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Color and Constitution: One Hundred Years of Research

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Summary. Useful theories and models of the color and constitution of unsaturated organic compounds have been sought for more than a century. The promises of quantum chemistry have not yet been realized satisfactorily. The polymethine concept, a modern chemical theory of constitution, is an auspicious development.

In 1976 there were two anniversaries in the field of color and chemical constitution. One hundred years before, Witt (*1*), at the Technical College of Berlin Charlottenburg, published the first comprehensive theory of color—the theory of chromophoric and auxochromic groups. Fifty years later W. König (*2*), at Dresden Technical University, presented his synopsis, "On the concept of 'polymethine dyes' and a general dye formula derived therefrom as the basis of a new systematics of dye chemistry."

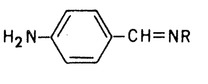
Since then, the theory of the constitution of unsaturated organic compounds, and hence the theory of color, has been enormously extended. In the 1930's, the concept of mesomerism was further developed, as E. Hückel derived the linear combination of atomic orbital-molecular orbital (LCAO-MO) model for the energetically stabilized aromatic state and L. Pauling introduced valence bond (VB) model. Thus in the 1940's and 1950's scientists were enthusiastic about the possibility of understanding the color and constitution of organic compounds on the basis of quantum chemistry (*3*). This enthusiasm has given way recently to a good deal of sobering. On the one hand, the limits and applicability of inductive theories, such as resonance and aromaticity, tended to narrow as these qualitative concepts were subjected to rigorous physical definitions. On the other, it proved impossible to satisfactorily solve the problem of an infinite variety of organic compounds in a purely deductive manner with aid of quantum theory. With quantum chemical approximations becoming more sophisticated, the interrelations of systems tended to be lost rapidly.

Binsch (*4*) aptly described the state of affairs in the following words: "Unless we learn how to deal with the problem of complexity [of chemistry] in a fundamentally new way, there is not much hope for a breakthrough, which is now desperately needed if we are to preserve the intellectual vigor of our science."

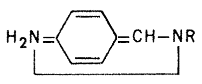
In this article I consider the present state of the general theory of color and constitution of unsaturated organic compounds (*5*).

Background

The point of departure of the modern chemical theory of color was V. A. Ismailsky's intuition in 1913 of the existence of an ideal chromo-state and his introduction of the term mesotropism to describe molecular states intermediate between two classical limiting structures, **1a** and **1b**, which can be formulated as



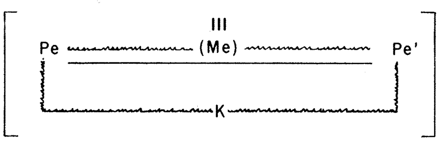
1a



1b

Ten years later mesotropism was being referred to in the literature as mesomerism or resonance in the work of many other authors. After another 10 years it was substantiated quantum chemically within the framework of the VB formalism, and, as is well known, it has affected the basic concepts of organic chemistry to this day (*3, 5*).

Independent of this development, König (*2*) incorporated the idea of the chromo-state as related to colored organic compounds in his polymethine conception, which markedly influenced future developments on two grounds. First, it was clearly understood that all organic dyes known at that time contained polymethine structural units of the general formula **2** where Me denotes



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formally trivalent, conjugated groups, such as $-CH=$, $-N=$, and $-SR=$; Pe and Pe′ are perichromes, terminal groups of the polymethine chain, such as $\sim NR_2$, $\sim O$, and $\sim CR_2$; and K denotes conjunction. Second, it was postulated that an alternating charge density distribution along the chain is an essential feature of those polymethine structures. Quantum chemically, the hypothesis of charge alternation in polymethines was justified in 1949 by H. Kuhn, using the free electron model and 1 year later by M. J. S. Dewar, using the LCAO-MO method. The first experimental proof was provided in 1963 by nuclear magnetic resonance (NMR) spectroscopic measurements (*6*).

