Progress in

PHYSICAL ORGANIC CHEMISTRY

VOLUME 15

Editor

ROBERT W. TAFT, *Department of Chemistry*
University of California, Irvine, California

An Interscience® Publication

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New York Chichester Brisbane Toronto Singapore

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Contributors to Volume 15

Michael J. Blandamer
Department of Chemistry
The University
Leicester, England

San-Yan Chu
Department of Chemistry
National Tsing Hua University
Hsinchu, Taiwan, Republic of China

S. Dähne
Central Institute of Optics and Spectroscopy
Academy of Sciences of the German Democratic Republic
Berlin, German Democratic Republic

Tieh-Sheng Lee
Department of Chemistry
National Tsing Hua University
Hsinchu, Taiwan, Republic of China

F. Moldenhauer
Central Institute of Optics and Spectroscopy
Academy of Sciences of the German Democratic Republic
Berlin, German Democratic Republic

Ross E. Robertson
Department of Chemistry
University of Calgary
Calgary, Alberta, Canada

John M. W. Scott
Department of Chemistry
Memorial University
St. John's, Newfoundland, Canada

Sason S. Shaik
Department of Chemistry
Ben Gurion University of the Negev
Beer Sheva, Israel

Introduction to the Series

Physical organic chemistry is a relatively modern field with deep roots in chemistry. The subject is concerned with investigations of organic chemistry by quantitative and mathematical methods. The wedding of physical and organic chemistry has provided a remarkable source of inspiration for both of these classical areas of chemical endeavor. Further, the potential for new developments resulting from this union appears to be still greater. A closing of ties with all aspects of molecular structure and spectroscopy is clearly anticipated. The field provides the proving ground for the development of basic tools for investigations in the areas of molecular biology and biophysics. The subject has an inherent association with phenomena in the condensed phase and thereby with the theories of this state of matter.

The chief directions of the field are: (a) the effects of structure and environment on reaction rates and equilibria; (b) mechanisms of reactions; and (c) applications of statistical and quantum mechanics to organic compounds and reactions. Taken broadly, of course, much of chemistry lies within these confines. The dominant theme that characterizes this field is the emphasis on interpretation and understanding which permits the effective practice of organic chemistry. The field gains its momentum from the application of basic theories and methods of physical chemistry to the broad areas of knowledge of organic reactions and organic structural theory. The nearly inexhaustible diversity of organic structures permits detailed and systematic investigations which have no peer. The reactions of complex natural products have contributed to the development of theories of physical organic chemistry, and, in turn, these theories have ultimately provided great aid in the elucidation of structures of natural products.

Fundamental advances are offered by the knowledge of energy states and their electronic distributions in organic compounds and the relationship of these to reaction mechanisms. The development, for example, of even an empirical and approximate general scheme for the estimation of activation energies would indeed be most notable.

The complexity of even the simplest organic compounds in terms of physical theory well endows the field of physical organic chemistry with the frustrations of approximations. The quantitative correlations employed in this field vary from purely empirical operational formulations to the approach of applying physical principles to a workable model. The most common procedures have involved the application of approximate theories to approximate models. Critical assess-

ment of the scope and limitations of these approximate applications of theory leads to further development and understanding.

Although he may wish to be a disclaimer, the physical organic chemist attempts to compensate his lack of physical rigor by the vigor of his efforts. There has indeed been recently a great outpouring of work in this field. We believe that a forum for exchange of views and for critical and authoritative reviews of topics is an essential need of this field. It is our hope that the projected periodical series of volumes under this title will help serve this need. The general organization and character of the scholarly presentations of our series will correspond to that of the several prototypes, e.g., *Advances in Enzymology, Advances in Chemical Physics,* and *Progress in Inorganic Chemistry.*

We have encouraged the authors to review topics in a style that is not only somewhat more speculative in character but which is also more detailed than presentations normally found in textbooks. Appropriate to this quantitative aspect of organic chemistry, authors have also been encouraged in the citation of numerical data. It is intended that these volumes will find wide use among graduate students as well as practicing organic chemists who are not necessarily expert in the field of these special topics. Aside from these rather obvious considerations, the emphasis in each chapter is the personal ideas of the author. We wish to express our gratitude to the authors for the excellence of their individual presentations.

We greatly welcome comments and suggestions on any aspect of these volumes.

Robert W. Taft

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Progress in

PHYSICAL ORGANIC CHEMISTRY

VOLUME 15

Structural Principles of Unsaturated Organic Compounds: Evidence by Quantum Chemical Calculations

BY S. DÄHNE AND F. MOLDENHAUER
Central Institute of Optics and Spectroscopy
Academy of Sciences of the German Democratic Republic
Berlin, German Democratic Republic

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I. INTRODUCTION

When the limitations of resonance theory, aromaticity, and quantum chemistry were realized at the end of the sixties (1–3), structure theory of unsaturated organic compounds (UOC) went into a crisis which has called forth many challenging, contemplating, or even pessimistic comments on the vigor of theoretical organic chemistry (4–8). This stagnant period has been overcome by and large with the development of triad theory (7, 9–11). The vast amount of UOCs can be classified phenomenologically by physical and chemical aspects on the basis of simple rules combining topological and electronic principles. This provides the chemist with a heuristic model by which he can readily estimate and foresee the physical and chemical properties of UOCs such as bond lengths, electron densities, light absorption, and reactivity as it is the hopeful intention of future molecular engineering.

