

state, it bears a charge of +0.74. Thus it is probable that water molecules will coordinate and stabilize the leaving proton, as we have discussed for water adsorbed to the iron electrode,^{7c} and this stability is responsible for the decrease in activation energy to 1 eV at potentials around 0.7–0.8 V in acidic solution.¹³ In alkaline solutions, the activation barrier increases and the current increases.¹³ The current increase has been associated with increased acetylene coverage,¹³ possibly CCH₂ standing vertically, a phase seen in vacuum studies^{4a} and studied theoretically.^{2b} CH bond activation in such a species is less likely to be aided by direct interaction with the metal surface atoms, and this may be responsible for the increased barrier in alkaline solutions.

Our calculations show a low CH activation barrier in the cathodic direction, where reduction to ethylene and ethane is known to take place.¹² This implies a low barrier for hydrogenation of acetylene, which will happen when water is reduced, forming surface hydrogen atoms on the cathode surface. We have not studied this process here, but the reader is referred to our earlier study of water dissociation on Pt(111), which shows a barrier comparable to the CH activation barrier.¹⁰

To our knowledge, there are no published studies of acetylene reactions on iron electrodes for comparison with our theoretical results. In the anodic range 0.20–1.2 V, the surface is covered by the passive film, a hydrated oxide of 40-Å thickness,¹⁴ which should prevent acetylene adsorption to iron metal. In the –0.45 to +0.20 V range, the iron electrode undergoes dissolution.^{14,7d} If the surface has regions active to acetylene in this potential range, it appears from our results that acetylene should reduce to methane by hydrogenation of surface CH species. A small amount of methane was sometimes seen in the reduction of acetylene on platinum.¹² If the concentration of surface hydroxyl species is great enough, acetylene dissociation might be blocked, with the result that ethylene or ethane would be the reduction products.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the research.

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Aromatic Stability of Heterocyclic Conjugated Systems[†]

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Abstract: The graph-theoretical approach for calculation of the aromatic stability of conjugated polycyclic hydrocarbons is extended here to polycyclic systems having a single heteroatom. Advantages of this algebraic approach, which yields *expressions* for the molecular resonance energies, are discussed. In particular, the relative stabilities of *positional* isomers have been predicted for many derivatives of benzenoid conjugated systems in which a carbon atom is replaced by a heteroatom. The basis for the analysis is conjugated circuits (circuits defined within individual Kekulé valence structures) and their enumeration. The results are illustrated on azabenzenoid systems (N-arenes), but the nonnumerical conclusions are valid for a broader class of heterocyclic compounds.

One of the first questions to be considered when one proposes the synthesis of a novel compound is its stability, or its intrinsic capability of not easily decomposing. For conjugated systems, molecular resonance energy (RE) is a parameter that gives a useful measure of this intrinsic stability. RE is defined as that part of the molecular binding energy which is not accounted for by bond additivity, which in the case of acyclic systems suffices to represent the molecular energy. This extra stability bequeathed on some polycyclic conjugated systems is associated with the "aromatic" character of the compounds, and one speaks of *aromatic stability* of polycyclic conjugated systems or heterocyclic conjugated systems. There are two fundamentally different approaches to the study of molecular resonance energy and aromaticity: (a) use of quantum chemical computations that will produce a *numerical value* for RE and (b) use of graph-theoretical enumerations that give *algebraic expressions* for RE. The former will yield absolute values for RE of molecules of interest; the latter offers an insight on relative values, even without a knowledge of precise individual magnitudes. Observe the profound difference of the two kinds

of results. In view of the complexity of rigorous computations on polycyclic conjugated hydrocarbons, not to mention heterocyclic conjugated systems of similar size, the choice is not between quantitative calculations of reliable accuracy and qualitative predictions of simple or apparently simplistic schemes that may properly account for some aspects of the bonding. What is needed is a scheme that, even if not comprehensive, can correctly answer some of the questions of interest. As will be argued here a graph-theoretical approach based on the concept of conjugated circuits¹ (vide infra) offers a theoretical model capable of answering some questions on molecular structure with utmost reliability. In order to illuminate the profound difference between quantum chemical calculations (such as SCF MO methods applicable to polycyclic conjugated hydrocarbons) and algebraic considerations of graph theory, let us consider the question, "which has greater aromatic stability, anthracene or phenanthrene?" There is no way to answer this question a priori within the quantum chemical domain. To find the answer, one has to perform the necessary calculations, obtain the relevant numerical data, and a posteriori deduce the answer. Through the use of a graph-theoretical concept of conjugated circuits, one can derive expressions for RE. These expressions, when combined with the very plausible assumption that smaller conjugated circuits (benzene is an illustration!) have larger RE than larger conjugated circuits,

[†] Dedicated to Professor R. G. Parr, who moved us away from simple Hückel MO method, without disregard for molecular topology.

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immediately show that phenanthrene will have greater RE than anthracene. Such an approach, however, will not yield numerical answers, and if one insists on numerical data, an *outside* source has to be used to provide the standards against which the graph-theoretical parameters will be scaled.

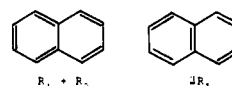
In this paper we will continue the application of "conjugated circuits" ideas to discussion of π -electron RE of conjugated systems and will show that they present a natural extension to the heterocyclic case of earlier work on homocyclic hydrocarbons. The utility of the so-developed algebraic RE expressions is argued from chemically appealing assumptions and from the great success already obtained for homocyclics² and their ions.³ A variety of qualitative and quantitative predictions are made on heterocyclics, particularly N-arenes. The approach is quite capable of yielding both reasonable qualitative statements and (given proper input) accurate quantitative values, even without explicit reference to quantum chemical calculations. The relation of this approach to quantum chemical ideas is nevertheless of major interest. Even though we emphasize graph-theoretical (i.e., combinatorial and topological) content and aspects of the approach, a reader should not misunderstand that there is no such relation. In fact, Herndon's work on resonance energies of aromatic hydrocarbons⁴ can be interpreted to indicate a relation of a semiempirical quantum chemical method and graph-theoretical approach based on enumeration of conjugated circuits.⁵

We start by outlining the basic graph-theoretical concepts and continue by considering polycyclic conjugated hydrocarbons having a single heteroatom. The approach is applied to selected azabenzenoid systems (N-arenes). Finally extension of the approach to heterocyclics having more than one heteroatom of a same kind is sketched. Initially we avoided numerical comparisons, as these presuppose a selection of number of parameters involving heteroatoms. An available review⁶ indicates disagreements among few available sources. After the introductory remarks in this section, it should be clear to the reader that lack of a useful source (experimental or computational) is the prime limitation for applications of the approach to a wider selection of compounds. In order, however, to better illustrate the potential of the approach we decided despite the situation to use relatively reliable results on pyridine and quinoline⁷ and estimate the parameters of interest. Nevertheless, the numerical results have to be considered tentative. The major contribution of this work is in offering the *frame* for discussing conjugation and aromatic stability in heterocyclic compounds. Despite some uncertainty about the absolute magnitudes for RE of discussed molecules, their relative magnitudes, and these are more often than not the most important to chemists, will show more durable qualities and may be considered as rather firm.

Graph-Theoretical Invariants

Graph theory is concerned with *relations*, and in chemistry, the relationships between molecular structure and molecular properties are of particular interest. These can be studied within graph theory by taking *bonding* between atoms as the relation. This transforms the molecular skeleton to the molecular graph, which is a well-defined mathematical object. A characterization of a structure then follows from considerations of various graph *invariants* (i.e., quantities that are independent of the details of molecular representation, either graphical or tabular, that is,

independent of how a molecule is drawn or how atoms are numbered). There are many useful invariants, e.g., paths, walks, self-returning walks, circuits, special polynomials, etc. One of the tasks of the chemical graph theory is to recognize for individual applications suitable invariants. This may be viewed as analogous to the search of a suitable coordinate system in applications of calculus, such as in evaluations of difficult molecular integrals. As is well-known, the *results* of such computations do not depend on the choice of the coordinates, but the amount of work and even the feasibility may critically depend on the choice! Hence, our first job is to decide upon graph invariants to be employed in the attempt to discuss the intrinsic stability of polycyclic systems. Here the concept of resonance energy plays a crucial role, and efforts were made in the past to report resonance energies for many molecules, as these can serve as the guide in discussion of aromaticity and aromatic stabilities of different molecules. Let us mention in particular a work of Dewar and de Llano,⁸ who reported, using a MINDO variant (a semiempirical SCF MO method suitable for computations on relatively large polycyclic conjugated hydrocarbons), RE for numerous benzenoid and nonbenzenoid conjugated hydrocarbons. There was no hint, nor at the time would one expect, that individual RE may be related. They were derived for each molecule separately and considered fully *independent*, and if similar calculations are today to be extended to additional polycyclic conjugated systems the same would be true. The RE numbers simply represent actual *deviations* of the molecular energy from a hypothetical energy based on the simple bond additivity model. It was recognized several years later,¹ and relatively late in view of the long history of quantum chemical calculations on such molecules, that these "independent" deviations from the simple bond additivity *themselves can be expressed as being additive*. But the additivity is now in terms of selected (qualified) circuits that one has to identify within the collection of Kekulé valence formulas of a considered conjugated hydrocarbon. The particular qualified circuits, referred to as *conjugated circuits*, are those circuits within an individual Kekulé valence form in which there is a regular alternation of CC single and CC double bonds. Benzene has two Kekulé valence structures, each of which contains a single conjugated circuit R_1 . Naphthalene has three Kekulé valence structures (two of these, as in benzene, are symmetry related) that give rise to conjugated circuits R_1 and R_2 , as shown below:



