Annulenes

# Aromaticity: The Alternating C–C Bond Length Structures of [14]-, [18]-, and [22]Annulene**

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*Dedicated to Professor Kurt Mislow*

[18]Annulene ($C_{18}H_{18}$)[1] is the critical signpost along the $4n+2$ π electron Hückel[2] route from benzene to the larger aromatic $(CH)_k$ rings. Although Mislow[1a] pointed out the steric problems of the planar $D_{6h}$ form very early, [18]annu-

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lene has been assigned[1b] the same essential $D_{6h}$ symmetry as benzene—"the bonds do *not* alternate in length"—for over four decades. However, geometries with nearly equal C–C bond lengths are not expected for the very large [4*n*+2]annulenes. Since the aromatic stabilization energy per carbon decreases with increasing size,[3,4] very large annulenes should approach the behavior of polyolefins. This was first predicted[5] in 1959 by Longuet-Higgins and Salem, who guessed that C–C bond-length alternation might begin with [30]annulene. Indeed, this result was obtained at the DFT-B3LYP and MP2 theoretical levels in the comprehensive computational annulene survey of Choi and Kertesz (CK) in 1998.[4] In contrast, herein we show that this crossover point occurs much earlier, at [14]annulene, which, along with [18]annulene, has alternating rather than equalized C–C bond lengths.

As stressed by Shaik, Hiberty et al., the σ framework of aromatic compounds favors regular geometries, but the π components prefer bond alternation owing to greater overlap of adjacent p orbitals when they are closer together.[6–8] The π system has two competing tendencies: the preference for pair-wise interactions when C–C separations are shorter (as in double bonds) competes with the gain in aromatic stabilization energy when the C–C separations are equalized, but longer (as in benzene). However, this equalization tendency is the weaker of these two π effects and cyclic electron delocalization is not eliminated, but only reduced slightly, by bond alternation.[3] Thus, benzene, rather than being the aromatic prototype in this sense, is the exception! Benzene favors the highly symmetric $D_{6h}$ structure[9] solely due to its σ skeleton.[6] Naphthalene and virtually all other polybenzenoid hydrocarbons, even in corronene (over 0.05 Å) which has $D_{6h}$ symmetry, exhibit appreciable C–C bond-length differences. This partial localization is fully consistent with their aromatic character. In the larger annulenes, the preference for either a bond alternating or a higher symmetry structure depends on the Shaik–Hiberty[8] "fine balance of σ resistance and π distortivity."

Hence, it is important to ascertain[3–5,10,11] the point in the annulene progression at which the σ skeleton ceases to be the dominating influence and is replaced by the inherent predilection for double-bond localization. We establish herein that the preference for bond-alternating structures along the 4*n*+2 Hückel π-electron series begins at [14]annulene. Additionally, we also show that the next higher homologue, [18]annulene also shows remarkable C–C bond alternation. Benzene is not the aromatic paradigm!

*[18]Annulene*: The structure of [18]annulene, the most extensively[11–15] investigated higher Hückel monocycle, is of critical importance in this context. But the seemingly secure and currently accepted experimental[14,15] and theoretical conclusion[4,13] that [18]annulene ($C_{18}H_{18}$) has a $D_{6h}$ structure cannot be correct. Like benzene, [18]annulene belongs to the [4*n*+2]aromatic subgroup with $6(2p+1)$ π electrons (where "*p*" is an integer), which permits but does not require the highly symmetrical $D_{6h}$ point group. Although well established to be aromatic, the $C_{18}H_{18}$ chemistry differs markedly from that of benzene: [18]annulene undergoes reactions typical of localized π systems. The 1965 X-ray structure determination at 80 K favored $D_{6h}$ symmetry[15] with somewhat different (but not alternating) 1.382 and 1.419 Å lengths for the 12 inner and the six outer C–C bonds, respectively. The 1995 X-ray reinvestigation at 111 K revealed some disorder in the [18]annulene crystal[14] but gave C–C bond lengths of 1.385 and 1.405 Å and confirmed the essential $D_{6h}$ symmetry.[16] Electron correlated MP2 and various DFT computations[4,13,17] reproduced the X-ray structure well and supported the experimental conclusions that $C_{18}H_{18}$ has a "highly delocalized $D_{6h}$ structure." Other indirect evidence based on IR, UV/Vis, fluorescence, and photoelectron spectroscopy[18,19] also was consistent with a $D_{6h}$ structure. However, data from such methods are not sensitive to geometry changes. In sharp contrast, the proton chemical shifts respond markedly even to slight variations in structure.[3,20]

