

Figure 13. Maximum speedup of 1.9.

example can be compared with example ii. Here, the granularity is larger, perhaps accounting for a small improvement in performance although fewer iterations are required to obtain a result: one iteration of the outer loop and three iterations of the inner loop. The result is Mismatch.

CONCLUSIONS

For substructure searching of specific structures with the relaxation algorithm, the simulation demonstrates that, on average, a 5-fold increase in computational speed can be expected for approximately 20 processors. In some cases, the speedup is as much as 12-fold over the serial algorithm, and some of the factors responsible for this variation have been discussed. The degree of variation found for the small sample of specific structures investigated here makes projections of the performance as applied to searching a file of generic structures difficult, although some general observations can be made. Generic structures are more variable in nature and, taking into account all substituent groups, are generally much larger, consisting of many more nodes. The amount of computation to be performed is much greater, especially with generic queries, suggesting an improved performance with respect to speedup, although the larger volume of information associated with generic structures will result in higher communication costs. The simulation was designed as a feasibility study and, therefore, some assumptions were necessary in modeling the algorithm for generalized multiprocessor systems, for instance, the estimating of communication overheads. Further enhancements could be made to the simulation, but

we are now working toward an actual implementation of the relaxation algorithm on networked Transputers.

ACKNOWLEDGMENT

The support of the Department of Education and Science through the award of an Information Science Studentship to V.J.G. is acknowledged. L. Kitchen is acknowledged for his useful comments.

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Logical Extension of an Isomeric Pseudoconversion of Polycyclic Aromatic Hydrocarbons into Acyclic Polyenyne

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Received October 16, 1985

An isomerism between polycyclic aromatic hydrocarbons and ring assembly compounds formed by replacing selected rings with acetylenic linkages was noted, but not developed, by Dias. A far more complete isomerism, which is the logical extension of the referenced isomerism, is mathematically possible and is based on a reaction pathway using Dewar benzene intermediates. This technique is applied first to benzene and then to the general class of polycyclic aromatic hydrocarbons formed from six-membered rings, with the formulation of a concomitant nomenclature. Applicability of this method to the entire class of cata-condensed polycyclic aromatic hydrocarbons formed from six-membered rings is shown; also, some problems associated with trying to apply this technique to peri-condensed polycyclic aromatic hydrocarbons are described.

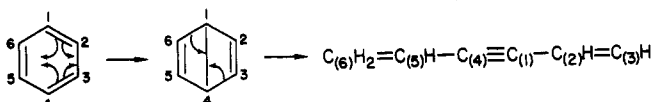
In the process of developing his "periodic table" for polycyclic aromatic hydrocarbons, Dias¹ used an isomerism of polycyclic aromatic hydrocarbons with a related set of alkynes.² This isomerism was only a minor part of Dias's focus, and no further development of this idea was presented. Nevertheless, this is the seed for the creation of a pseudoconversion scheme

that uniquely correlates a given polycyclic aromatic hydrocarbon with a corresponding acyclic polyenyne. Furthermore, in order for such an isomerism to have significance, it is imperative that a chemically viable pathway between "reactants" and "products" exists—irrespective how energetically unlikely such a pathway may be. Consequently, ignoring the chemical

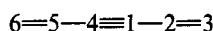
"reality" of such an isomerism, as well as any esoteric mathematics,³ the development of such an isomerism and pathway is herewith presented: The pathway chosen is one possible pathway for achieving the compounds shown by Dias. Additionally, it should be noted that the ring assembly compounds shown as Dias's "final product" can be further extended; i.e., instead of replacing only selected benzenoid modules,⁴ the entire set of benzene rings may be replaced by an appropriate set of acetylenic linkages.

For the case of cata-condensed⁵ polycyclic aromatic hydrocarbons formed from benzene modules, such a technique has as its "chemical logic" the representation of each such benzene module by its corresponding Dewar benzene form—followed by the shifting of electrons (and hydrogen atoms) to form the requisite triple bond.

(1) Benzene.