Modern Theory of Color and Constitution

As a theory concerning only dye chemistry, the polymethine concept existed for four decades almost unnoticed side by side with resonance theory, which was widely applied in organic chemistry, and the theory of the energetically stabilized aromatic state. It was

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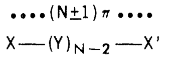
not until 1966 that the various theories were united by the concept of the existence of three ideal states of unsaturated organic compounds (*7-9*). An essential preliminary was the introduction of the modern notation **3** (*N* odd) for the general polymethine structural unit **2**, which represents a separate limiting structure within the framework of resonance theory. This made it possible, for instance, to extend the definition of a polymethine to colored organic radicals (**3**, *N* even) (*7, 10-12*), of which Wurster blue radicals are the best-known examples.



$$\overset{\cdots\cdots(N\pm1)\pi\cdots\cdots}{X—(Y)_{N-2}—X'}$$

3

In **3**, X, X′, and Y are elements of group IV, V, or VI of the periodic table; odd *N* corresponds to polymethine dyes; and even *N* corresponds to polymethine radicals.

The new interpretation was founded on the empirical deduction in 1966, based on Hückel molecular orbital (HMO) theoretical and experimental results, of an energetically stabilized ideal polymethine state, existing on a par with the energetically stabilized aromatic state (*9*). This brought theory back full circle to Ismailsky's chromo-state. Whereas resonance theory explained the color of organic compounds in terms of substituent effects in aromatic and polyenic basic structures, it is now possible to derive general relations between color and constitution on a physicochemical basis in terms of three ideal states: the aromatic state, the polymethine state, and the polyene state (*13*). This kind of interpretation was later justified by the results of Zahradnik (*14*), who obtained three different bonding types by comparing experimental and HMO-theoretical transition energies of several hundred unsaturated hydrocarbons.

The diversity of unsaturated organic compounds can be interpreted in terms of intermediates between these three ideal states. It was suggested that this approach be called triad theory (*13*), and the principles of this theory are shown schematically in Fig. 1.

The properties of the ideal aromatic state are reduced to those in Hückel's original definition. The state is characterized by a high degree of stability and very low chemical reactivity and is realized in cyclic hydrocarbons of ($4n + 2$) atoms. Typical features are identical π-bond orders between all atoms corresponding to a bond order of about 1½ and identical π-electron densities of approximately unity at all atoms.

