benzene remains and thus $\text{BLE} = \text{RE}(\text{phenanthrene-benzene})$. A check on the validity of this method can be seen for compound **59**, in which both Kekulé structures of the 14π -system leave a naphthalene, and thus delocalization of the 14π -system is not affected by the fusion; **59** should thus have the same chemical shift as the parent **4**. It does, $\delta(\text{Me}) = -4.20$ and -4.29 for **59** and $\delta(\text{Me}) = -4.25$ for **4**!

Table 6 shows values found¹⁴ for $\Delta\delta(\text{Ar})/\Delta\delta(\text{Bz})$ and BLE (based on Dewar RE's,⁵⁹ relative to benzene = 1.00 (=0.869 eV)) for several [a]-annelated dihydropyrenes [note $\Delta\delta(\text{Bz}) = -2.63$ ppm].

Similar data were obtained¹⁴ using the most distant proton chemical shifts, H_d (see Scheme 3).

Scheme 26

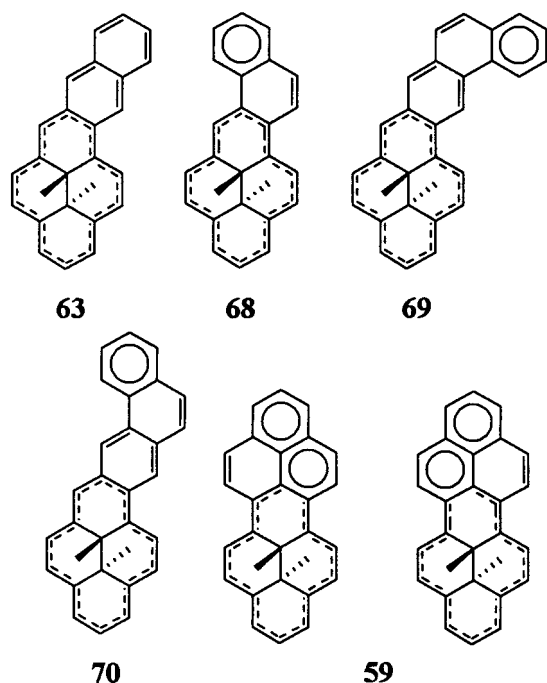


Table 6. Comparison of Experimentally Estimated Values of BLE from $\Delta\delta(\text{Ar})/\Delta\delta(\text{Bz})$ with Values Based on Dewar Resonance Energies

compd	annelating arene	$\Delta\delta(\text{Ar})/\Delta\delta(\text{Bz})$	BLE
4	none	0	0
59	see structure	0.00	0
58	1,2-naphthalene	0.56	0.52
47	benzene	1	1
69	2,3-phenanthrene	1.28	1.22
70	2,3-phenanthrene	1.27	1.22
63	2,3-naphthalene	1.45	1.52
56	benzene x 2	1.62	2.00

The relationship between $\Delta\delta(\text{Ar})/\Delta\delta(\text{Bz})$ and BLE appears to be approximately linear up to BLE = 1.5. Since $\Delta\delta(\text{Bz}) = \text{constant}$ (2.63) and since $\Delta\delta(\text{Ar}) = \text{constant} - \delta(\text{Ar})$, the relationship can be rewritten $\delta(\text{Ar}) = k(\text{BLE}) - c$.

A least-squares fit of the data (excluding **56**) gave

$$\delta(\text{Ar}) = 2.59(\text{BLE}) - 4.18 \quad (r^2 = 0.992) \quad (11)$$

where $\delta(\text{Ar})$ is the average chemical shift of the internal methyl protons and BLE is the bond localization energy (Dewar) of the annelating aromatic (Ar) relative to benzene = 1.00 (=0.869 eV).

Hence, for any other aromatic system, an estimate of its RE (BLE) can be obtained simply by measurement of the chemical shift of its internal methyl protons in **54** and then use of the equation

$$\text{BLE} = [4.18 + \delta(\text{Ar})]/2.59 \quad (12)$$

In reality, the relationship is not quite linear, as can be seen from Figure 1. As BLE becomes large, the ring current diminishes to zero and then $\delta(\text{Me}) = 0.97$. More data points are needed beyond BLE = 2 to obtain a better extrapolation of the trend. Most recently, we have been able to extend these equations (see section VI below).