The above can be viewed as *decomposition* of conjugation into cyclic conjugated components, instead of the customary Kekulé valence forms. By summing all the contributions in all Kekulé valence structures and averaging the sum (i.e., dividing it by the number of Kekulé valence structures K) one obtains an expression that can be viewed as an *algebraic formula* for the molecular RE.¹ In the case of naphthalene one obtains $(4R_1 + 2R_2)/3$. If one now uses as the outside source the SCF MO data, the graph-theoretical predictions will be at the level (and reliability) of the source computations—no better, no worse—except that now we succeeded in relating data initially considered to be independent. All this has been shown to hold for benzenoid conjugated hydrocarbons.^{2,3} Observe that the graph-theoretical approach just presented can be used in *reverse*, in order to verify the internal consistency of semiempirical quantum chemical computations.⁹

Conjugated Circuits in Heterocyclic Compounds

We will consider heterocyclic systems having a single heteroatom. If there are more than one heteroatom in a molecule, be it of the same kind or different, the approach can be extended as we will see later. Such extensions do not introduce novel computational difficulties; they do proliferate the number of adjustable parameters, just as do similar extensions in all semi-

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Table I. Count of Conjugated Circuits in Various Benzotetracene Derivatives^a

I $2R_1 + 2R_2 + X_1$	$2R_1 + X_2 + X_1 + X_2$	$2R_1 + R_2 + X_1 + X_2$	$3R_1 + R_2 + X_2$	$3R_1 + R_2 + X_2$
II $2R_1 + R_2 + R_3 + X_1$	$2R_1 + X_1 + X_2 + X_3$	$3R_1 + X_2 + X_3$	$2R_1 + R_2 + R_3 + X_1$	$3R_1 + R_2 + X_3$
III $2R_1 + R_2 + X_1 + X_3$	$2R_1 + R_3 + X_1 + X_2$	$2R_1 + R_2 + X_1 + X_3$	$3R_1 + R_3 + X_2$	$3R_1 + R_2 + X_3$
IV $2R_1 + R_2 + R_3 + X_1$	$3R_1 + X_2 + X_3$	$2R_1 + X_1 + X_2 + X_3$	$3R_1 + R_2 + X_3$	$2R_1 + R_2 + R_3 + X_1$
V $2R_1 + R_2 + X_1 + X_2$	$2R_1 + X_1 + X_2 + X_4$	$3R_1 + X_2 + X_4$	$2R_1 + R_2 + R_4 + X_1$	$3R_1 + R_2 + X_4$
VI $R_1 + R_2 + R_3 + X_1 + X_2$	$2R_1 + R_2 + X_2 + X_4$	$R_1 + R_2 + X_1 + X_2 + X_3$	$2R_1 + 2R_2 + X_3$	$2R_1 + R_2 + R_3 + X_2$
VII $R_1 + R_2 + R_3 + R_4 + X_1$	$2R_1 + X_2 + X_3 + X_4$	$2R_1 + R_2 + X_3 + X_4$	$R_1 + X_1 + X_2 + X_3 + X_4$	$2R_1 + R_2 + R_3 + X_4$
VIII $R_1 + R_2 + R_3 + X_1 + X_5$	$2R_1 + X_2 + X_3 + X_5$	$2R_1 + R_2 + X_3 + X_4$	$R_1 + X_1 + X_2 + X_3 + X_5$	$2R_1 + R_2 + R_3 + X_5$
IX $R_1 + R_2 + R_3 + R_4 + X_2$	$R_1 + 2R_2 + X_3 + X_4$	$R_1 + R_2 + X_2 + X_3 + X_4$	$R_1 + 2R_2 + R_3 + X_4$	$X_1 + 2X_2 + X_3 + X_4$
Total				
$14R_1 + 10R_2 + 6R_3 + 2R_4 +$ $8X_1 + 2X_2 + X_3 + X_4 + X_5$	$18R_1 + 4R_2 + R_3 +$ $4X_1 + 8X_2 + 6X_3 + 3X_4 + X_5$	$18R_1 + 6R_2 +$ $4X_1 + 6X_2 + 7X_3 + 3X_4 + X_5$	$18R_1 + 8R_2 + 3R_3 + R_4 +$ $4X_1 + 4X_2 + 4X_3 + 2X_4 + X_5$	$20R_1 + 8R_2 + 4R_3 +$ $2X_1 + 4X_2 + 3X_3 + 3X_4 + X_5$

^aKekulé valence structures of the parent benzotetracene, to which the numbering I-IX corresponds are shown in Figure 2.

Kekulé structures	Conjugated circuits
Total circuit count	$4R_1 + 2X_1 + 4X_2 + 2X_3$

Figure 1. Kekulé valence structures of acridine (the nitrogen atom is shown as a black circle) and their decomposition into conjugated circuits.

empirical calculations. In a heterocyclic system with a single heteroatom X, we may have conjugated circuits that incorporate the heteroatom besides conjugated circuits in which the heteroatom is not involved. The situation is illustrated for acridine (Figure 1). The graph-theoretical analysis consists in enumeration of conjugated circuits in all Kekulé valence structures. We will use symbol R_n ($n = 1, 2, 3, 4, \dots$) to represent conjugated circuits of size $4n + 2$ (i.e., of size 6, 10, 14, 18, ...) if only carbon atoms constitute the circuit and symbol X_n for conjugated circuits of size $4n + 2$ involving the heteroatom. As we see from Figure 1, in the case of acridine we have only R_1 conjugated circuits involving carbon atoms alone, while the heteroatom appears in conjugated circuits of sizes 6, 10, and 14. The overall contribution of the four Kekulé valence structures is $4R_1 + 2X_1 + 4X_2 + 2X_3$. If this is divided by four, the number of used Kekulé valence forms, we obtain the expression for the molecular RE: $(4R_1 + 2X_1 + 4X_2 + 2X_3)/4$. At this stage the above expression is a purely mathematical construction devoid of chemical content. In order to obtain a numerical value for the RE we need numerical values for the parameters R_n and X_n . These cannot be calculated by graph-theoretical methods: *graph theory does not supply ways of computing particular quantities on its own*. Even when Hückel's MO method is viewed as a graph-theoretical approach (in view of mathematical equivalence between the Hückel matrix and the adjacency matrix of the accompanying molecular graph) from which one can derive subsequently RE, this follows by implication, by tacit interpretation of the graph-theoretical adjacency matrix as a π -electron Hamiltonian! The way to obtain numerical values for molecular RE is to use *outside* (graph theory) source

I : $3R_1 + 2R_2$	II : $3R_1 + R_2 + R_3$	III : $3R_1 + R_2 + R_3$
IV : $3R_1 + R_2 + R_3$	V : $3R_1 + R_2 + R_4$	VI : $2R_1 + 2R_2 + R_3$
VII : $2R_1 + R_2 + R_3 + R_4$	VIII : $2R_1 + R_2 + R_3 + R_5$	IX : $R_1 + 2R_2 + R_3 + R_4$
Total		
$22R_1 + 12R_2 + 7R_3 + 4R_4 + 2R_5$		
Resonance Energy Expression: $(22R_1 + 12R_2 + 7R_3 + 4R_4 + 2R_5)/9$		

Figure 2. Nine Kekulé valence structures of benzotetracene. Each ring is labeled by the numbers 1-4 indicating the size of the conjugated circuits to which it contributes. Under each structure is indicated the partial contribution of that structure; structures have been ordered, I making the largest contribution to molecular RE and IX making the smallest such contribution. The total of all contributing structures leads to the expression for molecular resonance energy (bottom line).

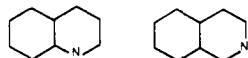
data, information on selected standard molecules, and calibrate the graph parameters (here R_n and X_n) accordingly. If standards are not available or information on the standards is very approximate, then the quantitative deductions from the graph-theoretical analysis will also be unavailable or very approximate. However, even if the numerical values for the parameters X_n may not be known, one can deduce a number of useful results relating to *relative* stabilities of selection of positional isomers, isomers in general, and even molecules of different size. We will postpone the discussion of numerical aspects of the graph-theoretical analysis for a later section dealing with nitrogen as heteroatom.