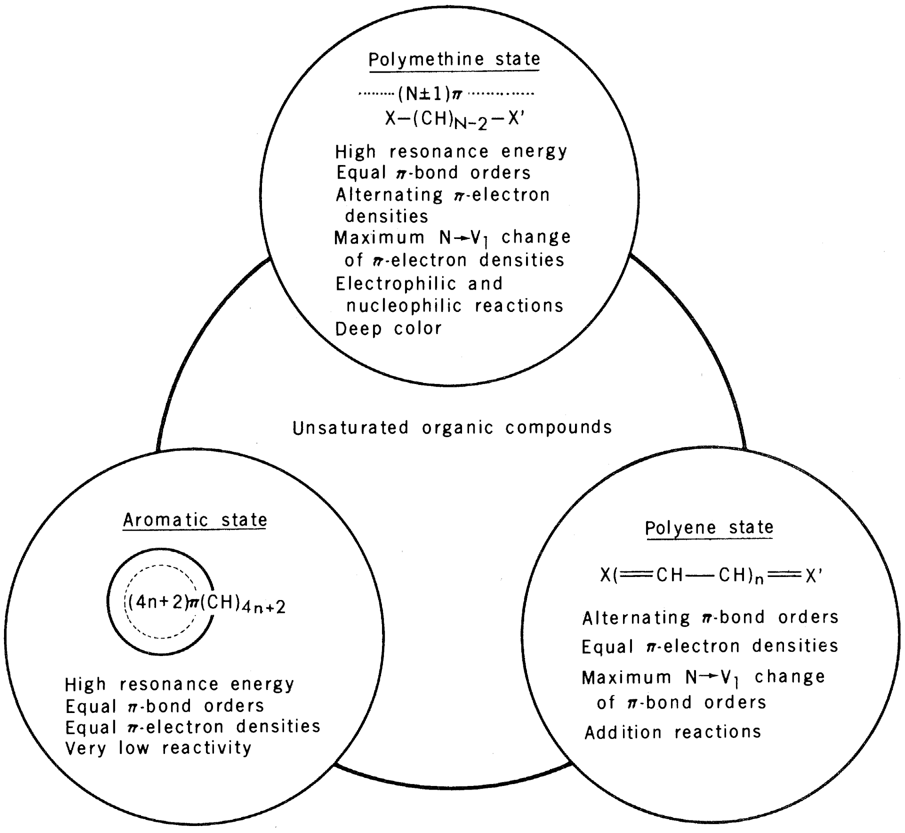


Fig. 1. Outline of the triad theory according to (*13*). The symbols are those used to date in the literature; *n* denotes zero and positive integers, and *N* stands for positive integers from 2 upward (see formula **3**).

The ideal polyene state is characterized by alternating double and single bonds in chain-shaped compounds which exhibit a relatively low degree of conjugation (resonance) in the ground state. On light absorption and transition from the ground state to the first excited singlet state ($N \rightarrow V_1$ in Fig. 1) a maximum change in the π-bond orders occurs such that double bonds acquire increased single-bond character and vice versa. Polyenes, like aromatics, have a π-electron density per atom of approximately unity. Because of their alternating π-bond orders, polyenes are destined for addition reactions.

The ideal polymethine state, like the aromatic state, is characterized by high resonance energy and identical π-bond orders of about 1½ attributable to a maximum delocalization of π-electrons in the ground state. In contrast to the aromatic state and the polyene state, polymethines feature a strongly alternating π-electron density distribution along the polymethine chain, which redistributes maximally on light excitation from the ground state to the first excited singlet state, in that atoms with a negative excess charge acquire a positive charge and vice versa. Because of the π-electron density alternation, polymethinic compounds preferentially enter nucleophilic and electrophilic substitution reactions (*15*). Where the numbers of π-electrons in compounds of comparable size are identical, compounds in the polymethine state will be deepest in color; that is, they combine a maximum transition probability (*16*) with a relatively low transition energy. Experimentally, cyanine dyes with an odd-numbered methine chain—for example, formula **3** with $N = 3, 5, 7, \ldots,$ and Y = (CH), symmetrically terminated by nitrogen atoms according to $X = X' = NR_2{}^{1/2\oplus}$—are particularly close to the ideal polymethine state.

According to the triad theory, in a particular unsaturated organic molecule as many independent, energetically stable, ideal polymethine or aromatic structural units (or both) are assigned as can be without branching of their conjugated system. Where for reasons of symmetry the conjugated system of the molecule is in fact branched, the ideal aromatic or polymethinic bonding system is weakened and polyenic structural units are formed with identifiable single- or double-bond character. Such bond variations can be described by the rule derived by K. Gebhard in 1911 and again by L. Pauling in 1947, according to which the sum of bond strengths of an atom is approximately constant (*17*).

Fabian and Hartmann (*10–12*) worked out a physical model for the ideal polymethine state which is very similar to the HMO model of the aromatic state. It is well known that unsaturated cyclic systems consisting of $2N$ carbon atoms (see Fig. 2) will be aromatic and thus energetically stabilized only if the number of atoms is $4n + 2$. Cycles consisting of $4n$ atoms are called antiaromatics. If we bisect a generalized ring system (either aromatic or antiaromatic), as illustrated in Fig. 2, and distribute the available $2N$ π-electrons unevenly over the two partial systems, we obtain two chain-shaped fragments of typical polymethinic character, one of which contains $(N + 1)$ π-electrons and the other $(N - 1)$ π-electrons. On bisecting aromatics with $(4n + 2)$ atoms, the two chains contain $2n + 1$ (odd) atoms and $2n$ or $2n + 2$ (even) π-electrons. These chain fragments correspond to the stable polymethine dyes. On the other hand, when antiaromatics with $4n$ atoms are bisected, the result will be chains with an even number of atoms and hence with an odd number of π-electrons. These compounds also have a deep color but are less stable; they are called polymethine radicals.