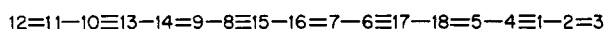
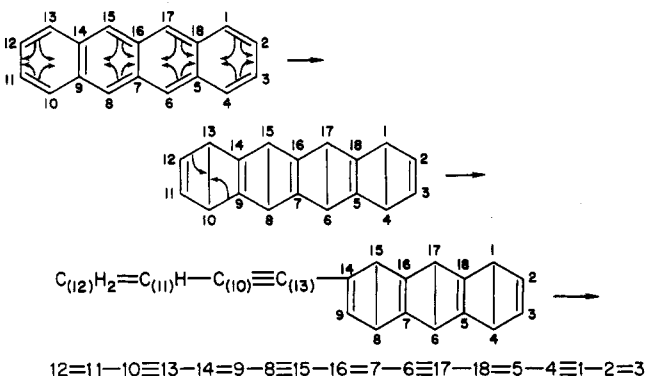
or by use of a simplified notation in which only the locant numbers are listed and the carbon and hydrogen atoms are implied



Notice that either of the two main Kekule structures, as well as any desired locant numbering of the carbon atoms, may be selected. Furthermore, an observation that will be useful in forming a nomenclature is that, using standard I.U.P.A.C.⁶ locant numbering, the lexicographically lowest numbering scheme of the three Dewar benzene resonance structures occurs when the triple bond occurs between C₃ and C₆, thereby yielding the name 1=2-3≡6-5=4.

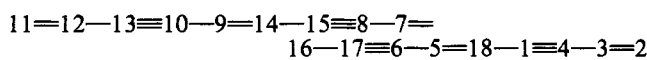
From an information perspective, whenever the sequence double bond—single bond—triple bond—single bond—double bond is encountered, it must be evaluated as to whether it is a code for an "opened" benzene ring or it is, actually, an acyclic six carbon chain. The codes for two such chains are distinguishable ONLY by the numbering; i.e., the open chain will be strictly sequential, 1=2-3≡4-5=6, vs. the simplified name, 1=2-3≡6-5=4, for benzene.

(2) An Acene. For example, tetracene, C₁₈H₁₂:



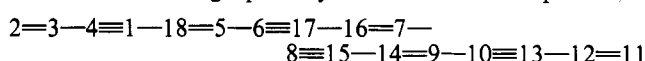
Notice that this is a much more complete isomeric conversion scheme than the one illustrated in reference 2—in which less than half of the benzene modules are replaced by alkynyl linkages.

Since there exist two end rings for an acene and each may be traversed either clockwise or counterclockwise, 2² = 4 possible combinations (using this standardized locant numbering) must be examined in order to choose a canonical name. The other three are

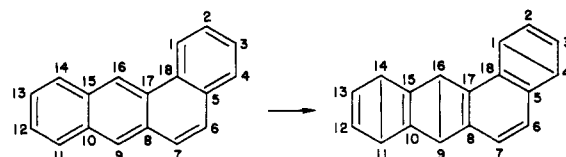


and the two sequences starting from the other end: i.e., 2=

3—.... The lexicographically lowest of these sequences is

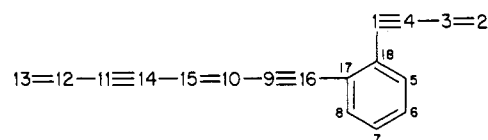


(3) An Aphen. For example, benz[*a*]anthracene, C₁₈H₁₂:

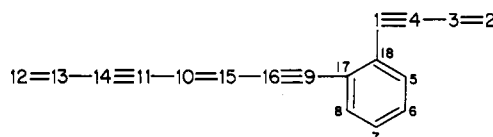


The Dewar benzene resonance structure chosen⁷ has the double bonds parallel to the common rings—as was intuitively done in the case of the acenes. In other words, start from each end ring and align the double bonds so that ring fusion will occur, whenever possible, at a double bond. This is always possible for cata-condensed hexagons (i.e., benzene modules) but may have to be sacrificed for peri-condensation or for different size rings.