In order to further illustrate the use of conjugated circuits for deriving the expressions for the molecular RE we will examine

more closely benzotetracene and isomers obtained by a substitution of a heteroatom X in selected positions in the carbon skeleton. In Figure 2 we illustrate the nine Kekulé valence structures of 1,2-benzotetracene, and in the first column of Table I we show the count of conjugated circuits for each individual valence structure. The Kekulé valence structures have been *ordered* according to their relative contributions to the molecular RE, if it is assumed that smaller conjugated circuits make dominant contributions. Observe how this single broad assumption suffices to almost fully order all the valence structures of 1,2-benzotetracene (if they have different contributions). Strictly speaking, Kekulé structures V and VI are not directly comparable, as we do not know relative magnitudes of the differences $(R_1 - R_2)$ and $(R_2 - R_3)$.¹⁰ The other columns of Table I show the count of conjugated circuits for the remaining heterosubstituted derivatives of 1,2-benzotetracene. Each time the heteroatom is situated in a different ring of the pentacyclic parent structure. One can reproduce the results simply by inspecting the Kekulé valence structures of Figure 2 and performing the enumerations, each time labeling one of the carbon atoms as X. If all X_n in Table I are replaced by the corresponding R_n , one should obtain in each case the same result, that of the parent 1,2-benzotetracene shown in Figure 2. Numbers from 1 to 5 have been inscribed into the individual rings of the Kekulé structures of Figure 2, indicating the size of the smallest conjugated circuit involving the particular ring. Hence, a ring labeled as "1" can also participate in additional conjugated circuits involving adjacent rings, but the presence of these additional conjugated circuits is noted by placing the digit "2" in the adjacent rings. Such labeling of individual rings was introduced in the discussion of local aromatic features¹¹ but is convenient also here, as it provides (a) an immediate reading of the partial contribution of individual Kekulé valence structure to molecular RE, (b) an easy detection of local variations in conjugation among different structures, (c) an easy check for erroneous count of the role of heteroatom, and (d) an easy check on omission or overlook of a contributing term, since each structure makes as many contributing terms as there are rings in the molecule. From Figure 2 one can directly derive the following count of conjugated circuits for the individual rings of 1,2-benzotetracene:

ring	R_1	R_2	R_3	R_4	R_5	sum
A	8	1				9
B	4	4	1			9
C	4	3	2			9
D	4	2	2	1		9
E	2	2	2	2	1	9
total	22	12	7	3	1	45

The sum of the entries in each row gives the number of Kekulé valence structures, while the sum along each column gives the count of conjugated circuits for the molecule as a whole. The entry in the right lower corner gives an independent check for the correctness of the counts. The first entry in each row gives also the X_1 count for each positional isomer having the heteroatom in the corresponding ring! If there are more than one non-equivalent site within a ring, *any* of them can be substituted by the heteroatom—the approach does not differentiate between positions within a single ring. For instance, the present theoretical approach cannot differentiate quinoline and isoquinoline:



They are expected to show the same RE. The difference between the two compounds is not beyond graph-theoretical analysis; it is outside the assumption of considered circuit additivity. If one

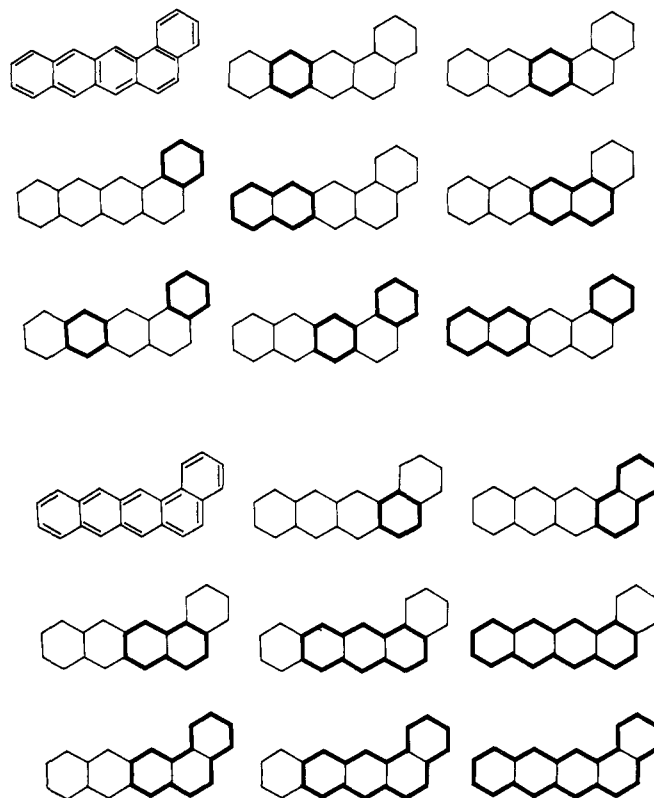


Figure 3. Decomposition of the first and the last Kekulé valence structures of Figure 2 illustrating the presence of disjoint conjugated circuits (in structure I) and linearly dependent conjugated circuits (in structure IX).

examines the bond types present in the two molecules we immediately see an important difference: Aromatic CN bonds in quinoline are of (2,2) and (2,3) type, while in the case of isoquinoline they are both of (2,2) type. Bond type is defined by the number of neighbors of the terminal atoms.¹²

The results for various derivatives of 1,2-benzotetracene are shown in the remaining columns of Table I. Normally we will be interested only in the total count of conjugated circuits for a compound. The individual entries in Table I serve only to illustrate underlying basic contributions, the individual Kekulé valence structures as well as the role of individual rings. The isomers have been *ordered* starting with the isomer showing the largest difference with the parent 1,2-benzotetracene. Observe that this ordering does not presuppose any knowledge of the relative values of R_n and X_n , except that the quantities monotonically decrease with n . The ordering shows that already at this qualitative level of examination of selected heterocyclic compounds, some deductions on their relative behavior are possible.

Before proceeding to analysis of other molecules a comment on disregard of some higher conjugated circuits is warranted. We choose, somewhat arbitrarily, to ignore contributions of higher conjugated circuits that are linear combination of smaller conjugated circuits. Such appear for the first time already in phenanthrene, where one R_3 conjugated circuit can be seen to be a combination of two smaller R_2 conjugated circuits and R_1 (with opposite sign).¹ It is doubtful if inclusion of all conjugated circuits would alter numerically significantly the results. Gomes¹³ confirmed these doubts in the case of conjugated hydrocarbons, which is not surprising when one recalls that numerically R_3 has been estimated to contribute 0.1 eV, and we talk of a fraction (a small multiple of $1/K$, K being the number of Kekulé valence structures) of that contribution. However, the present convenience of excluding these small terms (which makes enumerations simpler and

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Table II. The Count of Conjugated Circuits in Heterocyclic Structures Having Four and Five Condensed Benzenoid Rings^a

structure	coefficients in the resonance energy expressions							
	R_1	R_2	R_3	R_4	X_1	X_2	X_3	X_4
A	12	2			4	6	3	1
B	12	4	1		4	4	2	1
C	14	4			2	4	3	1
D	10	6	2		6	2	1	1
E	8	4			4	4	4	
F	10	4	1		2	4	3	
G	18	6			4	8	7	2
H	20	10	2		2	4	5	2
I	18	8	3	1	4	6	4	1
J	16	8	3		6	6	4	2
K	16	10	4		6	4	3	2
L	34	4	1		8	10	4	3
M	34	6	3	1	8	8	2	2
N	30	12	3	1	12	2	2	2

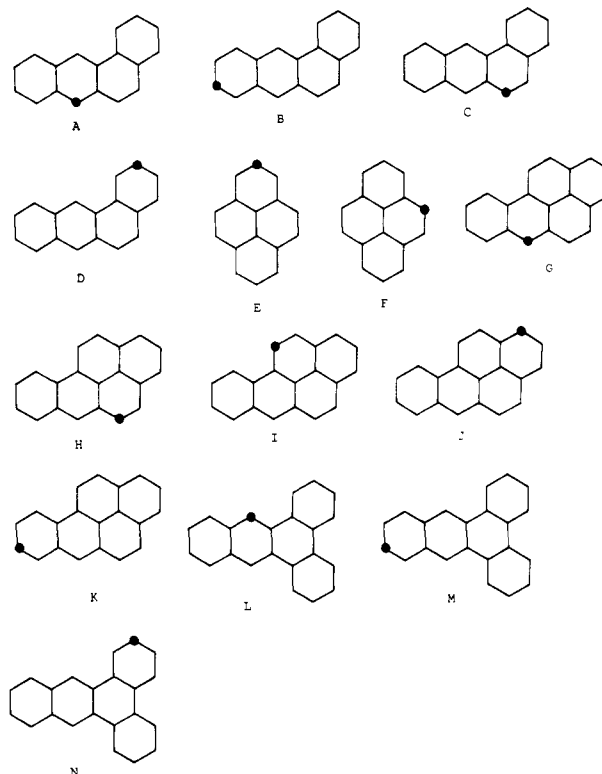
^aLabels A-N correspond to molecular skeletons shown in Figure 4. Symbols R_n and X_n represent conjugated circuits of size $4n + 2$ involving only carbon atoms and involving a heteroatom, respectively.

offer checks on the count of conjugated circuits) may not be prudent in future extensions. As described elsewhere,¹⁴ one finds simple regularity if one counts all conjugated circuits, including also combinations of disjoint conjugated circuits. In such instances one finds in all $(K - 1)$ contributing terms. In Figure 3 we illustrate this more general count of conjugated circuits for a pair of valence structures of 1,2-benzotetracene, one having disjoint contributions, the other having linearly dependent conjugated circuits. A consideration of disjoint conjugated circuits introduces additional parameters, such as $R_{1,1}$ representing contribution of two disjoint R_1 conjugated circuits. This parameter is characterizing the difference between RE of benzene and diphenyl (assuming the difference that can be traced solely to interactions of two π -sextets and compensating for other differences, like change in σ frame, nonbonding interactions, etc.). Currently, there is little evidence that $R_{1,1}$ and similar terms make a visible contribution.