Recently Michl and Thulstrup (*18*), on the basis of a simple MO picture, explained the deep color of nonalternant hydrocarbons by the fact that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of such compounds are localized largely in different parts of space, while in aromatics and polyenes they are localized in the same part of space. This conclusion seems to be general as nonalternant hydrocarbons are polymethinic in structure (*9*).

As indicated in Fig. 2, the sectioning procedure can be simulated by factorization of the Hückel determinant of a cyclic hydrocarbon consisting of $2N$ atoms. In this way we also obtain the molecular parameters of the polymethine dyes and polymethine radicals as algebraic solutions in closed form which describe the experimental behavior of this class of compounds surprisingly well (*10–12*).

Verification and Theoretical Implications of the Polymethine Concept

Many experimental and theoretical studies have confirmed the concept of the ideal polymethine state and have led to a clearer understanding of the correlation between the color of unsaturated organic compounds and their constitution.

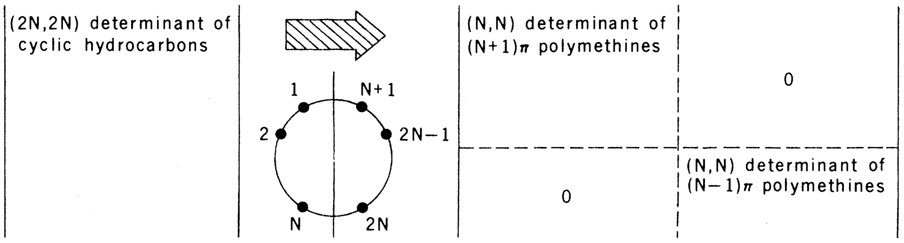
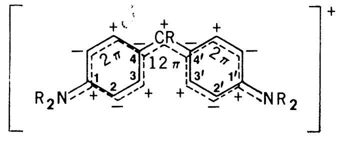


Fig. 2. Factorization of the Hückel determinant of a cyclic hydrocarbon consisting of $2N$ atoms (*11*). The symbols are those used to date in the literature; N stands for positive integers from 2 upward; $2N = 4n + 2$ for aromatics and $2N = 4n$ for antiaromatics.

The experimental work has led to the detection of a high resonance energy (*19*), to the electrochemical determination of relative orbital energies (*20*), and to the detection of an abnormally high electronic polarizability (*21*). Systematic x-ray structure analyses (*17, 22*) have not only confirmed the polymethinic bond lengths predicted by quantum chemical calculations but led to the discovery of interactions between π- and σ-electrons caused by polymethinic charge alternation (*23*). The structure analyses and carbon-13 nuclear magnetic resonance spectroscopy of organic dyes (*24*) have provided information about charge alternation and hybridization at the methine atoms. In this way it is possible to carry out detailed studies of the magnitude of charge alternation in polymethines and perturbations of this alternation in so-called nonalternant polymethines.

Theoretical work based on the polymethine concept. Qualitatively, the concept of alternant and nonalternant polymethines enables most organic dyes to be classified by their structural features (*25*). If charge alternation in a polymethine system is maintained on branching—for instance, in the diphenylmethane dyes (**4**)—then the resulting alternant polymethine will usually absorb at wavelengths slightly shorter than those of the unbranched basic chromophore. In addition, the bonds at branching points 1,1′ and 4,4′ are enlarged somewhat and hence the bond between C-2(2′) and C-3(3′) and the bond between C-5(5′) and C-6(6′) are shortened, according to Pauling's rule (*17*).



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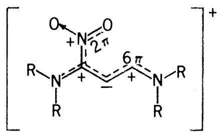
However, if the polymethinic charge alternation in a molecule is perturbed in such a way that two centers of high or low electron density lie close together, then we are concerned with nonalternant polymethines. The latter always absorb at much longer wavelengths than the constituent basic polymethine chromophores. Substituent effects, known as Witt-Dilthey-Wizinger's, Kendall's, Kauffmann's, and Caliezi's color rules, are part of the more general concept of alternant and nonalternant polymethines (*25*).

