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Chemical Graph Theory. V¹. On the Classification of Topological Biradicals*

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We have considered skeletal forms for topological (conjugated) biradicals and have examined alternative structural classification schemes for them. In particular, we have looked more closely at the classification proposed by Herndon and Ellzey, based on the multiplicity of the zero eigenvalue and have examined all acyclic forms having 12 or fewer carbon atoms, and all cyclic forms having 8 or fewer carbon atoms. While the present work does not contribute to resolving the controversy as to which type of biradical can be expected to have the singlet, and which the triplet ground state, it provides the possibility of grouping compounds of the same expected ground state and thus allows the deduction of similar properties for members of the same group. Hence, definitive theoretical or experimental results obtained for a new standard species can then be applied to a wider body of biradicals. Examination of the distribution of »unpaired« spin density and the character of bonds which have a constant body type (so-called essentially single or essentially double CC bonds) provided guidance for deriving a number of rules for the construction of larger topological biradical forms by the combination (as fragments) of smaller-sized biradicals or other molecular fragments.

INTRODUCTION

Classification as an operation can be used in structural chemistry in order to predict novel compounds with certain desired properties. Classification is used widely in data reduction, for example in cluster analysis and pattern recognition, where it is tied to *empirical* parametrization and hence is devoid of much of the structural background. In this paper we reconsider the use and rôle of classification, but insist on structural criteria as the only legitimate source for the grouping of molecular systems. We will give particular consideration to biradicals of conjugated hydrocarbons. Structural factors of interest here are *graph-theoretical invariants* and these themselves will belong to

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two groups: (1) basic graph invariants (independent of the chemical model assumed) and (2) invariants based on a model which reflects the chemical approach (or simplification) to a structure. In the first group we include concepts such as paths, circuits, conjugated circuits, Kekulé structures, et., as long as they are viewed as mathematical constructions. In the second group we have concepts such as NBMO's (non-bonding molecular orbitals), the characteristic polynomial interpreted as the secular determinant, and other concepts used in the Hückel molecular orbital (HMO) approach, or parametrized on certain SCF MO calculations. In each case a definitive model is involved.

Conjugated biradicals are molecular systems with two electrons in degenerate frontier π -orbitals, or in frontier π -orbitals which are very close to each other in energy so that the difference in orbital energies can be overcome by the loss of energy accompanying decoupling of paired electrons. Some biradicals are very stable molecules, such as, for example, the Tschitschibabin hydrocarbon biradical. More commonly they are of interest as intermediates in thermal² and photochemical³ reactions. Some pyrolytic reactions are supposed to occur via biradical intermediates.⁴ In addition, biradicals emerge in various theoretical considerations, for instance in structure-resonance theory.⁵

CLASSIFICATION SCHEMES

We have some freedom of choice in selecting the invariants on which a classification is to be based. In addition, one can use several classification criteria simultaneously to break up the population of objects into very many subgroups. We will examine here a few alternatives, and will finally concentrate on one particular classification criterion which appears to be the most relevant for differentiation of biradicals. Firstly, one can classify biradicals (but also other compounds) into acyclic, cyclic, bicyclic, etc., simply by inspecting their molecular skeletons. One continues by inspecting cycles present in a molecule and by distinguishing benzenoid radicals (consisting of fused benzene rings) and other structures. Depending on whether the cycles and rings are even or odd (i. e. having an even number of carbon atoms, or having an odd number of carbon atoms) one arrives at alternant (bipartite) and non-alternant (non-bipartite) biradicals. Within HMO such classification is already important because of the observations of Coulson and Rushbrooke⁶ on the distribution of orbital levels, which is symmetric for the former class. All this has been known for some time; nevertheless it was only relatively recently that Herndon and Ellzey⁷ recognized an additional important classification factor: *the multiplicity of the zero eigenvalue*. However, Dewar and Longuet-Higgins⁸ were first to point out the importance of the multiplicity of the zero eigenvalue. For example, in Figure 1 we show several derivatives of the azulene skeleton which are biradicals, but which belong to two substantially different classes.

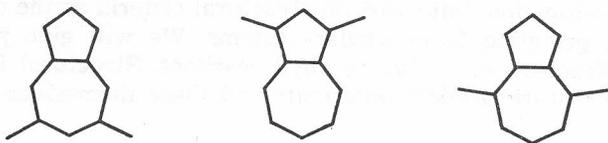


Figure 1. Biradicals derived from azulene skeleton which have apparent structural similarity yet belong to two substantially distinctive biradical types

By looking at Figure 1 one cannot, without further analysis, classify the structures, unless one is aware of the criterion used and unless one performs the necessary check. Figure 1 illustrates that superficially similar structures may behave quite differently and apparent forms for molecular structures (biradicals here) may be misleading. Once we know the criterion for classification we still have to make the necessary manipulations in order to find out the answer. In the case of the azulene derivatives in Figure 1, using, as suggested by Herndon and Ellzey, the multiplicity of the zero eigenvalue as the basis for classification, we still have to find if we have a single zero eigenvalue or a doubly degenerate one. This can be done in many ways.^{9,10}

In this paper we discuss the classification of topological biradicals, based on the multiplicity of the zero eigenvalue. Before engaging in the development of suitable schemes for classification and construction of biradicals let us emphasize that *the graph-theoretical approach can only distinguish two (or more) classes; it cannot predict properties*. The best approach then is to consider a few (or even a single) representative members of the class as a standard and to adjust the parametrization accordingly.

There has been some disagreement in the past about predictions of properties of members of each of the two classes. For instance, Mestechkin and Vysotskii,¹¹ using a variant of MO known as UHF MO LCAO, predicted the biradicals shown in Figure 2 to be in the triplet state, while Herndon and Ellzey⁷ predicted them to be singlet species.

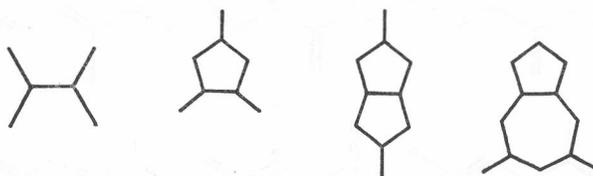


Figure 2. Biradicals which are predicted to be in a triplet state by UHF MO scheme, are predicted as singlets by several other MO models. VB theory also confirms spin singlet of these biradicals

Similar systems have also been predicted to be spin singlets, in many instances by use of the PPP and Hubbard models.¹²⁻¹⁴ In addition, *ab initio* calculations¹⁵ and VB theory^{14,16} also verify the spin singlet for these structures in all cases tested. All these MO and VB results are in clear disagreement with the results of the UHF MO LCAO approach.¹¹ Since it is generally accepted that the UHF procedure artificially favours higher spin states by about 25 kcal/mole, the ground state of structures in Figure 2 is likely to be singlet. We have emphasized 'likely' not in order to indicate that the matter should be reconsidered (which indeed may happen), but to stress that in this paper we do not take sides or contribute to resolving the dilemma. We are concerned with recognizing the structural factors which eventually decide if a molecule belongs to the first or to the second class, viewing the zero eigenvalue as the criterion for classification. If, and when, it is beyond any doubt that the molecules in Figure 2 are biradicals with a singlet spin state, then we could indicate other molecules which are also expected to be spin singlets. If it happens that the present prevailing support for the singlet state is shown to be doubtful, such a finding will not affect our classification. Only the

standards which suggests properties for the class as a whole will have to be revised accordingly.

ACYCLIC TOPOLOGICAL BIRADICALS

Topological biradicals cannot have Kekulé valence forms. If one attempts to construct a valence formula two non-adjacent carbon atoms remain "isolated". These "isolated" carbon atoms are sites of unpaired electrons and their presence will be indicated by a dot. The illustration in Figure 3 shows an acyclic system with six possible valence-type structures, the sites for the unpaired electrons being at terminal vertices and on one of the central carbon atoms.

Acyclic systems are necessarily alternant and the distribution of "dots" in Figure 3, summarized in the bottom diagram, happens to coincide with the customary division of carbon atoms in alternants into "starred" and "unstarred".¹⁷ In other acyclic conjugated biradicals we find that some of the "starred", which are available, are not used and that unpaired electrons may also occupy "unstarred" sites. In analysis of biradicals it appears that one should focus attention on unpaired electrons, rather than on the standard "starred" — "unstarred" partition of atoms, since the former are the essential component of such systems. In Figure 4 we show all biradicals having eight and fewer carbon atoms, while in Figure 5 we have listed all acyclic conjugated biradicals having ten carbon atoms.