Four- and Five-Ring Heterocyclic Systems

As the number of fused benzene rings increases, so generally does the number of isomers.¹⁵ The results for systems with fewer rings have been known for some time, but recently the difficult task of enumerating isomers for structures with a larger number of rings has been successfully completed.¹⁶ There are a number of alternative approaches to finding the number of isomers. The present state of art allows one even to let computers draw all possible structures.¹⁷ The count of isomers for heterocyclic systems is an even more formidable task. The difficulty again is primarily in recognizing duplicates (rather than in the possibility of having omissions, although this also should not be underestimated), due to a fast proliferation of structures. For example, while there are only 22 arenes with five fused benzene rings,¹⁸ the class of X-arenes (i.e., arenes with a single X heteroatom) with five rings consists of 210 members.¹⁹ In this section we have selected only a few from this populous class.

First we examine all significantly distinctive positional isomers having four fused benzene-type rings. By *significantly* distinctive we mean here positional isomers having the heteroatom in different

**Figure 4.** Heterocyclic compounds having four and five fused rings.

rings. In Figure 4 we show skeletons of selected heterocyclic systems, and in Table II are given the separate counts of conjugated circuits for circuits involving only carbon atoms and for circuits involving the nitrogen atom. The advantage of the algebraic approach becomes evident when we want to compare results for different structures. Frequently one can make valid deductions even without recourse to numerical values. For example, consider the difference in RE of structures A and B, which can be written as $2D_2 + D_3$, with D_n standing for $(R_n - X_n)$. Because we do not yet know these differences numerically, we cannot say if A or B has greater aromatic stability. But we notice that structures J and K, benzopyrene heterocycles, show the *same* difference: $2D_2 + D_3$. Hence, if A is more aromatic (as measured by RE) than B, then also J is more aromatic than K. Such a priori comparisons are simply not available within the standard quantum chemistry approaches, where there are no indications that the pair of isomers J, K may have anything in common to the pair A, B; *but they do!*

Selection of the Parameters for Computing RE

All previous results hold for *any* heteroatom; different heteroatoms will be associated with different numerical values for the graph-theoretical parameters X_1, X_2, X_3, \dots . We will now restrict discussion to aza compounds and illustrate how one can determine the value of the parameters X_n . As already mentioned, this requires some outside data that would allow one to assign numerical values to X_n quantities. Ideally, reliable computations on at least half a dozen molecules would be desirable so that the corresponding systems of equations, based on the expressions for RE of half a dozen standards, is overdetermined. However, the RE results for heterocyclics are scarce, particularly the results on different molecules from a same computational laboratory. Our task is to try to determine X_n 's from an underdetermined system of equations, not an overdetermined system. As will be shown, by a suitable curve-fitting approach, we have succeeded in deriving values for X_1, X_2, X_3 , and X_4 . Before we outline this, let us discuss the parameters R_1, R_2, R_3 , and R_4 for carbon-only conjugated circuits. The values adopted in the past were based on the reported RE of benzene, naphthalene, anthracene, and tetracene: 0.869, 1.323, 1.600, and 1.822 eV, respectively, computed by Dewar and de Llano.⁸ When these values are used in the expressions for the

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(17) Knop, J. V.; Szymanski, K.; Jeričević, Z.; Trinajstić, N. *J. Comput. Chem.* **1983**, *4*, 23.

(18) Trinajstić, N. "Chemical Graph Theory"; CRC Press: Boca Raton, FL, 1983.

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Table III. Numerical Values for the Parameters R_n and X_n Used in This Work^a

n	R_n , eV	X_n , eV	D_n , eV
1	0.869	0.908	0.039
2	0.246	0.367	0.121
3	0.100	0.148	0.048
4	0.041	0.059	0.018

^a While, as expected, R_n and X_n decrease with the size of the circuit, their difference does not decrease monotonically (last column).

corresponding RE, one obtains a simple system of linear equations (already in Gaussian triangular form convenient for subsequent substitution):

$$(2R_1)/2 = 0.689$$

$$(4R_1 + 2R_2)/3 = 1.323$$

$$(6R_1 + 4R_2 + 2R_3)/4 = 1.600$$

$$(8R_1 + 6R_2 + 4R_3 + 2R_4)/5 = 1.822$$

Any revision in the resonance energies of the above simple benzenoids will induce a novel parametrization. As discussed elsewhere⁹ one can impose restrictions on the solution of such a set of equations by demanding that $R_1, R_2, R_3, R_4 \dots$ monotonically decrease or approach zero or some small constant value as the size of the circuits increases. Because the values $R_1 = 0.869$ eV, $R_2 = 0.246$ eV, $R_3 = 0.100$ eV, and $R_4 = 0.041$ eV satisfy the condition, they have been adopted.²⁰ Now we need a similar set of equations to define X_n parameters. From comparison of SCF π -MO calculations^{7,8} of benzenoid hydrocarbons and the corresponding aza derivatives, it follows that $RE(N\text{-arene}) > RE(\text{arene})$. However, the $RE(N\text{-arene}) - RE(\text{arene})$ difference is generally quite small. It follows that N-arenes will show similar regularities found in arenes, but for discussion of finer details and differences among N-arene isomers we have to differentiate between conjugated circuits involving only carbon atoms and conjugate circuits involving nitrogen. Because the R_n parameters have been based on SCF-MO calculations, results of a similar quality ought to be used to determine X_n values. In Figure 5 we show graphically the monotonic decrease of R_n with n . The curve can be well approximated by a two-parameter exponential: $R_n = A \exp(-Bn)$. By using a nonlinear least-square regression, one obtains $A = 2.8 \pm 0.2$ and $B = 1.19 \pm 0.07$. Dewar, Harget, and Trinajstić⁷ reported SCF-MO resonance energies for pyridine and quinoline. These values suffice to determine two parameters, A' and B' , for a curve $X_n = A' \exp(-B'n)$ representing monotonic behavior of contributions from conjugated circuits involving nitrogen atom. The values for X_1 and X_2 one obtains are 0.908 and 0.367 eV, respectively. Thence $A' = 2.25$ and $B' = 0.91$. Thus we see that the curve for aza compounds has a smaller amplitude (measured by A') but is also somewhat slower in tailing off (measured by B'). By extrapolation, we find $X_3 = 0.148$ eV and $X_4 = 0.059$ eV. In Table III we show the parameters used and also show the difference, D_n , between the two sets of parameters belonging to hydrocarbons and aza compounds, respectively. After an initial relatively small difference in RE of benzene and pyridine, we observe an increasing difference involving X_2 and the gradual decrease with larger n , which justifies the neglect of contributions of larger conjugated circuits. However, some caution is required if we consider extending the discussion to even larger systems. It would be incorrect to suggest that in porphine only pyrrole rings (being the smallest) make significant contributions to RE. They make the dominant contributions, but we have not yet established that contributions from larger conjugated circuits (such as the molecular periphery) can be fully neglected,²¹ particularly as the

(20) The value for R_4 found by one of us (N.T.) was incorrect, but the correct value based on tetracene appears too large (out of the monotonic behavior); hence the value of 0.04 eV was retained.

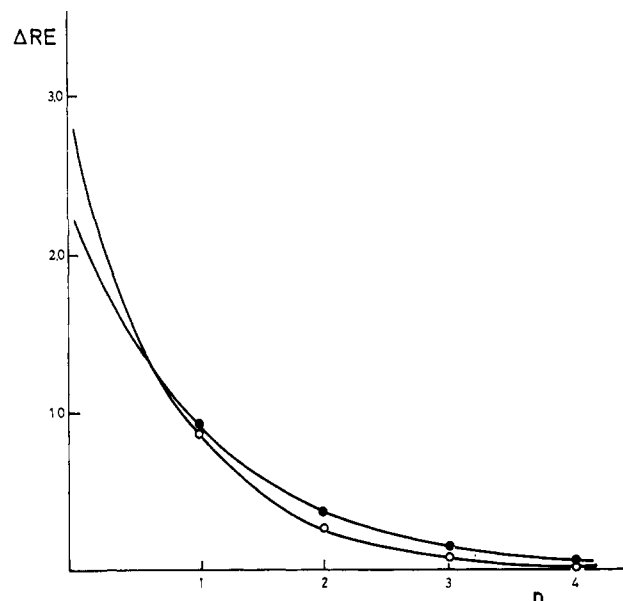


Figure 5. Dependence of contributions of rings of size $4n + 2$ ($n = 1, 2, 3, 4$). Open circles correspond to conjugated circuits involving only carbon atoms; black circles correspond to conjugated circuits involving nitrogen.