Bühl and Schleyer established and validated the use of ab initio/GIAO/NMR methods for structural determinations.[21,22] Based on the comparison of experimental and computed chemical shifts for a large number of boranes, carboranes, and nonclassical carbocation systems, Bühl and Schleyer found excellent agreement between the experimental and computed chemical shifts only when the geometries were correct,[21] and revealed many errors in experimental structures. Likewise, the $^1$H NMR chemical shifts of many arenes computed by GIAO-B3LYP/6-311 + G** are generally within 0.2 to 0.5 ppm of the experimental values.[23,24] Hence, accurate structures of [*n*]annulenes may be established by comparing computed with experimental chemical shifts. Excellent agreement is expected only when the geometries are correct. The results obtained by using this procedure demonstrate that [18]annulene cannot have a $D_{6h}$ structure. The evidence is decisive: the proton chemical shifts computed using the X-ray geometry[25] are in gross disagreement with those measured[26,27] experimentally.

This large disagreement has been found before, but its importance was not appreciated.[3,4,13b] CK[4] noted that the inner–outer proton chemical shift differences for all the higher aromatic annulenes, computed using the B3LYP/6-31G* geometries, were far from the available experimental NMR spectroscopic data, and stated that "the origin of this discrepancy is not clear." Baldridge and Siegel (BS)[13b] reported the chemical shifts of the inner and outer protons for $D_{6h}$, $D_{3h}$, and $D_3$ [18]annulene geometries; the later two were obtained at HF levels, but only a $D_{6h}$ minimum was found at MP2 and all the DFT levels employed. None of these geometries gave $\delta$ $^1$H values that agreed acceptably with the experimental values. But according to BS, the single $D_{6h}$ minimum obtained at MP2 and various DFT levels (e.g. BPW91/dz(d), B3PW91/dz(d,p), and B3PW91/dz(2df,2p)) and the agreement with the X-ray geometry, were decisive in supporting the $D_{6h}$ [18]annulene structure. BS speculated that the large discrepancy (12.3 ppm) between the observed and computed $^1$H NMR chemical shifts of the inner protons in the $D_{6h}$ structure might be due to the "strong temperature dependence" or to the deficiencies in the theory, stating that "the ring current is over-estimated at these computational levels." However, Stevenson and Kurth subsequently found only a small temperature dependence of the $\delta$ values of the inner protons of [18]annulene.[27] What then is the cause of the

  

discrepancy? Our explanation is simple: neither the X-ray nor the electron-correlated geometries are correct. [18]Annulene does not have a $D_{6h}$ structure.

The $^1$H NMR chemical shifts computed with numerous methods on $D_{6h}$ geometries, optimized at various HF, MP2, or various DFT levels by imposing $D_{6h}$ symmetry, failed completely in reproducing the experimental results (Figure 1 and Table 1). The solution of the disagreement is not the level of theory employed, but rather in the use of the lower symmetry geometries. Although $D_{3h}$ and $D_3$ structures gave results in closer agreement with the experimental values, as BS noted, these results are still unsatisfactory. We find that *only* the $C_2$ geometry gave acceptable computed chemical shifts (Table 1). These findings exclude the "highly delocalized" $D_{6h}$ structure for [18]annulene, as well as the $D_{3h}$ and $D_3$ alternatives.

While the degree of delocalization is overestimated by various DFT and MP2 methods, the HF level underestimates the delocalization in aromatic molecules.[3] Consequently, a hybrid density functional that has a larger HF component should give an intermediate structure on optimization. Indeed at the KMLYP and BHLYP levels, which include approximately 50% HF, reduced symmetry ($D_{3h}$, $D_3$, and $C_2$) [18]annulene structures are lower in energy than the $D_{6h}$. However, the $C_2$ geometry is the only minimum (Table 1). While the computed $\delta$H values of the outer protons of $D_{3h}$ and $D_3$ structures are acceptable compared with experiment (Table 1), the chemical shifts of the inner protons of the $D_3$ ($\delta H_{inner} = -4$ ppm) and $D_{3h}$ ($\delta H_{inner} = -5$ ppm) forms differ by 1 and 2 ppm, respectively. In contrast, the bond-length alternating $C_2$ KMLYP and BHLYP minima gives[28] outer and inner proton chemical shifts (average: 8.9 and −2.5 ppm