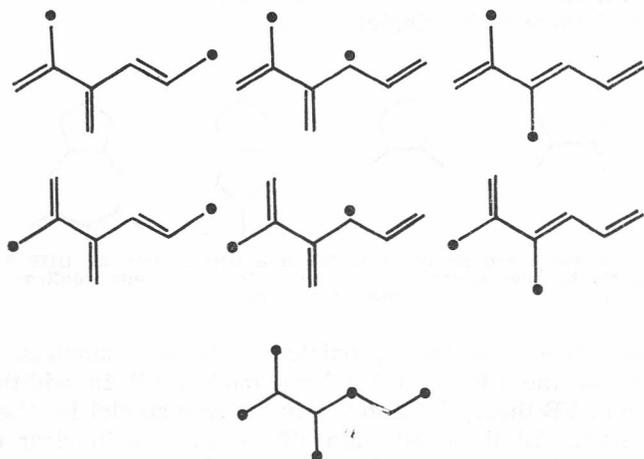


Figure 3. Valence-bond type structures for 2,3-dimethylhexatriene biradical. The last structure shows sites available for unpaired electrons

In both sets of diagrams we have indicated with a visible black circles those carbon atoms which share the density of unpaired π -electrons. A close look at Figure 4 and Figure 5 reveals important differences between various structures. For example, in the case of C_{10} biradicals we may have as few as four, and as many as six carbon sites participating in delocalization of unpaired spins.¹⁸ It seems that such differences in overall behavior deserve close examination. Clearly some parts of the molecular skeleton are "inactive" and in order to see better the similarities and differences between biradicals in Figure 4 and Figure 5, we will construct new graphic forms to represent them. The recipe for construction of these new graphic representation of biradicals

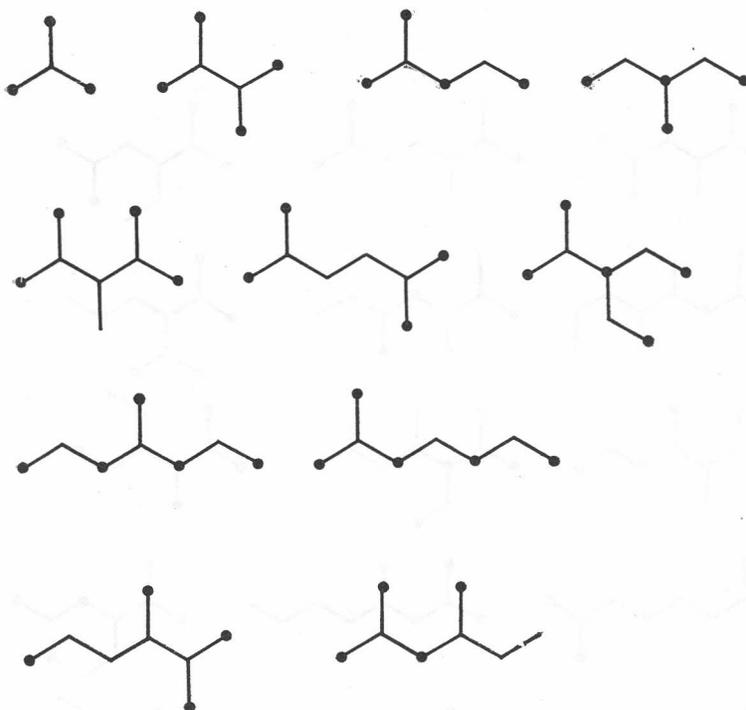
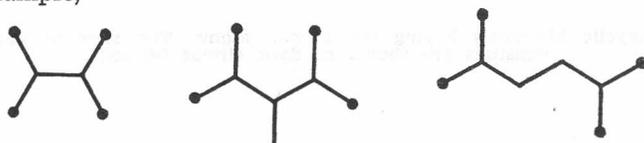


Figure 4. All acyclic biradicals having four to eight carbon atoms. The sites of unpaired electron densities are shown as dark circles (>dots<)

is as follows: Select as vertices only "dotted" carbon atoms and connect them in they are separated by a path of length two. Thus, for each graph in Figure 4 and Figure 5, a simpler graph may be derived. These new and simpler graphs are shown in Figure 6.

Observe that these new graphs, named *daughter* graphs, may be disconnected or may have a single component. In addition, several structures lead to the same daughter graph. Thus, the daughter graphs may serve for finer classification of acyclic conjugated biradicals. The connected daughter graphs correspond to biradicals that have attained the maximal number of delocalization sites for unpaired electron density for the relevant part of the skeleton. On the other hand, in disconnected graphs such sites are fewer than the maximum possible, or, even if the maximal number has been achieved, the sites do not belong to the same bipartite class.

The occurrence of a smaller number of different daughter graphs for biradicals than the original number of biradicals considered makes possible a classification of the biradicals into fewer groups. Observe that we can classify biradicals having a different number of carbon atoms by this scheme. Thus, for example,



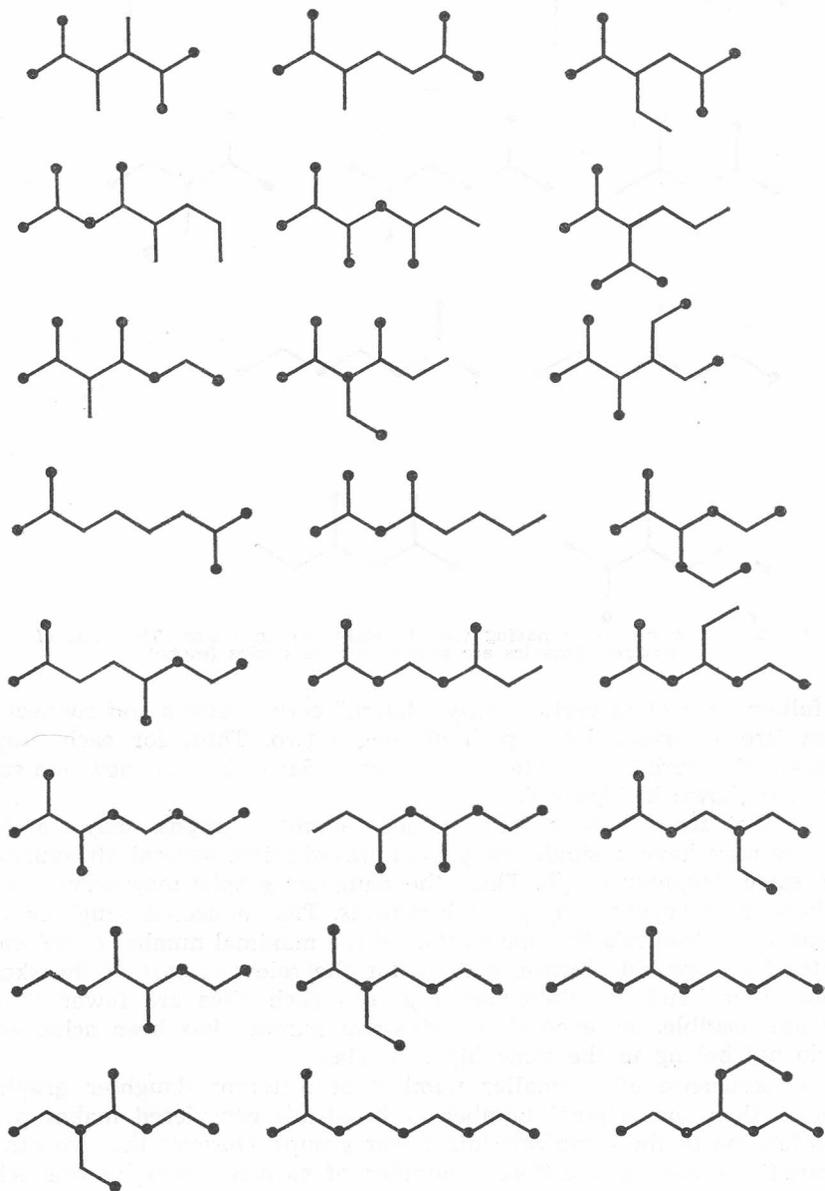
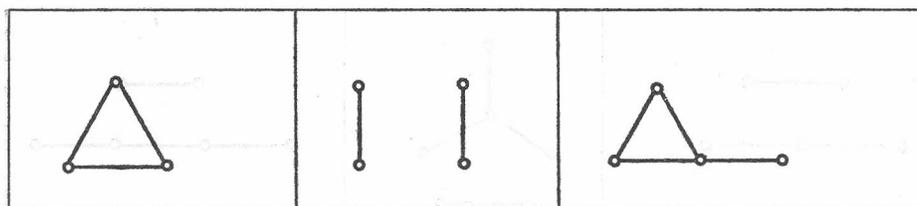
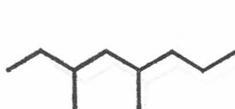
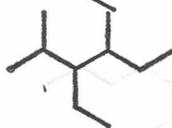
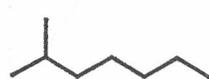
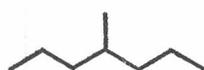
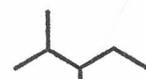
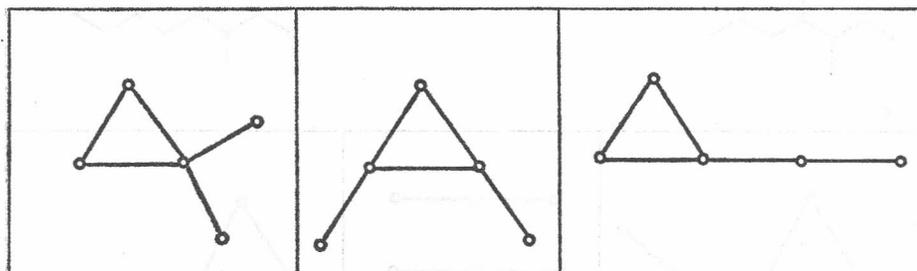
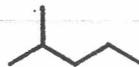
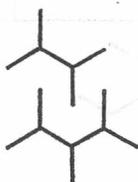
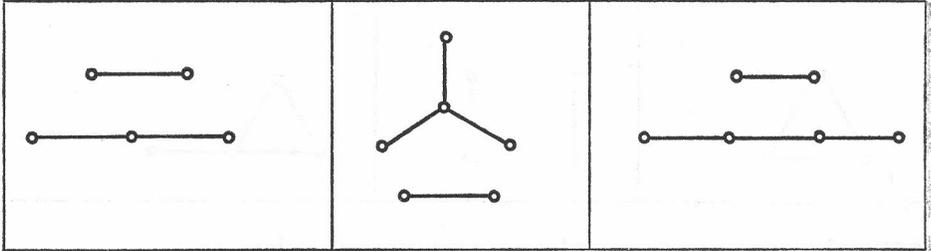