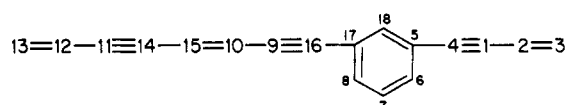
Reduction of the end rings to enynyl side chains on the common ring (5-6-7-8-17-18) yields either



1

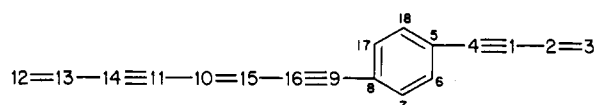


2



3

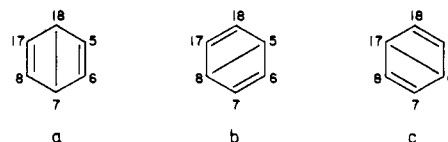
or



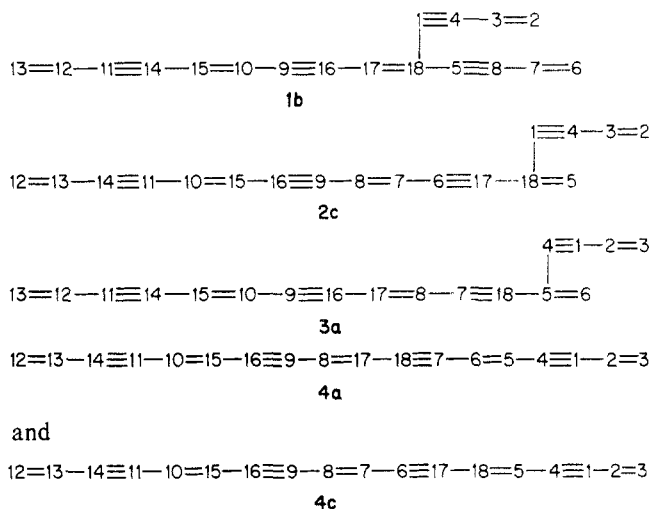
4

Note that the side chains on the common ring are ortho for 1, meta for 2 and 3, and para for 4.

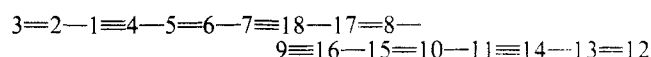
In order to further reduce this "common ring" to its corresponding alkyne, it is necessary to examine each of the three Dewar benzene resonance structures in combination with each of the four forms given above:



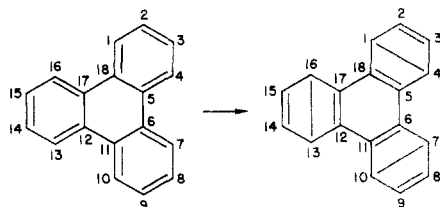
Focusing attention on just the common ring, note that structure a reduces to either 8=17-18≡7-6=5, 17=8-7=18-5=6, or the reverse of either of these. Furthermore, in all cases, it is desirable that any atom joined by a triple bond (such as 7 or 18 in structure a) not have a side chain, as this would cause five bonds to emanate from a single carbon atom.⁸ This is equivalent to saying that it is desirable to avoid using structure a with 1 or 2, structure b with 2, 3, or 4, and structure c with 1 or 3. The preferred combinations are



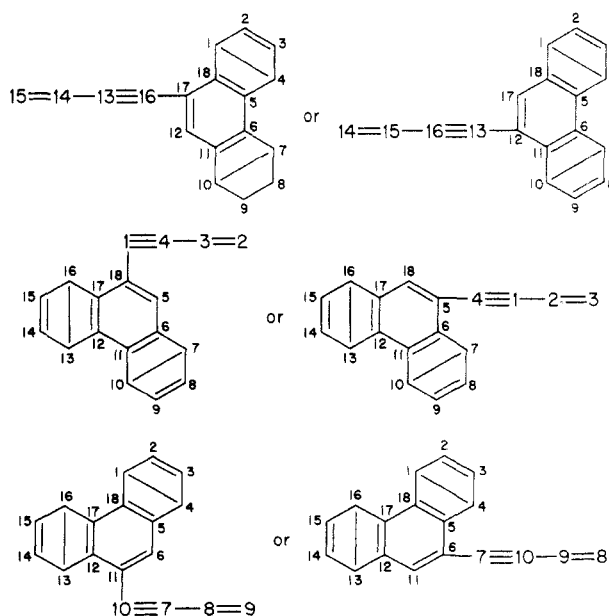
Notice that the presence of para side chains, as occurs with **4**, allows for an unbranched representation of this compound. Consequently, by use of the idea of longest main chain (as is commonly done in forming a nomenclature) and lexicographic order, this polycyclic aromatic hydrocarbon is named (from **4a** reversed)



