Communications to the Editor

On Enumeration and Classification of Condensed Polycyclic Benzenoid Aromatic Hydrocarbons

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The prototype polycyclic aromatic hydrocarbons (PAHs) consist solely of condensed six-membered benzenoid rings of sp^2-hybridized carbon atoms and any requisite attached hydrogen atoms. The carbon skeleton graphs of PAHs, which may be called polyhex graphs[1] or polyhex systems,[2] can be classified as catacondensed or pericondensed,[3] exemplified in Figure 1. The dual inner graph[1-4] of a pericondensed polyhex contains triangles; otherwise, the polyhex is catacondensed, likewise depicted in Figure 1. An important further distinction of pericondensed systems into those possessing and those not possessing Kekulé structures is also possible.[5] PAHs without Kekulé structures do not exist as stable, singlet ground-state species.[6]

Numerous mathematical and chemical works are concerned with enumeration of polyhex/PAH graphs with a specified number of rings.[3,7-16] A computerized coding system for benzenoids and structural analysis algorithms developed by Herndon and Bruce[17] can also be used for this purpose. The numbers and the classifications of the molecular PAHs (with Kekulé structures) associated with polyhexes containing up to 10 rings given in Table I were obtained by using these latter procedures.

The results in Table I differ critically from every previously published account. The only correspondence is for the numbers of polyhexes and graphite-connected polyhex graphs given in columns two and three of the table. The restrictive term "graphite-connected" refers exclusively to polyhex graphs that can be excised from the planar tesselation of regular hexagons (graphite graph). The tabulated figures lead one to infer that any purely graph theoretical itemization of molecular species using this restriction is highly misleading and conveys a limited amount of chemical information.

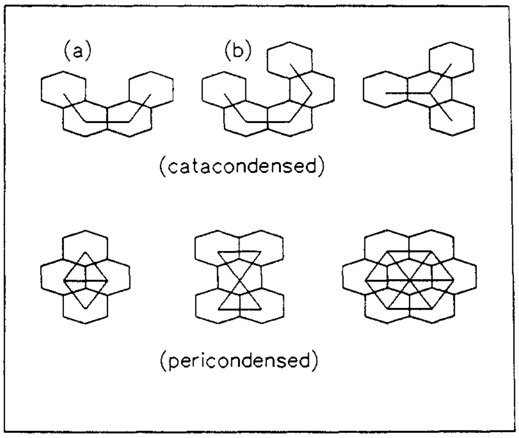

Figure 1. Polyhex groups and superimposed dual inner graphs for cata- and pericondensed benzenoids. (a) Benzo[*c*]phenanthrene. (b) Dibenzo[*c*,*g*]phenanthrene.

The data relevent to the actual number of benzenoid compounds is contained in the last four columns on the table. In analogy to all other enumerations of chemical structures, the potential number of molecular species is augmented due to the possible existence of stereoisomers.[18] In each case, the total number of possible PAHs is the sum of the number of planar species and nonplanar meso compounds plus twice the number of nonplanar enantiomer pairs. The stereoisomers include both structures with overlapping rings (helicenes) and systems whose polyhex graphs are graphite-connected. All planar species are required to belong to the graphite-connected class, but most graphite-connected polyhex graphs represent either a set of enantiomers or diastereoisomers.

The major structural features (stereocenters) that engender nonplanarity and stereoisomerism in PAHs are 1-5 and 1-6 H-H steric inteference terms as in benzo[*c*]phenanthrene and dibenzo[*c*,*g*]phenanthrene, respectively, and/or the presence of overlapping rings as found in hexahelicene and higher helicenes. The existence of enantiomers and nonplanar meso diastereoisomers for helicene structures is, of course, well-recognized;[19,20] meso and *d*,*l* forms of a catacondensed double helicene with 10 rings were reported as early as 1971.[21,22] Large degrees of nonplanarity that arise from the 1-5 and 1-6 H-H stereocenters are also fully established and discussed structural phenomena.[23-26] In fact, a large fraction of reported X-ray structures of PAHs actually describe highly nonplanar chiral species rather than planar or near-planar molecular systems.[19,20,27-37] The presence of a