The alternating charge distribution can be perturbed, for example, by substitution of an electron acceptor for a positively charged methine atom, as in **5**, or by substitution of an electron donor for a negatively charged methine atom, as in **6**. Nonalternant polymethines with two or more polymethinic fragments have been called coupled polymethines (*8*). Examples are the aminoquinones **7** and numerous other quinone and indanthrone dyes in which coupling causes especially strong deepening of the color. Furthermore, because of the adjacent positive charges at C-1 and C-2 and at C-4 and C-5, the interatomic distances are larger than the normal single-bond distance between sp_2 hybridized methine atoms (*26*).



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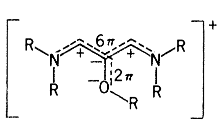

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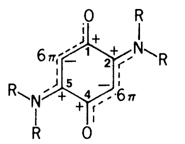

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Coupling between two polymethine fragments was first simulated by Leupold and Dähne (*27*), using HMO calculations. To describe light absorption by coupled polymethines, the resonance integral at the coupling bonds had to be appreciably less than the resonance integral of a polymethinic bond.

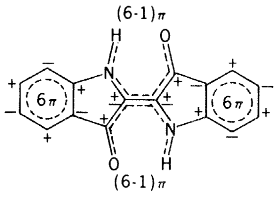
Fabian and co-workers (*12, 28*) found that the coupling concept follows from the HMO formalism. When the properties of unsaturated organic molecules are calculated by the same parametrization—that is, without regard to special structural features—it follows from configuration analyses that polymethinic and aromatic structural units are preferred. In fact, the calculated transition energy of the longest-wavelength absorption band is especially low in the case of nonalternant polymethines. Exceptions to this general color rule, however, will occur in a particular molecule whenever aromatic structural units are formed which compete successfully with the polymethine structure (*25*).

Other nonalternant polymethines with perturbed charge alternation have cross-conjugated or cross-coupled systems such as those which occur in indigo dyes. By linking together two polymethine structures through two or several common methine atoms, as in indigo (**8**), enlargement of the bonds is avoided while the strong bathochromic effect is maintained. As a result, these deeply colored indigoid systems are particularly stable.

Recently Hartmann (*29*) developed a more general physical model for describing relationships between color and constitution. The symmetry properties of the orbitals of structural fragments to be linked together in a larger chromophore enable us, by analogy with the Woodward-Hoffmann rules of reactivity, to predict in detail the shifts in color to be expected, as well as the relative orbital energies and hence the stability and reactivity of the systems. With perturbation theory, semiquantitative estimates can even be made. To illustrate this, formulas **9** to **11** show, respectively, a penta-, a hepta-, and a nonamethine fragment whose central methine atoms are linked together, forming a five-membered carbon ring.

It follows from the considerations in (*12, 29*) that the ground state in compounds **9** and **11** is destabilized on ring closure and light absorption is shifted bathochromically. Compound **10**, on the other hand, should be stabilized, with a hypsochromic shift in light absorption. Formally, all three models are nonalternant polymethines with a perturbed charge alternation, but in **10** an energetically stabilized, aromatic π-electron sextet (**10b**) competing with the polymethine structure can be formulated without double bonds emanating from the ring, which would counteract the trend toward aromatization. Consequently, only **9** and **11** represent nonalternant polymethines, whereas compounds of type **10** must be considered as substituted aromatics which absorb at relatively short wavelengths.

Studies of intermediates between ideal polymethines and ideal aromatics or ideal polyenes cover a wide field of modern color theoretical work. These intermediates can be produced by an increasingly unsymmetrical π-electron distribution within an ideal polymethine unit—for instance, by replacing one nitrogen atom at the chain end by an oxygen atom, as in **12** or **13**. Such intermediate structures exhibit all the features that would be expected—for instance, reduced charge alternation and a hypsochromic shift of the longest-wavelength absorption band in conjunction with a diminished polymethinic character. Especially in the polyenes of type **13b**, this is accompanied by growing bond alternation.