(4) A Starphene. For example, triphenylene, $C_{18}H_{12}$:

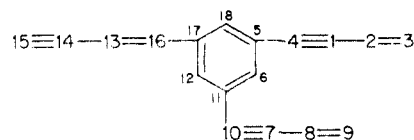


Since there are three end rings, $2^3 = 8$ possibilities must be examined. These may be reduced individually to

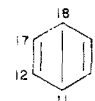


From a purely mathematical analysis approach, all eight permutations must be examined. Each, in turn, must be combined with one of the three possible Dewar benzene resonance structures of the common ring. In other words, there are 24 possible cases to be studied. However, rather than doing this, an important reduction in the number of cases is effected by the desire that the maximum number of bonds emanating

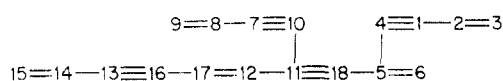
from a single point (carbon atom) is four. Because of this, having the acyclic polyenynyl side chains connected to the common ring in an all "meta" arrangement, as would seem to be preferable—inasmuch as the rings annellated to the common ring are staggered—is precluded. Consider



For this form, every one of the three Dewar benzene resonance structures will have the "elongated" bond common to one of the three carbon atoms already having a side chain. For example, let the elongated bond be 18-11:

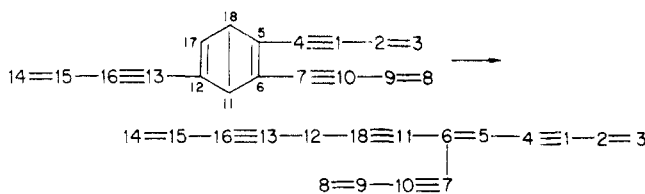


After isomeric conversion of this ring to $17=12-11\equiv 18-5=6$, there exists a triple bond as well as two single bonds at carbon 11. The resultant structure is

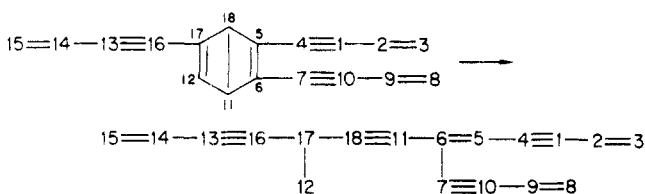


In other words, carbon 11 is oversaturated, and thus such a structure is undesirable. In a similar manner, an examination of other all-meta forms shows the same fault.

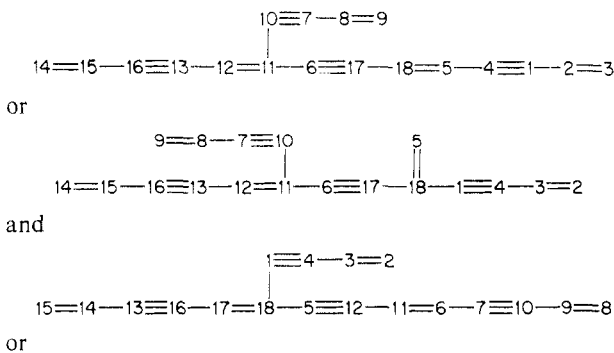
With the particular Dewar benzene resonance structure shown for the common ring, because carbons 11 and 18 are saturated, two of the side chains must be at carbons 5 and 6, respectively. Thus, the third side chain can be at either 12, i.e.