Table IV. Expression for the Resonance Energy for Known Heterocyclic Skeletons (X Corresponding to Nitrogen Substitution)^a

structure	expression for resonance energy
A-457	$(4R_1 + 2X_1 + 4X_2 + 2X_3)/4$
A-3811	$(8R_1 + 4R_2 + 4X_1 + 4X_2 + 4X_3)/6$
A-3859	$(2R_1 + 2X_1 + 2X_2)/3$
B-382, B-385, B-387	$(54R_1 + 20R_2 + 2R_3 + 12X_1 + 14X_2 + 9X_3 + 3X_4)/19$
B-383	$(44R_1 + 12R_2 + 2R_3 + 8X_1 + 12X_2 + 10X_3 + 6X_4 + 2X_5)/16$
B-384	$(61R_1 + 17R_2 + 2R_3 + 12X_1 + 16X_2 + 7X_3 + 4X_4 + X_5)/20$
B-386, N-38, N-39	$(24R_1 + 8R_2 + R_3 + 6X_1 + 10X_2 + 5X_3 + X_4)/11$
B-388, B-389, B-391	$(44R_1 + 20R_2 + 4R_3 + 12X_1 + 10X_2 + 7X_3 + 4X_4 + X_5)/17$
B-390	$(60R_1 + 32R_2 + 14R_3 + 16X_1 + 12X_2 + 8X_3 + 4X_4 + 3X_5 + X_1)/22$
B-410, B-411	$(34R_1 + 14R_2 + 2R_3 + 12X_1 + 4X_2 + 3X_3 + X_4)/14$
B-429	$(90R_1 + 30R_2 + 3R_3 + 6X_1 + 20X_2 + 22X_3 + 7X_4 + X_5)/27$
B-431, B-433, B-436	$(16R_1 + 4R_2 + 4X_1 + 6X_2 + 2X_3)/8$
B-432	$(14R_1 + 4R_2 + 2X_1 + 4X_2 + 3X_3 + X_4)/7$
B-491, B-493	$(6R_1 + 2R_2 + 4X_1 + 2X_2 + X_3)/5$
B-492	$(4R_1 + 2R_2 + 2X_1 + 2X_2 + 2X_3)/4$
D-1187	$(34R_1 + 4R_2 + R_3 + 8X_1 + 10X_2 + 4X_3 + 3X_4 + X_5)/13$
D-1188, D-1190, D-1192	$(28R_1 + 8R_2 + 8X_1 + 8X_2 + 6X_3 + 2X_4)/12$
D-1189, D-1191	$(18R_1 + 6R_2 + 4X_1 + 6X_2 + 7X_3 + 3X_4 + X_5)/9$
D-1313, D-1314	$(32R_1 + 12R_2 + 8X_1 + 8X_2 + 5X_3)/13$
N-211, N-213	$(10R_1 + 6R_2 + 2R_3 + 6X_1 + 2X_2 + X_3 + X_4)/7$
N-212	$(6R_1 + 4R_2 + 2R_3 + 2X_1 + 2X_2 + 2X_3 + 2X_4)/5$
P-836, P-838	$(36R_1 + 10R_2 + 4R_3 + R_4 + 10X_1 + 8X_2 + X_3)/14$
P-837	$(34R_1 + 6R_2 + 3R_3 + R_4 + 8X_1 + 8X_2 + 2X_3 + 2X_4 + X_5)/13$
P-2812	$(2x_1)/2$
T-206	$(160R_1 + 32R_2 + 8R_3 + 32X_1 + 16X_2 + 18X_3 + 12X_4 + 2X_5)/40$
T-2398	$(70R_1 + 16R_2 + 2R_3 + 16X_1 + 12X_2 + 10X_3 + 5X_4 + X_5)/22$

^a Labels are those of "The Dictionary of Organic Compounds".²² All the compounds of Table IV are depicted in Figure 6.

number of such larger circuits need not be small. To summarize the estimate of X_n parameters for aza compounds we may assume

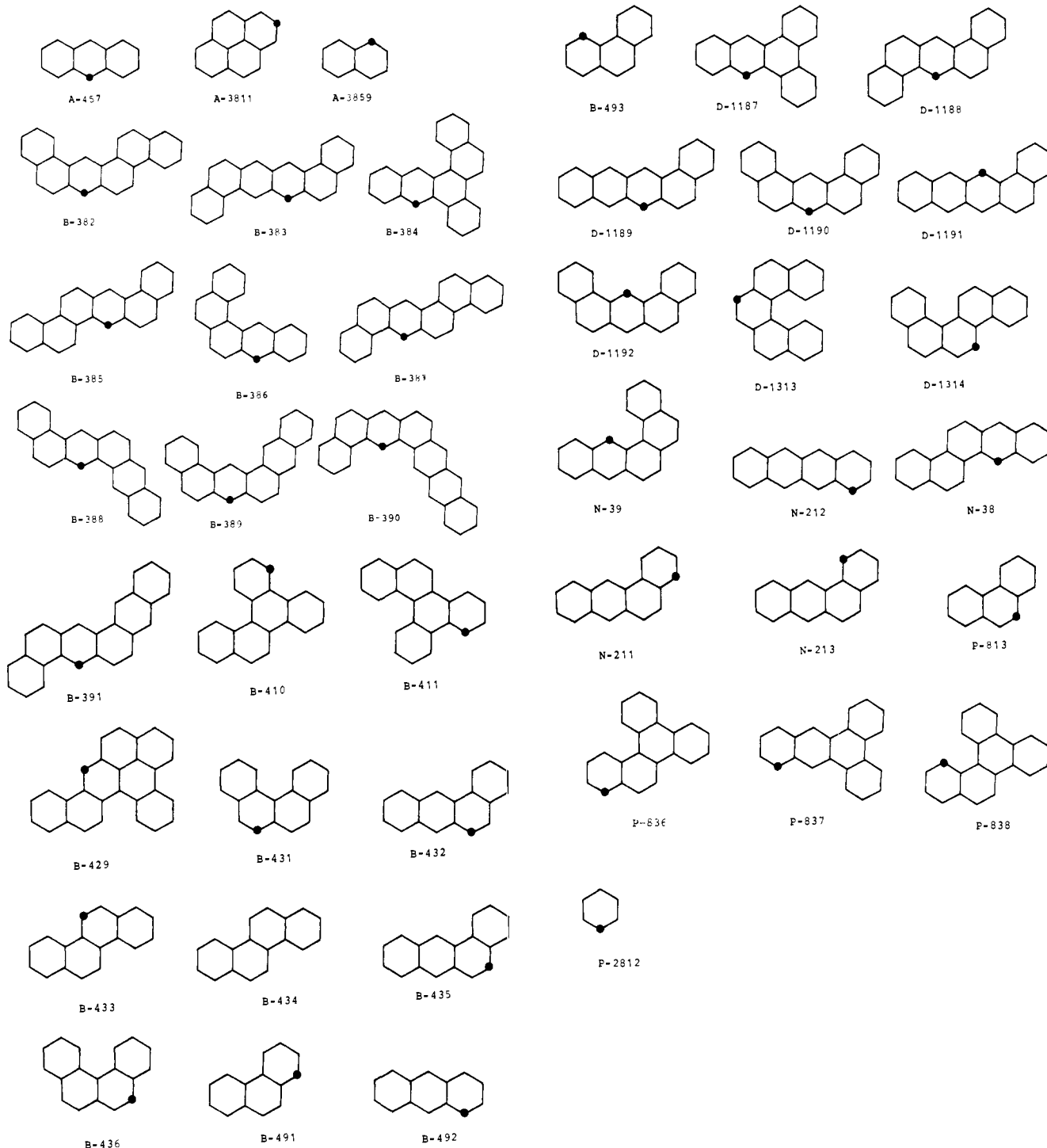


Figure 6. Known nitrogen heterocyclic compounds with their labels from the "Dictionary of Organic Compounds".²² Resonance energy expressions are shown in Table IV and the numerical values in Table V.

that, in general, the following holds: $X_n > R_n$ for small n , and (since magnitude decrease) $X_n \approx R_n$ for large n . At least this occurs in the SCF-MO calculations used here as standards. In view of relatively small differences in D_n it is not surprising that different authors have arrived at different RE's of selected aza

(21) According to MO calculations the size of reasonably planar annulenes has to be below a certain limit for ring size in order to ensure fully aromatic behavior. The calculations of Dewar and Gleicher (Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685) have indicated that the limit lies between the $n = 22$ and $n = 26$ membered ring compounds. Translated in the terminology of conjugated circuits, this would suggest that contributions arising with R_5 or R_6 would be zero. However, the above MO results have yet to be experimentally confirmed, and it appears that they may be artifacts of MO calculations and that even larger ring structures show fully delocalization of their π -electrons.

compounds, as pointed out in the review by George.⁶

We end this section by comparing the RE of acridine with that of anthracene: $RE(C_{13}NH_9) = 1.764$ eV and $RE(C_{14}H_{10}) = 1.600$ eV. The difference of 0.164 eV is significant but not dramatic.