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Table I. Numbers of Catacondensed and Pericondensed Polyhex Graphs and Associated Condensed Polycyclic Aromatic Hydrocarbon Molecular Species[a]

no. of rings	no. of polyhexes[b]	graphite-connected graphs[b]	graphs of nonplanar species	planar molec species	pairs of enantiomers	nonplanar meso compds	total molec species
			Catacondensed				
3	2	2	0	2	0	0	2
4	5	5	1	4	1	0	6
5	12	12	4	8	4	0	16
6	37	36	21	16	22	3	63
7	123	118	83	40	104	4	252
8	446	411	354	92	531	10	1164
9	1689	1489	1452	237	2559	21	5376
10	6693	5572	6093	600	12882	47	26411
			Pericondensed				
4	1	1	0	1	0	0	1
5	3	3	0	3	0	0	3
6	15	15	4	11	4	0	19
7	72	72	38	34	39	4	116
8	361	353	242	119	287	11	704
9	1824	1734	1432	392	1944	22	4302
10	9332	8535	7977	1355	12454	70	26333

[a] All figures are for systems with Kekulé structures. [b] These enumerations coincide with those obtained previously.[3,7-16]

stereocenter ensures a nonplanar structural moiety. The interplanar four-ring dihedral angle of 30° that is found in benzophenanthrene[28] is typical of the smallest nonplanar structural adjustments characterizing these molecular systems.

The reults obtained for the numbers of stable PAH stereochemical structural isomers have been verified by using molecular mechanics[38] and AM1[39] calculations for all possible chiral and planar structures through six rings,[40] and for over 30 selected examples of stereochemical pairs with seven to nine rings. Each stereoisomer examined is at a well-defined molecular mechanics energy minimum, and the most stable calculated nonplanar geometry always corresponds closely to the experimental X-ray structure (if known). In addition, the molecular mechanics calculations have also been shown to correlate the relatively sparse (11 compounds[41,42]) experimental $\Delta H_f°$ data for PAH structures with an average deviation of 1.1 kcal/mol.[40]

An intriguing aspect of the present work is the understanding that a *majority* of polycyclic benzenoids capable of existence will have highly nonplanar molecular structures. The planar polycyclic aromatics are therefore the unusual systems, since the planar molecules comprise only a small fraction of the potential realizable compounds.

The computerized examination of the structure code data used for this work also gives a detailed analysis of several types of other structural features (e.g., 1,2 and 1,4 addition reaction sites, bay regions, and fjord regions). The complete results of this finer delineation of molecular structure for the PAHs and extensions to larger systems will be presented in a complete paper.

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Coordination Geometry of Gaseous Hexamethyltungsten: Not Octahedral

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Wang, Albright, and Eisenstein[1] have shown that d^0 ML_6 complexes may prefer a trigonal-prismatic D_{3h} coordination geometry to the ubiquitous octahedral O_h configuration: ab initio molecular orbital calculations on the model compounds TiH_6^{2-} and CrH_6 with large, better than double ζ bases and electron correlation included at the fourth-order Møller–Plesset level indicate that the energy of the trigonal-prismatic configuration of TiH_6^{2-} is 9.2 kcal mol^{-1} lower than that of the octahedral. The calculations on CrH_6 indicate that the energy of the prismatic configuration is 157 kcal mol^{-1} lower than that of the octahedral, and further lowering of the symmetry from D_{3h} to C_{3v} reduces the energy by another 17.5 kcal mol^{-1}. Wang, Albright, and Eisenstein concluded that a trigonal-prismatic D_{3h} or C_{3v} configuration of d^0 ML_6 complexes is favored when M–L bonding is strong and nonpolar and when the ligand is not bulky and has little or no π-donating capability.

Very recently, Morse and Girolami[2] have reported the crystal structure of $[Li(tmeda)]_2[ZrMe_6]$, tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, Me = CH_3. The $[ZrMe_6]^{2-}$ anion is, of course, pseudoisoelectronic with TiH_6^{2-} and was indeed found to

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