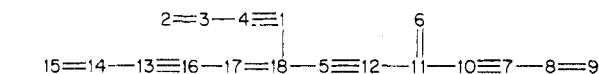
or at 17, i.e.



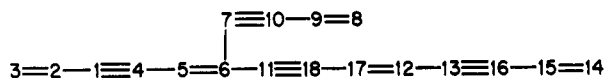
Similarly, using the other two Dewar structures yields



or



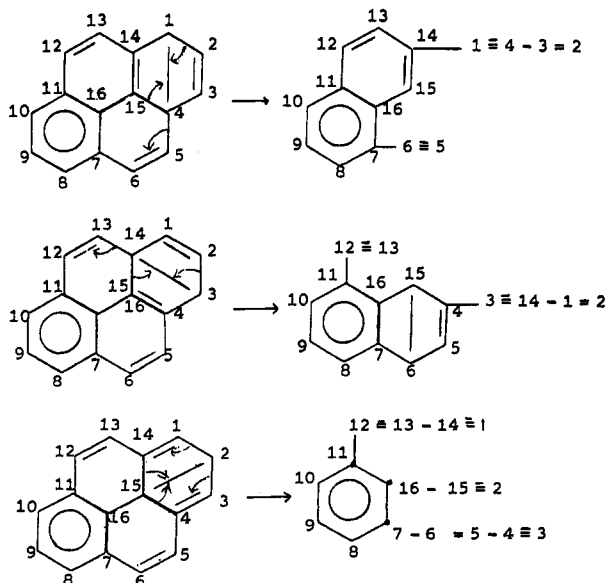
Therefore, the optimal name (with 14 carbons in the longest chain)¹⁰ is



(5) **Generalization for Cata-Condensed Compounds.** Starting from any cata-condensed polycyclic aromatic hydrocarbon, when an additional ring is annellated at a single edge, it will either elongate a given chain (section 2), cause a given chain to branch at an end ring, i.e., form an angle of $\pm 120^\circ$ with the rest of the chain (section 3), or start an internal new chain (section 4). Thus, the annellation of additional rings that still produce a cata-condensed ring system will be reducible to one of these methods. When annellation at two or more edges occurs, a peri-fused ring system is created. See section 6.

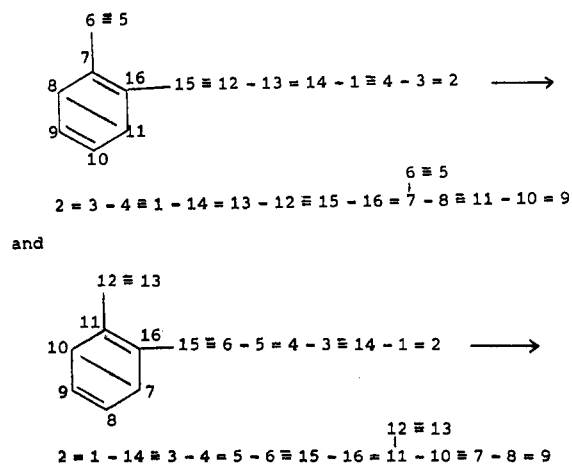
(6) **Peri-Condensed Compounds.** The absence of end rings annellated at a single edge in the peri-fused portion of a polycyclic aromatic hydrocarbon seems to preclude the existence of a similar pathway that will reduce such a compound by the above isomeric conversion to an acyclic polyenyne, as the algorithm to align the double bond with the "single" edge of ring fusion is no longer applicable. For a single-edge annellated ring, there exists a unique Dewar benzene resonance structure in which the central bond (which will become a triple bond after the conversion) is not adjacent to any other ring. Consequently, after conversion, there is always an adjacent single bond on each side of the triple bond and, thus, not oversaturation. For any peri-condensed structure, on the other hand, at least three adjacent carbon atoms and thus two adjacent edges are bonded to other rings; thus, any Dewar benzene resonance structure created by the above conversion would have at least five bonds at the "triple point".¹³ In other words, the simple technique used for cata-condensation is inapplicable for peri-condensation—within the constraint of four bonds.