Figure 5. All acyclic biradicals having ten carbon atoms. The sites of unpaired electron densities are shown as dark circles (»dots«)

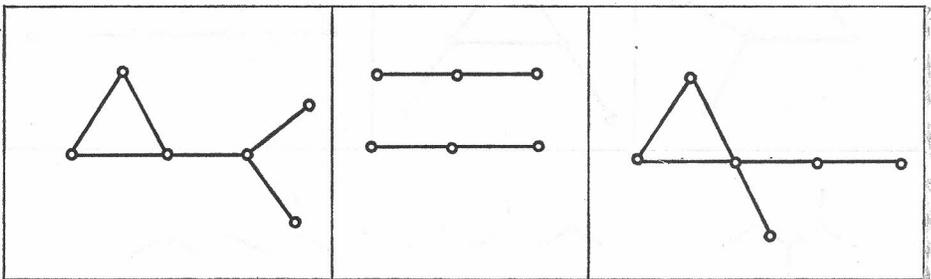
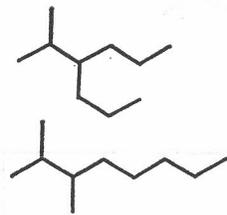
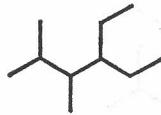
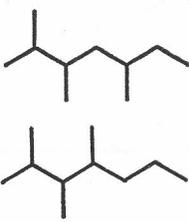


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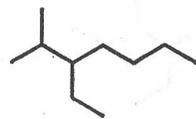
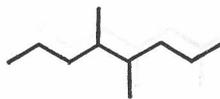
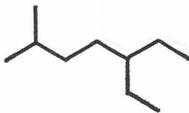


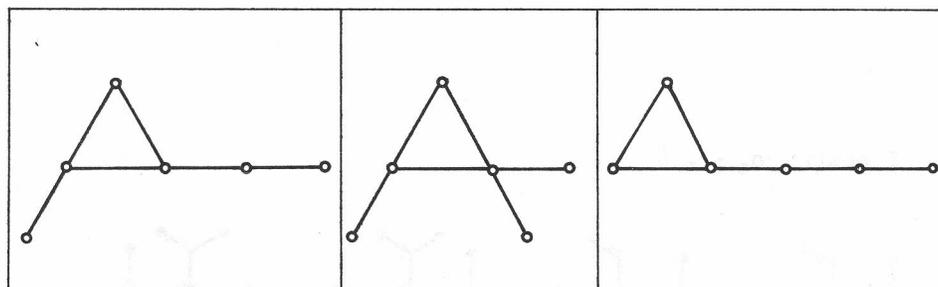


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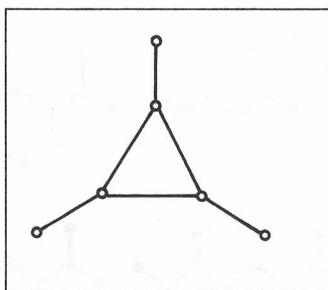
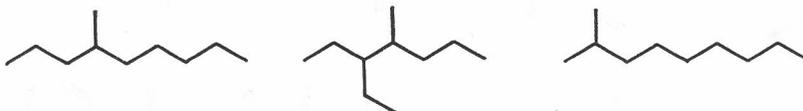


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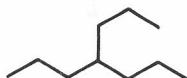
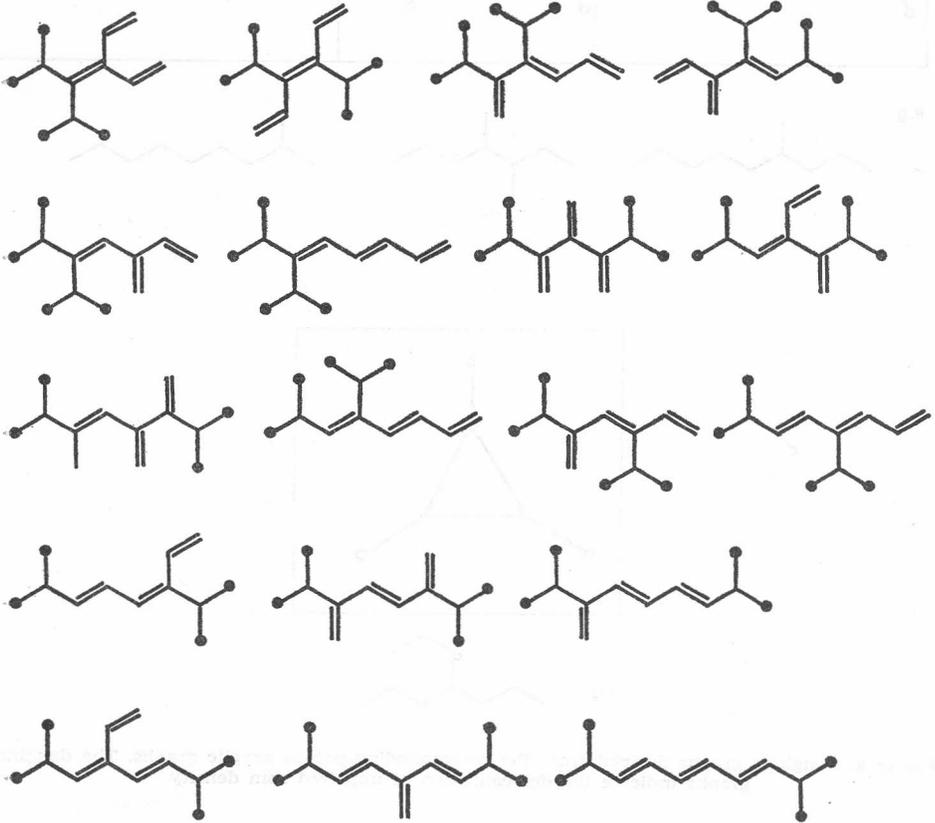


Figure 6. Daughter graphs derived from the corresponding parent acyclic graphs. The daughter-graphs indicate the delocalization of unpaired spin density

all have a common daughter graph: two disconnected K_2 units.¹⁹ This is a significant property of the classification: It appears to be sufficiently general, independent of the size, and, as we shall see later, also independent of the cyclic character of the structure. It is desirable therefore to investigate the classification scheme in more detail and for this purpose we selected acyclic biradicals with 12 carbon atoms. There are 95 acyclic biradicals with 12 carbon atoms. In all there are 551 acyclic graphs with 12 vertices,²⁰ but when one excludes those of valency greater than 3 and excludes those which correspond to polyenes, and those which correspond to higher radicals (e.g. tetraradicals), one is left with only 95 biradical structures, the skeletal forms of which are depicted in Figure 7.

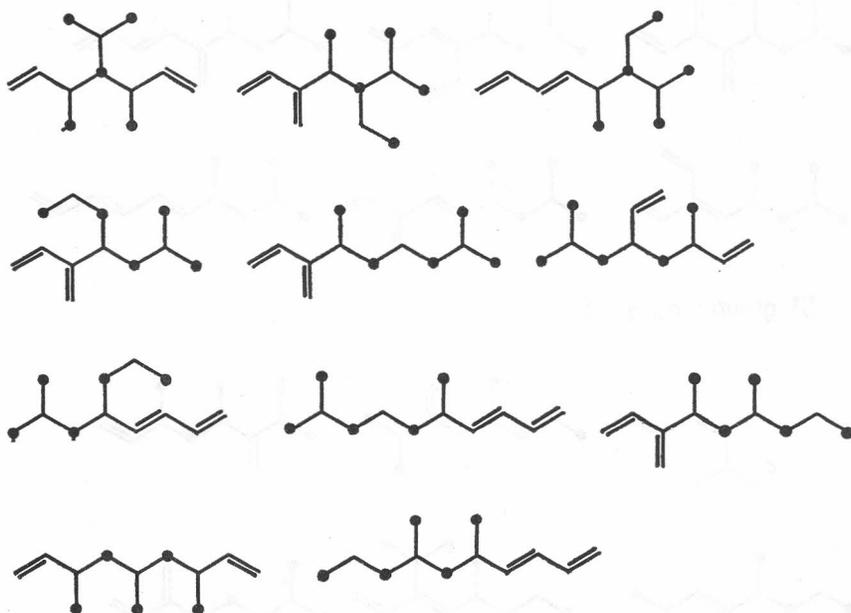
I. group : $\alpha_{n-2} = 4$



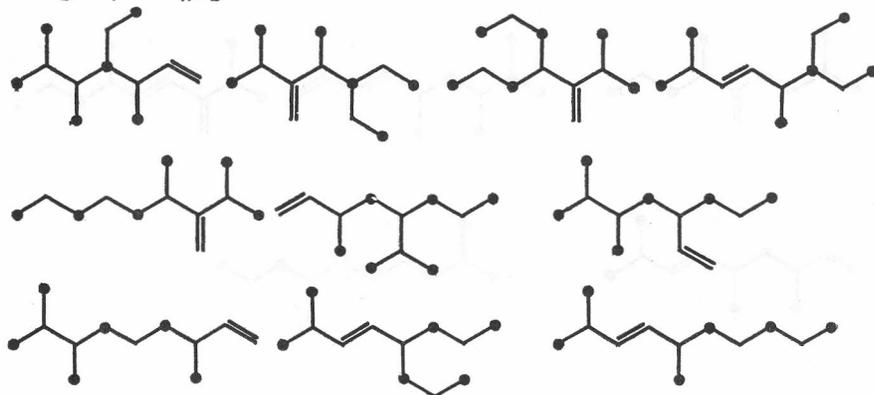
The following table lists the structures shown in Figure 1. The structures are numbered 1 through 20. The table provides the corresponding chemical formula for each structure, showing the number of carbon atoms (C), hydrogen atoms (H), and methyl groups (Me) attached to the chain.

