

The Energetics of Aromatic Hydrocarbons: An Experimental Thermochemical Perspective

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Contents

I. Introduction to Aromaticity and Antiaromaticity: Definitions and Scope of the Study	1541	B. Trialene and Bicyclohexatriene	1561
II. Benzene and the [n]Annulenes	1543	C. Pentalene	1562
A. Benzene ([6]Annulene)	1543	D. Acenaphthylene and Fluoranthene	1562
B. [4]Annulene	1544	E. Pyracylene, Aceplaidylene, and Some Related Species	1562
C. [8]Annulene	1544	F. Corannulene	1563
D. [10]Annulene	1545	G. Stabilization Energies in Nonalternant Hydrocarbons	1563
E. [12]Annulene	1546	XI. Fullerenes	1564
F. [14]Annulene	1546	XII. Acknowledgments	1564
G. [16]Annulene	1546	XIII. References	1564
H. [18]Annulene	1547		
III. Polycyclic Aromatic Hydrocarbons	1547		
A. Cata-Condensed Aromatic Hydrocarbons	1547		
1. Homologous Series	1548		
2. Three and Four Benzenoid Rings	1549		
3. Five or More Benzenoid Rings	1549		
B. Peri-Condensed Aromatic Hydrocarbons	1550		
1. Pyrene	1550		
2. Perylene	1550		
3. Coronene	1550		
C. Stabilization Energies in Benzenoid Hydrocarbons	1551		
IV. Effect of Alkylation	1552		
A. <i>n</i> -Alkyl-Substituted Benzenes: Homologous Series	1552		
B. Polyalkylation: Additivity of Small Substituents on Benzene	1552		
C. <i>tert</i> -Butylated Benzenes	1553		
D. Substituted Naphthalenes	1554		
E. Methylated 3- and 4-Ring Species	1554		
V. Energetics of Hydrogenation Reactions	1555		
VI. Cyclophanes	1556		
VII. Polyphenyl and Other Polyaryl Compounds	1557		
A. Biphenyl	1557		
B. Biaryls	1558		
C. Polyphenyls	1558		
D. Cyclic Polyphenyls: Biphenylene and Triphenylene	1559		
E. Polyphenyl Polyaromatic Compounds	1559		
VIII. Benzoannulation and Annulation of Benzene	1559		
A. Benzoannulation	1559		
B. Cyclobutadiene, Its Benzo Analogues, and the [M]Phenylenes	1559		
IX. Alternant [n]Annuleno[m]annulenes	1560		
X. Nonalternant Hydrocarbons	1561		
A. Azulene	1561		

I. Introduction to Aromaticity and Antiaromaticity: Definitions and Scope of the Study

Undeniably, the concept of aromaticity is theory-dependent and, as documented by the contributions to this thematic issue of *Chemical Reviews*, has numerous definitions, manifestations, and ramifications. The current study adopts an experimental thermochemical perspective in the examination of the aromatic (or nonaromatic or antiaromatic) character of organic compounds. The enthalpies of formation we cite are derived from such calorimetric measurements as enthalpies of combustion and hydrogenation reactions, accompanied by related determinations of phase change enthalpies. Most of the thermochemical data are from the evaluated archival source,¹ which contains all the original literature citations, unless stated otherwise. Following thermochemical convention, we use kJ/mol where by definition 4.184 kJ = 1 kcal. Since aromaticity and antiaromaticity are considered to be properties of isolated molecules, all thermochemical data herein refer to the gas phase (at standard temperature and pressure) unless another phase is specified. Fortunately, there are numerous data and some simple and reliable methods for estimating phase change enthalpies, at least for hydrocarbons. As such, data for enthalpies of formation in the condensed phase (liquid or solid) will generally be supplemented by the appropriate measured or estimated phase change enthalpy to allow for discussion of the idealized gas phase (i.e., at 1 atm and 25 °C). Enthalpies of vaporization (liquid to gas) of hydrocarbons will be derived using eq 1, taken from ref 2, and those of sublimation (solid to gas) by

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eq 2, recommended by ref 3. The former equation was suggested for any hydrocarbon, while the latter equation was initially used only for unsubstituted polycyclic aromatic hydrocarbons. We assume equal validity for both.

$$\Delta H_v = \Delta H_f(g) - \Delta H_f(l) = 4.7n_c + 1.3 \quad (1)$$

$$\Delta H_s = \Delta H_f(g) - \Delta H_f(s) = 6.0n_c \quad (2)$$

Since the phase change enthalpies are assumed to

depend solely on the number of carbons in the species, n_c , the comparison between isomeric hydrocarbons and pairs of hydrocarbons with the same number of carbons is presumed to be equally valid in any phase, although we will always prefer to use measured rather than estimated data for gas-phase species.

Although numerous classes of compounds exhibit aromatic character, almost all of the experimental thermochemical studies have been performed on carbocyclic species. This study, therefore, focuses on neutral, π -conjugated, carbocyclic systems and some of their alkylated and arylated derivatives. Even so-focused, the multiring carbocyclic systems of interest encompass a wide variety of structure. The alternant and nonalternant species may contain fused six-membered rings only (benzenoid, alternant), five- and/or seven-membered rings fused among the six-membered rings (nonbenzenoid, nonalternant), and four-membered rings fused among the six-membered rings (nonbenzenoid, alternant). The rings may be chain-linked (σ -bonded) as in polyphenyls or cyclophanes or fused to form acenes, phenacenes, phenes, erylenes, [N]phenylenes, circulenes, and helicenes. Although many compounds in these categories have been synthesized, isolated, and characterized by both their spectra and melting points, in fact, surprisingly few thermochemically relevant data have been determined. We will exclude charged species mostly obtained in solution such as cyclopropenyl cation and cyclopentadienyl anion as well as 3-dimensional aromatic species since thermochemical data are generally not available to deduce their aromatic character (except the C_{60} and C_{70} fullerenes).

Most of the heterocyclic species for which experimental enthalpies of formation are known have one or two nitrogen atoms or an oxygen, five- and/or six-membered rings, and at most three rings. This would appear to be a considerably rich chemical terrain, especially if substituted derivatives are included in the landscape. It is not. It is interesting, informative, but woefully incomplete. For example, while furan is well-understood by the thermochemist and organic chemist alike, the corresponding ring-contracted and ring-expanded oxirene and oxepin are not available for thermochemical investigation and subsequent comparison. For five-membered ring heterocycles with only nitrogen and carbon in the ring, the so-called azoles from pyrrole to pentazole, a bare majority are thermochemically characterized. For the corresponding six-membered ring species (the so-called azines from pyridine to pentazine), it is now a narrow majority that are not so understood. In both cases, data for the species with adjacent nitrogens are generally missing. Almost all of the possible two- or more-ring species are yet to be investigated by the thermochemical community except for benzo-analogues of the one-ring species.

Very often, other heterocyclic compounds of interest are too unstable for isolation in the necessary quantity and purity and/or of insufficient volatility necessary for combustion or even reaction analysis. Indeed, many of the desired species remain unknown except as transient intermediates and thus are not charac-

terized at all except for inference from a reaction product and perchance a spectroscopic signature. Such is the case for those species that are π isoelectronic to benzene (e.g., pentazines), naphthalene, and their multiring counterparts and those putatively aromatic species with 6-, 10-, and generally $(4n + 2)$ π electrons.⁴ This is even more painfully true for species that have $4n$ π electrons and so are often presumed to be non- or antiaromatic (e.g., 1*H*-azirines and 1*H*-azepines). Exacerbating the problem is the 40 kJ/mol range in the reported measured enthalpies of formation of methylenimine (formaldimine), the simplest acyclic species with a C=N double bond.^{5,6} We recognize this last species, H₂C=NH, to be an archetypal species for numerous nitrogenous heterocycles much as ethylene is for benzene and other unsaturated hydrocarbons. And while another nitrogen-containing paradigm, vinylamine, H₂C=CH-NH₂, seemingly has less ambiguity in its understanding, fewer measurements are available to contradict each other.⁷

Some comparisons will be made between the thermochemical description of aromaticity and other criteria such as magnetic, spectroscopic, or structural properties. Occasionally will we include comparisons between computational theory and calorimetric experiment. However, aromaticity is a "multidimensional" phenomenon,⁸ and as such, we concentrate on just one of its important aspects. Thorough surveys and comparisons of other models, methodologies, and results are included in other reviews in this issue. Some newer volumes are comprehensive in their outlook.⁹⁻¹²

In keeping with the oft-cited thermodynamic criterion for aromaticity,¹³ we consider an aromatic species as one in which cyclic π -electron delocalization results in an enthalpy of formation more negative than expected based on a related reference species, that is, it is stabilized relative to the reference. An antiaromatic species is one that is destabilized from cyclic delocalization, that is, its enthalpy of formation is more positive than expected, and a nonaromatic species is neither stabilized nor destabilized. We will make considerable use of the notion of "resonance energy", a concept comprising many different types of calculations with an unfortunate deficit of unique identifying technical names, that is, resonance energy is frequently defined differently by different investigators and so, unlike thermochemical entities, is neither additive nor transferable.

II. Benzene and the [*n*]Annulenes

A. Benzene ([6]Annulene)

The term "aromatic" was originally applied to many of the synthesized derivatives of benzene because they exhibited that olfactory feature. Benzene itself would never be so described. However, benzene is the quintessential and archetypal molecule which exhibits the concept of aromaticity in all its many structural and chemical manifestations.

One of the first quantitative measures of aromaticity was a thermochemical one—the classic measurement of enthalpies of hydrogenation of unsatur-

ated six-membered hydrocarbon rings by Kistiakowsky and colleagues.¹⁴ They measured hydrogenation enthalpies of cyclohexene, 1,3-cyclohexadiene, and benzene (**1**). The directly measured enthalpy of hydro-



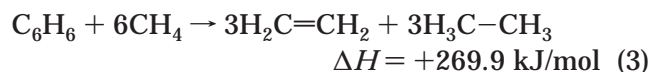
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genation of cyclohexene to form cyclohexane was -118.6 ± 0.4 kJ/mol¹⁵ at 355 K, comparable to that of typical acyclic *cis*-olefins.⁵ The likewise directly measured enthalpy of hydrogenation of 1,3-cyclohexadiene to form cyclohexane was not quite twice the value for cyclohexene to cyclohexane but instead was the somewhat smaller (less negative) -229.6 ± 0.4 kJ/mol. The 7.6 kJ/mol difference, neglecting any temperature effects, between the enthalpy of hydrogenation of 1,3-cyclohexadiene and twice that of cyclohexene is ascribed to a stabilizing interaction between the two conjugated double bonds of the diene due to the delocalization of four π electrons. One might, therefore, expect that the enthalpy of hydrogenation of the corresponding three-double-bond species, benzene (or "1,3,5-cyclohexatriene"¹⁶), to form cyclohexane would be $3(-118.6)$ with a $3(7.6)$ kJ/mol correction for the three pairwise conjugative interactions of the double bonds. In other words, an estimated hydrogenation enthalpy of benzene of ca. -333 kJ/mol appears plausible. However, the measured value¹⁷ was only -205.3 ± 0.7 kJ/mol. The phenomenal 127.7 kJ/mol difference between the experimental and calculated enthalpies of hydrogenation may be attributed to the energetic manifestation of the cyclic delocalization of the π electrons over and above that expected for "merely conjugated" double bonds. This net energy difference, termed the "Dewar resonance energy" (DRE),¹⁸ is ca. 21.3 kJ/mol per π electron. The full delocalization energy, or resonance energy (RE), may be calculated as the difference between the enthalpy of hydrogenation of the real, fully delocalized six π electrons of the benzene ring and the enthalpy of hydrogenation estimated for six π electrons as found in isolated, noninteracting double bonds. For benzene compared to three cyclohexenes, the difference of 150.5 kJ/mol, or 25.1 kJ/mol per π electron, is the largest of all compounds which we consider aromatic and for which we have requisite data.

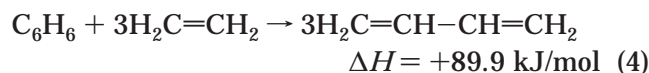
The calculated energy difference depends on the reference compound(s) chosen for comparison as well as on additional structural features such as σ -bond energy and steric strain which may affect the energetic analysis. A hypothetical molecule, "1,3,5-cyclohexatriene" is a reasonable choice for a reference comparison to benzene, as are the real cyclohexene and cyclohexadiene molecules which represent a portion of the π -electron energy of the hypothetical molecule. However, the hypothetical triene has alternating single and double C–C bonds of different lengths, while benzene's six C–C bond lengths are identical. One estimate of the energy required to equalize the bond lengths in the reference compound is ca. 113 kJ/mol, and, as a result the calculated

resonance energy of benzene¹⁹ becomes ca. 264 kJ/mol. Other strain estimates result in yet different REs which can be quite different from each other depending on the underlying assumptions.

Isodesmic and homodesmotic reaction schemes use small molecules which retain bond types on both sides of the equation to model the relevant structural components of the cyclic conjugated species.²⁰ The homodesmotic reactions match bond and hybridization types for C–C and C–H on both sides of the equation. Calculation of the isodesmic stabilization energy (ISE) from the additivity of the enthalpies of formation of CH₄, H₃C–CH₃, and H₂C=CH₂ is analogous to the RE derived above for benzene in that the reference system has noninteracting ethylenic double bonds and the calculated energy includes both the cyclic and noncyclic π -electron delocalization. Isodesmic reactions, like the RE calculation, tend to overestimate the stabilization because of the inclusion of the noncyclic delocalization energy.



The homodesmotic stabilization energy (HSE), analogous to the DRE derived above, uses *s-trans*-1,3-butadiene as a model for the single C_{sp²}–C_{sp²} bond and conjugated C=C bonds in benzene. Because the “merely conjugated” π -electron delocalization is stabilizing, the HSE is always of lower energy than the ISE and is thus a better estimation of aromaticity or antiaromaticity.²¹



Historically interesting to theorists attempting to improve their correlations and predictions of compound properties may be Kistiakowsky's remark¹⁴ that “the figures show the disproportionately great stabilization of benzene, which is not at all in quantitative agreement with the calculations of Pauling and his co-workers”.

B. [4]Annulene

After a demonstration of stabilization of the fully conjugated cyclic triene, a natural succeeding question concerns the stabilization of cyclic polyenes of different ring sizes. Benzene may be classified as a member of the homologous [*n*]annulenes—monocyclic compounds with alternating double and single bonds and, necessarily, an even number of ring carbon atoms, [*n*]. The only annulene smaller than [6]-annulene (benzene) is [4]annulene (cyclobutadiene, 2). Bypassing experimental detail and complexity and



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accompanying computational assumptions, the enthalpy of formation of this latter species was recently reported²² to be 477 ± 46 kJ/mol. The immediate questions paralleling those earlier for benzene are what is its enthalpy of hydrogenation and how does

this quantity compare with twice that of cyclobutene? Although no direct measurements are available for the enthalpies of hydrogenation of either cyclobutene or cyclobutadiene, enthalpies of hydrogenation are calculated as the difference between the enthalpies of formation of the unsaturated species and the hydrogenation product, eq 5

$$\Delta H_{\text{H}_2} = \Delta H_f(\text{product}) - \Delta H_f(\text{reactant}) \quad (5)$$

The enthalpies of formation of cyclobutene (156.7 ± 1.5 kJ/mol) and cyclobutane (28.4 ± 0.6 kJ/mol) are known, and so the enthalpy of hydrogenation of cyclobutene is thus -128.3 ± 1.6 kJ/mol. The more exothermic enthalpy of hydrogenation of cyclobutene compared to cyclohexene and other acyclic *cis*-alkenes is ascribed to greater ring strain in the four-membered ring species. From the cyclobutene hydrogenation value, a value for the hydrogenation enthalpy of cyclobutadiene is estimated to be $2(-128.3) = -256.6$ kJ/mol for isolated double bonds in the reference species and $2(-128.3) - 2(-7.6) = -241.4$ kJ/mol for double-bond delocalization in the reference species. However, these quantities are dwarfed by the -449 ± 46 kJ/mol that would have been obtained experimentally were cyclobutadiene stable enough to be isolated and subsequently hydrogenated to cyclobutane. The phenomenon of extraordinary destabilization is worthy of its descriptive name, antiaromaticity. Indeed, the derived $(-449 + 257)/4 = -48$ kJ/mol per π electron RE and the $(-449 + 241)/4 = -52$ kJ/mol per π electron DRE destabilizations for cyclobutadiene are considerably greater than the corresponding stabilizations for benzene of +21 and +25 kJ/mol per π electron. Making additional assumptions and corrections, the original authors²² derived a total destabilization of -364 kJ/mol and partitioned this into -134 kJ/mol of ring strain and -230 kJ/mol or -57 kJ/mol per π electron (DRE) due to antiaromaticity.