For the most part, the structural principles underlying this theory have been derived from chemical experience. Evaluation of many hundreds of X-ray structure analyses and generalization of structure analytical results have proved very helpful (11). This approach has been legitimately criticized, for many of the published structural data are too inaccurate and thus insignificant for evidence (12). Complementing earlier work by Fabian and Tröger-Naake (13) we calculated some thousand model compounds by the HMO method using the β-SC procedure of Golebiewski and Novakowski (14) to take into account bond lengths alternation. This gave consistent results better suited for comparison than X-ray structural data.

Not only do the results confirm the basic structural principles and color rules, but they also permit a more detailed classification of UOCs, which is applied here mostly to polymethinic compounds. There is no question that polyenic and aromatic compounds can be systematized in a similar way.

The main goal of this review, however, is not to convince theoreticians of the suitability of the triad theory or of certain quantum chemical calculations but to provide experimental chemists with simple implements to design and fit new UOCs with special electronic structures. The reader will find, therefore, in Chapters II through IV the description of hundreds of model compounds which follow the structural principles and rules of the triad theory outlined in Chapter I. Experimentalists who are preferentially interested in the architecture of molecules have to keep in mind only the instructions concerning the relation between

model structures and experimentally accessible compounds explained in Section I.B, and then they should look at the structures, which represent many compounds unsynthesized so far.

In order to save space only a few references have been made to experimentally known facts. Chemists will easily recognize, however, how experimental results are reflected by the triad theory.

A. Structural Principles and Color Rules

Three fundamental principles determine the main features of the electronic structure of UOCs; that is, their bond lengths and π-electron distribution:

1. *Triad Principle.* The diversity of UOCs can be interpreted in terms of intermediates between three ideal states: the *aromatic state*, the *polymethinic state*, and the *polyenic state*.
2. *Energy Principle.* The structure of the UOCs derives from their tendency to form as many *unbranched, energetically stabilized*, highly symmetric aromatic and/or polymethinic *structural units* as possible.
3. *Bonding Principle*
   a. The sum of bond strengths of an atom is approximately constant (*Gebhard–Pauling Rule*).
   b. The bond lengths between equicharged neighbored atoms are additionally enlarged and those between oppositely charged atoms are additionally shortened (*Kulpe's Rules*).

The characteristic features of the three ideal states are summarized in Fig. 1. Ideal aromatics of formula 1/1 (15) are pericycles consisting of $(4n + 2)$ atomic centers occupied by $(4n + 2)$ π-electrons. Pericycles consisting of $4n$ atomic centers and filled with $4n$ π-electrons are called antiaromatics, which exhibit polyenic features. Ideal polyenes 1/2 are linear chains of $2n$ atomic centers occupied by $2n$ π-electrons. Ideal polymethines 1/3 are chainlike molecules having N atomic centers occupied with $(N + 1)$ or $(N - 1)$ π-electrons (16) which are symmetrically distributed along the chain. Odd-membered polymethines are the polymethine dyes in closer sense, whereas even-membered polymethines occupied by an odd number of π-electrons are the polymethine radicals (17). Those are called synonymically push–pull or capto–dative, or otherwise stabilized radicals (18, 19).

Many theoretical and experimental studies have proved the practical utility of the triad principle (11, 20–30) and verified the energy principle (11, 31–34). The bonding principle first formulated by Gebhard (35) and Pauling (36) has been confirmed only empirically, so far by Bürgi (37). Later on it was extended by Kulpe et al. (38, 39), who took into account additional bond length alterations