Structure No.	Chemical Formula
1	$C_{10}H_{16}Me_4$
2	$C_{10}H_{16}Me_4$
3	$C_{10}H_{16}Me_4$
4	$C_{10}H_{16}Me_4$
5	$C_{10}H_{16}Me_4$
6	$C_{10}H_{16}Me_4$
7	$C_{10}H_{16}Me_4$
8	$C_{10}H_{16}Me_4$
9	$C_{10}H_{16}Me_4$
10	$C_{10}H_{16}Me_4$
11	$C_{10}H_{16}Me_4$
12	$C_{10}H_{16}Me_4$
13	$C_{10}H_{16}Me_4$
14	$C_{10}H_{16}Me_4$
15	$C_{10}H_{16}Me_4$
16	$C_{10}H_{16}Me_4$
17	$C_{10}H_{16}Me_4$
18	$C_{10}H_{16}Me_4$
19	$C_{10}H_{16}Me_4$
20	$C_{10}H_{16}Me_4$

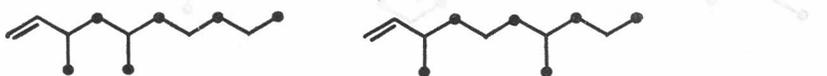
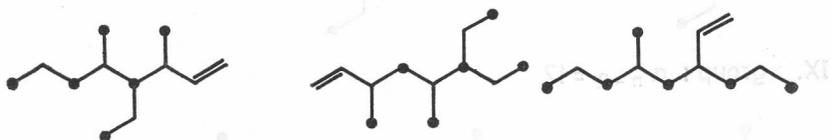
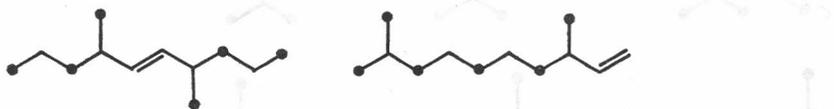
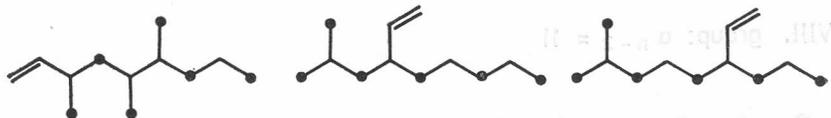
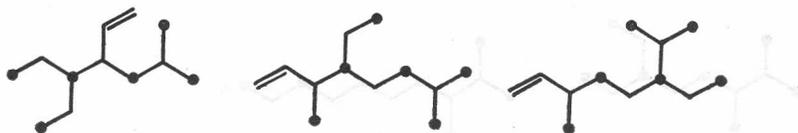
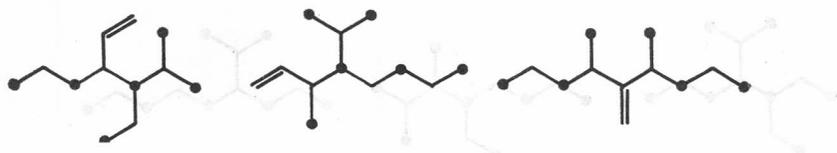
IV. group: $\alpha_{n-2} = 7$



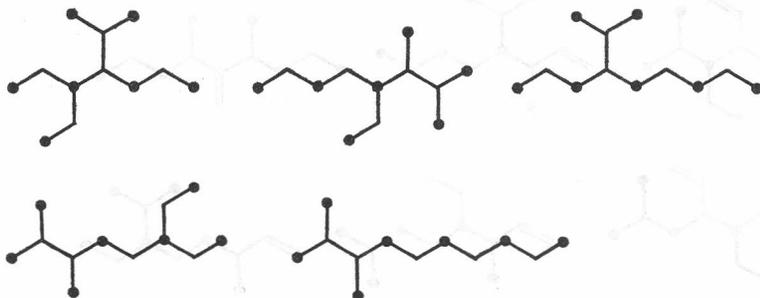
V. group: $\alpha_{n-2} = 8$



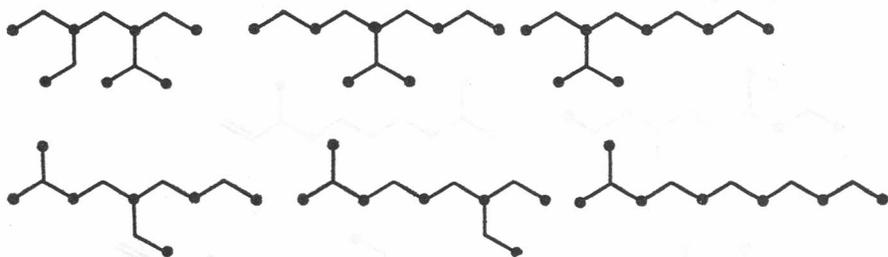
VI. group: $a_{n-2} = 9$



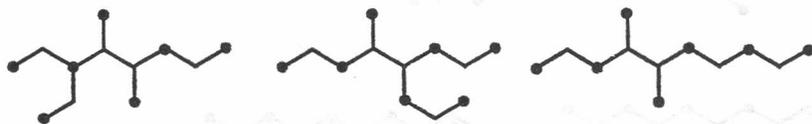
VII. group: $\alpha_{n-2} = 10$



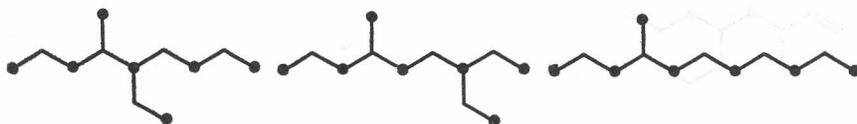
VIII. group: $\alpha_{n-2} = 11$



IX. group: $\alpha_{n-2} = 12$



X. group: $\alpha_{n-2} = 14$



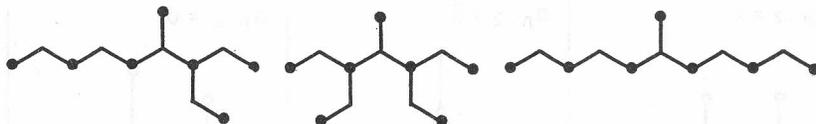
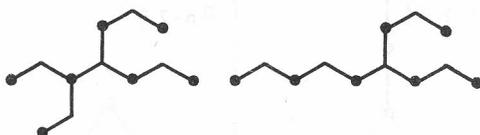
XI. group: $a_{n-2} = 15$

 XII. group: $a_{n-2} = 16$


Figure 7. All 95 acyclic biradicals having 12 carbon atoms grouped according to the coefficient a_{n-2} of the characteristic polynomial

The graphs in Figure 7 have been divided into groups with headings $a_{n-2} = 4$, $a_{n-2} = 5$, $a_{n-2} = 6$, etc., because it was observed that they shown (1) some common structural features and then (2) that such classification coincides with the value of the coefficient a_{n-2} of their characteristic polynomial.²¹ The common features of biradical graphs grouped together are even more clearly seen when we examine the corresponding daughter graphs shown in Figure 8.

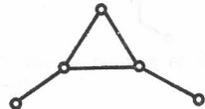
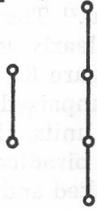
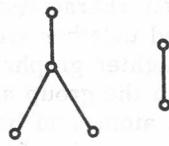
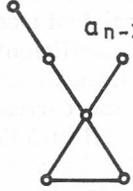
For example, all biradical graphs in the group $a_{n-2} = 4$ have unpaired electron sites separated by a single carbon atom, and have two such units, this being clearly evidenced in the single common daughter graph. All biradical graphs in group $a_{n-2} = 5$ have whole biradical electron density sites linked and attached to a remnant part which is triene. For higher a_{n-2} numbers some apparent diversity in participating compounds is noticed. For $a_{n-2} = 6$ the biradical part consists of two and three radical site units which are combined with a butadiene fragment or with two ethylene fragments. For $a_{n-2} = 7$ we have, in addition, two different radical fragments:

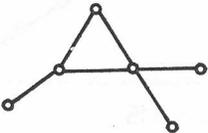
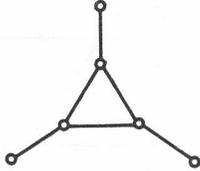
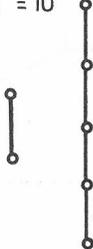
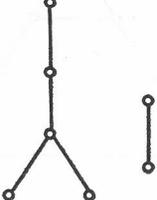
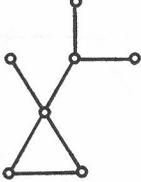
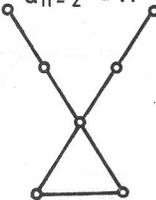
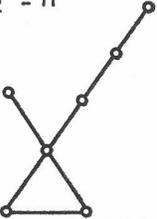
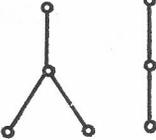
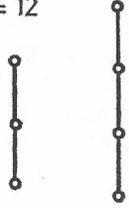


For higher a_{n-2} coefficients the number of components is even greater, although a more careful inspection of Figure 8 reveals some common features in the daughter graphs: They all have the same number of vertices for each a_{n-2} group which may or may not be different from the number of vertices in other a_{n-2} groups and some similarity in their patterns of branching.