Resonance Energies of Aza Conjugated Systems

In Table IV we have collected the expressions for the resonance energies of aza compounds of Figure 6. In a number of cases we see several structures have the same expression for RE. These include trivial cases of positional isomers where the N atom resides within the same ring. However, a number of cases correspond to isomers that have different connectivity. It is not difficult to recognize that fusion sites in polycyclic system can be exchanged, providing they have the same Pauling bond order, as illustrated on the skeleton of phenanthrene, which yields benzphenanthrene

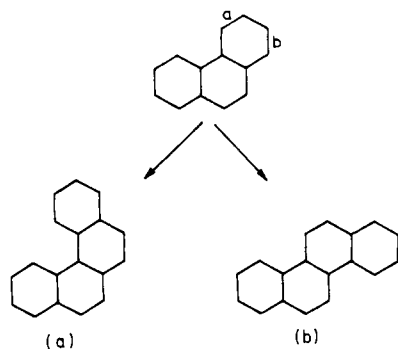
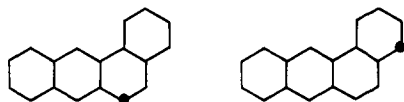


Figure 7. Phenanthrene with two nonequivalent CC bonds that yield distinctive isomers (benzphenanthrene and chrysene) having a same count of conjugated circuits.

and chrysene (Figure 7). Such a switch of the fusion sites will not affect the count of conjugated circuits, and consequently, apparently different molecular skeletons will result in an identical expression of RE.

In Table V we give numerical values for RE as computed with the parameters previously derived. The first column in Table V gives the label for the structure as indicated in Figure 6 and the "Dictionary of Organic Compounds".²² The next column gives RE (in electronvolts), from which one may derive RE/e (resonance energy per π -electron), a measure, advocated by Schaad and Hess,²³ of π -electron stabilization of conjugated structures. The next two columns show a partitioning of the total RE into parts, first, in which the heteroatom makes an explicit contribution (represented by RE(X) and derived by adding all contributions from conjugated circuits X_n ($n = 1, 2, 3, \dots$)) and, second, the remainder, RE(R), which is due to contributing conjugated circuits as expressed by terms involving R_n ($n = 1, 2, 3, \dots$). It is of some interest to observe a rather constant contribution of RE(X). It appears that the presence of a heteroatom does not make dramatic variations among the structures examined. The dominant contribution appears to depend primarily on the number of unsubstituted rings and their mode of fusion, as accounted for in the portion of RE shown as RE(R). The small variations in RE(X) among structurally related compounds are informative. Take, for instance, the two benzotetracene derivatives B-432 and N-211, which differ in their substitution rings:



Their total RE are similar: 2.420 and 2.394 eV for B-432 and N-211, respectively. Hence, if we pay attention *only* to total RE we would conclude that nitrogen substitution made hardly any effect. By partitioning RE in RE(X) and RE(R) parts we see that the corresponding parts show more dramatic variations: substitution of the central ring (the "weak" ring in the spirit of Clar's notion of aromatic sextets²⁴) makes the nitrogen contribution small, while substitution in the terminal rings makes it substantial. Such information is very relevant for anticipation of molecular properties (local properties in particular) and may be decisive for consideration of reaction intermediates and other speculative mechanistic contemplations. We suggest that quantities RE(X) and RE(R) and derivatives of these quantities shown in the next two columns of Table V be viewed as theoretical indices. $(RE(X) - RE(R))/K$ (K being the number of Kekulé valence structures) measures part of the X atom role, on the average, in dominating RE contributions, just as $(RE(X) + RE(R))/K$ gives the average contribution of Kekulé structures to molecular RE. We find a relatively constant (negative) contribution per structure, about -0.1 eV. Finally the last column in Table V gives the ratio of

Table V. Numerical Values for Molecular Resonance Energies of the Compounds of Figure 6^a and Their Partitioning into Contributions Arising from Carbon-Only Conjugation and Conjugated Circuits Involving Nitrogen^b

structure	total RE, eV	RE(X), eV	RE(R), eV	$\Delta RE/K$, eV	$\Delta RE/RE$, eV
A-457	1.764	0.895	0.869	0.007	0.015
A-3811	2.271	0.949	1.322	0.062	-0.576
A-3859	1.429	0.850	0.579	0.090	0.190
B-382	3.662	0.844	2.587	-0.095	-0.496
B-383	3.431	0.844	2.587	-0.109	-0.508
B-384	3.772	0.902	2.870	-0.098	-0.522
B-386	2.986	0.902	2.084	-0.108	-0.396
B-388	3.466	0.904	2.562	-0.098	-0.478
B-390	3.717	0.925	2.792	-0.085	-0.502
B-410	3.290	0.919	2.371	-0.104	-0.441
B-429	4.127	0.946	3.181	-0.082	-0.542
B-431	2.627	0.766	1.861	-0.137	-0.417
B-432	2.420	0.541	1.879	-0.191	-0.553
B-491	2.044	0.903	1.141	-0.048	-0.117
B-492	1.704	0.712	0.992	-0.070	-0.165
D-1187	3.325	0.900	2.425	-0.117	-0.459
D-1188	3.126	0.934	2.192	-0.105	-0.403
D-1189	2.685	0.783	1.902	-0.124	-0.556
D-1313	3.208	0.842	2.366	-0.117	-0.475
N-211	2.394	0.913	1.481	-0.081	-0.237
N-212	1.872	0.593	1.279	-0.137	-0.367
P-836	3.311	0.869	2.442	-0.112	-0.475
P-837	3.229	0.817	2.413	-0.123	-0.494
P-2812	0.908	0.908		0.454	1.000
T-206	4.650	0.958	3.693	-0.060	-0.517
T-2398	3.894	0.941	2.953	-0.091	-0.517

^aSecond column. ^bColumns three and four, respectively. The last two columns are derived indices based on the partitioning of the resonance energy, which more clearly indicate important variations among seemingly similar structures. $\Delta RE = RE(X) - RE(R)$.

$(RE(X) - RE(R))/(RE(X) + RE(R))$, a nondimensional number which for most aza derivatives is found between -0.400 and -0.500. A full use of the proposed indices may happen in the future when more data are analyzed. Currently these indices (or partial contributions to RE) should be used to single out some unusual feature of some compounds. All aza derivatives of Figure 6 appear remarkably uniform as a class, yet as we see from variations in the four last columns of Table V the class is far from homogeneous. Indeed we can immediately single out as special all structures for which a noticeable deviation from average values is observed in the last two columns. Each such case then requires a close examination. Such a case is N-211, in which nitrogen is substituted to a ring of low aromatic content.

Extension to Several Heteroatoms

Applications of the outlined approach to heterocycles having several heteroatoms is straightforward. In the case of two nitrogen atoms within a single ring (Figure 8) extension is trivial: all one has to do is to interpret X_n values as belonging to two-nitrogen rings and assign to them novel parameteric values. A use of symbol X_n' may represent the novel situation. If we have two identical heteroatoms in different rings (Figure 9 illustrates the case for phenanthrene derivatives), we discriminate between conjugated circuits involving a single heteroatom and conjugated circuits involving two heteroatoms. If the two heteroatoms are different, we differentiate their partial contributions, as shown in Table VI. Clearly these more general situations will require additional standards that will allow one to determine new parameters. Without reliable information for needed standard structures the application of the outlined graph-theoretical approach is hindered. The "defect", however, is not with graph-theoretical analysis but is due to the lack of believable quantum chemical calculations on molecules of this complexity.

In Figure 10 we illustrate two heterocyclic systems having two nitrogens, which, however, do not require additional parameters for computation of their RE. The smaller molecule, B-333, may be viewed as a derivative of perylene, the central CC bonds of which are *essentially single bonds*²⁵ (i.e., in all Kekulé valence

(22) "Dictionary of Organic Compounds", 5th ed.; Buckingham, J., Ed.; Chapman and Hall: New York, 1982.

(23) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.

(24) Clar, E. "The Aromatic Sextet"; Wiley: London, 1972.