Another enthalpy of formation for cyclobutadiene is based on the noncalorimetric experimental determination of the enthalpy of formation of benzocyclobutadiene,²³ a species which will be discussed later. Using that value, 427 kJ/mol, and the same logic as above, the various stabilization energies are RE = -36 kJ/mol per π electron and DRE = -40 kJ/mol per π electron. The ISE and HSE values (-192 and -312 kJ/mol, respectively) are close to those calculated at the MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + ZPE(HF/6-31G(d)) level for (*D*_{2h}) cyclobutadiene (-195.8 and -314.6 kJ/mol, respectively).²¹ When corrected by the calculated strain energy²⁴ of -140.6 kJ/mol, the ISE per π electron and HSE per π electron calculated here are -13 and -43 kJ/mol, respectively.

C. [8]Annulene

Cyclooctatetraene, or [8]annulene, is the third member of the [*n*]annulene series. Its enthalpy of formation of 295.9 ± 1.7 kJ/mol refers to the most stable all-(*Z*) isomer.²⁵ A recent high-level ab initio study²⁶ obtained an enthalpy of formation for the

most stable D_{2d} structure (**3**) of 293.2 kJ/mol, very close to the measured value. The hydrogenation



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enthalpy of (*Z,Z,Z,Z*)-cyclooctatetraene is -420.3 ± 2.0 kJ/mol.²⁷ From experimental enthalpy of formation data, the hydrogenation enthalpy of (*Z*)-cyclooctene²⁸ is -97.4 ± 0.4 kJ/mol. That this value is less exothermic than those for cyclohexene and cyclobutene arises partly from the strain energy of the cyclooctane product with its significant transannular H,H-repulsion.²⁹ We estimate an enthalpy of hydrogenation value of $4(-97.4) = -389.6$ kJ/mol for the reference cycle with isolated double bonds and $4(-97.4) - 4(-7.6) = -359.2$ kJ/mol for the reference cycle with delocalized double bonds. Cyclooctatetraene is thus destabilized with an RE of -30.7 kJ/mol or ca. -3.8 kJ/mol per π electron and with a DRE of -61.1 kJ/mol or ca. -7.6 kJ/mol per π electron. We hesitate to call this antiaromaticity—besides the above awareness of cyclooctane and its strain-derived instability, cyclooctatetraene itself is not planar and thus lacks even the relatively small conjugative stabilization found in the nonaromatic compound 1,3-cyclohexadiene and a fortiori the aromatic stabilization found in benzene.

Calculation of the ISE and HSE for planar D_{4h} cyclooctatetraene (**4**) at the same high level of theory as for cyclobutadiene²¹ gives a net stabilization of $+14.9$ kJ/mol per π electron (ISE) and destabilization due to cyclic delocalization of -14.9 kJ/mol per π electron (HSE). Calculated from the experimental



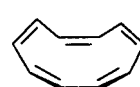
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enthalpies of formation and nonplanar cyclooctatetraene, the values are (kJ/mol per π electron): $+21.8$ (ISE) and -8.2 (HSE). Planar (D_{4h}) cyclooctatetraene is a transition state in the ring-inversion equilibration of tub (D_{2d}) cyclooctatetraene while the higher energy planar (D_{8h}) cyclooctatetraene is a transition state in the π -bond shift equilibration of D_{2d} .³⁰ If the D_{8h} structure is used for an HSE calculation, the destabilization due to cyclic π -electron delocalization over C–C bonds of equal length is even greater.

D. [10]Annulene

The syntheses of the [10]annulenes are fraught with difficulties. Apparently, the all-(*Z*) and *E,Z,Z,Z* isomers have significant angle strain while the *E,Z,E,Z,Z*-isomer suffers transannular H,H-repulsion. Solution enthalpy of hydrogenation measurements are perhaps plausible to suggest, but catalytically facilitated interconversion of *E,Z,E,Z,Z*-[10]-annulene into its valence isomer 4*a*,8*a*-dihydronaphthalene (bicyclo[4.4.0]deca-2,4,7,9-tetraene) is also expected. In addition, the transannular effect in both the annulene and cyclodecane hydrogenation product

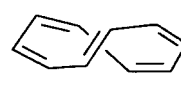
would confound interpretation of the aromaticity of the annulene except for the simplest comparison of it with five isolated double bonds. Also confounding have been theoretical studies of the [10]annulene potential energy surface. Both theoretical and experimental work showed the lowest energy all-*Z* structure to have a boat shape (**5**) with alternant single and double bonds.³¹ Calculations on the higher energy planar all-*Z* structure (**6**) show a slight bond alternation with D_{5h} symmetry and highly aromatic character.³² However, recent results suggest that only the high-order correlated methods will be able to correctly predict whether the *E,Z,Z,Z,Z*-[10]annulene is more stable in the C_2 “twist” (**7**) or the C_s “heart” (**8**) conformation.^{33,34}



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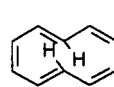


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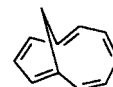


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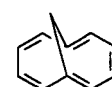
The transannular H,H-repulsion in *E,Z,E,Z,Z*-[10]-annulene (**9**) is relieved in the 1,5- and 1,6-methano derivatives, bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene (**10**) and bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**11**), respectively. These retain both substantial planarity



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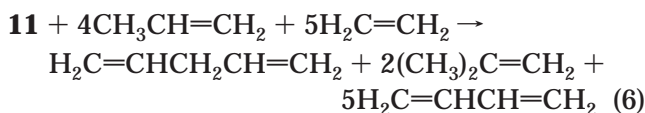


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and the 10 π -electron system around the periphery³⁵ and are sufficiently stable to have been thermochemically investigated, the former by hydrogenation reaction calorimetry and the latter by both this method and combustion calorimetry.³⁶ The difference between the derived enthalpies of formation of these isomers is ca. 85 kJ/mol, favoring the 1,6-isomer. This suggests that any stabilization conferred by the 10 π -annulene peripheries is mitigated by the position of the bridging group and resulting geometry. Indeed, because there may be some degree of transannular orbital interaction at the bridgehead carbons, these modified annulenes may be viewed as homoaromatic systems.³² Evidence other than thermochemical is required to distinguish the degree to which these compounds are homonaphthalene and homoazulene vs bridged annulenes.

Experimental NMR,³⁷ X-ray analysis,³⁸ and new MM3 calculations³⁴ suggest the 1,6-methano isomer to be a relatively planar structure with nonalternating outer-ring bond lengths, extensive conjugation, and aromatic character.³² A low-energy structure of the 1,5-methano isomer was likewise found by MM3 calculations³⁴ to have nonalternating bond lengths and relative planarity and to be in good agreement with the X-ray structure. An HSE calculated from

experimental enthalpies of formation for the reference molecules and an enthalpy of formation for the 1,6-methanoannulene from *ab initio* calculations including electron correlation is -41 ± 19 kJ/mol.³⁹ The authors speculate that the lack of any significant aromatic stabilization is due to the molecule's departure from planarity.

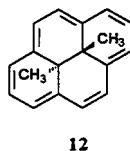


E. [12]Annulene

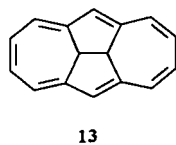
There are no thermochemical data for any of the [12]annulenes. In both a historical and conceptual sense, we may consider [12]annulenes as any species that have 12 π electrons in their outer perimeter. Even so doing, the only formal [12]annulene derivatives for which there are thermochemical measurements are biphenylene and pyracylene. Recent results indicate that these species with their contained benzenoid rings are better understood as benzene derivatives than as a perturbed [12]annulenes, and so they will be discussed later.

F. [14]Annulene

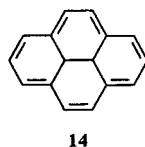
No thermochemical data are available for any of the [14]annulenes. However, combustion calorimetry and an estimated enthalpy of sublimation have been recently reported⁴⁰ for an ethanebisylidene-bridged analogue, *trans*-10*b*,10*c*-dimethyl-10*b*,10*c*-dihydropyrene (**12**) with an enthalpy of formation of (s) 231.2 ± 4.6 kJ/mol and (g) 338.8 ± 4.9 kJ/mol. There is



another species, 10*b*,10*c*-dihydroazuleno[2,1,8-*ija*]-azulene (**13**), with an enthalpy of formation of 466.1 kJ/mol derived from enthalpy of hydrogenation measurements.^{28c}



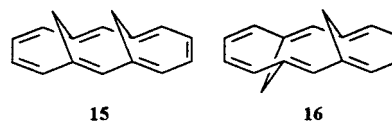
Interrelation of these two [14]annulene derivatives may be made directly once the former is "demethylated" to the parent 10*b*,10*c*-dihydropyrene (**14**). This



species and **13** are isomeric—they are both [14]annulenes with a bridging $>\text{CH}-\text{CH}<$ group. Assume the former demethylation process has about the

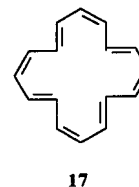
same enthalpy of formation difference as two other species with two adjacent methyl-bearing quaternary carbons: 2,2,3,3-tetramethylbutane transformed to 2,3-dimethylbutane and 2,2,3,3,4,4,5,5-octamethylhexane transformed to 2,2,3,4,5,5-hexamethylhexane. The average difference is 49.9 ± 3.4 kJ/mol. These are the only examples for which there is the requisite experimental enthalpy of formation data. Applying this average difference to the demethylation of **12** results in an estimation of an enthalpy of formation of **14** of ca. 389 kJ/mol, some 77 kJ/mol more stable than its isomer. We had not expected the two bridged annulenes to have identical enthalpies of formation—one has four six-membered rings and the other has two apiece of five- and seven-membered rings with an accompanying total strain energy of ca. 77 kJ/mol.⁴¹ The near equality is gratifying in terms of interrelating these two [14]annulene derivatives, but it tells us nothing about the aromaticity of either species or of [14]annulene itself.

The *syn*- and *anti*-bismethano[14]annulenes (**15**, **16**) were compared by several *ab initio* and density functional theory methods.⁴² Using the most accurate B3LYP results, the *syn*-delocalized structure was determined to be the global energy minimum. Its aromatic character was deduced from ¹H NMR chemical shifts, a large, negative magnetic susceptibility exaltation, and negative NICS (nucleus-independent chemical shift) values. In contrast, the *anti*-localized minimum energy structure is nonaromatic.



G. [16]Annulene

The enthalpy of formation of *E,Z,E,Z,E,Z,E,Z*-[16]annulene (**17**) is known from experiment only for the solid, 547.5 ± 11.7 kJ/mol. No data are available for

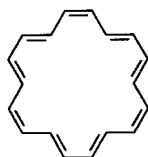


any partially hydrogenated species, and no enthalpy of hydrogenation to cyclohexadecane is known from experiment. From the measured enthalpy of formation of solid cyclohexadecane (from combustion measurements) of -403.4 ± 2.0 kJ/mol and the above data for the solid [16]annulene, the enthalpy of hydrogenation of the solid is -950 ± 12 kJ/mol. Estimated gaseous enthalpies of hydrogenation for the reference compounds, which assumes phase-independence of hydrogenation enthalpies, includes the enthalpies of hydrogenation for typical unbranched acyclic gaseous *cis*- and *trans*-alkenes⁵ of -119 and -115 kJ/mol, respectively: $4(-119) + 4(-115) = \text{ca. } -936$ kJ/mol for isolated double bonds in the reference compound and $4(-119) + 4(-115)$

$-4(-15) - 4(7.6) = \text{ca. } -846 \text{ kJ/mol}$ for delocalized double bonds in the reference compound.⁴³ The RE calculated from the difference between the experimental and estimated enthalpies of hydrogenation is thus $-0.9 \text{ kJ/mol per } \pi \text{ electron}$, and the DRE is $-7 \text{ kJ/mol per } \pi \text{ electron}$, comparable to the slight antiaromaticity of [8]annulene but well within the uncertainty of the experimental measurements. A rough estimate of the HSE for [16]annulene, assuming an enthalpy of sublimation calculated from eq 2, is ca. $-12 \text{ kJ/mol per } \pi \text{ electron}$. Neutral [16]annulene, although nonplanar because of the four sterically interacting internal protons, is known to exhibit a paramagnetic ring current consistent with antiaromatic character.⁴⁴

H. [18]Annulene

There are two determinations of the enthalpy of formation of [18]annulene (**18**). The first is $163.4 \pm$



18

16.7 kJ/mol for the solid from combustion measurements and ca. $280 \pm 25 \text{ kJ/mol}$ for the gas incorporating an estimated enthalpy of sublimation.⁴⁵ The second is $516 \pm 16 \text{ kJ/mol}$ for the gas derived from reaction calorimetry of its thermal decomposition into benzene and 3,4-benzo-1,3,5-cyclooctatriene and an enthalpy of formation estimate for the latter reaction product.⁴⁶ Of course, these two values are incompatible and the large error bars are suggestive of thermal instability. We might be able to choose one of them as being more plausible, however.

There are no experimental measurements of the enthalpy of hydrogenation or the enthalpy of formation of cyclooctadecane nor of any unsaturated derivative such as cyclooctadecene. Nonetheless, the value for the saturated alicycle is easily estimated. Cyclopentadecane, cyclohexadecane, and cycloheptadecane are all essentially strainless⁴⁷ with an average enthalpy of formation per $-\text{CH}_2-$ of -25.2 kJ/mol for the solids and -20.5 kJ/mol for the gases. Assuming cyclooctadecane is also strainless, its enthalpy of formation is calculated as -453.6 kJ/mol (s) and -369.0 kJ/mol (g). From the enthalpy of formation for gaseous [18]annulene of 280 kJ/mol , the enthalpy of hydrogenation is ca. -649 kJ/mol , and from the second enthalpy of formation value of ca. 516 kJ/mol , the enthalpy of hydrogenation is ca. -885 kJ/mol . A simple estimation for the gaseous enthalpies of hydrogenation of the two reference compounds, using the same assumptions and enthalpy values as for [16]annulene, are $3(-119) + 6(-115) = -1047 \text{ kJ/mol}$ and $3(-119) + 6(-115) - 3(-15) - 6(-7.6) = -953.4 \text{ kJ/mol}$. The enthalpy of hydrogenation differences between the real and reference species are thus the very different, RE = 398 and DRE = 304 for the first enthalpy of formation measurement and RE = 162 and DRE = 68 kJ/mol

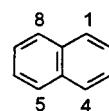
for the second enthalpy of formation measurement. For the first value, the DRE is ca. $17 \text{ kJ/mol per } \pi \text{ electron}$ which would demonstrate that [18]annulene is significantly aromatic but less so than benzene. The second value yields a DRE of ca. $4 \text{ kJ/mol per } \pi \text{ electron}$, very slightly aromatic. The HSEs for these two enthalpies of formation are 13.2 and 0.1 kJ/mol per π electron, respectively. From a thermochemical viewpoint only, none of these answers which value for the enthalpy of formation of [18]annulene is preferred.

