Translated from *Uspekhi Khimii*, **46**, 1835-1870 (1977) U. D. C. 539.199 + 541.655 + 541.67

The Electronic Structures and Properties of Polymeric Molecules with Conjugated Bonds

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Modern ideas about the electronic structure of the long molecules of polymers with conjugated bonds (CBP) are examined and their various physicochemical properties are discussed from the standpoint of these hypotheses.
The bibliography includes 162 references.

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I. INTRODUCTION

The modern theory of the electronic structure of molecules with conjugated bonds has had significant achievements in the qualitative and quantitative explanation of the properties of such systems. The possibility of applying semiempirical methods in order to explain and predict the properties of small molecules has been examined in reviews [1,2]. For large molecules (polymers), the employment of the usual quantum-chemical methods becomes impossible mainly owing to the large amount of computational work involved. On the other hand, methods usually employed in statistical physics and in solid-state physics are effective in such systems.

Large molecules have properties which their individual units or components do not possess [3]. Some of these properties are associated with the mechano-statistical properties of the macromolecular units joined together in succession and others are due to the continuous conjugated system or the appearance of long-range order. Irregularity of structure, defects, and heteroatoms have a considerable influence on the observed properties of large molecules and hinder their explanation.

In the present review, we shall consider the achievements and difficulties encountered in semiempirical theories when an attempt is made to explain and predict special properties (optical, magnetic, etc.) of long molecules of polymers with conjugated bonds (CBP). As for small molecules with conjugated bonds, the theoretical analysis of the properties of CBP macromolecules is based on the π-electron approximation using the corresponding model Hamiltonians [1,2].

Interest in long molecules with conjugated bonds has recently increased sharply after the work carried out by Little [4], who put forward the idea of synthesising on the basis of CBP an organic superconductor having a high critical temperature. These hopes were not fulfilled because CBP possess properties quite different from those postulated by Little. However, the idea of using organic compounds, one-dimensional and quasi-one-dimensional systems, in order to obtain substances with unusual properties is extremely fruitful. This is confirmed by the detection of metallic conduction in complexes of tetracyanoquinodimethane (TCNQ) with tetrathiafulvalene (TTF), *N*-methylphenazine (NMP), and alkali metals, for example TCNQ-TTF, NMP-TCNQ, Rb-TCNQ, etc. where the conduction is strongly anisotropic and takes place along stacks of TCNQ and acceptor species [5,6]. Stacks of identical molecules are weakly bound to one another, which makes it possible to employ for the analysis of such systems the same models as for CBP macromolecules. However, we may note that charge transfer in these donor–acceptor crystals leads to the need to take into account the Coulombic interaction throughout the bulk of the crystal. It has been found that the Coulombic energy of the crystals or the Madelung energy influences significantly the nature and degree of charge transfer from the donor to the acceptor [7,8], complicating the overall physical picture. Nevertheless, one-dimensional systems manifest their characteristic properties in any situation.

The unusual properties of CBP or quasi-one-dimensional systems are the first consequence of the "unidimensionality" of these systems. Naturally all such systems consist of three-dimensional atoms or molecules, so that the macromolecules or molecular stacks possess not only length but also "width" and "thickness". However, electrons or excitations (electronic or vibrational) in such systems can migrate only along a chain of atoms or a stack of molecules. Thus the motion of electrons or excitations is one-dimensional and in this sense the corresponding systems—macromolecules, chains of atoms, and stacks of molecules—are one-dimensional or quasi-one-dimensional. The prefix "quasi" emphasises that the systems are in fact three-dimensional, although

their most significant physicochemical properties are associated with the one-dimensional motion of electrons and excitations.

The limitations imposed on the number of spatial dimensions in which electrons or excitations can migrate diminish the number of possible situations and, in terms of the language of statistical physics, alter the phase volume. For example, when one electron is scattered by another, the electron moments before and after the collision are located on the same straight line. This finding permits the exact solutions for certain models of one-dimensional systems, since it is possible to recalculate all possible situations arising in the interaction of electrons.

The unidimensionality of the system leads to the appearance of interesting properties, which are much more rarely encountered in three-dimensional systems. A comparatively small number of quasi-one-dimensional systems, which manifested their unusual properties, as it were, at random, have so far been investigated. Now that the relation between the quasi-unidimensionality of the systems and their unusual properties has been understood, the problem arises of a purposeful search for and synthesis of quasi-one-dimensional systems and of the investigation of their properties. In the solution of this problem, theoretical ideas formulated at the present time will prove useful. They are in fact the main subject of the present review in relation to CBP macromolecules.

One-dimensional models have been fairly widely investigated in the theory of the condensed state of matter to test various theoretical constructions and approximations. Starting with the work of Bethe[9], Hulten[10], Orbach[11], and others[12,13], the investigators of one-dimensional models have been attracted by the possibility of obtaining exact solutions, so that these studies were in the main of methodological interest. However, the number of real one-dimensioal systems started to increase recently. Numerous CBP have been synthesised[14-17] and organometallic compounds with chains of metal atoms[18,19] and charge-transfer complexes based on TCNQ[5-8,20] have become available. Intensive investigation of the properties of polymers has begun; in particular the $-(SN)_n-$ polymer has been found to exhibit superconduction, albeit with a fairly low critical temperature ($T = 0.3$ K).[21] However, we may note that it became clear very soon that the polymeric sulphur nitride is not a quasi-one-dimensional crystal owing to the significant contribution of interchain interactions[22].