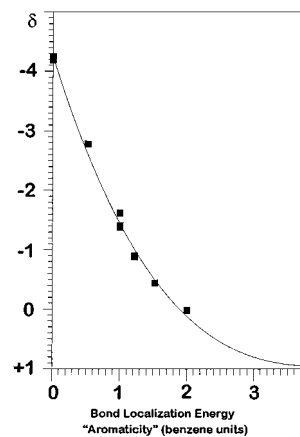


Figure 1. Chemical shift (δ) of the internal methyl protons for **54** vs BLE.

By synthesis of **71** and **72** and use of this approach (eq 12), an estimate of the resonance energy of cyclopentadienide to be about 0.55 that of benzene⁶⁰ and of biphenylene to be about 1.59 times that of benzene (Dewar value 1.55)⁶¹ has been made. This method has also been used for a number of organo-metallics¹² which will be discussed below.

A relationship was also derived¹⁴ for [e]-fused compounds **55**

$$\text{BLE} = [4.22 + \delta(\text{e-Ar})]/2.32 \quad (13)$$

and for compounds with *cis*-methyl groups derived from **23**

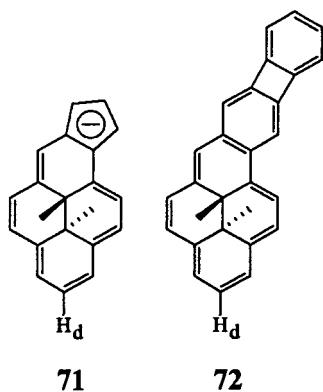
$$\text{BLE} = [1.95 + \delta(\text{cis-Ar})]/1.71 \quad (14)$$

but the number of examples known in these cases is less, however, see section VI below.

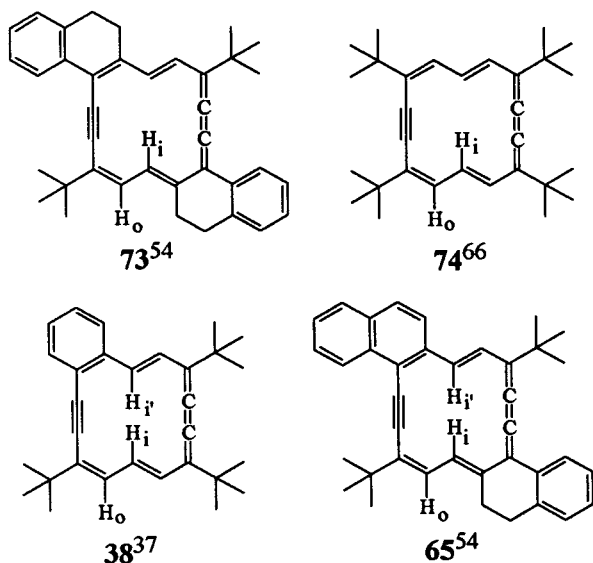
Lai also extensively studied the chemical shift changes in the dihydropyrenes, especially [e]-annelated ones^{62,63} and conjugated rather than fused aryl systems,^{64,65} and has been able to show that while conjugation of aryl groups, e.g., as in 2-phenyl-**4**, has a much smaller effect on the change in chemical shift of the internal methyl protons (it is about 0.48 ppm for each benzene resonance energy added),⁶⁵ it does behave in a regular fashion and can be used to estimate resonance energies of the conjugating groups. However, the shift differences are small, so care must be taken not to use systems where other anisotropic effects are introduced.

In principle, any suitable annulene could be used to derive similar relationships as for the dihydropyrenes above. However, the perimeter of the annulene must remain reasonably unchanged on annelation or conjugation and anisotropic effects must be small or at least constant. In the case of the [a]-annelated dihydropyrenes, **54**, of which **72** (see Scheme 27) is an example, the annelating rings are reasonably distant from the probe hydrogens (both the internal methyl protons and the most distant external hydrogens, H_d). Indeed, for **72**, the BLE found using the Me shift data was 0.56 and using the H_d shift data was 0.55.⁶¹ In fact, if two such different probes in the same molecule give such consistent data, then other effects apart from the ring current effect can be taken to be small. The extent to which this is true will