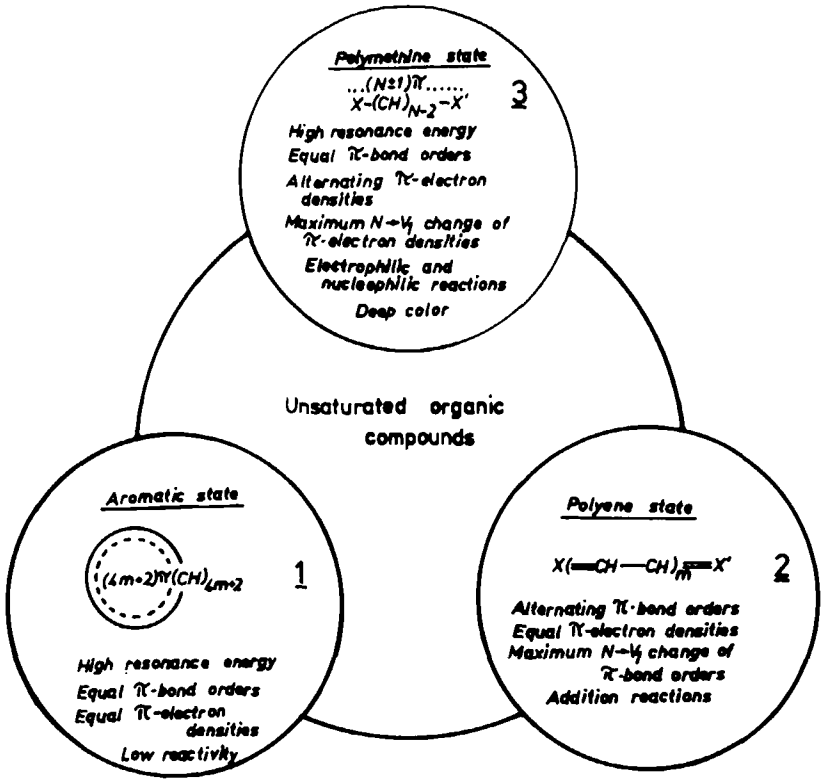


Figure 1 Outline of the triad theory (after References 7 and 10). The symbol m denotes zero and positive integers; N stands for positive integers from 2 upward and is identical with the number of the atomic centers in a molecule.

caused by Coulomb forces. However, neither the term bonding strength, as a measure of bond length, nor the term charge produced by the σ- and π-electrons have been clearly defined so far. A correlation with the π-bond orders may be expected to a rough approximation only. Within the framework of π-electron approximation, Gebhard–Pauling's rule follows from valence bond (VB) considerations. This has not yet been substantiated theoretically within the framework of MO formalism, obviously because the influence of the additional bonding effects according to Kulpe's rules had not been realized in the past.

Concerning the old question of "color and constitution," we need to add the following color rules to the fundamental principles (40). Again we shall confine ourselves to a discussion of the color of polymethinic compounds since these include more or less all typical dyes. It was Clar, first of all, who set up rules concerning the color and constitution of aromatic compounds (32), whereas

Kuhn and many others formulated certain rules concerning polyenic compounds (41, 42).

The *polymethine color rules* read:

1. *Polymethines* are *deepest* in *color* in comparison to aromatics and polyenes with the same number of π-electrons (43).
2. *Alternating polymethines* absorb at slightly shorter wavelengths than the longest constituent ideal polymethine unit.
3. *Nonalternating polymethines* absorb at substantially longer wavelengths than the longest constituent ideal polymethine unit.
4. If the polymethinic structure in alternating or nonalternating polymethines is weakened in favor of competing *aromatic structures*, the aromatic compound will absorb at shorter wavelengths than the longest ideal polymethine unit that can be formulated in the molecule.
5. If structural effects or terminal groups of unlike electronegativity remove the symmetry of π-electron distribution along a polymethine chain, compounds of a *polyenic structure* are formed; these absorb at shorter wavelengths than comparable polymethines having a symmetrical π-electron structure.

In these rules, as opposed to traditional approaches, no conclusions are drawn from light absorption as to the structure of a compound. On the contrary, the physical and chemical properties of a molecule—in our case, its color—are inferred by proper reasoning from its electron configuration.

To understand these rules we need to explain what we mean by alternating and nonalternating polymethines (40). The terms are intended to remind us of the well-known alternant and nonalternant hydrocarbons which are somewhat similar although not exactly identical. For this reason we follow the proposal made by Griffiths (27) to denominate both types of compounds by similar but not by identical terms.

Any attempt to classify the polymethines proceeds from their unique π-electron density alternation in the ground state, provided that heteroatoms with a larger electronegativity than carbon and heteroatoms with a lower electronegativity than carbon have a high respectively low π-electron density. This means that there are two possibilities in structural variations of polymethinic compounds: alternating polymethines retain this electron density alternation, whereas it is perturbed in nonalternating polymethines. This gives a pattern of classification as shown in Fig. 2, which we are going to use in this work.

Ideal, chain-shaped polymethine dyes having an odd number of chain atoms are alternating systems, whereas polymethine radicals with an even number of atoms belong to the nonalternating systems. Substitution of electron donor or electron acceptor groups for methine protons gives substituted alternating or nonalternating systems depending on whether a high or a low π-electron density prevails at the substituted position. Chain branching over ring systems is the