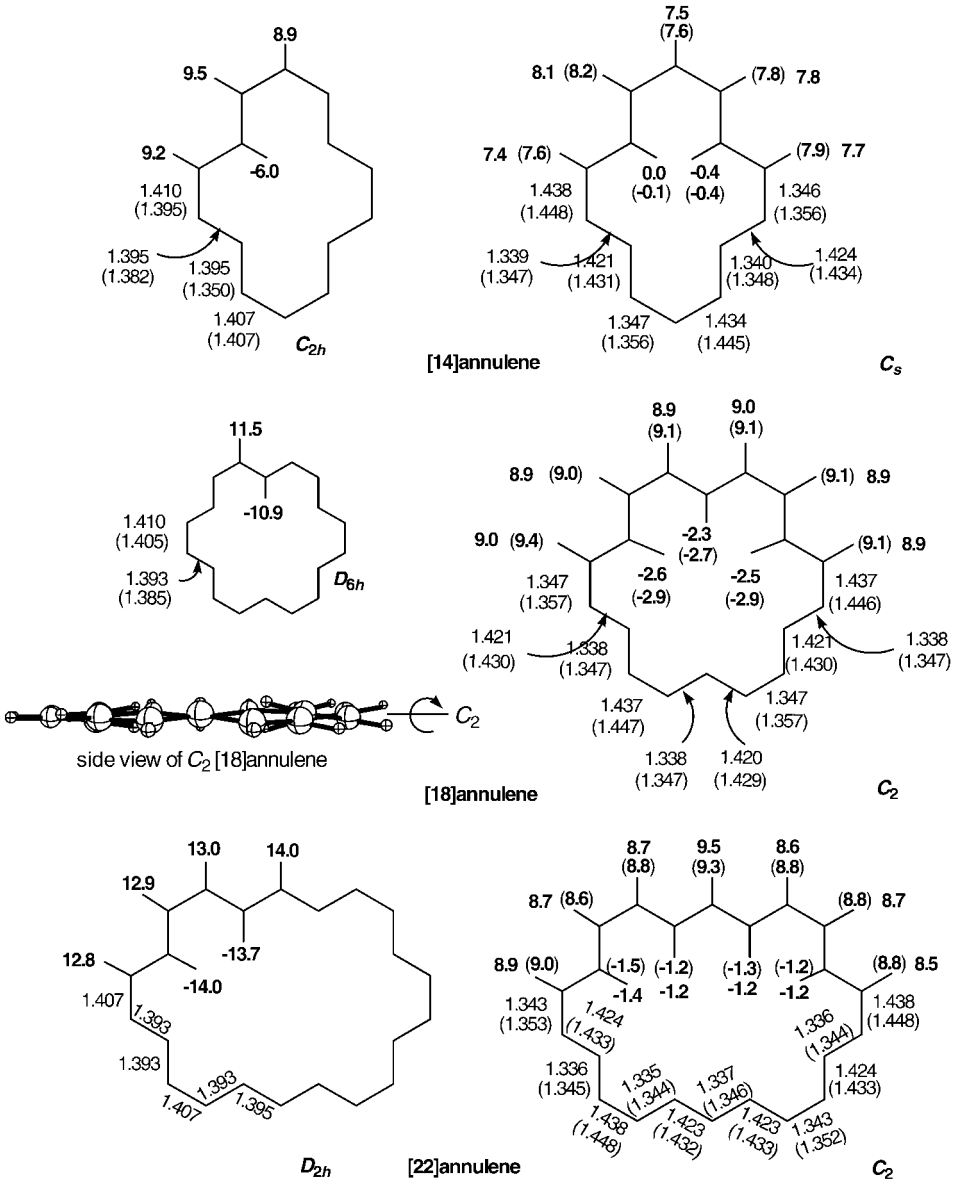


***Figure 1.*** Optimized geometries and chemical shifts (bold) of [14]-, [18]-, and [22]annulenes. The high symmetry structures on the left were optimized at B3LYP/6-311+G** (the numbers in parenthesis are the X-ray distances in Å) and the corresponding lower symmetry structures on right at KMLYP/6-311+G** and BHLYP/6-311+G** (in parenthesis). The $^1$H chemical shifts (in ppm) were computed on these geometries at GIAO-B3LYP/6-311+G**//. The experimental NMR values are given in Table 1.