Scheme 27



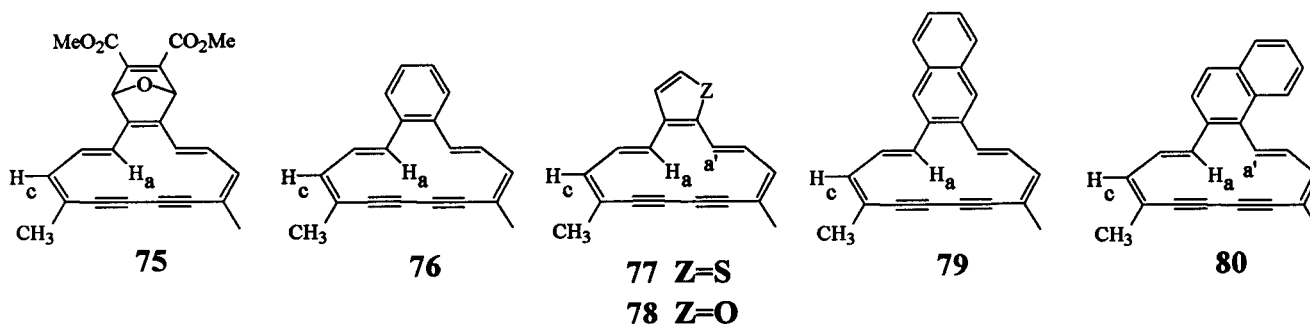
Scheme 28



obviously be different in other annulene series. Nakagawa's annulenes seem reasonably well behaved. For example, Lai⁶⁵ notes that $\delta(H_i)$ of **73** (a diphenyl derivative of **74**) are 0.92 ppm deshielded from those in **74**, in remarkable agreement with that predicted ($2 \times 0.48 = 0.96$ ppm) on the basis of the dihydropyrenes.

In any other annulene series, if the parent (**A**) and the benzannulene (**BA**) are known, then use of eq 15 (modified from eq 10), where **AA** is the annelated annulene, will provide an estimate for the resonance energy, RE (strictly BLE, see text above), of the annelating fragment of **AA**.

Scheme 29



$$\frac{\text{RE (annelating fragment)}}{\text{RE (benzene)}} = \frac{\delta H(\mathbf{A}) - \delta H(\mathbf{AA})}{\delta H(\mathbf{A}) - \delta H(\mathbf{BA})} \quad (15)$$

Thus, for Nakagawa's⁶⁶ annulene **74** (**A**), H_i is the probe and $\delta(H_i) = -4.39$; it is $+0.60$ for **38** (**BA**) and -1.53 for **65** (**AA**) (Scheme 28). Use of these in eq 15 above leads to a relative resonance energy for naphthalene of 1.57 (BLE = 0.57; RE = BLE + 1, see 1,2-naphthalene BLE discussion above), in good agreement with the Dewar value⁵⁹ of 1.52. Where possible, a second probe should always be used. However, if the other internal proton, $H_{i'}$, is used, then for **38** $\delta = 0.70$ and for **65** $\delta = -1.22$ and BLE = 0.62; the anisotropy of the annelating ring has an effect. On the other hand, if the external proton H_o is used, the chemical shift differences are rather small (solvent effects can be significant): δH_o for **74** = 9.42, δH_o for **38** = 8.41, and δH_o for **65** = 9.17. The resulting BLE of 0.25 is too small. Clearly the additional annelation introduces enough anisotropy to perturb the small shift changes enough to make the BLE value less reliable.

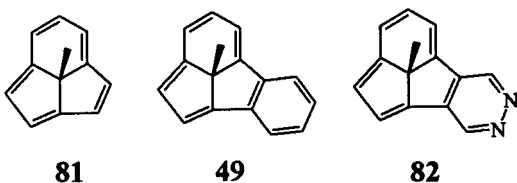
Sondheimer's dehydroannulenes provide an instructive example (Scheme 29). Their relevant shifts are shown in Table 7.