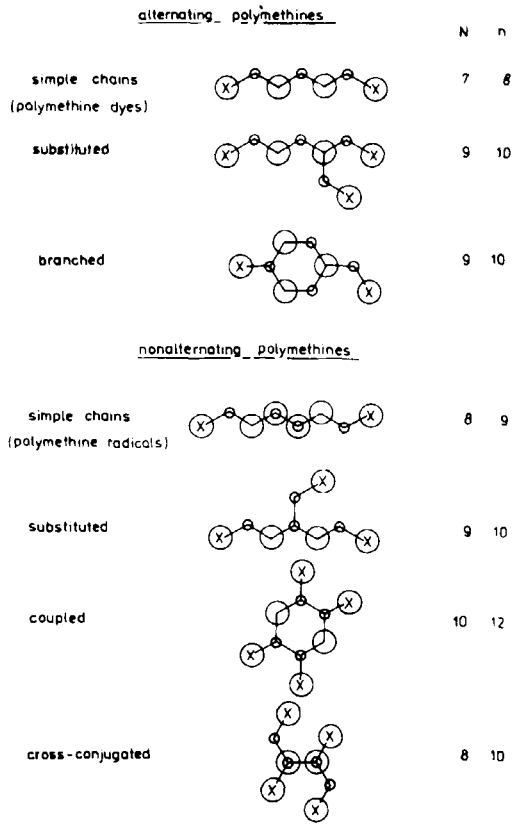


Figure 2 Classification of unsaturated organic compounds with heteroatoms by their electronic structure.

most common structural variation in alternating systems. Such compounds are termed branched polymethines. The simplest case of chain branching is a substituted alternating polymethine.

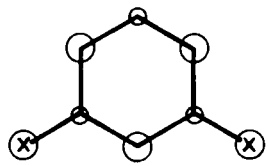
In structure variations of nonalternating polymethines we can distinguish between two essential situations: Two methine atoms of equal (high or low) π-electron density are directly adjacent to each other within a molecule. Such systems are called coupled polymethines. The simplest case of coupling is a substituted nonalternating polymethine. In the second situation π-electron density alternation in a molecule is canceled due to overlapping of two polymethine units. Such compounds are called cross-conjugated nonalternating polymethines; they include the indigoid dyes, in particular.

Two linear polymethine chains may also be crossed while alternation of π-electron density is being maintained. By contrast to nonalternating cross-conjugated polymethines, this is not accompanied by any noticeable changes in their

properties that would justify classification of such a system as a separate group.

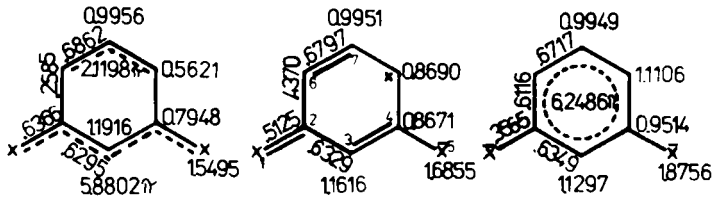
Frequently, a molecule will contain several structural variants: for instance, branching along with couplings and/or cross-conjugations. If so, the compound is included in the last position of the groups listed in Fig. 2.

When classifying a polymethine one must not disregard its overall π-electron structure. The importance of the polymethinic $(N + 1)$ π-electron occupation for the pattern of classification may be demonstrated in the *meta*-substituted benzenes **1** which should be alternating polymethines according to the principle of alternation. However, quantum chemical calculations show that when the



1

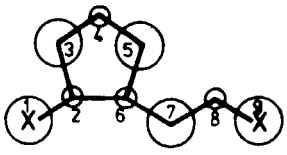
model compound is filled with 8 π-electrons light absorption is strongly red-shifted (44). If we count the π-electrons we will realize that in **1a** no branched, alternating polymethinic structure can be formulated whatever. On the contrary, the system is made up of a trimethine unit with 6 π-electrons on five atoms; this is coupled to an allyl cation fragment—that is a carbon monomethine occupied by $(N - 1)$ π-electrons (17)—whose light absorption should actually be red-shifted, according to color rule 3. When occupied by 10 π-electrons, a doubly donor-substituted aromatic structure **1c** is obtained. Its light absorption is blue-shifted, in accord with color rule 1. Only radical **1b** should have an alternating polymethinic structure whose trimethine chain (C^2, C^3, C^4) branches into a pentamethine chain (C^2, C^6, C^7, C^8, C^4) and vice versa, since it takes in this case 9 π-electrons to have $(N + 1)$ π-electrons per N chain atoms in each of the branched partial system. The molecular diagrams of $HMO_{\beta\text{-}SC}$ calculations of the three model structures show, indeed, the expected behavior. (For a better counting of the π-electron occupation per polymethine chain only one limiting structure is presented in formula **1b**.) Similar results are obtained using other quantum chemical methods such as HMO or PPP (44).



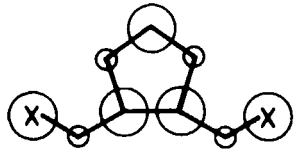
1a (8π) **1b** (9π) **1c** (10π)

In the coupled structure **1a** the bonds are equalized within the polymethine units while those of the coupling bonds are stretched considerably. In the aromatic compound **1c** the bonds are equalized inside the ring, which carries two substituents linked by nearly single bonds. In the branched polymethine **1b** the bonds tend to equalize likewise within the two polymethine chains. The bonds are stretched, however, at the branching points C^2 and C^4 in keeping with Gebhard–Pauling's rule. By the same rule, the next two bonds, C^6–C^7 and C^7–C^8, necessarily become narrower. Following color rule 2, light absorption in the branched polymethine radical should be blue-shifted in comparison to a nonbranched pentamethine. Unfortunately, nothing is known about the light absorption of such radicals.