Two questions are worth further examination:

(1) Can one construct topological biradicals from simpler structures?; and

<p>$a_{n-2} = 4$</p> 	<p>$a_{n-2} = 5$</p> 	<p>$a_{n-2} = 6$</p> 
<p>$a_{n-2} = 7$</p> 	<p>$a_{n-2} = 7$</p> 	<p>$a_{n-2} = 7$</p> 
<p>$a_{n-2} = 8$</p> 	<p>$a_{n-2} = 8$</p> 	<p>$a_{n-2} = 9$</p> 
<p>$a_{n-2} = 9$</p> 	<p>$a_{n-2} = 9$</p> 	<p>$a_{n-2} = 9$</p> 

$a_{n-2} = 9$ 	$a_{n-2} = 9$ 	$a_{n-2} = 10$ 
$a_{n-2} = 10$ 	$a_{n-2} = 11$ 	$a_{n-2} = 11$ 
$a_{n-2} = 11$ 	$a_{n-2} = 11$ 	$a_{n-2} = 11$ 
$a_{n-2} = 11$ 	$a_{n-2} = 12$ 	$a_{n-2} = 12$ 

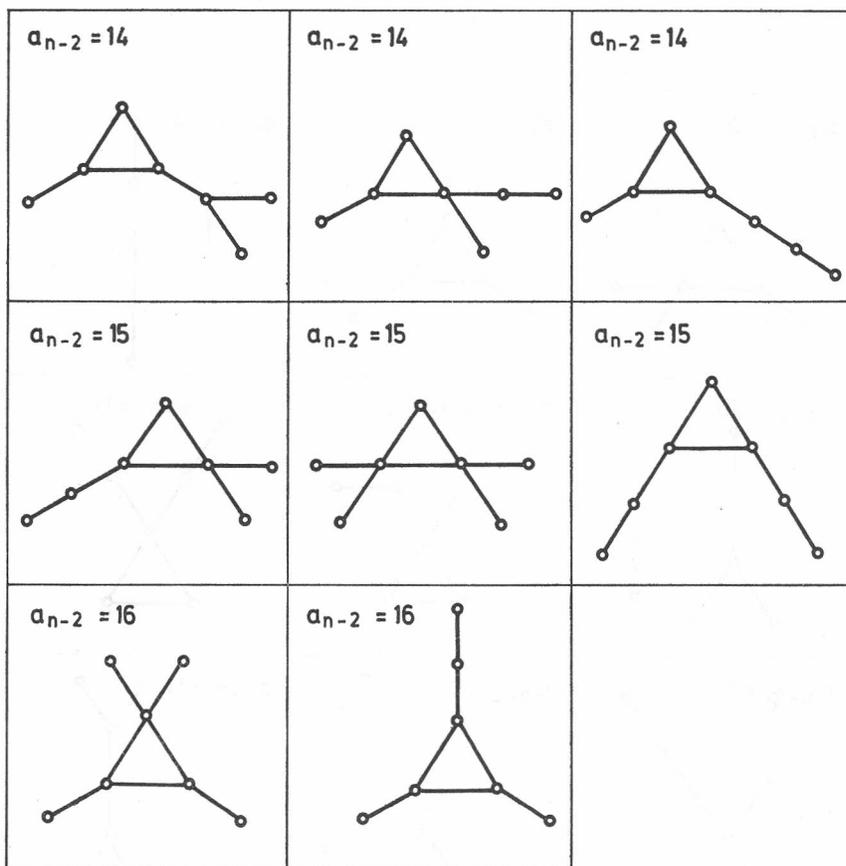
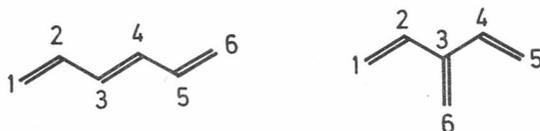


Figure 8. Daughter graphs depicting the degree of delocalization of the unpaired spin density in acyclic biradicals having 12 carbon atoms

(2) Is there some structural interpretation for the subdivision of the graphs into various a_{n-2} groups? In order to answer the first question we will consider the group $a_{n-2} = 4$. From Figure 7 we see that all biradicals in this group may be viewed as having been derived by substitution of two (equivalent) radical fragments of the type,



at the various sites of the two trienes,



If we assume the above numbering of carbon atoms, then only the following di-substitutions are possible for the first triene:

I: (1,1); (1,2); (1,3); (1,4); (1,5); (1,6); (2,3); (2,4); (2,5); (3,3)

Other combinations are ruled out due to the symmetry. Thus, for example, combination (3,5) is equivalent to the combination (2,4) already used. For the second triene:

II: (1,1); (1,2); (1,4); (1,5); (1,6); (2,4); (2,6); (6,6)

Carbon atom 3 cannot be used because it already has a valency of three, while a combination such as (2,5), due to the symmetry of the skeleton, is equivalent to (1,4).

In all we have ten biradicals of the first substitution class, and eight biradicals of the second substitution class; a total of 18. A similar construction

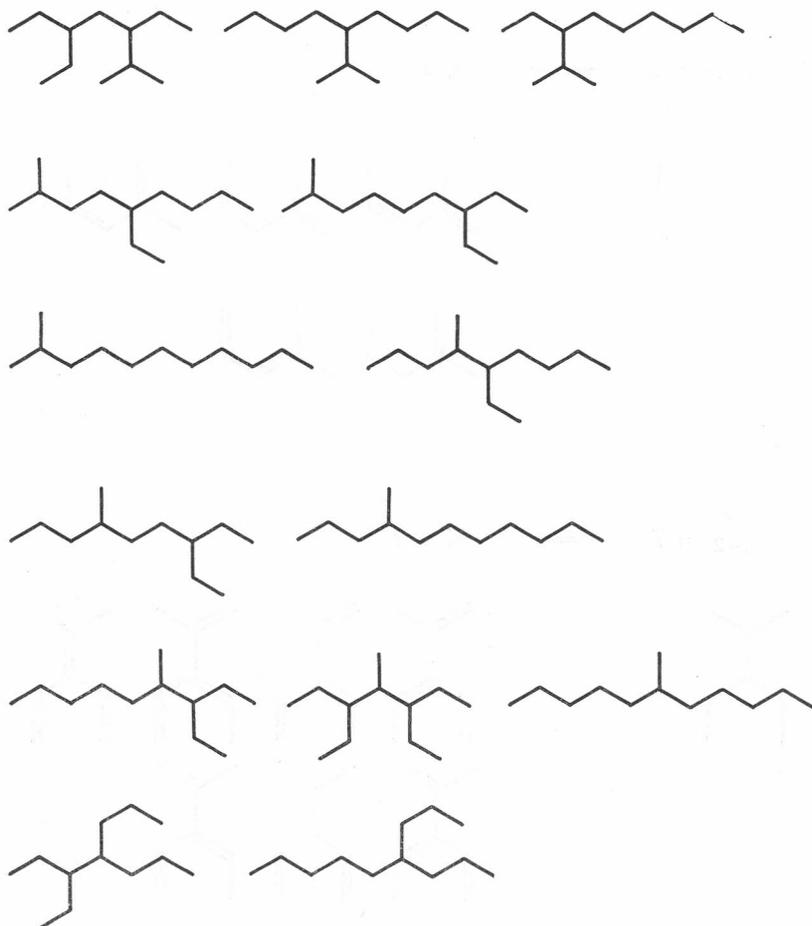


Figure 9. C_{12} biradical forms with maximally delocalized unpaired spin densities.

approach may be applied to other biradical forms. We see from Figure 7 that polyenes with $n-4$ carbon atoms lead to biradicals with $a_{n-2} = 4$ and $a_{n-2} = 5$ and all possible biradical structures may be generated in this way. The above method of constructing biradical forms is of some interest. It is more efficient than constructing all trees and then filtering out unqualified forms and it also allows the construction of a subclass of biradical forms. For instance, if we are hunting for biradical forms that have delocalized unpaired density, we find such a biradical in the case of $a_{n-2} = 11$, $a_{n-2} = 14$, $a_{n-2} = 15$ and $a_{n-2} = 16$. Figure 9 shows these skeletal forms with maximally »delocalized« unpaired spin density.

They should be contrasted with several biradical forms which also have the maximal number of carbon atoms participating in delocalization of spin density, but which do not have these sites fully delocalized — as evinced by their daughter graphs which have two components (case $a_{n-2} = 12$).