  

***Table 1:*** Theoretical results[41] for the [4*n*+2]π annulenes, Figure 1.[a]

| [N] | PG | Level | $\Delta r$ | $E_{rel}$ | $\tilde{\nu}$ | $\delta H_{inner}$ | $\delta H_{outer}$ |
|---|---|---|---|---|---|---|---|
| [14] | $D_2$ | B3LYP | 0.015 | 2.6 | 102.7 | −6.7 | 9.0 to 9.7 |
| | $C_{2h}$ | B3LYP | 0.015 | 0.0 | 97.8 | −6.0 | 8.9 to 9.5 |
| | $D_2$ | KMLYP | 0.013 | 5.3 | 741.0*i* | −7.0 | 8.7 to 9.4 |
| | $C_2$ | KMLYP | 0.105 | 1.7 | 97.8 | 0.4 to 1.0 | 7.3 to 7.9 |
| | $C_{2h}$ | KMLYP | 0.013 | 2.5 | 664.3*i* | −6.1 | 8.6 to 9.3 |
| | $C_s$ | KMLYP | 0.098 | 0.0 | 103.8 | 0.0 to −0.4 | 7.4 to 8.1 |
| | $D_2$ | BHLYP | 0.014 | 5.0 | 680.5*i* | −7.0 | 8.8 to 9.5 |
| | $C_2$ | BHLYP | 0.109 | 1.9 | 98.1 | 0.4 to 1.0 | 7.4 to 8.0 |
| | $C_{2h}$ | BHLYP | 0.014 | 2.2 | 608.0*i* | −6.1 | 8.7 to 9.4 |
| | $C_s$ | BHLYP | 0.101 | 0.0 | 104.0 | −0.1 to −0.4 | 7.6 to 8.2 |
| | $C_{2h}$ | Experiment[26] | 0.057 | | | 0.0 | 7.6 |
| [18] | $D_{6h}$ | B3LYP | 0.017 | 0.0 | 72.3 | −10.9 to −11.0 | 11.5 to 11.6 |
| | $D_{6h}$ | KMLYP | 0.015 | 3.2 | 1218.3*i* | −11.3 to −11.5 | 11.2 to 11.4 |
| | $D_{3h}$ | KMLYP | 0.095 | 0.6 | 97.5*i*, 95.4*i*, 45.8*i* | −4.9 to −5.0 | 9.3 to 9.8 |
| | $D_3$ | KMLYP | 0.095 | 0.4 | 74.9*i* | −4.2 to −4.5 | 9.4 to 9.5 |
| | $C_2$ | KMLYP | 0.099 | 0.0 | 73.0 | −2.3 to −2.6 | 8.9 to 9.0 |
| | $D_{6h}$ | BHLYP | 0.015 | 2.6 | 1073.0*i* | −11.2 to −11.4 | 11.2 to 11.5 |
| | $D_{3h}$ | BHLYP | 0.094 | 0.4 | 100.0*i*, 89.4*i*, 56.2*i* | −4.9 to −5.1 | 9.6 to 9.8 |
| | $D_3$ | BHLYP | 0.095 | 0.4 | 23.7*i*, 22.6*i* | −4.3 to −4.6 | 9.5 to 9.7 |
| | $C_2$ | BHLYP | 0.100 | 0.0 | 74.0 | −2.7 to −2.9 | 9.0 to 9.4 |
| | | Experiment[26,27] | 0.042 | | | −2.99 | 9.3 |
| [22] | $D_{2h}$ | B3LYP | 0.014 | | 48.3 | −13.7 to −14.0 | 12.8 to 14.0 |
| | $D_{2h}$ | KMLYP | 0.013 | 6.4 | 1840.0*i* | −14.0 to −14.6 | 12.4 to 13.9 |
| | $C_{2v}$ | KMLYP | 0.100 | 0.2 | 22.0 | −3.1 to −3.4 | 9.2 to 10.1 |
| | $C_2$ | KMLYP | 0.103 | 0.0 | 46.6 | −1.2 to −1.4 | 8.5 to 9.5 |
| | $D_{2h}$ | BHLYP | 0.014 | 5.4 | 1605.8*i* | −13.9 to −14.5 | 12.5 to 13.9 |
| | $C_{2v}$ | BHLYP | 0.101 | 0.2 | 104.7*i* | −3.0 to −3.3 | 9.3 to 10.1 |
| | $C_2$ | BHLYP | 0.104 | 0.0 | 97.8 | −1.2 to −1.5 | 8.6 to 9.3 |
| | | Experiment[37] | | | −0.4 to −1.2 | 8.5 to 9.7 | |