Observations and calculations concerning the two low-energy structures of [18]annulene, D_{6h} (bond equalized) or D_{3h} (bond alternant), have become fairly consistent. The [18]annulene in the solid phase is almost planar with dimensions⁴⁸ in essential agreement with the D_{6h} structure reported to be most stable by various SCF calculations that include electron correlation.^{49,50} In CDCl_3 , [18]annulene exhibits a diatropic ring current, consistent with aromaticity, the magnitude of which is sensitive to the steric interactions involving its internal protons.⁵¹ Ab initio calculations tend to agree with the more recent enthalpy of formation determination.^{49,52}

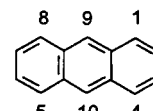
III. Polycyclic Aromatic Hydrocarbons

A. Cata-Condensed Aromatic Hydrocarbons

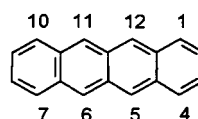
Cata-condensed polycyclic aromatic hydrocarbons contain benzenoid rings such that each fused carbon atom is common to no more than two rings.⁵³ The benzenoid rings may be linearly annelated (acenenes), as in the series naphthalene (**19**), anthracene (**20**), and naphthacene (**21**), or they may be angularly annelated, as in phenanthrene (**22**), benz[a]anthracene (**23**), benzo[c]phenanthrene (**24**), chrysene (**25**), and triphenylene (**26**). Except for some isolated examples



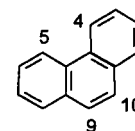
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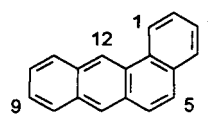
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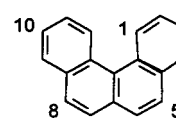
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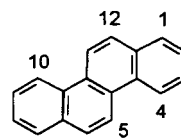
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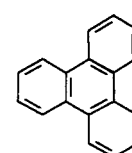
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Table 1. Enthalpies of Formation of Cata-Condensed Polycyclic Aromatic Hydrocarbons (kJ/mol)^a

compound	ΔH_f° (c)	ΔH_f° (g)
naphthalene (19)	77.9 ± 1.2	150.3 ± 1.5
anthracene ^b (20)	127.4 ± 5.9	229.1 ± 6.3
phenanthrene ^c (22)	113.0 ± 2.1	204.7 ± 2.9
naphthacene ^d (21)	158.8 ± 1.5; 177 (derived)	302 (derived)
benz[<i>a</i>]anthracene ^e (23)	170.8 ± 2.4	288.2 ± 4.3
benzo[<i>c</i>]phenanthrene (24)	184.9 ± 2.0	291.2 ± 4.6
chrysene ^f (25)	145.3 ± 2.1	263.5 ± 4.5
triphenylene ^g (26)	146.5 ± 1.5	265.5 ± 2.5

^a Data are from ref 1 unless otherwise noted. ^b The solid enthalpy of formation is the mean of the two most recent values, 127.4 ± 5.6 kJ/mol from ref 56 and 129.2 ± 1.8 kJ/mol from ref 57 as found in ref 1. The enthalpy of sublimation is the mean of the values given in ref 1, 101.7 ± 2.3 kJ/mol. ^c The solid-phase enthalpy of formation is the mean of the two most recent values, 109.8 ± 1.6 kJ/mol from ref 58 and 116.2 ± 1.3 kJ/mol from ref 57 as found in ref 1. The enthalpy of sublimation is the mean of the values given in ref 1, 91.7 ± 2.0 kJ/mol. ^d The solid-phase enthalpy of combustion is almost certainly incorrect. See discussion in text. ^e The enthalpy of sublimation, 117.4 ± 3.6 kJ/mol, is from ref 59. ^f The enthalpy of sublimation, 118.2 ± 4.0 kJ/mol, is from ref 54 and 60. ^g The solid-phase enthalpy of formation is the mean of the two values, 141.1 ± 0.7 kJ/mol from ref 61 as found in ref 1 and 151.8 ± 1.3 kJ/mol from ref 62 as found in ref 1. The mean of these two determinations is the same as that found in ref 63, 147.3 ± 2.3 kJ/mol. The enthalpy of sublimation, 119 ± 3 kJ/mol, is from ref 59.

that follow, these are the only cata-condensed polycyclic aromatics for which there are experimental enthalpies of formation. The enthalpies of formation which we have selected for the cata-condensed polycyclic aromatics are shown in Table 1. Some of these species, such as naphthalene, anthracene, and phenanthrene, have numerous references for the experimental determination of their enthalpies of combustion and of sublimation (they are all solids at 298 K and 1 atm). Usually, the evaluated archive¹ chose the more recent values from around 1966 onward. For many other of the compounds listed in Table 1, there has been only one experimental determination of the enthalpy of combustion but numerous and widely divergent measurements of the enthalpies of sublimation.^{54,55}

1. Homologous Series

Naphthalene, anthracene, and naphthacene constitute an homologous series in which each successive member is formed by benzo-fusion to the [*b*] side of the preceding member. As with other homologous series,⁶⁴ there should be a linear correlation between the enthalpies of formation of these species in the same phase vs the number of carbon atoms, n_c . Because each successive member of the series has one additional benzenoid ring, a more convenient independent variable is the number of such rings, n_r . A plot of the data for the solid phase shows that the reported enthalpy of formation of naphthacene is much too endothermic. A prediction for its solid-phase enthalpy of formation, based on those for naphthalene and anthracene, is ca. 177 kJ/mol. The two reported values¹ for the enthalpy of sublimation, 124.7 ± 4.2 and 143.7 ± 5.0 kJ/mol, are irreconcilably different. Using the estimated solid enthalpy of formation and each of the enthalpies of sublimation produces two values for the gaseous enthalpy of formation. When these are plotted with the enthalpy of formation values for the gaseous naphthalene and anthracene, only the less endothermic value for naphthacene, ca. 302 kJ/mol, lies close to the same straight line as its two homologues. By coincidence, this value is the same as one of the recommended values for naphthacene produced from the too-endothermic solid enthalpy of formation combined with the more endothermic enthalpy of sublimation. The

linear equations which may be used to estimate the solid and gaseous enthalpies of formation for naphthacene are

$$\Delta H_f^\circ (\text{s}) = [n_r(49.5)] + (-21.1) \quad (7a)$$

$$\Delta H_f^\circ (\text{g}) = [n_r(78.8)] + (-7.3) \quad (7b)$$

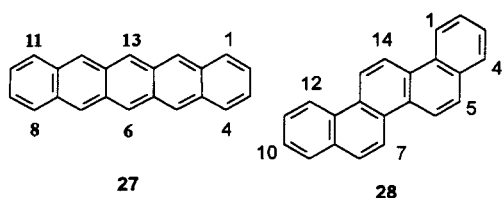
For naphthalene, phenanthrene, and chrysene considered as a benz[*a*]-fused homologous series, a plot of their solid enthalpies of formation vs n_r shows only a little scatter. Assuming the value for naphthalene is accurate, either the value for phenanthrene is slightly too endothermic or the value for chrysene is not endothermic enough or both. As found in ref 1, the only experimental value for chrysene is from the same source⁶³ as that for naphthacene and may also be not endothermic enough. The disparity is not as great for this series, however. Unfortunately, the enthalpies of sublimation for chrysene are exceedingly different. Between 1967 and 1995 there have been four independent measurements of the enthalpy of sublimation of chrysene: two of these (the earliest and the latest) average 118.2 ± 4.0 kJ/mol and the other two are the identical 131.0 ± 4.0 kJ/mol. When the resulting two gaseous enthalpies of formation are plotted with the others in the homologous series, the less endothermic of the chrysene values better fits a linear relationship. One of the less endothermic enthalpy of sublimation measurements of chrysene is from the same source as the less endothermic measurement of naphthacene.⁵⁴ Using the preferred values, the linear regression equations from weighted least-squares analyses of the solid and gaseous enthalpies of formation vs the number of benzenoid rings are

$$\Delta H_f^\circ (\text{s}) \pm 1.1 = [n_r(33.9 \pm 0.8)] + (10.3 \pm 2.5) \\ r^2 = 0.997 \quad (8a)$$

$$\Delta H_f^\circ (\text{g}) \pm 1.8 = [n_r(55.8 \pm 1.3)] + (38.3 \pm 3.9) \\ r^2 > 0.999 \quad (8b)$$

From these equations the gaseous enthalpies of formation of higher homologues can be estimated. For example, the enthalpy of formation of the 5-ring

acene, pentacene (**27**), is predicted to be ca. 387 kJ/mol and that for the 5-ring phenacene, picene (**28**), 317.3 kJ/mol.



2. Three and Four Benzenoid Rings

Clar proposed⁶⁵ that the maximum number of localized aromatic sextets (and thus the number of Kekulé structures) that can be drawn for benzenoid hydrocarbons correlates well with several properties of the compounds. For example, phenanthrene contains two localized sextets (five Kekulé resonance structures), while its isomer anthracene has only one localized sextet (four Kekulé resonance structures), and so might be considered to be “more aromatic”. Of the 4-ring benzenoid isomers, naphthalene has the fewest sextets (one), triphenylene has the most (three), and the others have two apiece. Generally, the cata-condensed species which have more phenanthrene subunits, and thus have greater “angularity”, also have more localized Clar sextets. How well does the Clar model correlate with the enthalpies of formation?

With respect to the enthalpies of formation, the angular phenanthrene itself is more stable in either the solid or gaseous phase than its isomer anthracene in the corresponding phase. Whatever 4,5-H,H-repulsion phenanthrene suffers is not sufficient to greatly destabilize it relative to anthracene. Of the 4-ring isomers, the order of stability based on experimental values for the solid polyaromatics is chrysene \approx triphenylene > naphthalene > benz[*a*]anthracene > benzo[*c*]phenanthrene. It is entirely unexpected for the linear naphthalene to be more stable than the angular benz[*a*]anthracene or for the highly angular triphenylene to be less stable than chrysene. For the former comparison, our estimated value for naphthalene seems more credible than the measured value. However, it is the gas-phase species that are most sensibly compared.

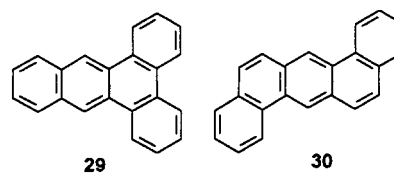
Chrysene is more stable than naphthalene, benz[*a*]anthracene, and benzo[*c*]phenanthrene whichever sublimation enthalpies, and thus gas-phase formation enthalpies are chosen. Benz[*a*]anthracene and benzo[*c*]phenanthrene have identical gas-phase enthalpies of formation within the uncertainty intervals. On the basis of the historical Clar or “angular effect”, it is expected that naphthalene would be the least stable, and so again our estimate, which fortuitously coincides with one of the recommended values, seems reasonable. That benz[*a*]anthracene and benzo[*c*]phenanthrene are of similar stabilities is compounded of two factors: although the greater angularity of benzo[*c*]phenanthrene should have a stabilizing effect similar to chrysene, the moderately severe 1,12-H,H-repulsion in the two terminal rings causes the molecule to be nonplanar and thus relatively destabilized. It is for this reason also that

chrysene, with the same angularity as benz[*c*]phenanthrene, is substantially more stable.

Triphenylene, containing three phenanthrene subunits, should be the most aromatic of the four-ring cata-condensed polycyclic aromatic hydrocarbons. The enthalpies of reaction are endothermic upon successive benzoannulation of benzene in the series: benzene to naphthalene (+67.7), naphthalene to phenanthrene (+54.4), and phenanthrene to triphenylene (+60.8).

3. Five or More Benzenoid Rings

We now turn to the thermochemistry of cata-condensed polycyclic aromatic hydrocarbons with five or more rings. There is disappointingly little data. For five-ring species, we have only been able to find an unsigned and otherwise unpublished institute report⁶⁶ that presents the enthalpies of formation of solid dibenz[*a,c*]anthracene (**29**) and its [*a,h*]-isomer (**30**).

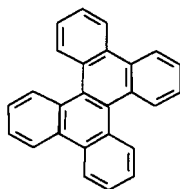


There is some ambiguity as to which isomer is which—however, the two values are the same within experimental error, 179 ± 10 and 184.3 ± 9.1 kJ/mol. Their enthalpies of sublimation⁵⁴ are also comparable, 159 ± 6 and 162 ± 6 kJ/mol. The enthalpies of formation of gaseous dibenz[*a,c*] and -[*a,h*]anthracene are therefore ca. 342 ± 12 kJ/mol. Since both species have the same number of Clar isolated sextets and neither apparently suffers a destabilizing interaction, the closeness of enthalpy values is unremarkable. Is the reported value plausible? From the regression eq 7b above, the estimated enthalpy of formation of gaseous pentacene is 387 kJ/mol. The isomerization enthalpy of linear naphthalene to angular benz[*a*]anthracene (using the best value for naphthalene) is -13.8 kJ/mol. Isomerizing pentacene twice, first to benz[*a*]naphthalene and then to dibenz[*a,h*]anthracene, would be exothermic by ca. 28 kJ/mol. The enthalpy of formation of benz[*a,h*]anthracene is thus estimated as 359 ± 15 kJ/mol. Summing the slope of eq 7b (78.8 kJ/mol), as an estimate of the enthalpy increment equivalent to adding a linearly annelated benzenoid ring, and the enthalpy of formation of triphenylene (265.5 kJ/mol) produces an enthalpy of formation of ca. 344 kJ/mol for dibenz[*a,c*]anthracene. Finally, assuming thermoneutrality of these two reactions



gives enthalpies of formation for the 5-ring compounds of ca. 351 and 327 kJ/mol, respectively. All of these values are consistent.

For six cata-condensed rings, there is the enthalpy of formation for dibenzo[*g,p*]chrysene (**31**)⁶⁷ of 574 kJ/mol for the gaseous species. Composed of two benzo[*c*]phenanthrene subunits, this is a very strained species as indicated by the large endothermic isomerization enthalpy of 110 kJ/mol from the estimated enthalpy of formation of the linear hexacene, 465.5 kJ/mol from eq 7b. Beyond six rings, there are no reported relevant measurements.



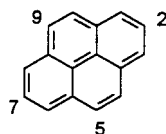
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B. Peri-Condensed Aromatic Hydrocarbons

Peri-condensed polycyclic hydrocarbons contain some rings which are fused to others at more than two carbons, e.g., the 1,8*a*,8 (and, hence, 1,8-*peri*) positions of naphthalene. These, like cata-condensed species, have been largely ignored by the thermochemical community.

1. Pyrene

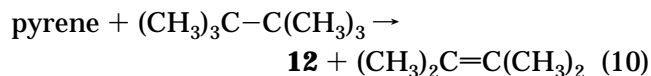
Pyrene (**32**), a polycyclic aromatic hydrocarbon with four rings, can be seen as comprising varied subunits: an ethylene-bridged [14]annulene, four fused benzene rings, two fused naphthalenes, a biphenyl or a phenanthrene. Its enthalpy of formation is 225.7



32

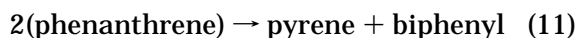
± 1.2 kJ/mol, which is ca. 76 kJ/mol less than the preferred enthalpy of formation of naphthacene, a cata-condensed species with the same number of benzenoid rings but with a different number of carbon atoms, π electrons, and Clar sextets.