Table 7. Chemical Shift Data and BLE Calculation (eq 16 for molecules of Scheme 29)

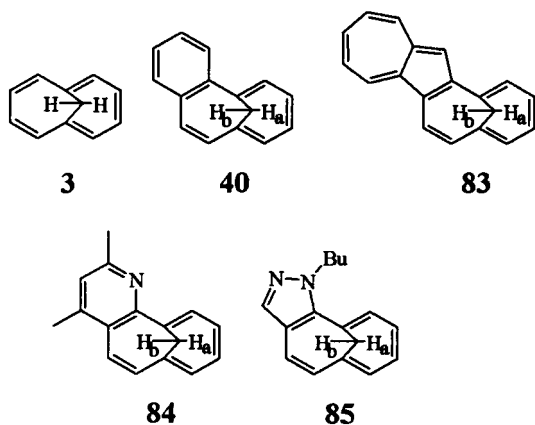
compd	75 ⁶⁷ (A)	76 ⁶⁸ (BA)	77 ⁶⁹ (AA)	78 ⁶⁹ (AA)	79 ⁷⁰ (AA)	80 ⁷⁰ (AA)
$\delta(H_a)$	-2.12	4.99	2.76	3.53	6.35	5.01
$\delta(H_{a'})$			2.76	3.89		5.18
$\delta(H_c)$	8.21	7.08	7.45	7.75	6.82	6.98
$\delta(\text{CH}_3)$	2.98	2.36	2.59	2.62	2.19	2.28
BLE (H_a)			0.69	0.79	1.19	1.00
BLE ($H_{a'}$)			0.69	0.85		1.03
BLE (H_c)			0.67	0.41	1.23	1.09
BLE (CH_3)			0.63	0.58	1.27	1.12

For the thiophene-annelated annulene **77**, the three BLE values obtained all agree reasonably well. This is not true for the furan-annelated case **78**, where the more electronegative oxygen atom introduces greater anisotropy. Unfortunately in this system, the biggest changes in chemical shift occur for H_a , which is also the proton that is most affected by the annelating ring. This is also true for the naphtho systems **79** and **80**, and the BLE value calculated for **79** is too small while that for **80** is too large. In this regard, these annulenes seem less satisfactory than Nakagawa's.

Scheme 30



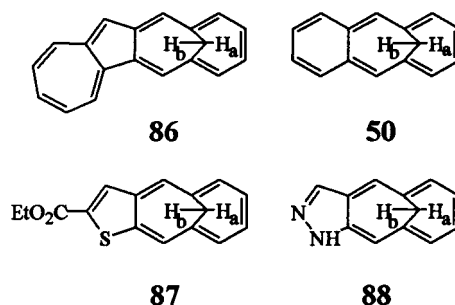
Scheme 31



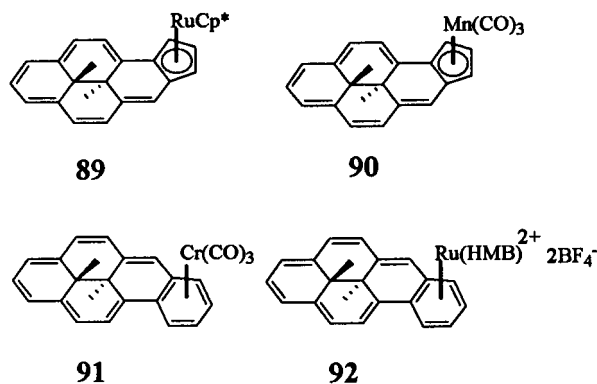
Relatively few suitable derivatives of Rees' annulenes are known⁴⁷ (Scheme 30). For the parent **81**, $\delta(\text{Me}) = -1.67$, for benzannulene **49**, $\delta(\text{Me}) = -0.79$, and for pyridizinoannulene **82**, $\delta(\text{Me}) = -1.06$. Using eq 15, BLE for pyridazine = 0.69. Bird⁷¹ gives the relative RE of pyridazine to benzene as 0.71, in excellent agreement with that measured using eq 15.

More of Vogel's annulenes are known than any other. Care must be exercised in using them, however, because the through-space anisotropy effects can be quite large. For example, in Scheme 31, the chemical shift of the two methylene bridge protons, H_a and H_b , of the benzannulene **40** are quite different, $\delta -0.06$ and 1.38 , respectively.³⁹ Use of H_a , the most distant one from the benzene ring should be most reliable, and comparison with those of **3** ($\delta -0.52$)^{3,23} and H_a of the azuleno-annulene **83** ($\delta -0.17$)⁷² using eq 15 yields the BLE (RE) of azulene as 0.76 benzene units. The experimental ratio⁷³ of resonance energies based on enthalpies of formation are $16.1/26.1 = 0.62$ benzene units, in quite good agreement with the NMR value. In the case⁷⁴ of pyridino-annulene **84**, H_a ($\delta -0.05$) and H_b ($\delta 1.30$) suffer an additional effect of the nitrogen making the calculated resonance energy for pyridine (based on eq 16) 1.02 benzene units too large. The result is worse for pyrazole **85**, $\delta(H_a) -0.02$.⁷⁵ In principle, 3,4-annulation rather than 2,3-annulation would place the annelating groups further away, and indeed the data for **50** (see Table 4 above) do suggest the annelating benzene ring has slightly less anisotropic effect relative to that in **40**: H_b at $\delta 1.18$ rather than at $\delta 1.38$. However, the azuleno derivative **86** has⁷⁶ H_a shielded ($\delta -0.76$) to a greater amount than those of the parent annulene, **3** ($\delta -0.52$). The authors claim that the [10]-annulene ring is delocalized and the azulene ring localized, though it is not clear to this author why that would shield H_a beyond that in **3**. A very recent paper by Lemal⁷⁷ does suggest that azulene is exceptionally easy to bond localize on