The fact that by color rule 4 formation of aromatic structures may be possible, is another important boundary condition in classifying UOCs by the triad system. If we take the two heptamethine structures **2** and **3**, which are



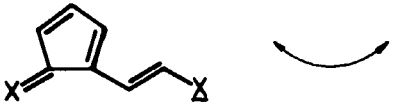
2



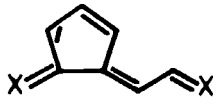
3

intramolecularly linked by the bonds C^2–C^6 and C^3–C^7, respectively, to form a five-membered ring, both are formally nonalternating polymethines as their π-electron density alternation is perturbed.

The resonance structures **2a,b** and **3a,b** are helpful in estimating the tendency for aromatization. Only in **3** the formation of an aromatic π-electron sextet

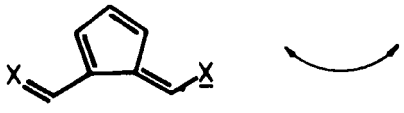


2a

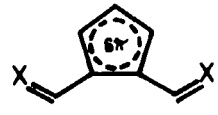


2b

substituted by single bonds with two acceptor groups is possible. To form a π-electron sextet in **2** requires that two double bonds emanate from the ring. By



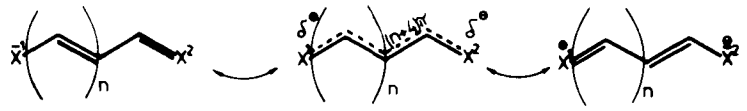
3a



3b

the second fundamental principle, these would oppose the trend toward aromatization. Hence, **2** should be, actually, a nonalternating polymethine. Its light absorption compared to the ideal heptamethine is therefore bathochromically shifted. **3**, on the other hand, is a substituted aromatic compound with a marked hypsochromic shift in light absorption.

Finally, ideal polymethinic behavior and thus, the validity of color rules 1 through 3, is strictly ensured only if the π-electrons are distributed in a fairly symmetrical way along the polymethine chain as in **4b**, in other words, if the classical resonance structures **4a** and **4c** have equal weight in terms of the VB formalism.

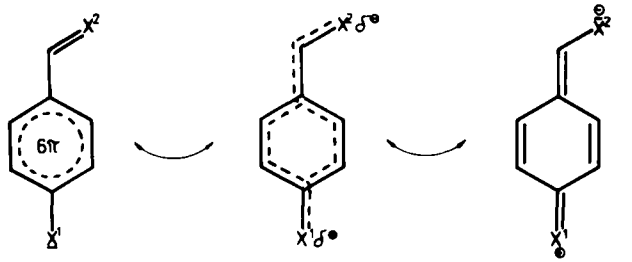


4a **4b** **4c**

Electronegativity:

$X^1 > X^2$ $X^1 = X^2$ $X^1 < X^2$

As the π-electrons become increasingly localized according to one or the other limiting structure polyenic structures and if possible aromatic structures are formed. Such perturbations in symmetry occur both in the event of structural asymmetries—in the nonalternating model **2**, for example—and in the case of polymethine chains substituted at the end with atoms of unlike electronegativity. The merocyanines **4** with $X^1 = NR_2$ and $X^2 = O$ are the best known examples, in which the terminal atoms have different electronegativity (17, 24). It has been overlooked, however, that even slight structural modifications, such as unsymmetrical substituent effects or ring branching, may lead to comparatively serious perturbations in symmetry. For example, if meropentamethinic structures **4**, $n = 2$, are branched across rings, as in the benzene derivatives **5**, a more or



Substituted aromatic **5a**

Branched polymethine **5b**

Branched polyene **5c**

Electronegativity of X^2

less pronounced symmetry deviation will occur resulting in the creation of aromatic and/or polyenic structural features. By triad theory, such structures must be interpreted as intermediates among all of the three ideal states.

B. Correspondence Between Ideal Model Structures and Real Organic Compounds

On a physico-chemical basis the structural principles provide the key to an understanding of the common features of UOCs. This requires the use of structural abstractions and generalizations, which have not yet been established in the literature, though the basis has already been provided in W. König's polymethine conception (45). We marked (17) terminal heteroatoms of polymethine chains with X,X′. They correspond to the perichromes as defined by König.

In practice, a X substituent is equivalent to an electron donor group, that is, to a substituent with a mesomeric +M effect. Examples are:

$$—Cl,\ —OH,\ —OR,\ —SR,\ —NH_2,\ —NR_2,$$

or

$$—O^{\ominus},\ —S^{\ominus},\ —NR^{\ominus}$$

and so on. Ring systems with heteroatoms also act as donor groups, provided there is a free electron pair in the π-electron plane available, as in pyrrole, imidazole, thiophene, and so on.