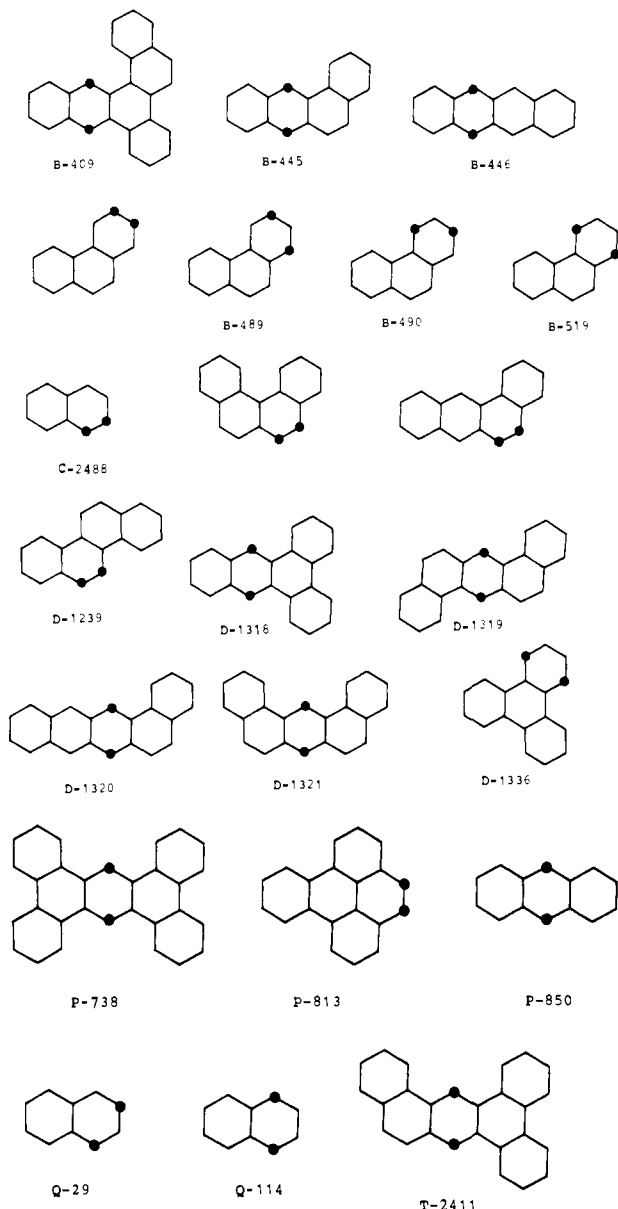


Figure 8. Heterocyclic nitrogen compounds having two nitrogen atoms in the same benzene ring and thus allowing immediate extension of the present analysis.

structures these bonds always appear as single). A consequence is the lack of "global" conjugation; that is, the molecule is equivalent to a union of two independent moieties. In the case of B-333 we have two phenanthrene-like moieties so that the molecular RE, $2(8R_1 + 2X_1 + 4X_2 + X_3)/5$, is twice that of azaphenanthrene (P-813). The other molecule, $C_{68}H_{32}N_2$, is the largest known polycondensed benzene-like skeleton, having 19 fused rings, two of which contain nitrogen. While in the case of B-333 we have a rigorous derivation of the expression for RE in terms of only R_n and X_n quantities, here the rigorous expression for RE involves several additional X_n' parameters. However, as one sees from the molecular skeleton, the two heterocycles are separated by seven rings, so that the smallest contributing conjugated circuits involving both nitrogen atoms will be X_9' . This we neglect, since we have already neglected X_n and R_n contributions involving five and more fused rings.

In summary, a few parameters suffice to characterize a large pool of structures. Moreover, because the count of conjugated circuits is not dependent on the substitution site for a heteroatom

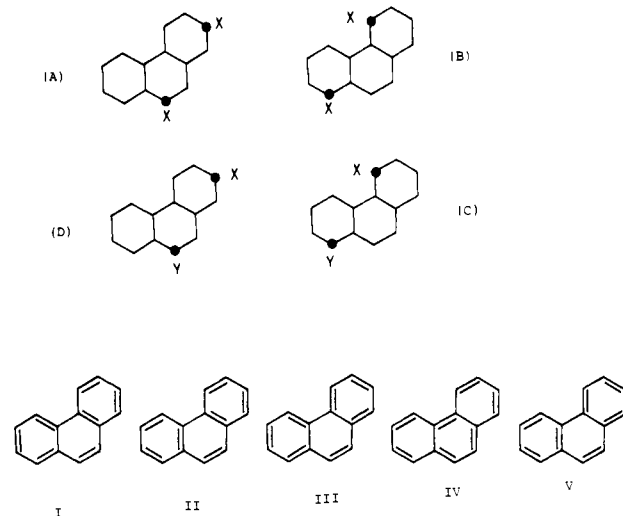


Figure 9. Heterocyclic systems having heteroatoms in different rings: structures A and B having identical heteroatoms (nitrogen); structures C and D having different heteroatoms. The five Kekulé structures of phenanthrene parent molecule are also shown.

Table VI. Illustration of Contributions Arising in Compounds Having More than a Single Heteroatom^a

structure A	structure B
$R_1 + X_1 + X_2$	$2X_1 + X_2$
$R_1 + 2X_1$	$R_1 + 2X_1$
$R_1 + X_1 + X_3'$	$2X_1 + X_3'$
$X_1 + X_2 + X_2'$	$R_1 + 2X_2$
$R_1 + X_1 + X_2'$	$2X_1 + X_2$
total	total
$(4R_1 + 6X_1 + 2X_2 + 2X_2' + X_3')/5$	$(2R_1 + 8X_1 + 4X_2 + X_3')/5$
structure C	structure D
$R_1 + X_1 + Y_2$	$X_1 + Y_1 + Y_2$
$R_1 + X_1 + Y_1$	$R_1 + X_1 + Y_1$
$R_1 + X_1 + Y_3$	$X_1 + Y_1 + (XY)_3$
$Y_1 + Y_2 + (XY)_2$	$R_1 + X_2 + Y_2$
$R_1 + X_1 + (XY)_2$	$X_1 + Y_1 + X_2$
total	total
$(4R_1 + 4X_1 + 2Y_1 + 2Y_2 + 2(XY)_2)/5$	$(2R_1 + 4X_1 + 4Y_1 + 2X_2 + 2Y_2 + (XY)_3)/5$

^aStructures A and B have two identical (nitrogen) heteroatoms while structures C and D have two different heteroatoms. The rows correspond to contributions from different Kekulé valence structures (illustrated in Figure 9).

within a ring, as well as on some rearrangements of the fusion sites, one finds a number of structures to have the same expression for the resonance energy. Thus coincidences that have been reported in the past for some compounds^{25b} can here be traced to their identical conjugation content, as measured by the count of different conjugated circuits. In Figure 11 we illustrate a number of aza derivatives, not included in Tables IV and V, which, however, do not require much analysis. The results for these molecules can be immediately read off by identifying the structure in the already available tables, which (a) differ in the position of the nitrogen atom within a ring or (b) differ only in the mode of fusion of rings, but the change does not produce change in the conjugated circuit counts. Finally, one should be reminded that the same expressions are valid for other than nitrogen heteroatoms.

Concluding Remarks

Graph theory²⁶ is not a substitute for quantum theory and quantum chemical calculations. Much of the confusion about and

(25) (a) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969. (b) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1975**, *31*, 295.

(26) There are a dozen text books on graph theory available; we recommend in particular for those not initiated in the subject: Wilson, R. J. "Introduction to Graph Theory"; Academic Press: New York, 1972. And as an advanced text, see: Harary, F. "Graph Theory"; Addison-Wesley: Reading, MA., 1969.

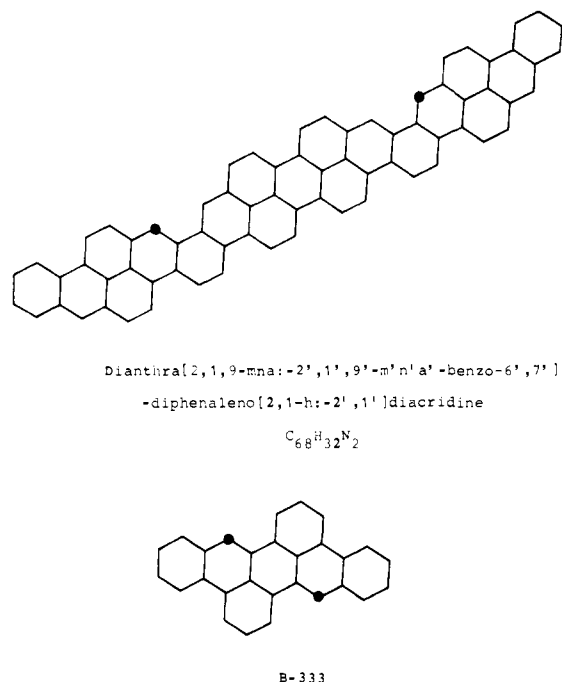


Figure 10. Heterocyclic compounds having two nitrogen atoms in different rings that do not require additional parameterization.

disregard of graph-theoretical approaches appears to originate with misconceptions about their supposedly simplistic and approximate character. But in fact graph-theoretic analyses are neither simplistic nor approximate; they are rigorous in providing one with *expressions* involving various structural *invariants*. In chemical applications at one stage of the analysis one attempts to *interpret* the mathematical results within chemical concepts, and here there are opportunities as well as uncertainties. Hückel's MO theory, as we know today, is one such interpretation of graph-theoretical quantities. HMO has played an important historical role, and it plays equally important educational role today. But the time of HMO has passed and the method is not of sufficient merit to be further pursued per se. It may still provide a useful frame for the consideration of selected structural features, such as some questions concerning π -electron correlations,²⁷ special properties,²⁸ and better understanding of nodal characteristics of orbitals.²⁹ In contrast to graph-theoretical approaches tied to MO formalisms, here we advocate the use of conjugated circuits as basic structural invariants for conjugated systems, including, of course, heterocyclic systems in particular. Conjugated circuits are mathematical constructions independent of quantum chemical concepts, such as those of MO, valence bond, or resonance theory. If one now seeks an *interpretation* for the mathematical concept, one may link conjugated circuits of size $4n + 2$ and $4n$ to the Hückel rule as well as to resonance theory (and associated exchange integrals).⁴ Because the results appear to agree with experience, conjugated circuits have become a chemical concept. Immediately they show how the Hückel rule can be extended to any polycyclic system. The congruence with the resonance theory of Herndon is particularly pleasing: on one hand, conjugated circuits indicate adequacy of considering only Kekulé valence structures within the resonance theory, while on the other hand the resonance theory offers a theoretical route in determining the numerical values for the parameters R_n , which have been hitherto derived empirically.³⁰ It is therefore somewhat surprising that the graph-theoretical approach based on conjugated circuits is

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(28) Klein, D. J.; Trinajstić, N. *J. Am. Chem. Soc.*, in press.