As stated in the discussion of the annulenes, there is enthalpy of formation data⁴⁰ for a bridged [14]-annulene, **12**. Were pyrene itself well-described as a [14]annulene, then the following reaction would be roughly thermoneutral:



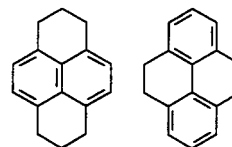
In fact, it is endothermic by the not insignificant ca. 270 kJ/mol, belying that description. Pyrene is better understood as a polycyclic aromatic hydrocarbon. One may also consider pyrene as a biphenyl bridged by two ethylenes in the 2,2'- and 6,6'-positions or as a phenanthrene bridged by an ethylene in the 4,5-positions. If these were meaningful comparisons, we

would expect the reaction



to be thermoneutral. In fact, it is exothermic by only 7.9 ± 3.4 kJ/mol, thereby supporting these alternative descriptions.

Two hydrogenated derivatives of pyrene are known, for both of which the enthalpy of formation is known: ⁶⁸ 1,2,3,6,7,8-hexahydropyrene (**33**) which retains a naphthalene subunit where adjacent *peri* positions are each linked by three methylene groups (40.7 ± 1.8 kJ/mol) and 4,5,9,10-tetrahydropyrene (**34**), a biphenyl derivative (90.2 ± 1.4 kJ/mol). In each case, the partial reduction of pyrene occurs so that by reorganization of the remaining double bonds an aromatic subunit is retained.

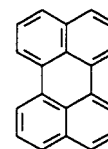


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2. Perylene

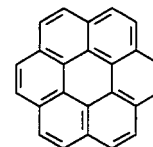
The enthalpy of formation of perylene (**35**) is 182.8 ± 0.8 (s)¹ and 306.0 ± 0.8 (g) kJ/mol.⁶⁰ The structure is most usefully described as being composed of two naphthalene rings conjoined by what has been called essential single bonds. In a later section, this description will be used to conceptually interrelate 1,1'-binaphthyl and perylene.



35

3. Coronene

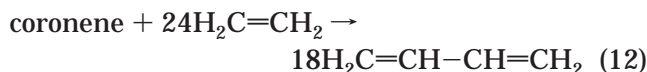
Coronene (**36**) may be variously described as six or seven fused benzenoid rings (hexabenzobenzene), or as [18]annulene circumscribing a central benzene ring, or as a small piece of graphite. The calculated



36

nucleus-independent chemical shifts (NICS) suggest the central ring is substantially less aromatic than the fully aromatic peripheral rings.⁶⁹ The enthalpy of the highly symmetric coronene has been determined⁷⁰ recently to be (solid) 146.5 ± 4.8 and (gas) 302.0 ± 8.0 kJ/mol. B3LYP/6-31G* and B3LYP/6-311G** calculations (300.8 and 300.4 kJ/mol) are in excellent agreement with the measured value, whereas the MP2/6-31G* results are not (274 kJ/mol).⁶⁹ Homodesmotic reaction enthalpies among aromatic spe-

cies producing coronene as a product are slightly exothermic, showing coronene to have enhanced aromatic character relative to other polycyclic aromatic hydrocarbons.⁶⁹ The homodesmotic reaction



results in 418.0 kJ/mol HSE or 17.4 kJ/mol per π electron. In this regard also, coronene is "super-aromatic" compared to benzene with its 15.0 kJ/mol per π electron.

Consider the enthalpy of reaction 13 and recall the incompatible suggested enthalpies of formation of [18]annulene from an earlier section (280 ± 25 and 516 ± 16 kJ/mol).



For the less positive endothermic enthalpy of formation of [18]annulene, the reaction enthalpy is -61 kJ/mol or -10 kJ/mol per C–C bond formed. For the more positive endothermic enthalpy of formation of [18]annulene, the reaction enthalpy is -297 kJ/mol or -50 kJ/mol per C–C bond formed. The latter exothermicity seems excessive. The smaller exothermic value is consistent with that for the related formal reaction of *o*-terphenyl to form triphenylene, ca. -14 kJ/mol, discussed in a later section, which suggests some interaction between the benzene rings of triphenylene as the new six-membered ring is formed. Both of these exothermicities and their relative magnitudes are consistent with the NICS(0) values for the central rings of triphenylene⁷¹ (-3.0) and coronene (0.8) compared to their outer rings (ca. -11).

C. Stabilization Energies in Benzenoid Hydrocarbons

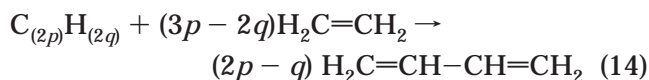
There are continuing efforts to correlate, predict, and understand the aromatic properties of polycyclic aromatic hydrocarbons. A volume devoted exclusively to polycyclic aromatic hydrocarbons⁷² recounts various schemes for calculating their "resonance" energies and sundry methods for quantitative physical measurements of their aromaticity. Some more recent attempts at quantitative assessment of aromaticity of these compounds involve high-level computational methods. For example, the energies of the linearly and angularly annelated cata-condensed compounds were calculated at the B3LYP/6-311G** level and their resonance energies derived.⁷³ The calculated and experimental energy differences were well-reproduced in those cases where the experimental enthalpies of formation were regarded as accurate. The resonance energies per C=C, as defined and derived therein, were essentially constant for the angularly condensed series from naphthalene to picene but decreased somewhat for the linearly annelated series from naphthalene to pentacene. Using the same optimization method, benzenoid ring aromaticity was studied⁷⁴ in terms of the HOMA index (harmonic oscillator model of aromaticity, containing both geometric and energetic components)

Table 2. Homodesmotic Stabilization Energies (HSE) of Polycyclic Aromatic Hydrocarbons (kJ/mol)

compound	HSE	HSE/ π -electron
benzene (1)	89.9	15.0
naphthalene (19)	137.2	13.7
anthracene (20)	173.4	12.4
naphthacene (21)	215.5	12.0
phenanthrene (22)	197.8	14.1
chrysene (25)	254.0	14.1
triphenylene (26)	252.0	14.0
benz[<i>a</i>]anthracene (23)	229.3	12.7
benzo[<i>c</i>]phenanthrene (24)	226.3	12.6
dibenz[<i>a,c</i>] and -[<i>a,h</i>]anthracene (29, 30)	290.5	13.2
dibenzo[<i>g,p</i>]chrysene (31)	173.5	6.7
pyrene (32)	249.3	15.6
perylene (35)	289.0	14.5
coronene (36)	418.0	17.4

as well as a thermochemical additivity scheme and computed NICS values. An increase in the number of rings of both the linear and angular acenes was associated with a substantial decrease in their aromaticity, the decrease being greater for the linear compounds. A very good correlation was shown between HOMA and NICS values for whole molecules, both cata- and peri-condensed.^{75,76}

Not considered were the simple homodesmotic reactions which have been used here. The HSEs calculated from eq 14 for neutral alternant polynuclear hydrocarbons using only ethylene and butadiene as the reference species appear in Table 2.



Consistent with all other studies, regardless of method of calculation, the angularly annelated compounds are more aromatic than the linearly annelated ones. If the angularly annelated hydrocarbons exhibit a constant rather than a decreasing HSE, then the reported enthalpies of formation of **29** and **30** are probably too endothermic. A more accurate determination would probably be somewhat lower than the 327 kJ/mol derived from eq 9b, from which the HSE would be 13.9 kJ/mol per π electron. The three peri-condensed examples all show greater stabilization energy than the cata-condensed species. As noted earlier, eq 14, as well as other homodesmotic reactions involving aromatic compounds, shows coronene to be more aromatic than benzene. Pyrene, too, appears to have greater stabilization than benzene. Whether this is a real effect or due to either inaccurate thermochemical measurements or the inadequacy of the same acyclic compounds to serve as reference species for both cata- and peri-condensed hydrocarbons is not known.

There has been a recent attempt to combine MP2/6-31G**//HF/6-31G* calculations with simple carbon substructure parameters as an accurate approach to correlating and predicting the enthalpies of formation of cata- and peri-condensed unsubstituted polycyclic aromatic hydrocarbons.⁷⁷ The electronic energies provide the nonadditive electronic effects, and the carbon-structure parameters model the additive effects. The quality of the multilinear regression was

Table 3. Enthalpies of Formation^a and Different Quantities $\delta(R_1,^*)$ for Monoalkyl-Substituted Benzenes (kJ/mol)

R_1	ΔH_f° (l)	ΔH_f° (g)	$\delta(R_1, \text{liquid})$	$\delta(R_1, \text{gas})$
H (benzene)	49.0 ± 0.6	82.6 ± 0.7		
CH ₃	12.4 ± 0.6	50.4 ± 0.6	36.6	32.2
CH ₂ CH ₃	-12.3 ± 0.9	29.9 ± 1.1	61.3	52.7
CH ₂ CH ₂ CH ₃	-38.3 ± 0.8	7.9 ± 0.8	87.3	74.7
CH(CH ₃) ₂	-41.1 ± 1.0	4.0 ± 1.0	90.1	78.6
CH ₂ CH ₂ CH ₂ CH ₃	-63.2 ± 1.1	-13.1 ± 1.1	112.2	95.7
CH(CH ₃)CH ₂ CH ₃	-66.4 ± 1.2	-17.4 ± 1.2	115.4	100.0
CH ₂ CH(CH ₃) ₂	-69.8 ± 1.3	-21.5 ± 1.3	118.8	104.1
C(CH ₃) ₃	-70.7 ± 1.2	-22.6 ± 1.2	119.7	105.2

^a All enthalpies of formation are from ref 1.

improved by omitting the experimental value for naphthalene of 302.5 kJ/mol. A correction term of -14.7 kJ/mol was required to correlate the naphthalene value with the other experimental values. If this correction term is an accurate predictor of naphthalene's enthalpy of formation, then it seems that the three linearly condensed hydrocarbons, naphthalene, anthracene, and naphthalene, are not homologous in terms of their enthalpies of formation. As the authors expected, the procedure was somewhat less accurate when used to predict the enthalpies of formation for the other compounds than when used to correlate the enthalpies.

IV. Effect of Alkylation

Alkyl substituent groups on an aromatic ring introduce new modes of interaction, and perhaps distortion, without the complicating effects of π -electron donation or withdrawal because alkyl groups are essentially electronically innocuous. Almost all of the thermochemical literature on substituted aromatic species relates to benzene derivatives. There are comparatively few enthalpy of formation measurements for substituted naphthalenes. It has been shown in those few cases that the difference between enthalpies of formation of the 1- and 2-isomers is generally small, and the difference between the naphthalene and benzene derivatives is largely independent of the substituent. For example, the enthalpies of formation of 1- and 2-bromonaphthalene are 174.3 ± 5.6 and 175.6 ± 2.3 kJ/mol.⁷⁸ These values differ from that of bromobenzene (105.4 ± 4.1 kJ/mol) by ca. 70 kJ/mol, very close to the enthalpy of formation difference between the parent hydrocarbons. For other aromatic hydrocarbons, there are almost no substituted derivatives other than methylated ones.

A. *n*-Alkyl-Substituted Benzenes: Homologous Series

There are both gas- and liquid-phase data for toluene and the *n*-alkyl substituents ethyl, propyl, butyl, pentyl (liquid only), and decyl. Since these constitute a classic homologous series, we derive eqs 15 from a weighted least-squares analysis where n_R is the number of carbon atoms in the substituent group. For most homologous series, *n*-RZ, the methyl-substituted derivative CH₃Z is an outlier from the otherwise straight line.⁶⁴ In the case of the *n*-alkyl benzenes, the correlation ($r^2 > 0.9998$) is not im-

proved by omitting toluene.

$$\Delta H_f^\circ (\text{l}) \pm 0.56 = [n_R(-25.5 \pm 0.13)] + (38.3 \pm 0.37) \quad (15a)$$

$$\Delta H_f^\circ (\text{g}) \pm 0.45 = [n_R(-21.1 \pm 0.10)] + (71.4 \pm 0.30) \quad (15b)$$

From eq 15b, the missing gas-phase enthalpy of formation for *n*-pentyl benzene is estimated to be -34.1 kJ/mol.

B. Polyalkylation: Additivity of Small Substituents on Benzene

Although the polyalkyl-substituted benzenes cannot be treated as homologous series, they can be understood in terms of additivity of substituent effects. We define the difference quantity, $\delta(R_1\dots R_n)$ as

$$\delta(R_1\dots R_n,^*) = \Delta H_f^\circ(\text{PhH}) - \Delta H_f^\circ(\text{Ph}-R_1\dots R_n) \quad (16)$$

where the asterisk (*) denotes the phase and (R₁...R_n) is one or more substituents attached to a benzene ring. The difference quantities for the simple monoalkyl-substituted benzenes, $\delta(R_1)$, are summarized in Table 3.

We are interested in discovering whether, and by how much, the difference quantity for a multiply substituted benzene deviates from the additive difference quantities listed in Table 3. The deviation difference quantity is defined as

$$D(^*) = \Sigma \delta(R_1,^*) - \delta(R_1\dots R_n,^*) \quad (17)$$

where (R₁...R_n) are the several substituents attached to benzene and the asterisk (*) denotes the phase.

There are directly measured enthalpy of formation data for the *ortho*, *meta*, and *para* isomers of the disubstituted benzenes: R, R' = Me, Me (l, g); Me, Et (l, g); Me, *n*-Pr (l); Me, *i*-Pr (l); Me, *t*-Bu (g);⁷⁹ Et, Et (l). For all the *meta*- and *para*-disubstituted species and for *o*-xylene, the $D(\text{g}, \text{l})$ are less than the root-mean-square (rms) of the experimental uncertainty levels. All of these compounds are, therefore, unstrained and so too presumably would be the *meta* and *para* isomers of other dialkyl-substituted benzenes. Enthalpies of formation for those compounds where $D(^*)$ is about 0 can be estimated from eqs 16 and 17 and the parameters in Table 3.

Table 4. Deviation Difference Quantities D^* for *Ortho*-Disubstituted Benzenes (kJ/mol)

R ₁ , R ₂	$D(\text{liquid})$	$D(\text{gas})$
Me, Me	0	0
Me, Et	2.5	3.6
Me, <i>n</i> -Pr	2.4	
Me, ^{<i>i</i>} Pr	4.4	
Me, <i>t</i> -Bu		21.8
Et, Et	5.1	

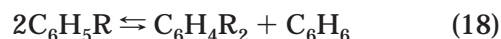
The *ortho* compounds definitely deviate from additivity, as shown in Table 4, and if ethyl methyl benzene is typical, the gas-phase deviation is greater than the liquid-phase deviation. That the deviations are positive indicates the real species is actually less stable than the model compound calculated by additivity. The destabilization is attributed to a steric effect between the two *ortho* groups. The deviations are about the same for the ethyl and *n*-propyl groups when they are *ortho* to a methyl group. Since two methyl groups *ortho* to each other exhibit no deviation, we can ascribe the full deviations to the ethyl and *n*-propyl groups and by extension to other *n*-alkyl groups as well when they are *ortho* to methyl. It is not surprising, then, to observe a deviation for diethyl which is twice that for (methyl, ethyl). The larger secondary group, isopropyl, causes a larger deviation due to its greater steric requirements. If additivity holds, the deviation for two *ortho* isopropyl groups would be about 9 kJ/mol. Unfortunately, there are no enthalpy of formation data available for any of the diisopropylbenzene isomers. The steric effect of the *t*-Bu group is predictably large.