[a] The 6-311+G** basis set was used throughout for optimization of the structures. [N] indicates the number of carbon atoms in the annulene ring. PG is the point group. $\Delta r$ [Å] is the difference between the shortest and the longest C–C bond length. $E_{rel}$ [kcal mol$^{-1}$] is the relative energy[41] with respect to the energetically most stable structure, at various levels of theory. $\tilde{\nu}$ gives the imaginary (indicated with *i*) or the smallest real vibrational frequency. $\delta H_{inner}$ and $\delta H_{outer}$ [ppm] are the GIAO-B3LYP/6-311+G** $^1$H NMR chemical shifts evaluated relative to TMS (with a computed proton shielding of 31.98).

KMLYP; 9.2 and −2.8 ppm BHLYP, Figure 1) remarkably close to the experimental data, 9.3 and −3.0.

In addition to this NMR spectroscopic evidence, $C_2$ [18]annulene is appreciably lower in energy than the $D_{6h}$ form at KMLYP and BHLYP as well as at MPW1PW91 (Table 2). The same is true at the current cutting edge of theory: single-point energy comparisons using the highly correlated CCSD(T) method (with DZP(C)+DZ(H)) also predict the $C_2$ form to be more stable than the $D_{6h}$ structure. The different energy ordering at B3LYP and at MP2 (Table 2) is suspect: Schaefer and co-workers[29] have stressed that these methods "overestimate the delocalization." While the KMLYP and BHLYP energy differences between the $C_2$ and the $D_3$ and $D_{3h}$ geometries are small (Table 1), the $D_3$ and $D_{3h}$ forms are higher order saddle points rather than minima. $D_{6h}$ [18]annulene is a transition structure, rather than a minimum. The eigenvectors of the sizable imaginary frequencies, 1218*i* at KMLYP and 1073*i* cm$^{-1}$ at BHLYP (Table 1), indicate the strong preference for C–C bond alternation. Hence, we conclude that [18]annulene prefers a bond alternating $C_2$ (or closely related) geometry over the currently accepted bond equalized $D_{6h}$ (or slightly nonplanar) structure. Grimme's newly introduced SCS-MP2 method overcomes the delocalization overestimation problem of MP2[30] and yields similar results for [18]annulene as CCSD(T): the $C_2$ form is favored over $D_{6h}$ by 1.2 kcal mol$^{-1}$ at SCS-MP2/TZV(d,p)//SCS-MP2/TZV(d,p).[31]

Why does [18]annulene prefer the $C_2$ structure? In 1952, Mislow predicted that the higher annulenes should not be planar owing to the steric repulsion between the inner hydrogen atoms.[1a] As Mislow foresaw, the average 1.88 Å H···H nonbonded distance in the $D_3$ structure is 0.03 Å larger than that in the $D_{6h}$ form (1.85 Å). However, the average H···H separation in the $C_2$ form is appreciably larger (1.94 Å) and this helps explain the preference for lower symmetry $C_2$ form for [18]annulene.

***Table 2:*** Single-point energy $C_2$ versus $D_{6h}$ [18]annulene energy differences, $E_{rel}$ [kcal mol$^{-1}$].

| Level | $C_2$ | $D_{6h}$ | $E_{rel}$[a] |
|---|---|---|---|
| HF/6-311+G**//KMLYP/6-311+G** | −692.11092 | −692.07832 | 20.45 |
| KMLYP/6-311+G**//KMLYP/6-311+G** | −695.38249 | −695.37735 | 3.22 |
| CCSD(T)/DZP(C)+DZ(H)(fc)//KMLYP/6-311+G** | −694.47008 | −694.46674 | 2.10 |
| CCSD(T)/DZ(fc)//KMLYP/6-311+G** | −693.44243 | −693.43812 | 2.70 |
| BHLYP/6-311+G**//KMLYP/6-311+G** | −696.34217 | −696.33821 | 2.49 |
| MPW1PW91/6-311+G**//KMLYP/6-311+G** | −696.61875 | −696.61819 | 0.35 |
| B3LYP/6-311+G**//KMLYP/6-311+G** | −696.80933 | −696.81557 | −3.91 |
| BLYP/6-311+G**//KMLYP/6-311+G** | −696.48006 | −696.49043 | −6.51 |
| BP86/6-311+G**//KMLYP/6-311+G** | −696.78056 | −696.79173 | −7.00 |
| MP2/6-31G*//KMLYP/6-311+G** | −694.23195 | −694.25595 | −15.06 |

Positive values of $E_{rel}$ indicate that the $C_2$ structure is more stable whereas negative $E_{rel}$ values signify the greater stability of $D_{6h}$.