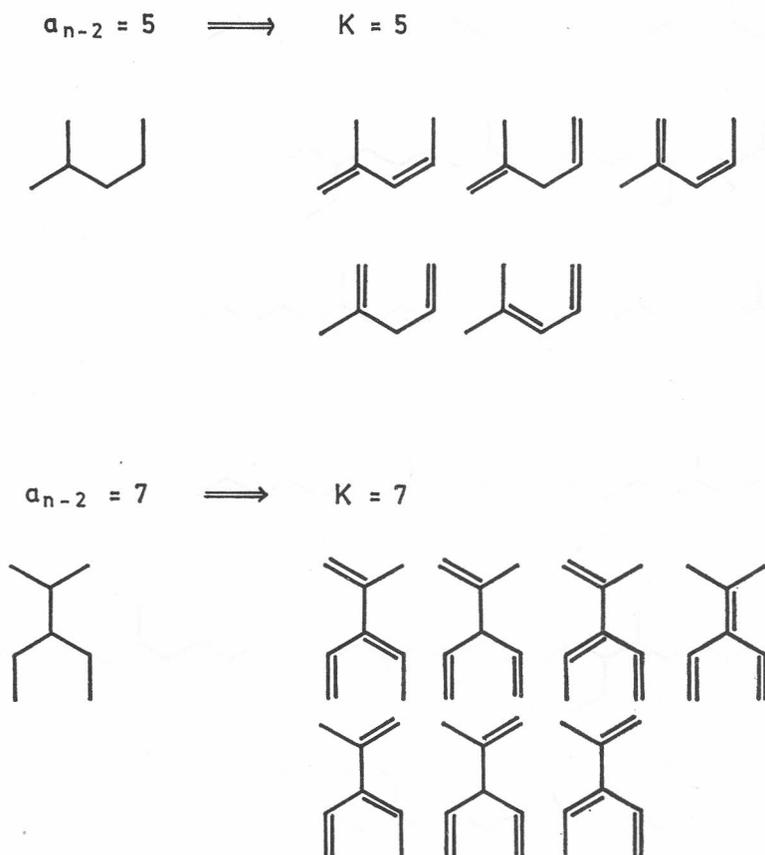


Figure 10. Valence structures for several acyclic biradicals demonstrating the connections of a_{n-2} with the number of Kekulé-type valence structures

$$a_{n-2} = 8 \implies K = 8$$

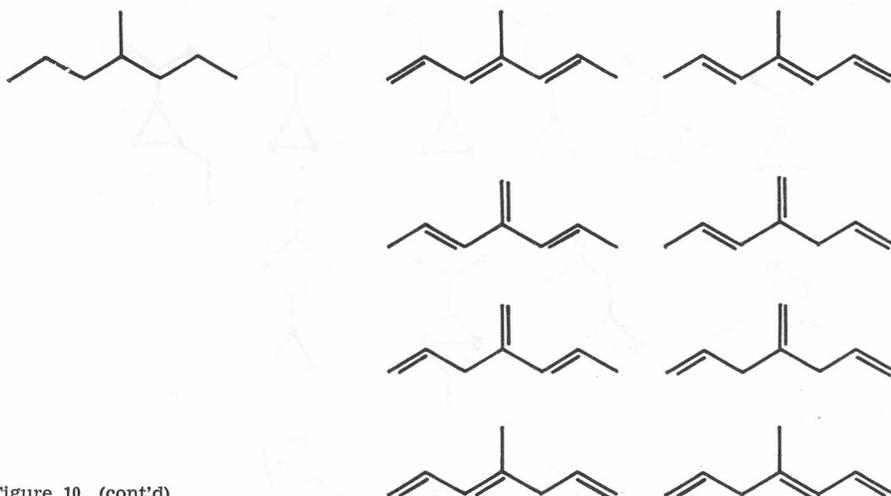


Figure 10. (cont'd).

Clearly, the classification of the topological biradicals based on the coefficient a_{n-2} appears to reflect considerable structural content and one wonders if the relationship is even deeper. It is not difficult to see that in the case when $a_{n-2} = 4$ all biradicals belonging to this group have four valence structures. Similarly, biradical forms having $a_{n-2} = 5$, as one can verify, can have five valence structures. One can continue and examine biradicals forms having $a_{n-2} = 6, 7, 8$, etc., and thus can confirm that the corresponding number of valence structures is in all cases given by a_{n-2} . Several illustrative examples are given in Figure 10.

CYCLIC TOPOLOGICAL BIRADICALS

Cyclic topological biradicals fall into two classes: (a) *alternant biradicals* and (b) *non-alternant biradicals*. In order to determine where a given cyclic biradical should be classified, it is enough to see whether it contains at least one odd-membered cycle. In that case it belongs to the non-alternant biradicals. The above classification correlates well with the criterion based on the multiplicity of the zero eigenvalue. Thus, cyclic alternant biradicals have a zero eigenvalue of multiplicity two, while cyclic non-alternant biradicals have a zero eigenvalue of multiplicity one. This results is connected with the following: It can be shown that the cases with spin density only in non-adjacent sites, which resembles bipartite (alternant) structures, for which the same is true, have characteristic polynomials where $a_{n-1} = 0$. Thus, the smallest non-zero coefficient is a_{n-2} which implies a doubly degenerate zero eigenvalue. On the other hand, the cases with adjacent spin density sites, which resembles non-bipartite (non-alternant) structures, are associated with characteristic polynomials where $a_{n-1} \neq 0$, and consequently are associated with a zero eigen-

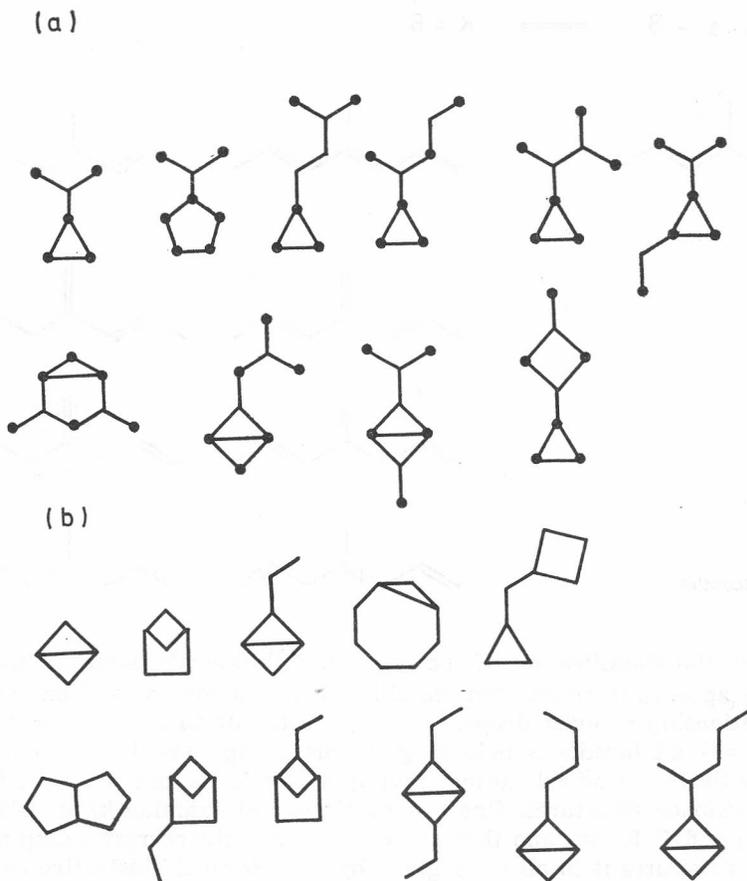


Figure 11. All non-alternant cyclic biradicals having 8 or fewer carbon atoms. Structures in part (a) of the Figure have a single zero eigenvalue and no Kekulé valence structures (proper biradicals), while those in part (b) have a single zero eigenvalue and *have* Kekulé structures (biradicaloids)

value of multiplicity one. In practice it is relatively easy to see if a biradical form can support adjacent or only non-adjacent spin density sites: one only has to examine a few (not even all) Kekulé-type valence structures. With this observation it is not difficult to verify that the azulene biradical forms of Figure 1 belong to two different classes as already mentioned. As an example, all monocyclic and bicyclic non-alternant biradicals having 8 or fewer carbon atoms are shown in Figure 11.

The structures in Figure 11 are divided into two groups: the first group is characterized by having $K = 0$, while the second group has $K \neq 0$. Structures characterized by a single zero eigenvalue and $K = 0$ are non-alternant »proper« biradicals. However, structures typified by a single zero eigenvalues and $K \neq 0$ exhibit partial biradical character and are sometimes called biradicaloids.²²⁻²⁶

As has already pointed out, cyclic alternant biradicals must have a doubly degenerate zero eigenvalue. Examples of monocyclic and bicyclic alternant biradical forms are presented in Figure 12.

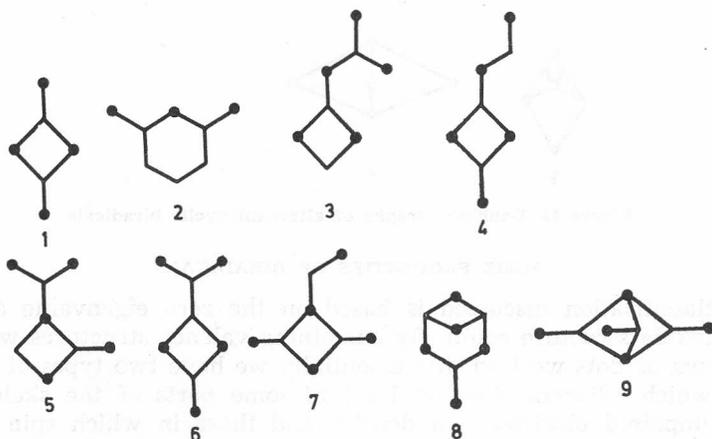
Structures in Figure 12 are also partitioned into two groups:

- (a) »proper« biradicals characterized by a doubly degenerate zero eigenvalue and $K = 0$, and
- (b) biradicaloids typified by a doubly degenerate zero eigenvalue and $K \neq 0$.

The corresponding daughter graphs are given in Figure 13.

Because two carbon radical sites may now be connected by more than a single path the daughter graphs of alternant cyclic biradicals show »double« connections.