Accordingly, mesomeric substituents having a −M effect, that is, electron acceptor groups, are represented by a —C=X′ grouping. Consequently, acceptor groups consist of a methine atom and of a X′ terminal atom from a polymethine chain. Examples are:

$$—C{=}NR,\ —NO_2,\ —CHO,\ —CRO,\ —SO_3H,\ —COOH,\ —CN,\ —SO_2NH_2$$

or

$$—C{=}\overset{\oplus}{N}R_2,\ —C{=}\overset{\oplus}{O}R,\ —CO_2^{\ominus}\ —SO_3^{\ominus}$$

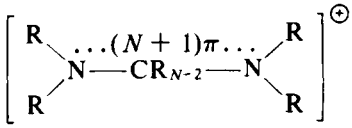
and so on.

In a nitro or sulfonyl group the methine atom adjacent to the heteroatom is again hetero-substituted. Hence, nitro compounds are to be interpreted as aza-substituted and sulfo compounds as thio-substituted polymethines.

Here again, heteroaromatics may act as acceptor groups if the heteroatom is incorporated in the ring by a double bond as in pyridine, quinoline, diazines, and triazines, for example.

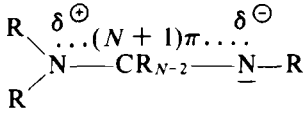
Whether a polymethine exists as an anion, cation, or electroneutral zwitterion depends on whether the polymethine chain is occupied by $(N + 1)$ or by $(N - 1)$ π-electrons and on the number of substituents bound at the heteroatom by σ-electrons.

For example, when occupied by $(N + 1)$ π-electrons, a cyanine-like dye (N = odd-numbered) or a polymethine radical (N = even-numbered) may take any of the following forms:



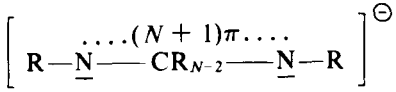
Cation, N = 2, 3, 4, . . .

6a



Electroneutral Zwitterion, N = 2, 3, 4, . . .

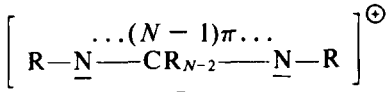
6b



Anion, N = 2, 3, 4, . . .

6c

When occupied by $(N - 1)$ π-electrons the following form is conceivable, provided we exclude the presence of multiply charged ions:



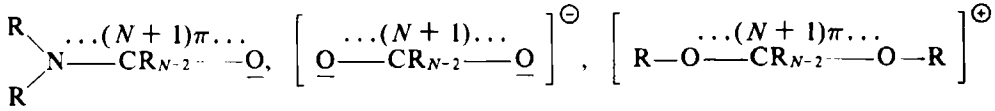
7

To facilitate transfer of the X,X′ groups to real substituents, we should write the substituents in semi-ionic form, for example:

$$-NR_2^{1/2\oplus},\quad -O^{1/2\ominus},\quad -OR^{1/2\oplus}$$

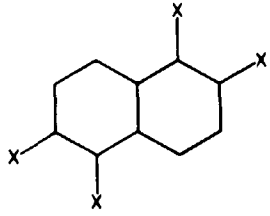
and so on. Having made the proper substitution, the general polymethine formula

1/3 turns into the cyanine **6a**, a merocyanine **8**, an oxonol **9**, or an oxonium polymethine **10**, and so on.



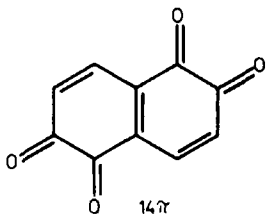
8 **9** **10**

As has been shown both empirically (17) and theoretically (23) the ideal polymethine state approaches with chains substituted by nitrogen terminal atoms. Hence it depends on the strengths of the mesomeric and inductive substituent effects to what extent polymethine features are realized. A periodic table of substituent effects similar to that proposed recently by Hall (46) may be helpful in estimating the mutual interaction of the terminal groups.

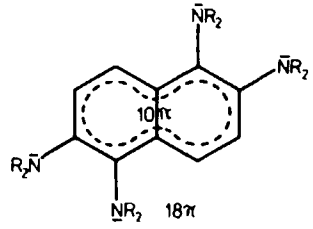


11

To demonstrate the influence of the overall π-electron occupation on the electronic structure, model **11** may be occupied by 14, 16, or 18 π-electrons. The occupation by 14 π-electrons results in the yellow bis-*ortho*-naphthoquinone **11a** and the occupation by 18 π-electrons in the colorless 1,2,5,6-tetraamino-naphthalene **11b**.