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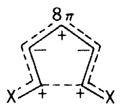

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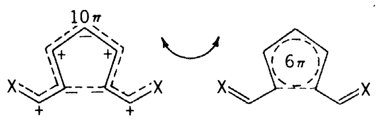
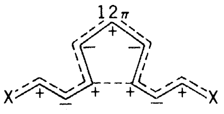


10a 10b



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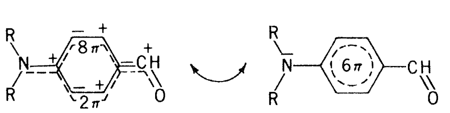
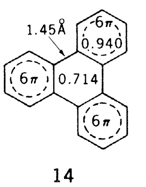


12a 12b

13a 13b



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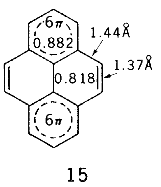

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Related Problems

Especially interesting and convenient for many purposes is the property of intermediate systems whose electronic structure—and hence their color—can be modified toward one or another ideal state by solvents of different polarity, as indicated in formulas **13a** and **13b**. This property is known in the literature as solvatochromism. Experimental evidence for such solvent-induced changes in the electronic structure in the ground state was provided by NMR spectroscopy (*30*). As early as 1939, a physical model for describing light absorption in such intermediates was developed by Förster (*31*) on the basis of the VB formalism. Recently, solvent-induced changes in color and electronic structure were simulated in microstructural models of solvatochromism based on self-consistent field LCAO-MO (PPP) calculations (*32*).

Although they are less relevant to color theory, similar approaches have been taken in the study of intermediates between aromatic and polyenic structures, on which extensive experimental data have been collected in the past 40 years, especially by Clar (*33*). As many as possible independent and energetically stabilized aromatic structural units are formed in an unsaturated hydrocarbon. Triphenylene, for instance, has structural features of the limiting structure **14**, while pyrene has structural features conforming to **15**, with bond lengths clearly differing in the less aromatic rings from those of benzene (1.39 angstroms).

This fact was represented in a physical model by Polansky and co-workers (*34*). The model was used to derive benzenoid and polyenoid characterograms by configuration analysis of the HMO wave functions. The closer the benzenoid character orders in **14** and **15** are to unity, the more pronounced is the aromatic character of the π-electron sextets.

Outlook

In the last 10 years new avenues have been opened up through which color theory can be integrated into the general theory of unsaturated organic compounds. At the beginning of the second century of a scientific theory of color, the experimental and theoretical equipment is available to elucidate the relationship between color and constitution and to classify unsaturated organic compounds according to general physicochemical properties.

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Chemical Ecology: Studies from East Africa

Interdisciplinary studies at the ICIPE laboratories in Nairobi are yielding exciting chemical results.

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The difficulties associated with the control of insect and other arthropod pests by means of conventional insecticides are widely recognized. Environmental pollution, lack of species specificity, and the development of resistant insect populations are among the main factors that make it highly desirable to develop new methods of pest control. A rational approach to this worldwide problem, however, requires a greater understanding than we now have of the physiology, ecology, behavior, and chemistry of insects. Many laboratories are engaged in research programs aimed at obtaining a more detailed knowledge of insect endocrinology; insect defense and communication systems are also receiving considerable attention. Work in these areas may ultimately provide the basis for new, biologically sound control techniques that utilize insect hormones and pheromones or their analogs. Perhaps an even more promising avenue of investigation involves the examination of plants for naturally occurring secondary metabolites that may have insect-repelling, insecticidal, antihormonal, or antifeeding characteristics on which novel ways to influence insect behavior or development (or both) might be based. From a chemical viewpoint, our knowledge of many of these areas is still in an embryonic state.

One important motive behind the founding of the International Centre of Insect Physiology and Ecology (ICIPE) was to establish an interdisciplinary laboratory where biologists and chemists from all over the world could collaborate on fundamental studies of arthropods, and concentrate chiefly on species of agricultural and medical importance. An equally important motive, however, was expressed by Djerassi just ten years ago (*1*). At that time, he put forward an intriguing model for the accelerated ad-

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