(a)



(b)

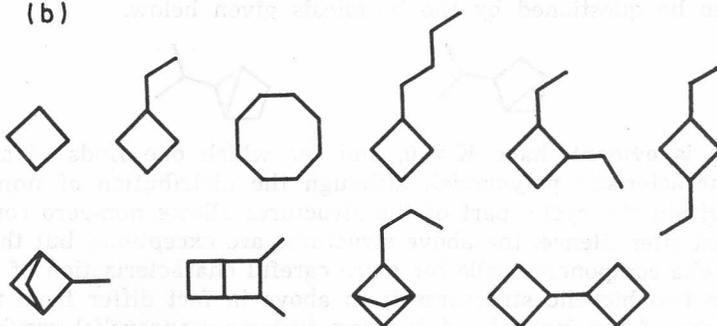


Figure 12. Examples of alternant cyclic biradicals. Structures in part (a) of the Figure have doubly degenerate zero eigenvalue and no Kekulé valence structures (proper biradicals), while those in part (b) have doubly degenerate zero eigenvalue and have Kekulé structures (biradicaloids)

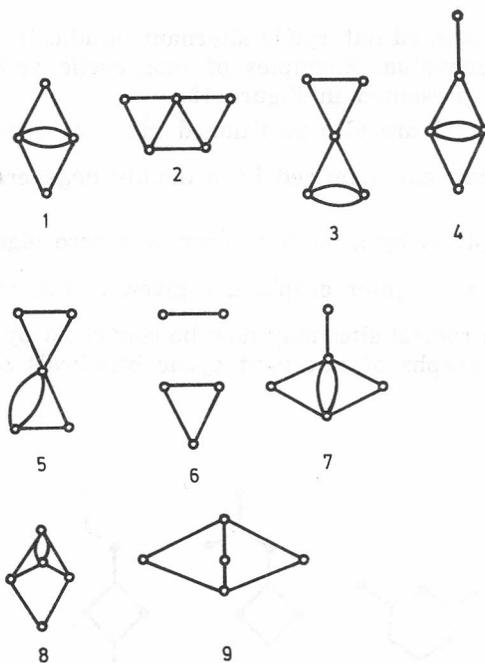


Figure 13. Daughter graphs of alternant cyclic biradicals

SOME PROPERTIES OF BIRADICALS

The classification discussed is based on the zero eigenvalue degeneracy and the Kekulé structure count. By examining valence structures with radical points shown as dots we find that essentially we have two types of biradicals: those in which adjacent sites (at least in some parts of the skeleton) have non-zero unpaired electron spin density and those in which spin density is not in adjacent sites. It appears that the first class has a single zero eigenvalue, while the second has a doubly degenerate zero eigenvalue. This is certainly the case with all acyclic structures (which belong to the latter case) and monocyclic structures. In the case of bicyclic structures the observed regularity appears to be questioned by the biradicals given below,



which, as is evident, have $K = 0$, and for which one finds x^2 as a factor of the characteristic polynomial, although the distribution of unpaired spin density within the cyclic part of the structures allows non-zero contributions in adjacent sites. Hence, the above structures are exceptions, but the presence of two cyclic components calls for more careful characterization of the second class. The two bicyclic structures from above in fact differ from the rest in that erasure of the inner bond (making systems monocyclic) results in biradicals of the class $K = 0$ and a single zero eigenvalue, while a similar operation on any of the remaining bonds, as well as on any of the remaining members, always produces a member of the same class. In other words, the

two bicyclic structures have spanning subgraphs¹⁹ which do not belong to the same class. Hence, the structures have different properties and constitute a class in themselves.

The graphs representing delocalization of unpaired spin density shown in Figure 7 have been grouped according to the value of the coefficient a_{n-2} and, as one can verify, have a_{n-2} valence forms for biradical structures. This finding, demonstrated on several C_{12} biradicals, is also true for biradical skeletal forms having fewer carbon atoms. Hence, if the coefficient a_{n-2} is, for example, 4 then, regardless of the number of carbon atoms, the skeletal form for the biradical will be one that can sustain four valence structures. Recognition of the »biradical« part and the »olefinic« part of the molecular skeleton is important as it is one of the prime factors in the classification of biradicals that partitions structures into groups for which similar properties are expected. However, the same structural feature is of interest in the process of construction of biradical forms.

CONSTRUCTION OF BIRADICAL FORMS

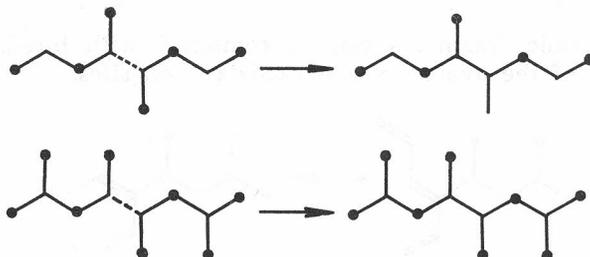
One of the advantages of chemical graph theory is its ability to generate structures of some anticipated class. By focussing attention on several structural components and using the model of Hückel, the $(4m + 2)$ rule (which is generally valid even if the HMO model has limitations) one can derive construction rules,²⁷ for example, that insertion of four CC bonds into any single cycle will not change the Hückel character of the structure (such as the pattern of orbital levels). In the same spirit we can now formulate a number of construction criteria for biradicals. Most of these may be recognized by close inspection of the reported biradical skeletons.

We give below the set of construction rules that embrace proper biradicals and biradicaloids:

- (i) Acyclic biradicals with n carbon atoms can be constructed from acyclic biradicals with $n-2$ carbon atoms by attaching a K_2 , i. e. $\text{O} \text{---} \text{O}$, fragment to any »dotted« carbon



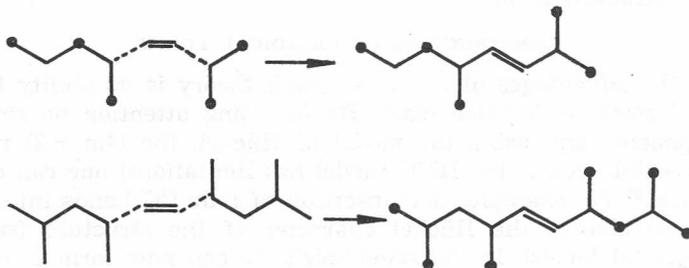
- (ii) Two acyclic radicals or biradicals can be joined by linking any two »undotted« carbon atoms to produce a biradical with the maximum number of »dotted« carbon atoms. The coefficient a_{n-2} of the new biradical is equal to the product of the coefficients a_{n-1} (a_{n-2}) for the two component radicals (biradicals).



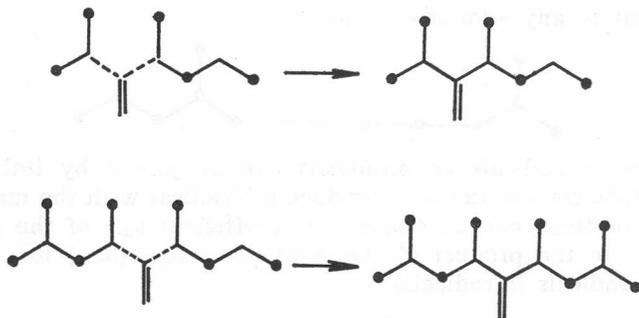
- (iii) The olefinic C=C fragment can be attached to any »undotted« carbon atom of a proper biradical to produce a novel biradical form with a fragment with essentially single and double CC bonds. The coefficient a_{n-2} is determined by the form of the associated »proper« fragment.



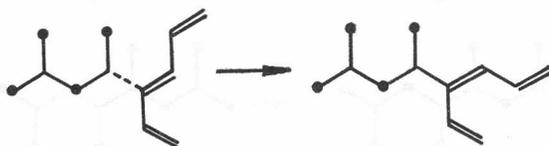
- (iv) The olefinic C=C fragment can be inserted between two adjacent »undotted« sites of a pair of radicals or biradicals, i. e. it can link two radicals or biradicals, leading to a novel biradical structure. The coefficient a_{n-2} is given by the product of the coefficients a_{n-1} (a_{n-2}) for the two radical (biradical) fragments.



- (v) The olefinic C=C fragment can link two radicals (biradicals) at the »undotted« position by the same carbon atom. The coefficient a_{n-2} of the composite biradical (tetraradical) is given as the product of the corresponding radical (biradical) coefficients a_{n-1} (a_{n-2}).



- (vi) Larger olefinic fragments can be combined with biradical fragments using any of the available »undotted« carbon sites.



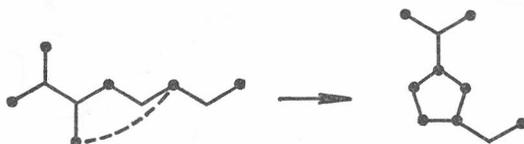
- (vii) Cyclization of an acyclic biradical by linking »dotted« and »undotted« carbon atoms produces a proper cyclic biradical.



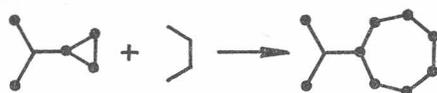
- (viii) Cyclization of an acyclic biradical by linking two »undotted« carbon atoms produces a biradical. This operation does not change the value of a_{n-2} .



- (ix) Cyclization of acyclic radicals by linking two »dotted« carbon atoms results in a new biradical structure which has all »dotted« ring carbon atoms and belongs to a subclass which is different from the parent structure.



- (x) Insertion of a linear chain with an even number of atoms into a cyclic structure does not change its biradical character.