There are enthalpy of formation data for three trimethyl-substituted benzene isomers: 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene. The second compound, with only one *ortho* interaction, has a deviation within the rms of the experimental uncertainty levels. The first compound, with a methyl group which is *ortho* to two other methyl groups, has deviations of 2.3 (l) and 4.5 (g), somewhat larger than might be expected. The all-*meta* isomer exhibits a negative deviation in both phases (−2.6 (l), −1.9 (g)), indicating that its experimental enthalpy of formation is more negative, and thus more stable, than predicted by additivity. Of the six isomers substituted with two methyl and one ethyl group (liquid only), the same negative deviation as above (−2.3) is exhibited by the all-*meta* 1-ethyl-3,5-dimethylbenzene.⁸⁰ The remaining isomers with only one *ortho* interaction have deviations within the rms, even the two which have an ethyl/methyl *ortho* interaction. The two compounds with two *ortho* interactions, the 1-ethyl-2,3-dimethyl- and 2-ethyl-1,3-dimethylbenzenes, have deviations consistent with additivity (a methyl/ethyl interaction and a 1,2,3-all-*ortho* interaction), 5.0 and 5.4, respectively. For the tetrasubstituted 1,2,3,4-tetramethylbenzene, the deviation of 7.2 (l) is larger than expected by additivity of two 1,2,3-trimethyl interactions. For the isomeric 1,2,3,5-tetramethylbenzene, additivity predicts a near cancellation of the 1,2,3-destabilizing and 1,3,5-stabilizing interactions. The actual deviation is 1.0 (l). The fully loaded hexamethylbenzene's deviation is the very large 23.8 (g), accounted for by six 1,2,3- and two 1,3,5-interactions in the gas phase.

The HOMA index of aromaticity for the various methyl-substituted benzene rings shows a much smaller variation in aromaticity compared to phenyl rings embedded in benzenoid hydrocarbons with analogous substitution patterns, thus demonstrating the importance of topological requirements.⁸¹ Further, the dearomatization in the methyl-substituted rings is mostly due to the geometric term (GEO) component of HOMA. Although the deviations from additivity discussed above do not correlate with either GEO or HOMA, there is a qualitative association between them. The rings with one or more *o*-dimethyl interactions show a larger GEO (and HOMA) value than *m*- and *p*-xylene, and the all-*meta* 1,3,5-trimethylbenzene shows by far the smallest GEO/HOMA value. However, the hexamethylbenzene's GEO value is less than the several tetramethyl benzenes.

C. *tert*-Butylated Benzenes

Because there are no directly measured enthalpy of formation data from combustion calorimetry for the isomeric di-*tert*-butylated benzenes, we must take a slightly different approach to study their energetics. For any R, the enthalpy of reaction of the isodesmic, or transalkylation, reaction 18 is equivalent to the expression for D^* , eq 17. If the *m*- and *p*-*tert*-butyl substituents behave similarly to methyl and ethyl substituents, then the desired enthalpy of formation for these di-*tert*-butyl benzenes can be obtained experimentally from reaction/equilibrium calorimetry for reaction 18, R = *tert*-butyl in the presence of a Lewis acid catalyst.



It was found that these reaction enthalpies too are very nearly thermoneutral, resulting in enthalpy of formation values of -187.4 ± 1.5 and -188.9 ± 1.5 kJ/mol for the liquid *m*- and *p*-di-*tert*-butylbenzenes respectively.⁸² No *o*-di-*tert*-butylbenzene was observed in this study as an equilibration product. This absence is not surprising since we expect considerable steric destabilization for this species. Equivalently, the isomerization enthalpy of *o*-di-*tert*-butylbenzene is expected to be large, and so it is reasonable to expect it to be directly observable calorimetrically. Since the equilibrium product mixtures from isomerization of *o*-, *m*-, or *p*-di-*tert*-butylbenzene should be identical, the difference between enthalpies of reaction of the *o*- and *m*-isomers (and/or *o*- and *p*-isomers) equals the desired difference between the enthalpies of formation of the isomers. This last study has been performed, and the difference of 93 ± 3 kJ/mol was found.⁸³ The somewhat larger value of 103 ± 7 kJ/mol was found in the same study from the difference between the appearance energies of the gas-phase reactions



of either Ar = *m*- and *p*-*tert*-butylphenyl and their *o*-isomer. The enthalpy of formation of liquid *o*-di-

Table 5. Enthalpies of Formation of Substituted Naphthalenes (kJ/mol)^a

compound	ΔH_f° (s)	ΔH_f° (l)	ΔH_f° (g)
naphthalene	77.9 ± 1.2		150.3 ± 1.5
1-methylnaphthalene		56.3 ± 1.7	113.5 ± 1.7 ^b
2-methylnaphthalene	44.9 ± 1.5		110.7 ± 1.7 ^b
2- <i>tert</i> -butylnaphthalene		-26.3 ± 1.4	
1,8-dimethylnaphthalene	25.9 ± 1.5	41.8 ± 1.8	108.7 ± 1.5
2,3-dimethylnaphthalene	-2.3 ± 1.0 ^c		76.1 ± 1.0 ^d
2,6-dimethylnaphthalene	-5.7 ± 1.7 ^c	19.4 ^e	78.4 ^f
2,7-dimethylnaphthalene	-5.1 ± 1.0 ^c		79.5 ± 0.6 ^g
1,4,5,8-tetramethylnaphthalene	-18.2 ± 2.8	5.7 ± 3.0	81.6 ± 3.2

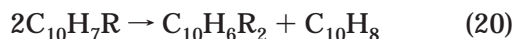
^a Data are from ref 1 unless otherwise noted. ^b Enthalpies of vaporization and sublimation are from ref 85. ^c Enthalpy of formation is from ref 86. ^d Enthalpy of sublimation is from ref 87. ^e Enthalpy of fusion from ref 88 is uncorrected and without error bars. ^f Enthalpy of sublimation from ref 89 is uncorrected and without error bars. ^g Enthalpy of sublimation is from ref 90.

tert-butylbenzene is thus ca. -95 kJ/mol, and $D(l)$ for the two substituents *ortho* to each other is the very large 95 kJ/mol.

There are three benzene isomers with three *tert*-butyl substituents: the 1,2,3-, 1,2,4-, and 1,3,5-tri-*tert*-butylbenzenes. There are no thermochemical data for the first. Equilibration thermochemistry⁸² shows the mutually *m-tert*-butyl groups in the 1,3,5-isomer to have a small destabilizing effect, $D(l) = 3.3$, but within the rms of the experimental uncertainty level, contrary to the small stabilizing effect seen for the smaller alkyl groups. Thus, the archival enthalpy of formation difference between the 1,2,4- and 1,3,5-tri-*tert*-butylbenzenes in the solid phase, 70.3 ± 5.1 kJ/mol, suggests that this energy difference is the destabilization energy associated with adjacent or *o-tert*-butyl groups in the solid phase. The enthalpy of formation for 1,2,4,5-tetra-*tert*-butylbenzene is -297.9 ± 9.7 kJ/mol. However, these data are only for the solid phase and earlier experience⁸⁴ shows how ill-advised it is to estimate phase change enthalpies for species with numerous quaternary carbons as found here in the *tert*-butyl groups.

D. Substituted Naphthalenes

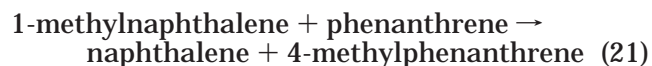
The thermochemical database for substituted naphthalenes is far less extensive than for substituted benzenes and is reproduced in Table 5. For a given R, there are two isomeric monosubstituted naphthalenes, the 1-R and the 2-R. The latter might be expected to be more stable because it lacks the 1,8- or *peri*-repulsion found in the former between the substituent and a small, but unavoidably nearby, hydrogen. For a methyl substituent, the difference between the enthalpies of formation of 1- and 2-methylnaphthalene, 113.5 ± 1.7 and 110.7 ± 1.7 kJ/mol, respectively, reveals a very small 2.8 ± 2.4 kJ/mol *peri* effect. For identical substituents, there are the following naphthalene isomers: 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6-, and 2,7-isomers. There is no substituent for which all 10 isomers have been thermochemically characterized. Furthermore, there is only one substituent for which there are enthalpy of formation data for the isomer of greatest interest—1,8-dimethylnaphthalene. Equation 20, analogous to eq 18, is now recast for mono- and disubstituted naphthalenes:



For R, R = 1-methyl, 8-methyl, the enthalpy of reaction is 32.0 ± 3.2 kJ/mol, signifying a quite large steric effect between the two *peri* methyl groups. In 1,4,5,8-tetramethylnaphthalene, there are two sets of *peri* methyl groups and the reaction enthalpy (R, R = 1,8-dimethyl), 78.5 ± 4.1 kJ/mol, is somewhat more than twice that for one *peri* set. Difficult to reconcile are the reaction enthalpies for R,R = 2-methyl, 6-methyl⁹⁰ and 2-methyl, 7-methyl, which are 7.3 ± 3.3 and 8.4 ± 2.5 kJ/mol, respectively, signifying some small destabilizing effect. And even though the two methyl groups are *ortho* for R, R = 2-methyl, 3-methyl,⁸⁷ which should have little thermochemical consequence, the reaction enthalpy is the slightly less endothermic 5.0 ± 2.5 kJ/mol.

E. Methylated 3- and 4-Ring Species

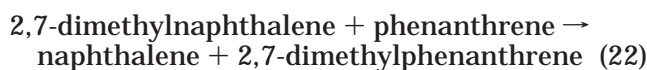
With 3-ring species there are new opportunities for destabilization. Consider phenanthrene with its two naphthalene subunits and the *peri* carbons thereon. In the "bay" region of phenanthrene, one *peri* carbon per naphthalene is still available for substitution while the other is now replaced by a carbon in the third ring of the phenanthrene. Enthalpy data for monomethylation, indeed for any monoalkylation, of phenanthrene is available only for 4-methyl phenanthrene.⁹¹ Since the methyl group is *peri* to a ring carbon, a convenient comparison is the enthalpy of reaction 21, 25.1 ± 3.0 kJ/mol. The steric effect between two *peri* methyl groups in naphthalene (32.0 ± 3.2 kJ/mol) is slightly greater than the effect between a methyl group *peri* to an aromatic ring carbon and its attached hydrogen.



The $D(g)$ for 4,5-dimethylphenanthrene is only 9.5 ± 6.4 kJ/mol. Since 4-methylphenanthrene is the only monomethylated species available for comparison, it appears that introduction of another methyl in the bay region is not significantly more destabilizing than the first, inasmuch as both compounds are likely nonplanar.

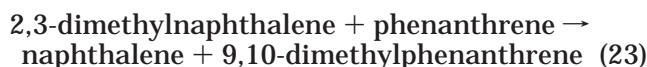
In both 2,7-dimethylnaphthalene and 2,7-dimethylphenanthrene, the methyl groups should have similar interactions. Accordingly, the enthalpy of reaction 22 is only 6.4 ± 3.2 kJ/mol, very nearly

thermoneutral.



The 50.5 ± 6.3 kJ/mol difference between the 2,7- and 4,5-dimethylphenanthrene enthalpies of formation more clearly illustrates the large destabilizing steric effect of two methyl groups in the bay region of phenanthrene.

9,10-Dimethylphenanthrene contains *ortho* methyl groups, and each of the methyl groups is *peri* to a ring hydrogen. Because the methyl, hydrogen *peri* effect is negligible in naphthalene, it is expected to be negligible in phenanthrene also. The enthalpy of reaction 23 should reveal the magnitude of the *ortho* interaction in phenanthrene compared to naphthalene and benzene:



The enthalpy of this reaction, 33.8 ± 8.9 kJ/mol, is very large compared to the small-to-vanishing *ortho* interactions in naphthalene and benzene.

For substituted benz[*a*]anthracenes and benzo[*c*]phenanthrenes, there is related destabilization. Examples include the 3,9- and 1,12-dimethylbenz[*a*]anthracenes with their gas-phase enthalpies of formation of 188.7 ± 3.9 and 251.5 ± 3.9 kJ/mol, although why the latter should be more stable than the 7,12-isomer with its enthalpy of formation of 277.7 ± 4.4 kJ/mol is not apparent. The same trends apply to both, qualitatively and quantitatively, in the solid state. This is fortunate because the corresponding examples for dimethylbenzo[*c*]phenanthrene, the 5,8- and 1,12-dimethyl derivatives are documented only for the solids with enthalpies of formation of 76.2 ± 2.1 and 154.5 ± 3.4 kJ/mol, respectively.

V. Energetics of Hydrogenation Reactions

The enthalpy of hydrogenation of benzene, compared to that of the hypothetical 1,3,5-cyclohexatriene, is the classic measure of aromaticity.¹⁴ In the section on [*n*]annulenes, we continued to use hydrogenation enthalpies as a convenient thermochemical evaluation tool. Important for the comparison of the results for different annulenes, however, is the correction for differences in strain energy in the reactants and products. Benzene and cyclohexane are both understood as strainless, but most of the [*n*]annulenes and their hydrogenation products are not. A valid conclusion regarding the antiaromaticity of cyclobutadiene, for example, must explicitly account for the strain energies of cyclobutane and cyclobutadiene. If we wished to compare the enthalpies of hydrogenation of *o*-, *m*-, and *p*-xylene, it is necessary to recognize that even though there is virtually no steric strain in the disubstituted benzene compounds as calculated in the previous section, this is not true for the dimethylcyclohexanes. The formal hydrogenation products chosen for comparison can be either the *cis*- or *trans*-isomers, and depending on which set is chosen, there are a different number of gauche interactions between the substituents themselves

and between the substituents and the ring methylene groups. For example, the *cis*-1,2-dimethyl groups from syn hydrogenation of *o*-xylene have a methyl–methyl gauche interaction of ca. 5 kJ/mol. The unsaturated reference compounds must also be adjusted. Although cyclohexene is an adequate model for the double bonds in benzene, 1-methylcyclohexene is a better model for the double bond in a methyl-substituted benzene. The difference between the enthalpy of hydrogenation of cyclohexene and 1-methylcyclohexane is 7.0 kJ/mol. Taking these various factors into account, the stabilization energy is about 2 kJ/mol less for the dimethyl-substituted benzenes than for benzene itself.⁹²

Because of similar considerations, enthalpies of hydrogenation by themselves cannot be used as a reliable quantitative measure of aromaticity for polycyclic aromatic hydrocarbons. The enthalpy of hydrogenation of complete formal reduction of naphthalene to *trans*-decalin is -332.4 ± 2.7 kJ/mol. The reference Kekulé structure for the reduction of naphthalene to tetralin and then to decalin has three cyclohexene-type double bonds and two methylcyclohexene-type double bonds (there is no enthalpy of formation data for 1,2-dimethylcyclohexene). The calculated enthalpy of hydrogenation is thus -578.6 ± 1.3 , and the resonance energy, RE, is -246.2 ± 3.0 or 49.2 kJ/mol per π bond. The same calculation procedure for anthracene with an enthalpy of hydrogenation to *trans-syn-trans*-perhydroanthracene ($\Delta H_f(\text{g}) = -243.2 \pm 3.8$ kJ/mol) of -470.6 ± 6.8 kJ/mol yields an RE of 47.3 kJ/mol per π bond. Unfortunately, there is no enthalpy of formation data for perhydronaphthacene or any other fully reduced benzenoid hydrocarbon. However, the most stable hydrogenation products from this homologous series also form an homologous series, and so their gaseous enthalpies of formation vs number of rings would be linearly correlated. The difference between the enthalpies of formation of *trans*-decalin and the perhydroanthracene is 61.1 kJ/mol, and therefore, an estimated enthalpy of formation of *trans-syn-trans-syn-trans*-perhydronaphthacene is -304.3 kJ/mol. The resonance stabilization energy is calculated as 46.4 kJ/mol per π bond using the preferred enthalpy of formation value for naphthacene. It is clear that the stabilization energy per π bond decreases as the number of benzenoid rings increases, although the measured effect is very small.

It might have been tempting to observe that because the hydrogenation enthalpy is the difference between the enthalpies of formation of the saturated and unsaturated compounds

$$\Delta H_{\text{H}_2} = \Delta H_f(\text{satd, g}) - \Delta H_f(\text{unsatd, g}) \quad (24)$$

and because both the saturated and unsaturated compounds form a homologous series, that a linear equation which includes a constant for the enthalpy of hydrogenation can be written.