To compensate for the above problem, two or more rings simultaneously can be "dismantled". However, we are now dabbling in an "art", rather than a "science". For example, consider the pyrene molecule—the smallest peri-condensed hexagonal module compound that does not have a break in the conjugation. Note that the smallest number of edges by which any ring is annellated to the other rings is two. Thus, the term "end ring" (if it is used at all) *can* be applied to either "corner" ring. In the case of cata-condensed rings, a pair of opposite edges of an end ring are "displaced" in order to make the central single ("Dewar") bond into a triple bond. For pyrene, this is supplemented by "removing" a third bond to achieve balance. For each such corner ring there are three possibilities:



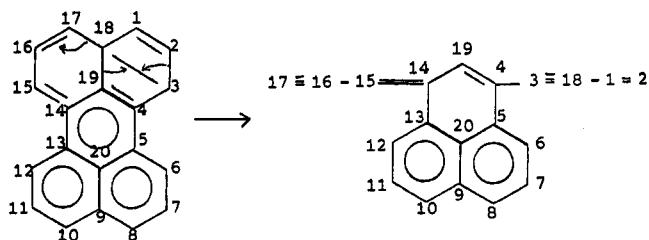
Notice that when the Dewar bond chosen is at a triple point,

three adjacent vertices have connected chains; thus, if these are the vertices of a hexagon, this hexagon cannot be further reduced without having five bonds at a vertex. In other words, only the first two of the above structures are viable. Since these are now cata-condensed systems, they can be further reduced to

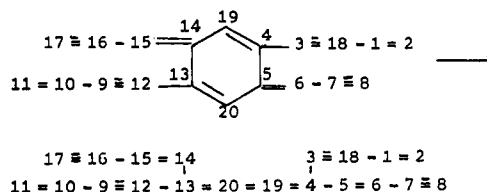


respectively, as well as two other forms having a smaller longest chain.

The pseudoconversion of two adjacent rings in a peri-condensed system, however, may not be sufficient. Consider the perylene molecule: The pseudoconversion of two contiguous rings produces an interim structure with an odd number of triple points (one) and a side chain that is doubly bonded to one of the rings:



Pseudoconversion of another pair of rings produces a "quinone"-type structure, which may be further converted to produce a triple allene structure:



From the above two examples, it may be noted that there does not appear to be a common structural form that would be machine recognizable for peri-condensed systems; unlike the cata-condensed pseudoreductions that give the "signature" double bond—single bond—triple bond—single bond, repeated for each pseudoreduced ring after the initial ring and the same signature followed by a final double bond for the initial ring.

The problem becomes even more acute when we examine the various combinations of six annellated benzene modules. Of the 82 different combinations mathematically possible,¹⁴ 36 are cata-condensed, 18 are peri-condensed (14 have two triple points, 3 have 4 triple points, 1—the induced seven-ring system coronene—has either 6 triple points as the simply connected 7-ring figure or else 0 as the multiply connected 6-ring figure), and 28 are chemically unattainable—due to having an odd number of triple points. Furthermore, of these 18 peri-condensed forms, two cannot be represented by a

Kekule structure^{15,16} and are not aromatic.

From the above paragraph, it may be concluded that a systematic complete pseudoreduction from peri-fused ring system to an acyclic polyenyne is beyond our grasp. Although a less ambitious task, as suggested in reference 2, is not precluded, nevertheless, because a chemically viable (regardless of how energetically undesirable) pathway from "reactant" to "product" is not evident, the isomorphisms shown in reference 2 for coronene and ovalene appear to be merely a convenient balancing of bonds and hydrogen atoms between the initial and final forms—rather than there existing an actual pathway that *could* achieve this conversion.