Scheme 32



Scheme 33



fusion to other rings; however, the question then arises, why not in **83**? The heterocycles **87** and **88** have⁷⁵ H_a at $\delta -0.53$ and -0.44 , respectively, at higher field than would be expected on the basis of **3**; some X-ray data for these compounds would be useful. Organometallics present an interesting challenge, perhaps first because exactly what does the aromaticity of an organometallic mean? Interpretation of NMR spectra requires care because a metal center could introduce quite a large anisotropy effect. Fortunately, McGlinchey⁷⁸ determined diamagnetic anisotropy values for a number of organometallic moieties and showed that the through-space shielding or deshielding of such a group at a distant position can be calculated. We used¹² his method on the organometallic species of Scheme 33 and compared their effects to that of benzene on the [14]-annulene. Each organometallic species bond-fixed the annulene ring more than the benzene ring of **47**. The relative BLE found for the fragments pentamethylcyclopentadienyl(Cp^*)ruthenium-cyclopentadienide, tricarbonylmanganese-cyclopentadienide, tricarbonylchromium-benzene, and hexamethylbenzene(HMB)ruthenium($2+$)-benzene of compounds **89**–**92** were found to be 1.38, 1.33, 1.27, and 1.34, respectively,¹² relative to benzene. In addition, analysis of the coupling constants of the organometallic moiety indicated that they all resisted bond fixation by the annulene, more than did the benzene ring of **47**. Thus, by our method, the molecules Cp-Ru-Cp^* , benzene- Ru^{2+} -HMB, $\text{Cp-Mn}(\text{CO})_3$, and benzene- $\text{Cr}(\text{CO})_3$ are all 30–40% more aromatic than benzene! Note: our method effectively measures bond localization energy, and the 2–3 bond of naphthalene has greater BLE than benzene. Whether naphthalene is more aromatic is debatable.

Nevertheless, such metal complexes behave as if they were like an aromatic. Few would doubt that

ferrocene and, hence, Cp–Ru–Cp are aromatic. Benzene–Cr(CO)₃ is more contentious. Simion and Sorensen^{79a} originally argued on the basis of susceptibility exaltation calculations that it is *antiaromatic*. We disagreed¹² on the basis of both our shift data and analysis of coupling constants and Günther's Q values (see above), which for **89**–**92** are all characteristic of strongly aromatic annelating systems. A more recent paper^{79b} by Schleyer and Sorensen supports our view.

V. Other Probes

Siegel⁸⁰ suggested that the barrier to rotation of the tricarbonylchromium group attached to an arene depends on the bond orders present in the arene, and if enough experimental points can be obtained to calibrate the system, it might provide a gauge of aromatic character.

In principle, ¹³C NMR shifts ought to yield similar information to their proton counterparts. However, ¹³C shifts seem to be more sensitive to geometry than their proton counterparts and are affected by additional β -substitutions more than are protons.⁸¹ Boekelheide⁸² reported ¹³C NMR data for the dihydropyrenes shown in Scheme 34 and Table 8.