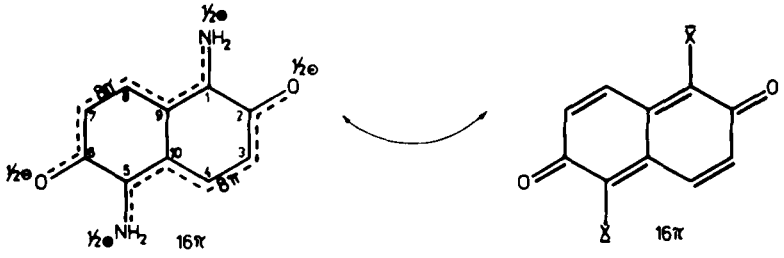


11a



11b

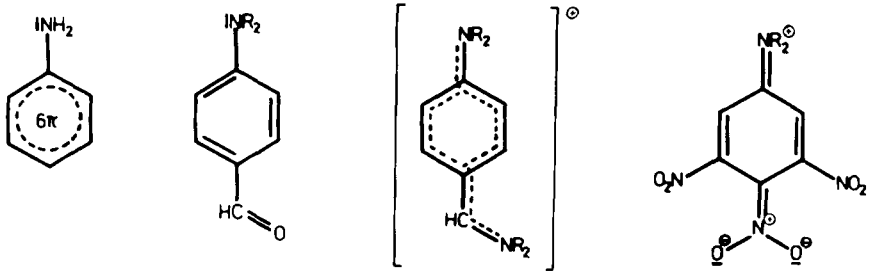
The deep-blue 1,5-diamino-naphthoquinone(2,6) **11c**, is filled with 16 π-electrons. It contains two pentamethine chains each having 8 π-electrons distributed among seven atomic centers, which are coupled to each other by the C^1–C^2–, C^5–C^6, and C^9–C^{10} bonds (20, 47). Because of the unlike electronegativity of the terminal atoms in the pentamethine chains the π-electrons are distributed not totally symmetrically along the chain, but deviate slightly toward a more polyenic structure **11d**. Only the diimmonium compound of the diaminonaphthoquinone or the dianion of the 1,5-dihydroxy-naphthoquinone (2,6) would have an ideal polymethinic structure with a fairly balanced π-electron distribution along the two pentamethine chains. An aromatization of system **11d** can be



11c **11d**

excluded as there is no resonance structure with 10 π-electrons within the two rings where only single bonds emanate from the cycle.

In the analogous way we may present the variety of substituted aromatic and polyenic compounds in the triad system, as previously indicated in formulas **4a** to **4c** and **5a** to **5c**. Even simple donor-substituted benzenes, such as the aniline **12**, are slightly polymethinic due to conjugation of the donor group with the benzene ring. However, the "lone pair" of the donor group is largely localized. It is reasonable, therefore, to consider these compounds as substituted aromatics:



12 **13** **14** **15**

Compounds such as *para*-aminobenzaldehyde **13** and similar derivatives as *para*-nitraniline behave like merocyanines **8** having 8 π-electrons on seven chain atoms. A polymethinic structure with an even more symmetrical π-electron distribution along the polymethine chain exists in the immonium compound of the *para*-dimethylaminobenzaldehyde **14**. As a result, this compound behaves similarly to the simple, chainlike pentamethine cyanine **6a**, $N = 7$. Any differences between the two compounds, obviously, are due to branching of the conjugation in the benzene ring of **14**. A largely polyenic, that is, in this case, a quinoid structure, is found in the highly polar compounds such as anion of picric acid or the 3,4,5-trinitroaniline **15** (11).

The effective electronegativity of the terminal substituents of polymethine chains can be changed in the sense of formulas **4** and **5** not only by different substituents but also by solvents of different polarity (48, 49). The effect has been known for a long time as solvatochromism (24).

C. The Quantum Chemical Method

For calculating the model structures, we were looking for a simple quantum chemical method in one-electron approximation. Such a method is obviously the Hückel method (HMO). However, it describes only polymethinic compounds reasonably well (21, 22, 23). To allow us to model polyenes and aromatics in an adequate way within the framework of triad theory, we decided to use the $HMO_{\beta\text{-}SC}$ method of Golebiewski et al. (14). The parametrization starts with HMO wave functions, with $\alpha_X = \alpha_C + h_X\beta_{CC}$ and $\beta_{CX} = k_{CX}\beta_{CC}$. In the first step of the calculations all bond parameters β (resonance integrals) are taken as identical using $k_{CX} = k_{CC} = 1$. In an iterative calculation based on the relationship $k = \exp[0.72\ (p - \frac{2}{3})]$ the resonance integrals involved are corrected in respect to the π-bond order p until self-consistency (SC) has been reached.

As a result of this SC procedure, orbital energies and π-bond orders both depend on the number of MOs filled with π-electrons. Therefore, if a particular molecule was occupied by different numbers of π-electrons, calculations had to be carried out separately for each occupation number.

Usually we considered model structures having X,X′ terminal atoms of greater electronegativity than carbon. These entered the calculations with an atomic parameter α_X (Coulomb integral) taking $h_X = 1$. As had been shown, this set of parameters describes particularly well simple polymethinecyanines 1/3 with X = X′ = $-NR_2^{1/2\oplus}$ (17, 23).