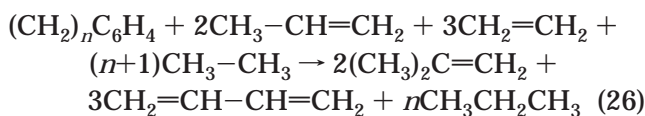
$$\Delta H_f(\text{satd, g}) = [m\Delta H_f(\text{unsatd, g})] + \Delta H_{\text{H}_2} \quad (25)$$

However, only in the case where the absolute value of the slope for the saturated compounds is identical

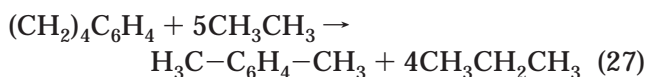
to the absolute value of the slope for the unsaturated compounds is the enthalpy of hydrogenation per π bond constant and equal to the y -intercept (" ΔH_{H_2} ") of eq 25. If the absolute values of the two slopes are significantly different, the enthalpy of hydrogenation per π bond will not be constant for the members of the unsaturated series but instead will exhibit a regular increase or decrease. In the present case, the relevant slopes are 17.5 and -15.3 and thus the hydrogenation enthalpies per π bond decrease slightly throughout the series.

VI. Cyclophanes

In cyclophanes, the aromatic rings are multiply attached by aliphatic chains. The simplest type of cyclophane consists of a benzene with a methylene chain affixed to nonadjacent carbons of the ring. In fact, this description results in two classes of compounds, the $[n]$ metacyclophanes and $[n]$ paracyclophanes corresponding to 1,3- and 1,4-bridging. Quite surprisingly and disappointingly, there are no experimentally thermochemically characterized species of either class with which to quantitatively confirm the expectation that the smaller the value of n , the more strained the cyclophane. Qualitatively, the effect of increasing ring strain was experienced in the increasing difficulty of synthesis. The strain of greatest interest is the deviation of the benzene ring from planarity into a boatlike structure and its effect on aromaticity. Early ^1H NMR spectra indicated a ring current and thus retention of aromaticity in the [6]- and [7]paracyclophanes,⁹³ although an even earlier ultraviolet spectrum of [8]paracyclophane suggested the benzene ring was "seriously bent" from a planar structure.⁹⁴ Even [5]paracyclophane was reported from its UV and ^1H NMR spectra⁹⁵ and from its theoretical infrared spectrum⁹⁶ to be aromatic. In a series of papers^{96–98} describing ab initio quantum mechanical studies of [6]-, [5]-, and [4]paracyclophanes, Schaefer and co-workers conclude, in answer to their question "Is [the] paracyclophane aromatic?", that it depends on what is looked at and thus what is particularly needed is "an unambiguous operational definition of aromaticity". On the basis of the above-mentioned spectral evidence and the small degree of bond alternation, the paracyclophanes are judged to be aromatic or at least "benzene-like".⁹⁹ On the basis of calculated energies, structure, and homodesmotic reactions, the molecules are judged not to be aromatic. For the [5]- and [6]paracyclophanes, the homodesmotic reactions the authors used are of the type^{96,97}



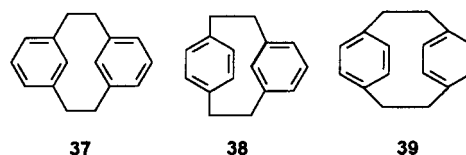
For [4]paracyclophane, a modified reaction was employed to evaluate the strain energy



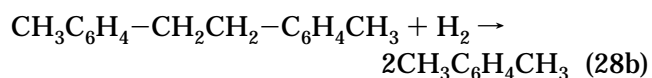
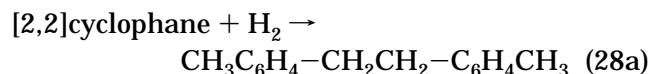
and its enthalpy of formation was predicted to be 365.7 kJ/mol.⁹⁸ Compared to benzene's +89.9 kJ/mol HSE, the [6]-, [5]-, and [4]paracyclophanes are destabilized by HSEs of -111 , -210 , and -266.8 kJ/mol, respectively, using eq 26 for all three determinations. Grimme suggested that [4]paracyclophane is best classified as a strained molecule with diradicaloid character.¹⁰⁰

Polymethylene-bridged aromatics have appeared elsewhere in the current study. There are the two isomeric [1]–[10]annulenophanes which are more commonly identified as the earlier mentioned **11** and **11**.¹⁰¹ We know of no equilibration of **10** with the benzenoid [5]metacyclophanedienes, and so cannot compare bridged benzenes and [10]annulenes. At least for **10**, the somewhat longer bridge is seemingly comparatively destabilizing as shown by the preference of many derivatives (but not the parent) for the [4.4.1]propellatetraene (tetracyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene) structure. As such, these cases show behavior unlike the simple benzenoid cyclophane paradigm.

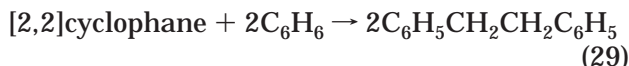
The second type of bridged aromatic rings have two polymethylene chains joining two benzene rings. These are the $[m,n]$ cyclophanes for there is no conceptual, synthetic, or existential reason the two chains need be the same length. Again ignoring the case of methylenes bridging *ortho* carbons, there are three types of species: *meta,meta* (conventionally called "*meta*"), *meta,para*, and *para,para* (conventionally called "*para*"). There is but one set of m and n where all three isomers can be directly compared, $m = n = 2$ (**37**–**39**). In this case, the thermodynamic



stability decreases dramatically in the order *meta* > *meta,para* > *para*—the enthalpies of formation are 170.5 ± 6.5 , 218.4 ± 1.7 , and 244.1 ± 2.6 kJ/mol, respectively. Remembering that *meta*- and *para*-disubstituted benzenes generally have very nearly the same enthalpies of formation, we conclude that the strain increases dramatically in the order *meta* < *meta,para* < *para*. The unique structural feature of these compounds is ring distortion in an attempt to minimize angle strain and hydrogen eclipsing in the bridging polymethylene chains and to minimize inter-ring repulsion. Such buckling forces the benzene rings to be nonplanar with resulting lessened π overlap, bonding, and aromaticity. The shorter the polymethylene chains, the more buckling and presumably the greater loss of aromaticity. The strain energy may be related¹⁰² to the difference in exothermicities of the two hydrogenolysis reactions



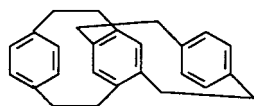
Assuming the enthalpy of the second reaction is the same as the corresponding reaction for bibenzyl (-42.1 ± 1.4 kJ/mol) so that the enthalpy of formation of the intermediate can be derived, the strain energies are 51.7, 98.9, and 123.9 kJ/mol for the *meta*, *meta,para*, and *para* species, respectively. The strain energies derived from the exothermicity of the reaction



are the equivalent 49.9, 97.8, and 123.5 kJ/mol.

For all other combinations of *m* and *n*, enthalpies of formation are available only for the *para* isomers. The number pairs are [1,8], [3,3], and [6,6] with enthalpies of formation of 28.9 ± 9.2 , 129.4 ± 3.7 , and -77.4 ± 11.7 kJ/mol, respectively. Are these cyclophanes strained? After all, much of the strain arises from distortion of the benzene ring or of the chain or their steric congestion or molecular geometry, and so for large enough values of *m* and *n*, we expect the strain to disappear. From reactions corresponding to eqs 28, the strain energies are¹⁰³ 3.6, 51.6, and -28.0 kJ/mol for the [1,8]-, [3,3]-, and [6,6]-paracyclophanes, respectively. As expected, compared to the [2,2] species, the [3,3] has considerably less strain energy. Taking into account the uncertainty, the [1,8]cyclophane has essentially no strain while the [6,6]cyclophane possesses negative strain. Negative strain in this context means the species is more stable than its reference species, here the planar benzene rings and acyclic alkyl groups. Intriguingly, the [6,6]cyclophane is only a slightly larger cycle than cycloheptadecane, which is 15 kJ/mol more stable than calculated from the "strainless" $-\text{CH}_2-$ increment derived from cyclohexane⁴⁷ Attractive van der Waals forces between the rings, i.e., intramolecular solvation, may contribute to the negative strain found in the cyclophane.

We close this discussion by mentioning three more cyclophanes. The first is a triply layered species, all *para* in its benzene substitution, all with two methylene groups as linkages, 1,4:2,5-[2.2.2.2]cyclophane (**40**). For the purpose of calculating strain energy, this



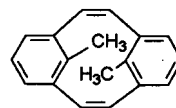
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compound can be related to methylated benzenes such as *p*-xylene and 1,2,4,5-tetramethylbenzene or to various diphenylethanes. Perhaps even simpler is the reaction enthalpy for



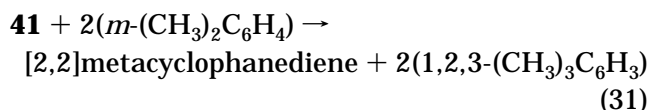
From the archival measured enthalpy of formation of the cyclophane, 409.5 ± 4.4 kJ/mol, the enthalpy of reaction is 3.9 ± 5.8 kJ/mol, statistically thermo-neutral. It appears that triple layering has but little effect beyond that of the two double-layering paracyclophanes found therein.

The penultimate species is 2,2'-dimethyl[2,2]metacyclophanediene (**41**)¹⁰⁴ shown by equilibration¹⁰⁵ to be ca. 15 kJ/mol less stable than **12**. The enthalpy of



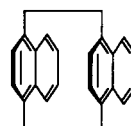
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formation has been calorimetrically determined only for the latter⁴⁰ (338.8 ± 4.9 kJ/mol). Assuming media independence of this equilibration enthalpy and thermoneutrality of the "demethylation" reaction

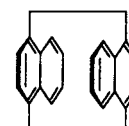


results in a derived enthalpy of formation of [2,2]-metacyclophanediene of ca. 407 kJ/mol. Recalling that the enthalpy of formation of [2,2]metacyclophane is 170.3 kJ/mol results in a formal enthalpy of hydrogenation of the diene of ca. 237 kJ/mol or some 118 kJ/mol per double bond. This result for metacyclophanediene is identical to the enthalpy of hydrogenation of unstrained *cis*-olefins. By analogy to [2,2]paracyclophanediene,¹⁰⁶ this is not surprising because the molecular strain twists the alkene double bonds out of conjugation with the benzene rings.

The last species are the two isomeric *syn*- and *anti*-[2.2](1,4)naphthalenophanes (**42**, **43**). As shown by solution-phase equilibration, the *syn* isomer is 27 ± 5 kJ/mol less stable than the *anti* isomer.¹⁰⁷ The enthalpy of formation of neither form has been measured, but measurements of their polymerization enthalpies show the *anti* isomer to be strained by ca. 90 kJ/mol, some 40 kJ/mol less than [2,2]paracyclophane.



42



43

VII. Polyphenyl and Other Polyaryl Compounds

A. Biphenyl

Polyphenyl and polyaryl compounds are formally formed by conjoining two aromatic hydrocarbon molecules with a single, or σ , bond. It is well-established that the simplest example of this class of molecules, biphenyl, is nonplanar in the gaseous state (but planar in the solid), and presumably so are the other species of this type. The nonplanarity of biphenyl obviates consideration of resonance contributors involving double-bond character between the rings and formal zwitterionic or biradical character. Although these types of structures are invoked to explain the conjugation or delocalization energy

of butadiene, such π -electron interaction between the rings in biphenyl is accompanied by a loss of aromaticity.

The enthalpy of the formal reaction where Ar = Ar' is phenyl



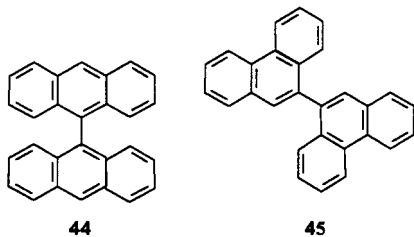
is $+16.2 \pm 2.2$ kJ/mol in the gas phase and the not too different $+23$ kJ/mol in the solid phase.¹⁰⁸ The endothermicity indicates negligible interaction between the rings, whatever the physical state. Interestingly, the gas-phase reaction enthalpy between benzene and toluene to form 4-methylbiphenyl¹⁰⁹ is $+5.5 \pm 3.0$ kJ/mol, which is about the same as the reaction enthalpy for two ethylenes reacting to form 1,3-butadiene, a molecule for which there is indisputably some conjugation between the double bonds. The related reaction enthalpy to form 4,4'-dimethylbiphenyl¹⁰⁹ is $+10.5 \pm 3.6$ kJ/mol, which, within the uncertainty, is the same as the aforementioned one for 4-methylbiphenyl.

B. Biaryls

There are three isomeric binaphthyls: 1,1', the 1,2', and 2,2'. There is enthalpy of formation data only for the first one as the solid,¹¹⁰ 170 kJ/mol. No doubt it is nonplanar in the gas phase, thus minimizing any steric interaction between the 8,8' peri hydrogens. The enthalpy of reaction 32 where Ar, Ar' = 1-naphthyl is $+14$ kJ/mol in the solid phase. Evidently, the more aromatic benzene undergoes a more endothermic reaction to form biphenyl.

The formal reaction to produce perylene (35) from 1,1'-binaphthyl is $+13$ kJ/mol for the solid phase, and so we deduce very little strain upon forming the second single bond. Despite the appearance of a new six-membered ring, there is no increase in aromaticity and the number of isolated aromatic sextets cannot change.

Because 9,9'-bianthryl (44) is composed of two linearly annelated polyaromatics and 9,9'-biphenanthryl (45) is composed of two angularly annelated polyaromatics, we expect the latter to be more stable, confirmed by the archival values of 326.2 ± 3.2 and 212.8 ± 2.8 kJ/mol for the two solids, respectively. The dihedral angles between the two anthryl ring systems of the former, determined by X-ray diffraction to consist of two discrete molecules in the asymmetric unit,¹¹¹ are $(74.65 \pm 4)^\circ$ and $(81.76 \pm 5)^\circ$.

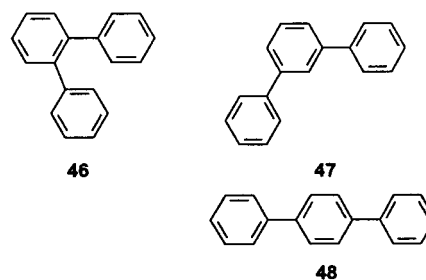


However, their enthalpy of formation difference, ca. 113 kJ/mol, seems too large. The enthalpies of the formal reaction 32 which relate the dimers to their three-ring monomers are $+71.4 \pm 4.1$ kJ/mol for bianthryl and -19.6 ± 3.3 kJ/mol for biphenanthryl.

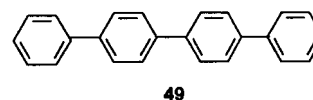
The exothermicity of the latter reaction is not credible. We would expect the enthalpy of reaction for either of these to be about the same as for formation of biphenyl and binaphthyl, ca. 18 kJ/mol. An enthalpy of formation for solid bianthryl of ca. 270 kJ/mol and for solid biphenanthryl of ca. 250 kJ/mol seems more plausible. The gas-phase enthalpy of formation value for 9,9'-bianthryl of 454.3 ± 5.3 kJ/mol gives an enthalpy of reaction 32 of ca. $+16$ kJ/mol.