In the study of the properties of real quasi-one-dimensional systems, both the most rigorous and approximate methods have been used. The old theoretical results, which were seemingly obtained in the course of purely academic research, unexpectedly provided a key to the explanation of the properties of macromolecules which had been previously rejected. The sudden success of the theory can be explained or, more correctly, is associated with fairly general features of the development of modern science. On the one hand, physical chemistry accumulated numerous interesting facts about the properties of one-dimensional systems, mainly CBP molecules. In order to explain these facts, all the known concepts of quantum-chemistry were used, but they proved to be inadequate and we now understand that the reason is that the correct allowance for the interaction of electrons (electronic correlations) is the key factor in these problems. The problem of the interaction of electrons has been usually solved in quantum chemistry for small molecules and the consequences of allowing for the interaction of electrons in macromolecules, for which semi-empirical versions of the self-consistent field (SCF) approximation were usually employed, were not evident. On the other hand, various models for one-dimensional systems have been discussed for a long time in theoretical physics in order to discover the qualitatively new features resulting from a more accurate allowance for the interaction of electrons. These models have names which are fairly unusual for chemists and even quantum chemists: the Ising model, the Heisenberg chain, the spin Hamiltonian... For a long time, the results of these two groups of investigations were published independently in the form of two separate streams of informations addressed to different scientific circles. In the middle 1960s, these two streams finally combined and, as a result, it was possible to achieve considerable progress both in the solution of exact problems and in the explanation and prediction of physicochemical properties. This process has continued, since it became possible to synthesise specific substances with unusual properties.

In order to create quasi-one-dimensional systems and new types of polymers, it is necessary to employ the rich experience gained in modern organic chemistry. For this purpose, one must begin at least with the formulation of a general scientific view concerning the problem as a whole. At the present time investigators prefer to work on "projects", whose likely outcome is known *a priori*. We believe that in such a situation the synthesis of a one-dimensional or quasi-one-dimensional compound is a still more favourable project, because one is very likely to obtain a substance with unusual properties.

An interesting example is the observation of the very high hyperpolarisability $\chi^{(3)}$ of single crystals of polydiacetylene (PDA), which makes the substance very promising for use in non-linear optics and laser engineering[23]. PDA single crystals are large, contain no amorphous phase, and are almost free from defects and impurities[24,25], which is to a large extent caused by the method of their synthesis by solid-phase polymerisation from the crystalline phase of the initial monomers at a moderate temperature[26].

Returning to the problem of the electronic structure of CBP, one should note that the description of this problem in Soviet and foreign literature lags far behind the actual present level of its understanding. This is due to a phenomenon, familiar in science, where whole blocks of references are transferred from one source to another when books, papers, and handbooks are written, which temporarily protects the given research field from being penetrated by new concepts and ideas. One of the aims of the present review is to shorten this period.

II. THE EVOLUTION OF VIEWS ON THE STRUCTURE OF CBP MACROMOLECULES

The first quasi-one-dimensional object investigated was a polyene chain, to which the theoretical studies by Lennard-Jones[27] and Coulson[28] were devoted. At that time it was known that the bond lengths in short polyenes alternate in accordance with the familiar Kekulé structures. The problem of whether the alternation of bond lengths in the polyene persists with increase of its length or whether the bond lengths become equalised, formulated in the above investigations, was solved using the "bond length–bond order" formula obtained by Lennard-Jones[27] in terms of the Hückel molecular orbital approximation for π electrons,

taking into account the elasticity of the σ skeleton [the Hückel–Lennard-Jones (HLJ) approximation].

At the same time Broocker and coworkers[29-35] investigated the absorption spectra of compounds with polyene chains, which made it possible to establish[36] the following relations. In the spectra of symmetrical cyanine dyes with an odd number of carbon atoms in the polyene chain, the wavelength of the first electronic transition increases by $\lambda_C = 1000 \pm 50$ Å following the addition of each CH=CH group to the polyene chain. This "red" shift does not diminish with increase of the length of the polyene chain, so that the energy of the first optical excitation ΔE tends to zero with increase of the length of the polyene chain. On the other hand, in asymmetric dyes with an even number of carbon atoms in the main conjugation chain and in polyenes with an even number of atoms, the intense optical absorption band ceases to shift with increase of the conjugation length, so that ΔE tends to a finite limit. The limiting value for polyenes $\Delta E_\infty \simeq 2.25$ eV (Fig. 1) has been obtained by extrapolating data obtained in studies on linear polyenes and annulenes[37-40].