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- (2) *Ibid.*, p 128.
- (3) For purposes of this paper, "rings" will have the implication of being nondegenerate (i.e., a triple bond will not be viewed as a conjugated two-atom ring) and simply closed (i.e., the only Dewar benzene structures considered will have parallel bonds. Crossed bond structures will be disallowed).
- (4) From a mathematical bias, this particular set of polycyclic aromatic hydrocarbons may be formulated by starting with a "stack" of benzene "modules" and successively annellating one module at a time to the previous structure in order to form the final compound.
- (5) Balaban, A. T.; Harary, F. "Chemical Graphs—V. Enumeration and Proposed Nomenclature of Benzenoid Cata-condensed Polycyclic Aromatic Hydrocarbons". *Tetrahedron* **1968**, *24*, 2505-2516.
- (6) International Union of Pure and Applied Chemistry *Nomenclature of Organic Chemistry: Section A*; Pergamon: Oxford, England, 1979; p 23.
- (7) The reason for this particular choice, or more precisely the problem with any other choice, will be described later in this section.
- (8) Although pentavalent, and even hexavalent, carbon compounds do exist,⁹ they are rare in occurrence; therefore, in this proposed pseudo-conversion scheme they have been purposefully excluded as an allowed product.
- (9) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; pp 375-385.
- (10) Within the constraint of a maximum of four bonds per atom, polyfilar¹¹ fused ring systems do not lend themselves to strictly linear names; i.e., there does not exist an 18-atom linear name for this starphene. The correlation of this nonlinearity with the fact that it is not possible for all three rings of a starphene to be in aromatic conjugation at the same time¹² may be more than coincidence; however, because this is a *pseudoconversion*, rather than an observed reaction, formulation of a mechanism for this has not been investigated.
- (11) Taylor, F. L. "Enumerative Nomenclature for Organic Ring Systems". *Ind. Eng. Chem.* **1948**, *40*, 735.
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Heuristic Approaches to the Design of a Cybernetic Electroanalytical Instrument

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Received November 6, 1985

The design of a "cybernetic" electroanalytical instrument requires consideration of both heuristic and deterministic procedures. The former brings to bear expert knowledge to obtain a solution at minimum cost. Heuristic knowledge is most conveniently represented in an expert system structure where the knowledge base is separated from the inference procedure. A system design based on PROLOG is described that obtains a solution by a heuristic depth-first search of an AND/OR graph.

INTRODUCTION

The rapid development of microelectronics technology has had a major impact on electroanalytical instrumentation. Although up to the late 1970s the major advancements have been in speed, accuracy, and sensitivity, we appear to be reaching the practical limits to further improvements in the sheer physical performance of the hardware. There is, for example, little point in improving sensitivity if interferences mask or distort the analytical signal. Rather, what is needed is better and more subtle qualitative information as well as new ways of assessing experimental data. This perception may be seen as the driving force for the future development of electroanalytical instrumentation.¹⁻³

Recent work has sought to use computer-based techniques to improve the information content of electroanalysis. A number of software packages with limited inferential capabilities have been developed that enable the extraction and interpretation of information from the raw experimental data. In general, these packages employ rigorously defined algorithms based on statistical and computational methodologies to transform the raw experimental data. The transformed data are then compared with a theoretical model, and the conformity or deviation from the model guides the inference. With

the advent of inexpensive personal computers, work in the area of software development has gained impetus.

Examples of analytical and inferential software include the following: use of a stored library of reaction schemes that could be automatically fitted to experimental data by computer developed by Harrison and Small;⁴ automated analysis of data from a number of techniques by simplex fitting by Hanafay et al.;⁵ pattern recognition for classifying Fourier-transformed cyclic voltammograms by Schachterle and Perone;⁶ automatic classification of coulometry data with deviation-pattern recognition by Meites and Shia;⁷ mechanistic classification with deviation-pattern recognition by Rusling et al.;⁸⁻¹¹ use of a computed function to assess electroanalytical data by Malloy;^{12,13} automatic feature extraction from cyclic voltammograms by Speiser.¹⁴ The above software were mainly applied to mechanistic analysis.

The computer can also be used to enhance the information content of electroanalysis by the intelligent control of the experiment itself. For example, complex potential waveforms and current-measurement protocols may be applied.¹⁵ However, perhaps the most important use of the computer in experimental control lies in the fact that it can bring to bear a number of electroanalytical techniques to solve a problem.