C. Polyphenyls

If there is negligible interaction between the benzene rings of biphenyl, then the isomeric terphenyls (46–48) should have very nearly the same enthalpy of formation, at least for the unhindered *m*- and *p*-isomers. This is realized¹¹² with enthalpies of



formation of 279.9 ± 2.0 and 272.9 ± 2.0 kJ/mol for the *m*- and *p*-species, respectively, and 279.5 ± 1.3 kJ/mol for the *o*-isomer. If the three terphenyls have essentially the same enthalpy of formation, then all of the isomeric quaterphenyls should also have a nearly identical enthalpy of formation. In fact, the enthalpies of formation for *p,p'*-quaterphenyl (49)¹¹³ and 1,3,5-triphenylbenzene are 382 ± 7.5 and 373.4 ± 1.5 kJ/mol, respectively.¹¹² Indeed, for extrapola-



tion purposes, it is sensible to invoke a linear relationship to which all of the above species belong. The following is the weighted least-squares regression equation for their enthalpies of formation vs the number of aromatic rings, n_r ($n_r = 1-4$; $r^2 = 0.999$).

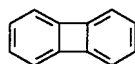
$$\Delta H_f(\text{g}) \pm 3.9 = [n_r(97.3 \pm 1.5)] + (-14.5 \pm 4.5) \quad (33)$$

Although the correlation is very good, a plot of the data for the homologous series benzene, biphenyl, *p*-terphenyl, and *p,p'*-quaterphenyl shows the values for the terphenyl to be ca. 9 kJ/mol too low compared to the essentially straight line upon which the other values lie. This conclusion is corroborated by the results from eq 32 involving various combinations of benzene, biphenyl, and *p,p'*-quaterphenyl where the average of the enthalpies of reaction is $+17.5 \pm 1.5$ kJ/mol while the enthalpies of reaction incorporating

p-terphenyl as either reactant or product are larger or smaller, respectively.

D. Cyclic Polyphenyls: Biphenylene and Triphenylene

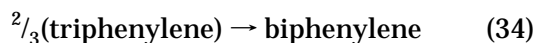
Biphenylene (**50**) and triphenylene (**26**), like several other compounds mentioned in this review, can be considered as comprising different subunits depending upon which Kekulé resonance contributor is drawn. Triphenylene was included in the cata-



50

condensed section along with its 4-ring isomers. It can also be seen as a cyclic *o*-terphenyl. Likewise, biphenylene can be regarded as a cyclic *o*-biphenyl or a dibenzocyclobutadiene. However, X-ray analysis¹¹⁴ and chemical evidence¹¹⁵ show that the main resonance contributor, of the five which can be drawn, is the one shown as **50** with alternating double and single bonds.

Taking the enthalpy of formation of biphenylene of 417.9 ± 3.3 kJ/mol, reaction 32 that conjoins the 2- and 2'-carbons of biphenyl to form biphenylene is the very endothermic $+236.5 \pm 3.8$ kJ/mol. The ca. 220 kJ/mol excess energy required to form the second bond is partitioned between the strain energies of the four- and six-membered rings and the destabilization attendant upon the degree to which biphenylene is an antiaromatic dibenzocyclobutadiene. The simple formal reaction



is endothermic by some 244 kJ/mol, also attesting to the profound thermodynamic if not kinetic, instability, of biphenylene.

The ring-closure enthalpy of reaction which converts *o*-terphenyl to triphenylene is -14 kJ/mol. Previously we suggested that the reported enthalpy of formation of *p*-terphenyl might be too low, and if so, the *o*-terphenyl enthalpy of formation is probably also too low if we expect the *para* isomer to be at least as stable as the *ortho* one. Even after making this small adjustment and acknowledging possible inaccuracy in the solid enthalpy of formation value for triphenylene, the reaction enthalpy is still exothermic. We deduce a nonnegligible interaction between the benzene rings in triphenylene which, on a smaller scale, is analogous to the ca. -90 kJ/mol exothermic formal closure of (*Z*)-1,3,5-hexatriene⁴³ to aromatic benzene.

E. Polyphenyl Polyaromatic Compounds

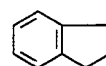
9,10-Diphenylanthracene and 5,6,11,12-tetraphenylnaphthacene (rubrene) are the sole examples of phenylated polyaromatic hydrocarbons for which there are enthalpy of formation data, 465.6 ± 5.1 and 446.2 ± 5.1 kJ/mol⁶⁰ for the former and 780.9 ± 21.8 kJ/mol for the latter. The phenyl rings are twisted (67.63 ± 5)° out of the anthracene plane in the

crystalline centrosymmetric 9,10-diphenylanthracene unit cell.¹¹¹ The normalized values for the enthalpies of reaction corresponding to eq 32 are ca. 35 and 25 kJ/mol for anthracene and two benzenes reacting to form 9,10-diphenylanthracene and ca. 37 kJ/mol for naphthacene and four benzenes reacting to form 5,6,11,12-tetraphenylnaphthacene. Even considering the uncertainty in the enthalpies of sublimation for all the substances, the values are much more endothermic for these compounds than for those discussed earlier.

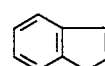
VIII. Benzoannulation and Annelation of Benzene

A. Benzoannulation

It has been recognized¹¹⁶ that benzoannulation of relatively unstrained olefins is accompanied by a ca. 28 kJ/mol increase in the enthalpy of formation. For example, the formal transformation of (*Z*)-2-butene to *o*-xylene, cyclopentene to indane (**51**), and cyclohexene to tetralin is accompanied by enthalpy of formation changes of 26.2 ± 1.5 , 26.8 ± 2.2 , and 31.0 ± 2.1 kJ/mol, respectively. The conjugated cyclopentadiene to indene (**52**) and styrene to biphenyl examples show the comparable differences of 29.1 ± 2.6 and 33.5 ± 2.5 kJ/mol, respectively. In contrast,



51



52

benzoannulation of aromatic benzene to form naphthalene shows a much larger, more positive difference, 67.7 ± 1.7 kJ/mol. The two successive benzoannulations in the series naphthalene to phenanthrene ($+54.4 \pm 3.3$ kJ/mol) and phenanthrene to triphenylene ($+60.8 \pm 3.8$ kJ/mol) are relatively constant, considering the error bars, and approximately twice that for the alkenes and dienes.

B. Cyclobutadiene, Its Benzo Analogues, and the [M]Phenylenes

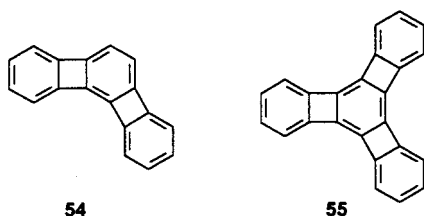
The strained cyclobutene shows an increase of $+42.7 \pm 1.7$ kJ/mol upon benzoannulation.¹¹⁷ As mentioned earlier, the very endothermic enthalpy of formation of cyclobutadiene^{22,23} is evidence of considerable instability of this species. Kinetic reactivity accompanies this thermodynamic instability, and so it is not surprising that this species is not isolable under ambient conditions. Benzoannulation results in benzocyclobutadiene (**53**), a somewhat more stable species, both thermodynamically and kinetically, for which recent gas-phase ion measurements²³ result in an enthalpy of formation of 406 ± 17 kJ/mol. That the enthalpy of formation of cyclobutadiene becomes less positive on benzoannulation supports the conclusion for considerable antiaromatic character of cyclobutadiene.



53

Dibenzoannulation of cyclobutadiene results in biphenylene (**50**), a long-known isolable hydrocarbon with an archival gas-phase enthalpy of 417.9 ± 3.3 kJ/mol. That its enthalpy of formation is essentially the same as the monobenzoannulated cyclobutadiene speaks to the antiaromaticity of the latter. An ab initio study of benzocyclobutadiene and biphenylene found that the “intrinsic destabilization energy” is ca. 33 kJ/mol greater in the former compound.¹¹⁸ This does not mean biphenylene is not destabilized relative to benzenoid expectations. The destabilization of biphenylene of more than 200 kJ/mol relative to triphenylene or biphenyl as explained earlier is huge, although not as large as for cyclobutadiene itself. The benzene rings clearly ameliorate the antiaromaticity of cyclobutadiene.

The annulation of benzene by benzocyclobutadiene to form biphenylene generates the first member of the $[N]$ phenylene series.¹¹⁹ The annulation results in an enthalpy of formation increase to benzene of ca. 336 kJ/mol. Very recently, the enthalpies of formation of angular[3]- and C_3 -symmetric [4]phenylenes (benzobis[1,2-*a*:3,4-*a'*]benzocyclobutadiene (**54**) and benzotris[1,2-*a*:3,4-*a'*:5,6-*a''*]benzocyclobutadiene (**55**)) were reported¹²⁰ to be 729.3 ± 3.8 and 1045.6 ± 7.9 kJ/mol. Annulation of biphenylene to give **54** results in ca. 311 kJ/mol increase, and a third annulation to **55** is another 316 kJ/mol increase in enthalpy of formation. As for the benzoannulation of benzene, above, the largest increase is in the first annulation of benzene itself while the two subsequent annulations are slightly less endothermic and relatively constant. In comparison, the B3LYP/6-31G* calculated enthalpies of formation for these species are 739.3 and 1046.4 kJ/mol, respectively.¹²¹



The enthalpies of the formal reaction for transforming a condensed benzenoid to the corresponding C_2 -interpolated $[N]$ phenylene using the experimental enthalpies of formation for naphthalene, phenanthrene, chrysene and biphenylene and the calculated enthalpies of formation for **54** and **55** were the nearly constant ca. 267 kJ/mol.¹²¹ From the extensive $[N]$ phenylene enthalpies of formation provided and the enthalpies of formation in Table 1, the enthalpies of reaction of other cata- and peri-condensed hydrocarbons are (kJ/mol) as follows: anthracene, 260; triphenylene, 260; benzo[*c*]phenanthrene, 259; benz[*a*]anthracene, 259. From our derived enthalpies of formation for naphthalene and picene, the reaction enthalpies are 260 and 268 kJ/mol, respectively, demonstrating the plausibility of our estimates.

Proton chemical shifts and NICS values have been calculated for several $[N]$ phenylenes.¹²² Both show diminished aromatic character in the six-membered

rings as well as diminished antiaromatic character in the four-membered rings. The central six-membered ring of branched phenylenes is only slightly aromatic compared to the terminal rings.

As stated in an earlier section, the formal reaction of biphenyl to biphenylene was accompanied by a reaction enthalpy of $+236.5 \pm 3.8$ kJ/mol. The formal reactions to give **54** from either *o*-, *m*-, or *p*-terphenyl are, per covalent bond formed, $+224.9 \pm 4.0$, $+224.7 \pm 4.3$, and $+228.2 \pm 4.3$ kJ/mol, respectively. The formal reaction of 1,3,5-triphenylbenzene to produce **55** is the remarkably similar $+224.1 \pm 8.0$ kJ/mol per covalent bond formed.

The enthalpies of partial hydrogenation of **54** and **55** were also reported¹²⁰ wherein only the central six-membered ring was totally saturated, -279.5 ± 4.2 and -299.6 ± 6.3 kJ/mol. The latter hydrogenation resulted in a product containing a strained, planar cyclohexane ring, and accordingly, an associated strain energy correction of 47.7 kJ/mol was applied to the experimental measurement. That is, if it were not for the strain in the product, the hydrogenation of **55** would be expected to give a more exothermic enthalpy of hydrogenation of ca. -347 kJ/mol. This quantity is very nearly what would have been predicted in the absence of benzene aromatic resonance. The center ring of **55** is neither aromatic nor antiaromatic—benzene with its three annulated benzocyclobutadienes has seemingly reacted as the classical nonbenzenoid cyclohexatriene.

IX. Alternant $[n]$ Annuleno[n']annulenes

$[n]$ Annuleno[n']annulenes are formally formed by conjoining two carbon atoms of an $[n + n' - 2]$ -annulene with concomitant loss of two hydrogen atoms and formation of a bicyclic molecule having conjugated double bonds. One way to understand these compounds is in terms of the component $[n]$ - and $[n']$ annulenes. Implicitly we have already done this when we considered the cata-condensed polycyclic aromatic hydrocarbon naphthalene ($n = n' = 6$) where the fused carbon atoms common to the two rings are the conjoined carbon atoms. For naphthalene and other cases where n and n' are both even, the component rings are totally conjugated and have “closed shell” singlet ground states.

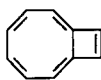
For the case of $n = n' = 4$, the compound butalene (**56**) is predicted¹²³ to be an almost rectangular molecule with a very low energy barrier of conversion (6.7 kJ/mol) to its “bond stretch” isomer, *p*-benzyne, a transient of considerable interest to theoretical and medicinal chemists alike.¹²⁴ We know of no experimental evidence for butalene, much less any thermochemical data from which we would deduce aromatic behavior, given its 6 π -electron periphery, or antiaromatic behavior, given its component cyclobutadienes.



56

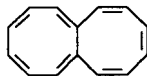
The $n = 6$, $n' = 4$ species, benzocyclobutadiene (**53**), conceptually interpolates the archetypal antiaromatic

species cyclobutadiene and the bis-benzenoid dibenzocyclobutadiene, or biphenylene (**50**), as discussed earlier. NICS calculations for these three species result in very large positive values in the four-membered ring center, decreasing from the mono- to the di- to the tricyclic compounds.¹²⁵ Neither need we discuss naphthalene further. However, its isomer, bicyclo[6.2.0]deca-1,3,5,7,9-pentaene (**57**), is neither aromatic nor antiaromatic with its enthalpy of formation of 514.2 kJ/mol¹²⁶ deduced from its hydrogenation enthalpy, -567.4 ± 3.3 kJ/mol, to form bicyclo[6.2.0]decane. The sum of the enthalpies of



57

hydrogenation of cyclobutene and cyclooctatetraene, as reported earlier, is -548.6 kJ/mol, which is not too different from the total hydrogenation enthalpy of the bicyclic pentaene (**57**). The results of limited computational studies are not at all clear regarding the planarity of the compound, the relative energies of the different resonance structures, and most important whether the compound is slightly aromatic because of its 10 π -electron periphery or is slightly antiaromatic because of the $4n\pi$ electron systems of its component rings.^{34,127} The same considerations apply to the $n = n' = 8$ case of octalene (**58**) with its two 8-carbon rings.^{128,129} The enthalpy of formation



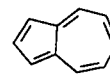
58

is 555.5 kJ/mol as deduced from the enthalpy of hydrogenation of -657.7 ± 1.3 kJ/mol.^{28c} It would appear that the [10]- and [14]annulenes themselves are not so aromatic as to confer a pronounced aromaticity on their perturbed annulene counterparts, the annulenoannulenes.

X. Nonalternant Hydrocarbons

In this section we will consider the thermochemistry of nonalternant species. In principle, the study of these compounds is at least as voluminous as those of alternant species. After all, every time two six-membered rings are found fused in a polynuclear aromatic hydrocarbon, one can form the corresponding nonalternant with a five-membered/seven-membered ring fusion. Indeed, there are two or more nonalternants that are related to the corresponding alternant arising from the choice of which six-membered ring is expanded to the seven-membered ring and which is contracted to the five-membered ring when the six-membered rings are not related by symmetry. In addition, the five- and seven-membered rings need not even be contiguous. The resulting nonalternant species are generally of lower symmetry than the original alternant species. Therefore, there are more isomers associated with the benzo-fusing locations of any remaining (i.e., unexpanded and

noncontracted) rings. For example, while naphthalene has but two monobenzoannulated derivatives forming only anthracene and phenanthrene, azulene (**59**) (formed from the formal contraction and expansion of naphthalene) has three monobenzoannulated derivatives. As such, corresponding to the isomeric



59

alternant benzenoid species anthracene and phenanthrene, there are five isomeric nonalternants: benz[*a*]azulene, benz[*b*]azulene, benz[*g*]azulene, cyclohepta[*a*]indene, and cyclohepta[*b*]indene. However, experimentally measured or derivable enthalpies of formation are absent for all five of the above, and indeed, to the best of our knowledge, no counterparts to any cata-condensed polynuclear hydrocarbons (save naphthalene and azulene) are accompanied by the desired data. The laboratory study of the energetics of nonalternant species pales by comparison to that of their benzenoid counterparts.