Why did the X-ray structure determination fail to find the correct geometry? Both static and dynamic disorders are possible reasons. Static disorder is due to a superposition of a lower symmetry structure leading to apparent higher symmetry. According to Gorter et al.,[14] the diameters determined by X-ray analysis for [18]annulene excluded the possibility of a 50:50 inversion disorder model of bond alternating $D_{3h}$ structures. However, their reference model was based on an early[32] HF/6-31G* geometry, which had "calculated ring diameters up to 0.20 Å

  

too large" (Table 3). In contradiction, the data in Table 3 demonstrate that the 50:50 inversion disorder $C_2$ (or $D_{3h}$) model of [18]annulene cannot be excluded, since the computed major and minor ring diameters for the $C_2$, $D_{3h}$, as well as the $D_{6h}$ structures have deviations less than 0.06 Å from the experimental values. Furthermore, the 50:50 $C_2$ [18]annulene superposition shown in Figure 2 also yields an averaged "$D_{6h}$ structure" with internal (1.379 Å) and external (1.392 Å) C–C bond lengths close to the reputed X-ray separations,[14] 1.385 and 1.405 Å, respectively. Consequently we believe that the X-ray evidence does not forbid 50:50 inversion disorder for a bond alternating $C_2$ (or $D_{3h}$) [18]annulene structure.[9,16]

***Table 3:*** Comparison of C–C major and minor interatomic distances [Å] across the ring for the X-ray [18]annulene structure[14] with those computed[41] at different levels of theory.

| | | C···C across the ring | | Deviations from X-ray | |
|---|---|---|---|---|---|
| | | Minor [Å] | Major [Å] | Minor [Å] | Major [Å] |
| **X-ray** | $D_{6h}$ | 5.91 | 7.54 | 0.00 | 0.00 |
| //HF/6-31G* | $D_{6h}$ | 5.93 | 7.56 | +0.02 | +0.02 |
| //B3LYP/6-311+G** | $D_{6h}$ | 5.96 | 7.60 | +0.05 | +0.06 |
| //KMLYP/6-311+G** | $D_{6h}$ | 5.86 | 7.48 | −0.05 | −0.06 |
| **50:50 Distortion models**: | | | | | |
| //HF/6–31G* | $D_{3h}$ | 5.95 | 7.60 | +0.04 | +0.06 |
| //KMLYP/6-311+G** | $D_{3h}$ | 5.86 | 7.49 | −0.05 | −0.05 |
| //KMLYP/6-311+G** | $C_2$ | 5.86 | 7.48 | −0.05 | −0.06 |
| //BHLYP/6-311+G** | $C_2$ | 5.92 | 7.54 | +0.01 | 0.00 |

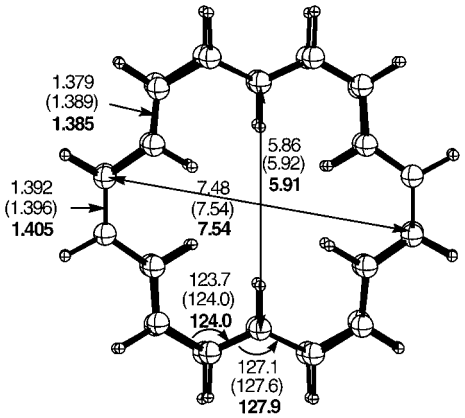


***Figure 2.*** 50:50 Inversion disorder (superposition) of KMLYP and BHLYP optimized $C_2$ [18]annulene. The values in parentheses are the corresponding BHLYP geometries while those in bold are from the X-ray data (1995)[14] measured at 111 K.

Dynamic disorder is a further complication. $D_{6h}$ [18]annulene is a transition state joining the two $C_2$ structures with an interconversion barrier of only about 3 kcal mol$^{-1}$ at KMLYP and BHLYP (2.1 kcal mol$^{-1}$ at our highest CCSD(T) level, Table 2). Hence, the symmetrization of [18]annulene takes place rapidly even at 111 K (the temperature of the 1995 X-ray investigation) which should result in a time-averaged $D_{6h}$ structure and compromises the interpretation of the experimental data. Haddon[16] also pointed out that "unfortunately the X-ray study cannot be regarded as definitive in the present case" since the "C–C distances are averaged over time and over a large number of unit cells by the diffraction process."