(29) Randić, M., unpublished results.

(30) It is true that Herndon⁴ has determined his parameters also empirically (from a comparison with calculations of Dewar and de Llano⁸), but in principle the parameters that have been identified with particular molecular integrals could be computed.

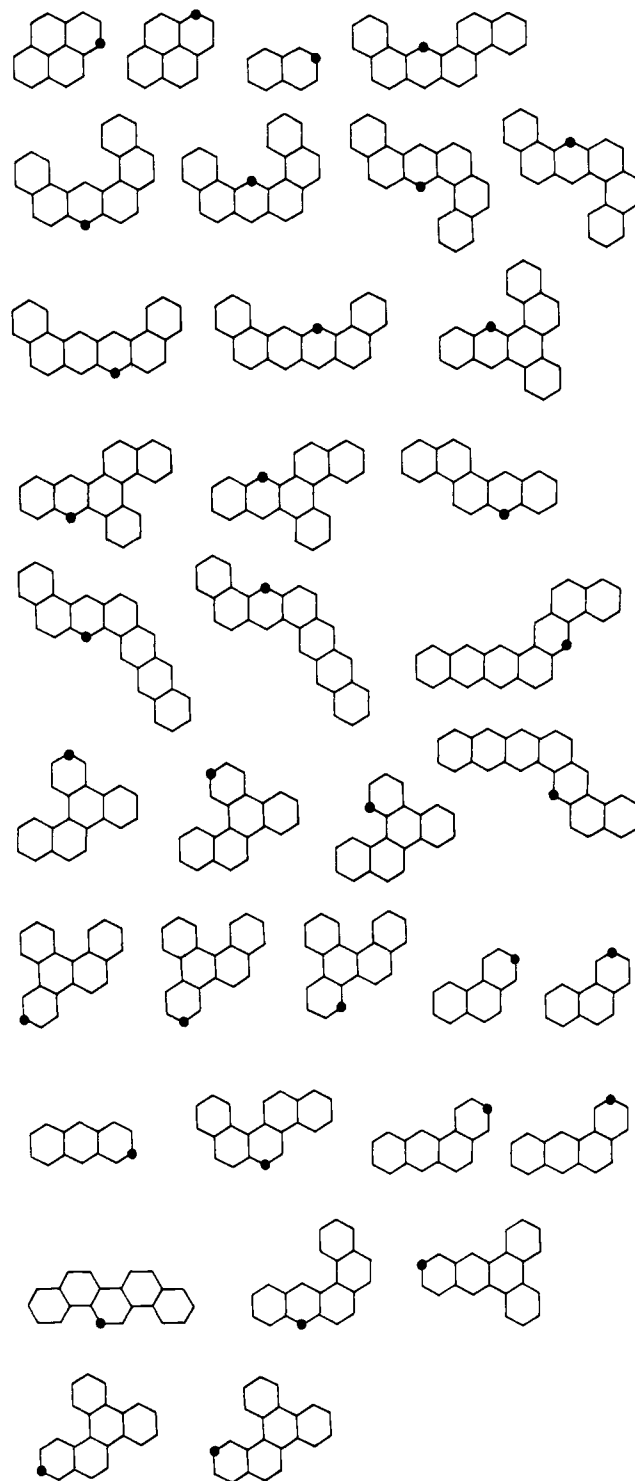


Figure 11. Various polycyclic compounds having a single heteroatom (nitrogen) for which the expression for resonance energy can be read directly from Table IV by identifying the corresponding structure having the same count of conjugated circuits.

so slowly accepted in some circles. Quantum chemistry appears to be preoccupied with the evaluation of the wave functions and potential surfaces—a worthy goal—but of limited use when one considers whole families of molecules (rather than an individual structure) and when one is concerned with *structure–property relationships*. Given a wave function one can proceed to calculate selected properties, but observe that that is just one component of the structure–property relationship: the other is *structure*. Critics, as well as neutral bystanders, should pause for a moment and try to figure out how to approach the other half of the dilemma *without* graph theory. What is structure? “What she is not, I

can easily perceive—what she *is* I fear it is impossible to say," a quote of Edgar Allan Poe's,³¹ well illustrates the situation. Graph theory offers an alternative way to characterize a structure—a structure is replaced by collection of its *mathematical properties* (graph invariants). Thus the impossible task of correlating structure with property becomes a somewhat less hopeless task when mathematical properties are correlated with physical properties of compounds. Conjugated circuits proved singularly

(31) Poe, E. A. "The Complete Edgar Allan Poe Tales"; Avenel Books: New York, 1981.

useful when aromaticity, conjugation, and related molecular properties of homocycles are involved, and the present paper has demonstrated the generality of the method to encompass heterocyclic systems.

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MNDO and ab Initio Study of the Mechanism of Organolithium Amination by Lithium Alkoxyamides

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Abstract: The MNDO method has been used to propose a plausible mechanism for the amination of organolithiums by lithium alkoxyamides. According to this mechanism, an initial lithium complex, formed between a lithium alkoxyamide and an organolithium and having two lithiums bridging the nitrogen and carbon, passes through a transition state which is best described as a trigonal bipyramid with two axial lithium cations and equatorial alkoxy, methyl, and alkyl nitrene substituents. The product is a more stable complex containing two lithiums bridging carbon and oxygen positions. The specific reactions studied by MNDO were the reaction of methyllithium with lithium methylmethoxyamide and with *N*-lithium hydroxyamide. The former reaction has a calculated barrier of 42.0 kcal/mol and the latter a calculated barrier of 68.9 kcal/mol. Ab initio calculations at the 3-21G and 3-21+G levels were carried out for the reaction between lithium hydroxyamide with methyllithium. At the 3-21G level the barrier is approximately 56 kcal/mol, and this value is reduced to 34.2 kcal/mol at the 3-21+G level. Comparisons have been made between MNDO and ab initio calculations at the 3-21G level for complexation energies. Both methods predict that stabilization of complexes of mixed monomers (such as $\text{LiNH}_2\cdot\text{LiCH}_3$) is approximately the average of the simple dimers $1/2[(\text{LiNH}_2)_2 + (\text{LiCH}_3)_2]$. Finally the MNDO model has been applied to rationalize recent experimental observations which indicate that intermolecular addition occurs preferentially to intramolecular addition in the rearrangement of *N*,2-dilithio-*N*-methylbenzyloxyamide.

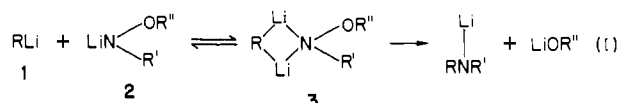
Lithium chemistry has experienced a very rapid growth over the last 5 years. The progress has been led rather than followed by theoretical calculations¹⁻¹² which have been generated largely in Schleyer's group. It is gratifying that many predictions^{1,3} have already been confirmed by experimental observations. Unfortunately the known chemistry of lithium is limited in comparison with other second-row elements due to the instability of lithium

compounds. However, this instability is somewhat offset by the stabilization gained by dimer and tetramer formation.⁸ Although covalent bonding plays an identifiable role, electrostatic attractions seem to predominate. In calculations² in which all lithiums are replaced by a point charge, relative energies are still reproduced.

Results and Discussion

Efforts to date have been largely directed toward determining the most stable structure of a lithium compound given a particular formula.¹⁻¹² The purpose of the present work is to investigate a displacement reaction which has recently¹³ been observed for lithium amide complexes.

This reaction, which is shown in eq 1a, occurs rapidly at -15 °C despite the fact that a nucleophilic carbon appears to be reacting with a nucleophilic nitrogen. In order to rationalize the



- (a) $\text{R} = n\text{-C}_4\text{H}_9$, $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$, $\text{R}'' = \text{CH}_3$
 (b) $\text{R} = \text{CH}_3$, $\text{R}' = \text{CH}_3$, $\text{R}'' = \text{CH}_3$
 (c) $\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$, $\text{R}'' = \text{H}$

facility of this reaction, an initial complex, **3**, has been proposed.¹³

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