Comparison of the external annulene C_a for **4**, **93**, and **95** shows a 2.1 ppm difference between the Me, Et, and Pr annulenes and of the internal bridge carbon C_b, a 5.1 ppm difference between **4** (CH₃ attached) and **93** (CH₂ attached) and a 0.2 ppm difference between **93** and **95** (both CH₂ attached). The ring current shielding of C_a is thus not significant. The bridge carbons C_b are better placed to experience the ring current and shielded 9–10 ppm. Comparisons between different systems can thus be made, but they must be carefully chosen to ensure

Scheme 34

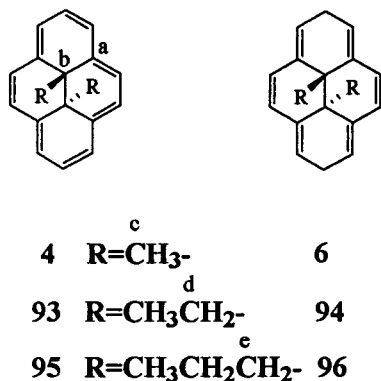


Table 8. ¹³C NMR Data for Molecules of Scheme 34^a

molecule	δ	C _a	C _b	C _c	C _d	C _e
4		136.6	30.0	14.0		
	$\Delta\delta$		9.2	9.6		
6		138.7	39.2	23.6		
93		134.5	35.1	5.1	20.3	
	$\Delta\delta$		9.6	3.6	6.9	
94		135.9	44.7	8.7	27.2	
95		135.0	34.9	13.3	13.9	29.8
	$\Delta\delta$		9.2	1.2	3.7	7.0
96		136.4	44.1	14.5	17.6	36.8

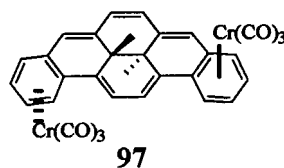
^a $\Delta\delta$ is for 6 – 4, 94 – 93, 96 – 95.

Table 9. Selected ¹H and ¹³C NMR Data for **4**, **47**, **91**, **56**, and **97**

compd	4	47	91	56	97
δ (CH ₃)	–4.25	–1.62	–0.97	+0.02	+0.64
RC shielding ^a	5.22	2.59	1.94	0.95	0.33
RC (¹ H) ^b	100%	50%	37%	18%	6%
δ (CH ₃)	14.0	17.0, 17.7	18.4, 20.0	19.2	21.5
RC shielding ^c	9.6	6.6, 5.9	5.2, 3.6	4.4	2.1
RC (¹³ C) ^b	100%	69%, 61%	54%, 38%	46%	22%
δ (bridge-C)	30.0	35.5, 36.0	36.9, 37.7	39.5	41.0
RC shielding ^d	9.2	3.7, 3.2	2.3, 1.5	–0.3	–1.8
RC (¹³ C) ^b	100%	40%, 35%	25%, 16%		

^a 0.97 – δ (CH₃). ^b RC relative to **4**. ^c 23.6 – δ (CH₃). ^d 39.2 – δ (bridge-C).

Scheme 35



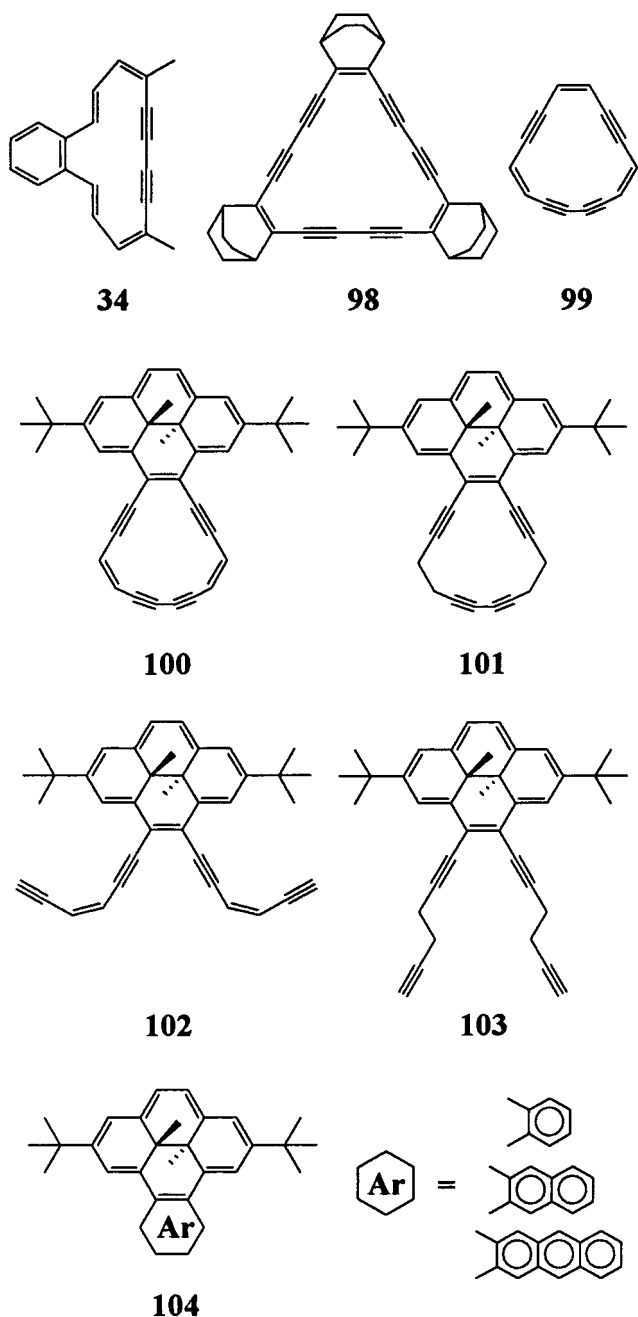
the same groups are attached. Even then, the 2 ppm difference for C_a is a substantial portion of the ring current effect and the difference of 0.6 ppm between C_b of **94** and **96** but 0.2 ppm between **93** and **95** means that quantitative measurements of aromaticity may be difficult. An interesting set of data⁸³ is shown in Table 9.