Unlike the NMR spectroscopic data, the presently available low-resolution experimental IR spectrum[1b] does not permit differentiation among the geometrical alternatives. Although the agreement between the experimental[1b] and computed[17] IR spectra (BLYP/6-311G*) for $D_{6h}$ [18]annulene was said to lend "further support to the delocalized structure," not only the $D_{6h}$, but also the $D_{3h}$, $D_3$, and particularly the $C_2$ optimized [18]annulene structures all give computed IR frequencies in the same range. For example, on average, corresponding frequencies for all these structures differ by merely 2.3 %, which is in marked contrast to the large variation (> 200 % for inner protons and > 25 % for outer protons, Table 1) for the $\delta$ values. The same relative insensitivity to structural changes (and the lack of high resolution data) characterizes other spectroscopic methods which have been applied to [18]annulene.[18,19]

*[14]Annulene*: Although the highest possible symmetry of [14]annulene is $D_{2h}$, this lower homologue of $C_{18}H_{18}$ suffers from having more severe nonbonded repulsions among the intra-annular hydrogen atoms. These are ameliorated in nonplanar geometries. The X-ray structure determination[33] at 283–303 K found $C_{2h}$ symmetry and moderate C–C bond alternation ($\Delta r = R_{single} - R_{double} = 0.057$ Å, the same alternation as in the naphthalene perimeter). However, the $^1$H NMR chemical shifts of the inner hydrogen atoms ($\delta H_{inner} = -5.4$ to $-7.0$ ppm), computed using the X-ray geometry,[25] are far from the measured $\delta = 0.0$ ppm value.[26] Hence, the experimental structure of [14]annulene also requires revision.

While all the DFT levels (Table 1) find the $C_{2h}$ form to be slightly more stable (2.5 kcal mol$^{-1}$) than the $D_2$, the local $C_{2h}$ B3LYP/6-311+G** minimum gives computed proton chemical shifts far from the experimental values. The $C_{2h}$ form is a transition state at both the BHLYP and KMLYP levels; the single imaginary frequency (> 600$i$ cm$^{-1}$) leads to the most stable $C_s$ structure. The computed $^1$H NMR chemical shifts of the $C_s$ inner ($\delta = 0.0$ to $-0.4$ ppm) and outer ($\delta = 7.4$ to 8.2 ppm) protons are in good agreement with experiment (Table 1). Note that the substantial ($\Delta r = 0.10$ Å) C–C bond alternation in the optimized $C_s$ structure (Table 1 and Figure 1) is nearly twice as large as the X-ray finding. We conclude that the currently accepted bond-length equalized $C_{2h}$ structure of [14]annulene is not correct; instead, a bond-length alternating $C_s$ geometry is favored.

*[10]Annulene*: The second member of the neutral aromatic hydrocarbon series after benzene, [10]annulene, cannot adopt $D_{10h}$ symmetry owing to ring strain. No X-ray structure[34] of [10]annulene is available, but computational studies reveal many possible (azulene-like, naphthalene-like, twist, boat, and heart) conformations all of which are nonplanar. Employing the "cutting edge" CCSD(T) method, two investigations concluded that the non-aromatic twist $C_2$ form is best.[29,35] Schaefer and co-workers demonstrated that HF underestimates, whereas MP2, B3LYP, and several other DFT

  

levels overestimate the degree of delocalization in the minimally nonplanar aromatic conformations.[29] In contrast, we find that the KMLYP and BHLYP methods, which have a larger HF component than B3LYP, give optimized geometries and relative energies of [10]annulene isomers which agree well[36] with the much more computational-resource demanding CCSD(T). This result further supports our use of KMLYP and BHLYP to optimize the [14]-, [18]-, and [22]annulene geometries, since this is not feasible at CCSD(T).

*[22]Annulene*: Although [22]annulene was prepared by Sondheimer and co-workers[37] in 1971, its X-ray structure is not known. The NMR $^1$H chemical shifts of the inner and outer protons are $\delta = -0.4$ to $-1.2$ and 8.5 to 9.7 ppm, respectively. CK reported[4] a bond-length equalized $D_{2h}$ structure at B3LYP/6-31G*, but the very large disagreement between the computed and experimental $^1$H NMR chemical shifts (Table 1) clearly excludes such high symmetries for [22]annulene. The eigenvector of the large imaginary vibrational frequency of the $D_{2h}$ form ($\tilde{\nu}_i > 1600i\ \mathrm{cm}^{-1}$ at KMLYP and BHLYP) points towards bond-alternating structures.