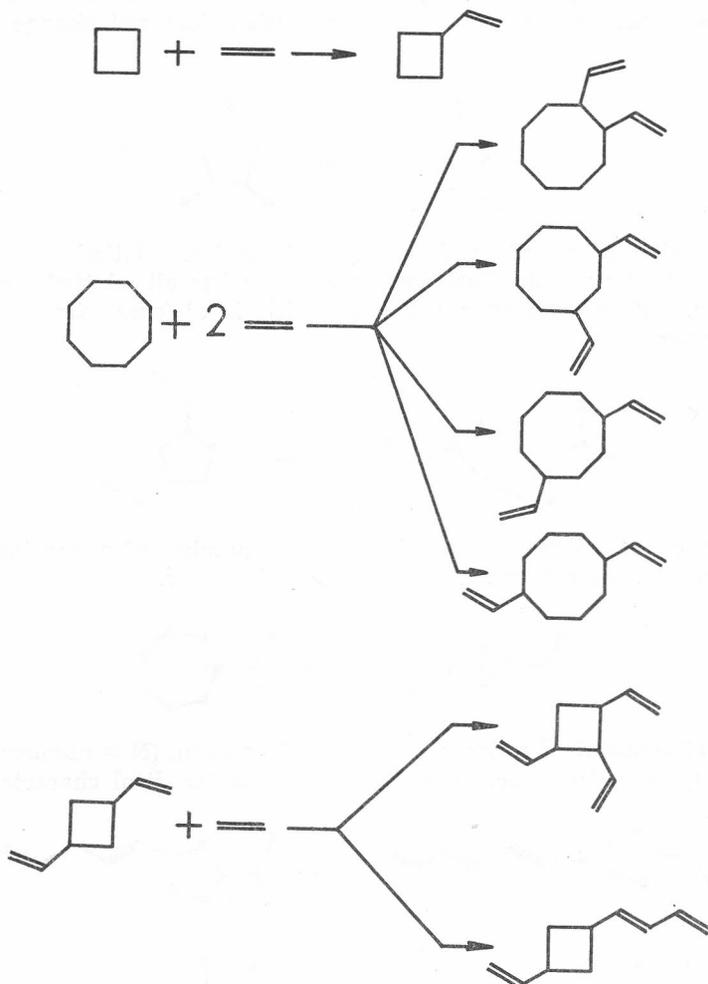
- (xi) The attachment of a linear chain with $N = \text{even}$, ($N = \text{number of atoms}$) to a (poly)cyclic structure will not alter its biradical character.



- (xii) The insertion of linear chains with $N = \text{even}$ ($N = \text{number of atoms}$) as bridges in (poly)cyclic structures does not change the biradical character of the generated structure.



- (xiii) The attachment of an even-membered linear chain at any position on (4m)-annulene or on its polyene exocyclic derivative will not alter their biradicaloid character.



Some of the above results are given in a different way by Döhnert and Koutecký.¹³

The significance of the recognition of »building« units and construction criteria is in their use in the derivation of structures having certain predetermined structural requirements. For instance if one desires to derive all bira-

dical forms that consist of *two equal radical fragments* with a separation of one CC double bond one can use the available rules to obtain all cases which will have coefficients $a_{n-2} = 4$, $a_{n-2} = 9$, etc., and within each such group one constructs or selects only structures complying with the requirement. In this way a number of structures which, for this purpose, are uninteresting, are avoided, thus increasing the efficiency of the search.

DISCUSSION

With the current expansion of chemistry, the problem of characterization, classification, ordering, etc., of structural forms is more important than might appear to a superficial observer. Over four million structures have already been registered, nevertheless, within any selected subgroup, a number of structures that are mathematically possible have not yet been observed. Computer programming of structures generates conceivable forms²⁸, which then have to be further analyzed in order to select those most likely to be of interest in experimental chemistry. One needs selection rules or criteria, and one pragmatic approach is to require that »candidate« structures be as »similar« as possible to naturally occurring substances.²⁹ The definition of »similarity« has yet to be specified, but the use of path codes has been shown to provide a useful criterion. Another approach — not yet properly developed — is to search for ordering of structures. Again, the requirement for »ordering« rules has to be defined, and may vary from application to application. If one »strikes« at some rule that would order (or only partially order) desired structures close to one another one again has a useful scheme for »filtering« structures and discarding undesirables. The important aspect of graph construction is not an exhaustive construction of all possible graphs of a given size (although this is also important for some very special considerations^{30,31}), but construction of forms having the desired qualities. Furthermore, if such a construction can be combined with derivation of the structures in some definite *order*, one achieves two goals in one step. *Order* for constructions was indicated as being an important component several years ago,³² however it seems that this has only recently been appreciated.^{33,34} It will depend on the algorithm used whether the derived structures are ordered or not. Of course, one has to recognize that different ordering schemes are possible, even desirable, if one is comparing experimental data. Our present construction of biradical forms has not been based on any ordering scheme. However, as a construction scheme, or set of rules it had an advantage which should be indicated as an alternative to what was discussed above. Biradicals normally are not stable systems, and many forms may be viewed as transient forms of interest for the *mechanism* of chemical transformations. By being able to discern several structurally different classes of such biradical forms we are offering those involved in the analysis of mechanisms a basis for differentiation of alternatives. It is quite conceivable that a chemical transformation (rearrangement for instance) can be thought of as involving several non-equivalent intermediate steps. Depending on energetics, barriers, etc. some of these are more likely and some less likely, and one can imagine that the nature of the biradicals involved may be a critical factor here. It is beyond the scope of the present work to speculate or even attempt to suggest (or rank) forms, but such a project, using empirical data, may in the future arrive at useful

structural rules and indicate which type of radical is of more relevance for the chemical processes under consideration. Finally, biradicals are also of interest for the clarification of properties of large systems in which »parts« of the structure are weakly coupled. We have only mentioned the Tschitschibabin hydrocarbon, which raises the question: is the system to be viewed as »weakly« coupled radicals or as a single molecule (in which one Kekulé type form allows coupling of unpaired spins)? Biradicals for which one can write the Kekulé valence form have not been examined here in much detail, but they also allow considerable delocalization of the unpaired spin density and would have some common properties with the biradicals considered here — such a delocalization is at least formally possible. Whether the spin density is localized or delocalized will be determined by experiment. Once this is known the results for many related structures can be deduced from the graph-theoretical characteristics of the structure.

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REFERENCES

1. Part IV: J. Seibert and N. Trinajstić, *Int. J. Quantum Chem.* **23** (1983) 1829.
2. R. G. Bergmann, in: *Free Radicals*, Edited by J. K. Kochi, Vol. 1, Wiley, New York 1973, p. 1.
3. J. Michl, *Topics Curr. Chem.* **46** (1974) 1.
4. P. Daud, *Accounts Chem. Res.* **5** (1972) 242.
5. W. C. Herndon, *Israel J. Chem.* **20** (1980) 270.
6. C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **36** (1940) 193.
7. W. C. Herndon and M. L. Ellzey, Jr., *Tetrahedron Lett.* (1974) 1399.
8. M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A 214** (1952) 482.
9. A. Graovac, I. Gutman, and N. Trinajstić, *Lecture Notes in Chemistry*, Vol. 4, Springer, Berlin 1977.
10. N. Trinajstić, *Chemical Graph Theory*, CRC, Boca Raton, in press.
11. M. Mestechnik and Yu. Visotskii, *Tetrahedron Lett.* (1975) 109.
12. D. Döhnert, Ph. D. Thesis, Freie Universität, Berlin 1979.
13. D. Döhnert and J. Koutecký, *J. Am. Chem. Soc.* **102** (1980) 1789.
14. D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Matsen, *J. Chem. Phys.*, in press.
15. W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **99** (1977) 4587.
16. A. A. Ovchinnikov, *Theoret. Chim. Acta* **47** (1978) 297.
17. C. A. Coulson, B. O'Leary, and R. B. Mallion, *Hückel Theory for Organic Chemists*, Academic, London 1978, pp. 88—90.
18. We speak of »unpaired« spins merely to avoid a commitment to the triplet or the singlet spin state, hence very informally.
19. F. Harary, *Graph Theory*, Addison-Wesley, Reading, Mass. 1971, second printing.
20. J. V. Knop, W. R. Müller, Ž. Jeričević, and N. Trinajstić, *J. Chem. Inf. Comp. Sci.* **21** (1981) 91.
21. The coefficient $a_n = 0$ for biradicals. Thus, a_{n-2} is the smallest non-zero coefficient of the characteristic polynomial.
22. R. Daudel, *Advances Quantum Chem.* **3** (1967) 161.
23. J. Michl, *Mol. Photochem.* **4** (1972) 257.
24. L. Salem and C. Rowland, *Angew. Chem. Int. Edit. Engl.* **11** (1972) 92.

25. J. Kolec and J. Michl, *J. Am. Chem. Soc.* **95** (1973) 7392.
26. C. Flynn and J. Michl, *J. Am. Chem. Soc.* **96** (1974) 3280.
27. D. Cvetković, I. Gutman, and N. Trinajstić, *Croat. Chem. Acta* **44** (1972) 365.
28. D. H. Smith and R. E. Carhart, *Tetrahedron* **32** (1976) 2513.
29. M. Randić and C. L. Wilkins, *J. Chem. Inf. Comp. Sci.* **19** (1979) 31.
30. F. Harary and E. D. Palmer, *Graphical Enumeration*, Academic, New York 1973.
31. K. Balasubramanian, J. J. Kaufman, W. S. Koski, and A. T. Balaban, *J. Comput. Chem.* **1** (1980) 149.
32. M. Randić, *Acta Cryst. A* **34** (1978) 275.
33. C. J. Colburn and R. C. Read, *J. Graph Theory* **3** (1979) 187.
34. M. F. Delaney and F. V. Warren, Jr., *J. Chem. Educ.* **58** 646.

SAŽETAK

Kemijska teorija crteža. V. O klasifikaciji topologijskih biradikala

J. V. Knop, D. Plavšić, M. Randić i N. Trinajstić

Predložena je klasifikacija topologijskih biradikala (biradikaloida) koja se temelji na mnogostrukosti nulte vlastite vrijednosti i na neposjedovanju (ili posjedovanju) Kekuléovih struktura. Izvedena su pravila za konstruiranje novih biradikala (biradikaloida).