The [14]-annulene proton ring current decreases from **4** to **97**. This is also true for the carbon ring currents for both the methyl and bridge carbons but differently than from the protons. Note that in **47** and **91** the two methyl and the two bridge carbons are differentiated and lead to a fair variation in the determined ring current; those for the corresponding protons are not significantly differentiated (**47**: δ -(Me) –1.618 and –1.626).¹⁴ In this author's opinion, it is better to use proton data to compare aromaticities. Bird⁷¹ showed that there is no relationship between ¹⁵N NMR data and the aromaticity of a variety of heterocycles.

VI. Concluding Remarks

There are many papers that calculate ring currents, other magnetic effects, resonance energies, and the like and thus comment on aromaticity; however, unless they specifically mention some experimental measurement to gauge aromaticity, they will not have been included here. However, there are papers elsewhere in this thematic issue of *Chemical Reviews* which deal with many of these aspects of aromaticity, for example, susceptibility exaltation, ring currents, resonance energies, etc. There are thousands of papers that report chemical shifts of aromatic compounds, but again, unless the authors mention that such data can be used to gauge aromaticity or unless this author deems the data so important that he has extracted the information, then these also will not have been covered. Nevertheless, this review shows that annulenes can be synthesized such that analysis of NMR data can yield information on their relative aromaticities or that of the annelating groups. π -Elec-

Scheme 36



trons are, however, fickle things: we may think we understand them but do we?

Since Günther³⁵ found that the [14]-annulene **34** was strongly diatropic and since Komatsu⁸⁴ found the [18]-annulene **98** to be likewise, we had every reason to believe that the [14]-annulene **99** would be similarly so. Given the considerable experience of Haley⁸⁵ in synthesizing dehydrobenzannulenes, as a joint project⁸⁶ we made the dihydropyreno-annulene **100**, as well as the models **101**–**103**, to access the relative aromaticity of the dehydro[14]-annulene system, **99**. To our surprise, the annulene **100** had the most shielded internal methyl protons, δ –3.91 [**101**: δ –3.77. **102**: –3.68. **103**: –3.80). I expected them to be much more deshielded, consistent with the many examples above. Clearly the dehydroannulene ring in **100** either has almost **no** ring current or something else is going on. We now have two systems, **100**

and the azulene fused system **86**, in which both have more diatropic bridged annulene rings than expected. We do not understand everything yet! Nevertheless, we continue to investigate this seductive area of chemistry. In our most recent work,⁸⁷ by synthesis of a series of [e]-fused dihydropyrenes (**104**), we have been able to develop eqs 16 and 17

$$\text{BLE} = 2.825 - [0.97 - \delta(\text{Me})]^{0.643} \quad (\rho > 0.9999) \quad \text{for [e]-series (16)}$$

$$\text{BLE} = 2.80 - [0.97 - \delta(\text{Me})]^{0.620} \quad \text{for [a]-series (17)}$$

which enable the range of values for BLE referred to in eqs 12–14 above to go beyond 2 and thus extend the range of annelated annulenes to which these are applicable.

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VIII. References

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