The computed $^1$H NMR chemical shifts (Table 1) of the $C_2$ [22]annulene outer ($\delta_{\mathrm{outer}} = 8.4$ to 9.5 ppm) and inner ($\delta_{\mathrm{inner}} = -1.2$ to $-1.4$ ppm) protons agree with the experimental[37] NMR spectroscopy values; those computed for the higher-energy $C_{2v}$ forms differ by 2 ppm. Hence, we predict that [22]annulene favors a bond-alternating structure. By implication, this should be true of all the higher annulenes.

*Bridged annulenes*: The inner hydrogen repulsion and conformational flexibility problems in larger annulenes, as in Vogel and Roth's 1,6-methano[10]annulene,[38] have been overcome in bridged structures. Both X-ray data and DFT computations[39] show various bridged [10]annulenes to have C–C bond-equalized structures. The same is true for many of the bridged [14]annulenes. The X-ray geometries of both bis(methano)[14]annulene conformers, *syn* and *anti*, are reproduced by B3LYP/6-31G* computations.[40] While the *syn* form is aromatic, the small C–C bond-length range (1.427 to 1.389 Å) may be due, at least in part, to the restraints of the bridging $CH_2$ groups. Conversely, the non-aromatic behavior (1.486 to 1.356 Å C–C range) of the *anti* conformer is partly due to the steric constraints of the bridges. KMLYP and BHLYP give geometries in equally good agreement with the X-ray data. *trans*-Dihydropyrene, another bridged [14]annulene, favors $C_{2h}$ symmetry at B3LYP (the C–C bond-length range is only 1.393 to 1.401 Å) but a lower symmetry $C_2$ form (1.364 to 1.394 Å) at KMLYP.

In contrast, the bridged [18]annulene, hexahydrocoronene, behaves distinctly differently at B3LYP than at KMLYP and BHLYP. While the B3LYP structure is highly C–C bond equalized at the $D_{3\mathrm{d}}$ minimum, this $D_{3d}$ geometry is a transition state ($\tilde{\nu} = 1069i\ \mathrm{cm}^{-1}$) at KMLYP and BHLYP. Instead, the $D_3$ form, with moderate bond alternation ($\Delta r = 0.077$ Å), is a minimum at KMLYP and BHLYP. The inner six-membered ring in hexahydrocoronene has essentially equal C–C bond lengths owing to the tendency of the σ framework to favor regular geometries.

In summary, our evidence establishes that the crossover point from the more symmetrical to bond-alternating Hückel monocycles occurs at [14]annulene. The currently accepted highest possible symmetry structures of [14]-, [18]-, and [22]annulene can be ruled out as they give computed $^1$H chemical shifts which disagree grossly with the experimental values. The correct structures, which can be obtained by optimization at the KMLYP and BHLYP DFT levels, give excellent $\delta$ $^1$H chemical shift agreement. All three annulenes have lower symmetries and exhibit considerable C–C bond-length alternation ($\Delta r = 0.1$ Å, Table 1). Nonetheless, they are clearly aromatic, judging from their abnormal inner and outer proton chemical shifts as well as their appreciable aromatic stabilization energies.[3,4] Equal C–C bond lengths in $[4n+2]\pi$ systems are not required for aromaticity, and actually reduce the stability of the [14]-, [18]-, and [22]annulenes by about 2.0, 2.8, and 5.8 kcal mol$^{-1}$, respectively (Table 1). As we have noted herein and earlier,[3,20] changes in geometry have much greater effects on the magnetic properties, which appear to be the most sensitive measures of the degree of cyclic electron delocalization. The commonly used descriptive terms, "localized, " for bond alternating,[3] and "delocalized," for bond equalized, are deceptive and misleading; they should be abandoned in the context of aromaticity or specified explicitly. The structures of fully conjugated $4n+2$ π-electron systems may have appreciable bond alternation and still be delocalized and aromatic.[3] Shaik, Hiberty, and co-workers have emphasized the strong global distortive tendency of π components towards localized bonding.[6–8] This tendency is not overcome in the most symmetrical geometries of the [14]-, [18]-, and [22]annulenes by the modest gain in delocalization energy resulting from bond-length equalization, even when combined with the preference of the σ C–C bonds to have the same length.

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