The parameters h_X and k_{CX} have to be varied as a matter of course if the compounds to be modeled are of a special type; that is, if the electronegativity and the bond strength of their terminal atoms differ markedly from that of a sp_2-

bound nitrogen atom. In this work we shall omit such variations of parameters, which serve to improve description of experimental data, since our concern at this stage is to portray the fundamental relationships between the constitution and the physico–chemical properties of UOCs by a consistent model.

In model compounds of unsymmetrical structure the calculations showed that the π-electrons were distributed unsymmetrically along the polymethine chain. Here again some deviations from experimental values occurred in such a way that the β-SC procedure overestimates the structurally induced dissymmetry. But the trend was described correctly in all cases under consideration. The structurally induced dissymmetry can be compensated by varying the electronegativity of the X,X′ heteroatoms. This was done in some instances by systematical variation of the Coulomb integral of the terminal X,X′ heteroatoms (as $\alpha_C = 0$ and $\beta_{CC} = 1$ were used the parameter h_X is identical with α_X depicted in the figures). In this way, we again obtained ideal polymethinic structures, in which the π-electrons were disposed symmetrically along the chain.

The $HMO_{\beta\text{-}SC}$ method in one-electron approximation does not consider influences arising from the special geometry of a compound, as they occur in *cis–trans* isomerism and other stereoisomeric forms. Since the interrelations between color and constitution in such cases represent higher-order approximations we shall not deal with them here.

Considering the limited information to be derived from the HMO method we shall also confine ourselves to closed shell systems having an even number of π-electrons. In our first contribution on the ideal polymethine state (21), we pointed out before, and others confirmed later by experiments (18, 19, 50, 51), that open shell polymethine radicals behave in many ways like closed shell polymethine dyes. The reason is that opposed to polyene radicals in polymethine radicals the essential electronic features are not determined by the singly occupied MO (SOMO) but by the doubly occupied HOMO and the empty LUMO which are related to those of the closed shell polymethines (52).

Because of the limitations of the HMO method we likewise did not consider molecules in the triplet state which are to be expected by single occupation of degenerate MOs. The calculated double occupation of one of the degenerate MO may be realistic, however, if Jahn–Teller distortions are taken into account.

Despite the fact that the parametrization used corresponds to an ideal polymethine system whose π-bond orders are fully equalized in the simple HMO formalism (21, 23), the $HMO_{\beta\text{-}SC}$ procedure slightly upsets this situation even in highly symmetrical polymethines (see molecular diagrams in Chapter II, Table 1). When the result is being compared with X-ray structural data (11) and H,H-coupling constants in the ^{1}H–NMR spectrum (53, 54), we find that those small differences are not an artifact of the method but that they reflect experimental behavior.

Configuration analyses carried out on coupled polymethines are added proof of the utility of the $HMO_{\beta\text{-}SC}$ procedure; they have been shown to give a very good account of the experimental findings (13).

However, we should emphasize that the conclusions drawn in this work do not depend on the particular kind of quantum chemical method of approximation chosen. Simple HMO computations will give the same information, though the approximation is less good. Even considerations by perturbational theory within the framework of HMO formalism will suggest correct trends (55).

Since electron density alternation within the polymethine chains is of special concern to the triad theory, Fabian made some test calculations using the ω-technique of Wheland and Mann (56). This method makes explicit allowance for the effect of electron repulsion within the simple LCAO–MO method using an SC procedure according to $\alpha_r = \alpha_0 + (1 - q_r)\omega\beta_0$ (with $\omega = 1.4$). The calculations produce a decrease in polymethinic electron density alternation while wave functions and eigenvalues that might affect the predictions by the triad theory are not changed by any appreciable amount (57). For this reason, we decided against a general application of the ω technique.

Also, when more advanced many-electron models were used, particularly the SCF procedure after Pariser, Parr, and Pople (PPP), the predictions were, in principle, consistent with the present model computations in nearly all of the cases studied (58–62).

D. Relevant Molecular Parameters

To assess molecular properties we used the quantum chemical quantities outlined as follows. N gives the number of atomic centers which is identical with the number of the atomic p_π orbitals in the z-direction of conjugated molecules and n gives the number of π-electrons.

The relative position of the frontier orbitals is related to a molecule's tendency to redox reactions (63) and spectral sensitization and desensitization effects as well (64–67). the *orbital energy* ϵ_j of the highest occupied molecular orbital (HOMO) describes the electron-donating ability in the ground state. Consequently, the ϵ_{HOMO} are correlated with the oxidation potentials E_{ox} which will be the more positive the more positive the ϵ_{HOMO} are. In this case oxidation will be rendered more difficult. A comparison of the calculated ϵ_{HOMO} of relevant model substances with their experimental stability reveals that compounds having bonding HOMOs, that is, $\epsilon_{HOMO} \geq 0$, do exist. If there are powerful electron donors (see Fig. 11) the HOMO may become slightly antibonding in nature and may assume values up to -0.3 β units.