A. Azulene

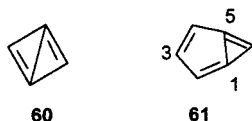
Azulene is the archetypal nonalternant hydrocarbon with its fused five- and seven-membered rings. It is also the simplest isolated nonalternant hydrocarbon. Azulene is often considered a perturbed[10]-annulene since the C5a–C8a bond that conjoins the rings is essentially a single bond, in that there cannot be a double bond between those carbons in any nonzwitterionic or nonbiradical (or Dewar long bond) resonance structures, and so the 10 π electrons are around the periphery. Azulene has only two Kekulé resonance structures compared to three for the isomeric, alternant naphthalene. The enthalpy of formation of azulene is 289.0 ± 3.8 kJ/mol,¹³⁰ some 139 kJ/mol more positive than that of the isomeric naphthalene. Despite this considerable enthalpy difference, azulene enjoys high thermodynamic and kinetic stability which has often been explained in terms of the high stability of the putative component 6 π (and, hence, aromatic) tropylium and cyclopentadienide ions. The sublimation enthalpy of azulene is not that much higher than its nonpolar isomer naphthalene (76.9 ± 1.6 ¹³¹ and 72.6 ± 0.6 kJ/mol) and so would seem to belie considerable contribution from these zwitterionic contributors.

At MP2 and MR–SDCI¹³² and B3LYP/6-311+G**⁴² levels of theory, the delocalized azulene structure is the energy minimum with the localized structure about 11–17 kJ/mol higher. Both structures are deemed aromatic on the basis of their NICS values for the five- and seven-membered rings: -21.5 – 8.3 for the delocalized structure and -18.1 and -5.9 for the localized structure.⁴²

B. Trialene and Bicyclohexatriene

The smallest, if not simplest, nonalternant of all is trialene (**60**) (also known as bicyclobuta-1,3-diene). There are no measurements of its enthalpy of formation or that of any of its derivatives. The next

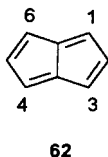
smallest example is bicyclo[3.1.0]hexa-1,3,5-triene (**61**). This species may be recognized as related by



bond stretch isomerism to the transient *m*-benzyne.¹²⁴ Unlike this perhaps more exotic looking *m*-benzyne, this nonalternant is also thermochemically uncharacterized in the experimental literature.

C. Pentalene

The enthalpy of hydrogenation of 1,3,5-tri-*tert*-butylpentalene has been measured, and combined with a molecular mechanically derived enthalpy of formation of the resulting substituted bicyclo[3.3.0]octane, the enthalpy of formation of the substituted pentalene has been obtained.^{28c} Assuming alkylation enthalpies for pentalene are the same as for benzene, the enthalpy of formation of pentalene (**62**) has been deduced to be 330 kJ/mol.¹³³



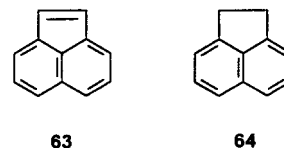
Pentalene necessarily has a zero dipole moment as an immediate consequence of its at least 2-fold symmetry. X-ray analysis showed 1,3,5-tri-*tert*-butylpentalene to have a localized electronic structure.¹³⁴ NICS and paramagnetic exalted susceptibility calculations indicate pentalene to be antiaromatic.¹³⁵ Kinetically, pentalene is much less stable than azulene, reflecting the considerable difference in stability between the 8 π and, hence, antiaromatic bicyclic system of the former and the 10 π and, hence, aromatic bicyclic system of the latter.

Pentalene has an essential single bond between the 3a and 6a carbons. Accordingly, the structural difference between pentalene and azulene is one $-\text{CH}=\text{CH}-$ group and the difference between strain in a component five- vs seven-membered ring. As found in the parent cycloalkanes²⁹ (and likewise the cycloalkenes from that source), the strain energies of five- and seven-membered ring species are comparable and therefore the difference between them can be ignored. The $-\text{CH}=\text{CH}-$ group enthalpy is ca. 57 kJ/mol,¹³³ that is, azulene should have the more positive enthalpy of formation by 57 kJ/mol barring any effects from aromaticity or antiaromaticity. From the "real molecules" we find a difference of 330–289 = 41 kJ/mol favoring azulene. Azulene apparently enjoys (57 + 41) or ca. 100 kJ/mol greater stability than pentalene.

D. Acenaphthylene and Fluoranthene

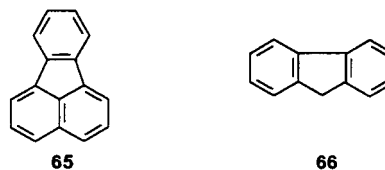
Acenaphthylene (**63**) is related to acenaphthene (**64**) much as cyclopentadiene and indene are related to cyclopentene and indane. In each of these cases, a double bond in a five-membered ring of the first

species is formally hydrogenated to form the second species. The enthalpy of formation of gas-phase



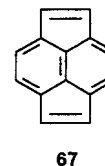
acenaphthylene is 259.7 ± 4.6 kJ/mol, and that of acenaphthene is 156.0 ± 3.1 kJ/mol. The formal hydrogenation enthalpy of acenaphthylene is thus 103.7 ± 5.5 kJ/mol. This value is the same within error bars for the values corresponding to the aforementioned two cases: 100.4 ± 2.1 and 102.7 ± 2.7 kJ/mol. This suggests negligible additional conjugation between the ace double bond and the naphthalene ring.

Fluoranthene (**65**) is formally a benzoannulated acenaphthylene and has an enthalpy of formation of 289.0 ± 1.0 kJ/mol. The enthalpy of benzoannulation is ca. 30 kJ/mol, which is typical for benzoannulation of unstrained olefins (see the related discussion earlier in this text). By contrast, the related benzoannulation of indene to form fluorene (**66**)¹³⁶ corresponds to an increase of enthalpy of formation of only 10 kJ/mol. It is not apparent why the two values for benzoannulation are so different.



E. Pyracylene, Aceplaidylene, and Some Related Species

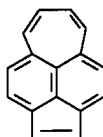
Pyracylene (**67**) is a highly unstable/reactive hydrocarbon, consonant with historical assumptions of its antiaromaticity due to its 12 π electron periphery around a central double bond. Nonetheless, ac-



companying a recent, simple, and elegant synthesis was the observation that it is indefinitely stable at -20 °C.¹³⁷ This allowed for enthalpy of combustion measurements and a resulting enthalpy of formation of 324.1 ± 3.6 kJ/mol for the solid species. As pyracylene readily decomposes/polymerizes between 323 and 398 K; reproducible, and therefore reliable, measurements of the enthalpy of sublimation are precluded.¹³⁸ Nonetheless, using an estimated enthalpy of sublimation from ref 137 (or using eq 2), a plausible enthalpy of formation of gaseous pyracylene is 409.0 ± 6.2 kJ/mol. An earlier ab initio study¹³⁹ calculated the value as 430 kJ/mol.

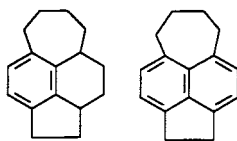
Aceplaidylene (**68**) is related to pyracylene rather much like azulene is related to pentalene. The stable azulene has a 10 π , hence, aromatic [10]annulene

perimeter. The unstable pentalene has an 8π , hence, antiaromatic cyclooctatetraene perimeter. Aceplaidylene with its seven- and five-membered rings and 14 π electron perimeter is plausibly aromatically stabilized while pyracylene with its two five-membered rings and 12 π electron perimeter would be antiaromatically destabilized. However, *ab initio* π electron first-order current density maps point to the naphthalene core rather than the annulene perimeter as the fundamental unit of current flow.¹⁴⁰



68

Regrettably, there are no enthalpy of formation data for aceplaidylene. However, there are enthalpy of hydrogenation data¹⁴¹ that we can utilize to derive a "plausible" value for the desired quantity. The hydrogenation of aceplaidylene to form aceplaidane (69), a decahydro derivative, is exothermic by 369.7 ± 1.9 kJ/mol. The hydrogenation of a hexahydro derivative (70, 1,8-butano-4,5-ethanonaphthalene) to form (most probably) the same aceplaidane is but -125.5 ± 0.5 kJ/mol.¹⁴² By use of a thermochemical cycle, we deduce the enthalpy of hydrogenation of aceplaidylene to its hexahydro derivative is ($-369.7 + 125.5$) or ca. -244 kJ/mol.



69

70

Let us now relate the hexahydroaceplaidylene with its isomer, 1,4:5,8-bis(propano)naphthalene (33). More commonly known as 1,2,3,6,7,8-hexahydropyrene, its enthalpy of formation is 40.7 ± 1.8 kJ/mol.⁶⁸ The difference between the enthalpies of formation of these doubly bridged naphthalenes may be expected to be ca. 77 kJ/mol, corresponding roughly to the sum of the strain energies of a five- and seven-membered ring in lieu of two six-membered rings.²⁹ We thus deduce an enthalpy of formation of aceplaidylene of ca. $(41 + 77 + 244) = 362$ kJ/mol.

Is this last number "plausible"? We may use this value in several comparisons. The first comparison is with aceplaidylene's isomers, pyrene and 13, referred to in a previous section. Replacing two noncontiguous six-membered rings in pyrene with the five- and seven-membered rings of aceplaidylene would result in an enthalpy of formation difference of (ca. $362 - 225$) = 137 kJ/mol, a number which is essentially identical to the 139 kJ/mol given above for the difference between azulene and naphthalene. In the latter case, the rings being exchanged are contiguous. Replacing two contiguous six-membered rings of aceplaidylene with five- and seven-membered rings and then rearranging the resulting tetracycle produces azuleno[2,1,8:*ija*]azulene and an enthalpy

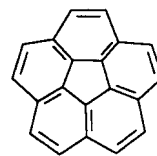
Table 6. Homodesmotic Stabilization Energies (HSE) of Nonalternant Hydrocarbons (kJ/mol)

compound	HSE	HSE/ π -electron
azulene (59)	-1.5	-0.2
acenaphthylene (63)	95.3	7.9
pyracylene (67)	8.5	0.6
fluoranthrene (65)	186.0	11.6
aceplaidylene (68)	113.0	7.1
azuleno[2,1,8: <i>ija</i>]azulene (13)	29.0	1.8
corannulene (71)	136.3	6.8

of formation difference of $(446 - 362) =$ ca. 84 kJ/mol. We have no readily accessible corrections for the ring replacements and rearrangements,¹⁴³ but intuition tells us that the qualitative stability order of all-benzenoid pyrene > partially benzenoid aceplaidylene > nonbenzenoid azulenoazulene is reasonable. Finally, the difference between the enthalpies of formation of aceplaidylene and pyracylene would be ca. -47 kJ/mol, remarkably similar to the -41 kJ/mol difference between azulene and pentalene.

F. Corannulene

If a C_{60} or C_{70} fullerene were dissected, corannulene (71) would be the smallest segment with a curvature similar to that of the spheroids. Gas-phase electron diffraction analysis, aided by B3LYP/6-31(d) calculations, shows the corannulene carbon skeleton is unlike the C_{60} one in that the hexagonal rings are not planar but bent out so as to flatten the molecule.¹⁴⁴ In two dimensions, corannulene resembles a contracted coronene but the nonplanarity of the corannulene would be expected to mitigate its aromaticity compared to the larger, planar coronene. In fact, not only is corannulene not 5/6 of coronene (252 kJ/mol), its gaseous enthalpy of formation,¹⁴⁵ 463.7 ± 7.3 kJ/mol, is more endothermic than that of coronene (302.0 kJ/mol). Of the many semiempirical and *ab initio* calculations of the enthalpy of formation quoted for corannulene,^{145,146} only two are close to the reported experimental value. Those two values are even closer (460.7 from MM2¹⁴⁷ and 459.6 kJ/mol from additivity¹⁴⁸) if a recommended value of 118.6 ± 4.7 kJ/mol for the enthalpy of sublimation⁵⁹ is accepted.



71

G. Stabilization Energies in Nonalternant Hydrocarbons

Homodesmotic stabilization energies for the non-alternant hydrocarbons are calculated in the same way as for the alternant polycyclic aromatic hydrocarbons, eq 14. The results for the compounds considered in these sections are shown in Table 6. Azulene, pyracylene, and azulenoazulene are all on the nonaromatic borderline by the HSE criterion, although that conclusion is unexpected for azulene

despite some strain associated with the nonbenzenoid rings. Acenaphthylene, aceplaidylene (derived), and corannulene have about one-half as much HSE per π electron as benzene. Fluoranthrene is nearly as stabilized as the polycyclic aromatic hydrocarbons it resembles.

XI. Fullerenes

Fullerenes represent a novel and extensive class of 3-dimensional delocalized and often aromatic species.¹⁴⁹ Sometimes fullerenes are composed solely of carbon; other times there are additional atoms as part of the cage (analogous to heterocycles), sometimes inside the cage itself (endohedral derivatives) and sometimes affixed to specific carbon atoms (and may be viewed as addition products to formal C=C double bonds or as substituted derivatives of partially hydrogenated cages). Despite the variety of species, calorimetric investigations have been limited almost exclusively to enthalpy of combustion, sublimation, and formation measurements of the initially discovered species, buckminsterfullerene (C₆₀) and the related somewhat larger C₇₀-fullerene, C₇₀. For both species, a ca. 150 kJ/mol range of enthalpy values has been reported.¹⁵⁰ For C₆₀, the average is 2509 kJ/mol for seven reports, with a standard deviation of 55 kJ/mol. The average experimental uncertainty is 13.6 ± 2.6 kJ/mol. The average of three reports for C₇₀ is 2713 ± 111 kJ/mol. The experimental uncertainty is ca. 22 kJ/mol in each of the three. Although the uncertainties are large, they are not particularly oppressive for species with so many carbons. Ab initio and MM3 calculations tend to support the experimental determinations.¹⁵⁰

Difficulties in the experimental measurements that have not always been acknowledged or ameliorated include the following: (a) Since polycyclic aromatic hydrocarbons often readily react with oxygen and other atmospheric components in both the synthesis and workup processes, fullerenes also should be similarly reactive. Furthermore, for many fullerene derivatives, there are numerous isomers that are difficult to separate. (b) Fullerenes have numerous exposed atoms and so considerable surface area (i.e., they are molecular forms of activated charcoal). As such, adsorption of solvent or other extraneous compounds is hard to avoid. (c) As mentioned before in this review in the context of polycyclic aromatic hydrocarbons, problems arise in determining sublimation enthalpies for species of low volatility. Reliable, as well as reproducible, formation enthalpies for fullerenes are thus hard to come by.

From the exothermic formal reactions as calculated by eq 14, the HSE values for C₆₀ and C₇₀ are ca. -11 and -8 kJ/mol, respectively. These numbers suggest that neither C₆₀ nor C₇₀ is aromatic and, indeed, are better described as antiaromatic. This result is not so surprising because the fullerenes are nonplanar and strained. As with some other species discussed earlier such as the smaller cyclophanes and substituted polynuclear aromatic hydrocarbons, many C-C bond angles found here in the fullerenes are rather different from the idealized 120° and, more importantly, the π orbitals are splayed and do not

properly overlap. However, despite all of the above complications, a seemingly unequivocal conclusion may be offered:¹⁵¹ per carbon, C₇₀ is more stable than the smaller, archetypal, highly symmetric C₆₀.

XII. Acknowledgments

The authors thank the referees for their careful reading and constructive comments during the preparation of the manuscript. J.F.L. thanks the U.S. National Institute of Standards and Technology for partial support of his thermochemical studies.

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