The behaviour of ΔE for symmetrical dyes appeared natural from the standpoint of the molecular orbital method[41,42] or the metallic model[43,44]. According to these ideas, the distance between the levels and hence ΔE is inversely proportional to the chain length and a satisfactory theoretical estimate of the "red" shift was obtained: $\lambda_C \simeq 900$ Å.[32,43,44] From this point of view, the finite value of ΔE_∞ for polyenes and asymmetric dyes was completely incomprehensible. This constituted a serious theoretical problem, since it did not concern a hypothetical infinite polyene, as in the earlier investigations[27,28], but real molecules with finite dimensions: a limiting value of $\Delta E(N)$ was approcched when the number of atoms was $N \simeq 10$–12 (Fig. 1).

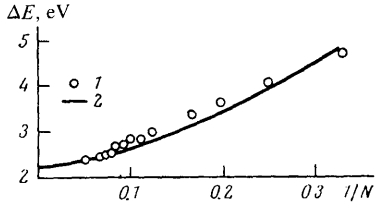


Figure 1. Dependence of the energy of the first electronic transition ΔE on $1/N$ in the polyene $(CH)_{2N}$: 1) experimental values[37]; 2) line drawn through points calculated by Eqn. (14).

The hypothesis of the alternation of bond lengths as the cause of the appearance of a ΔE_∞ gap in the spectra of excited polyenes was put forward for the first time by Kuhn[43,45,46], who proposed a model in which the non-interacting π electrons migrate in a field with a sinusoidal potential, the minima of which correspond to the region of double bonds. By selecting a parameter V_0 associated with the amplitude of the potential, it was possible to make the ΔE–N relation consistent with experiment. However, it remained obscure which factors distinguish the double bonds in the chain. If we note that the early investigations[27,28] indicated that the bond lengths in an infinite polyene are equalised (a result which appeared erroneous in the light of the above ideas), then, apart from the intuitive feeling associated with Kekulé structures, there is no reason why the double bonds should be distinguishable. The problem of bond lengths in a polyene was soon solved in terms of the SCF approximation[47]. It was found that in the HLJ model[27,28] a long polyene with equal bond lengths passes to the energetically more favourable state with alternating bond lengths, provided that $N > N_{cr}$, where N_{cr} depends on the model parameters.

In terms of the Hückel approximation, the energies of the molecular orbitals of π electrons are given by

$$\varepsilon_n = \alpha_0 + 2\beta_0 \cos\frac{\pi n}{N}, \quad n = -N+1, \ldots, N, \tag{1}$$

where α_0 is the Coulomb integral and β_0 the resonance integral for the C–C bond. The total energy of the molecule is

$$E = E_\pi + E_\sigma,$$

where the energy of the σ skeleton is additive with respect to the bonds:

$$E_\sigma = \sum_l E_{\sigma l}$$

and the energy of π electrons is given by

$$E_\pi = 2\sum_{n=-\nu}^{\nu} \varepsilon_n, \quad \nu = \frac{N-1}{2}.$$

The number of levels (1) is equal to the number of π electrons, so that in the ground state exactly half of the band defined by Eqn. (1) is occupied by two electrons in each molecular orbital. When the bond lengths alternate, the energies of the occupied molecular orbitals diminish and those of vacant orbitals increase, so that a gap ΔE_{alt} appears and E_π decreases. However, under these conditions E_σ increases because of the necessity to expend work against the elastic forces of the σ skeleton during the extension and construction of bonds. As a result, the total energy minimum is reached for certain values of the alternating bond lengths. In the solid state theory, the alternation of bond lengths in a one-dimensional metal became known as the "Peierls theorem"[48]. In quantum chemistry, this result has been formulated in relation to polyenes[49-51].

In the light of the above ideas, it was natural to identify the optical gap with the gap obtained as a result of alternation:

$$\Delta E_\infty = \Delta E_{alt}. \tag{2}$$

This view has been reflected in monographs[14-17,39] and became firmly established in the literature on CBP for a long time.

We may note that the alternation of bond lengths in the SCF or HLJ model is only fortuitously consistent with the ideas in theoretical chemistry on the alternation of double and single bonds. In fact, the bonds alternate (in the given models) because the number of π electrons is equal to the number of atoms and the polyene π band (1) with equal bond lengths is exactly half-filled; for this reason the gap ΔE_{alt} arises precisely above the filled band with a reduction of the energy of the latter, which is energetically favourable. If the polyene π band (1) was one-third or two-thirds filled, then the state in which groups of three different bonds alternate forming three bands with a gap above the filled band, etc. would have become favourable for the same reasons. This problem has been investigated by the present authors[52].

In terms of the Hückel approximation, the spectrum of the molecular orbital energies of the polyene $(CH)_2N$ with alternating bond lengths (we shall consider a cyclic model to avoid the complication due to end effects) has the following form:

$$E_{\pm}(k) = \alpha_0 \pm |\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(\pi k/N)|^{1/2} \quad -\nu \leqslant k \leqslant \nu, \quad \nu = (N-1)/2, \tag{3}$$

where β_1 and β_2 are two resonance integrals corresponding to short and long bonds. In the ground state, the $E_-(k)$ levels are twice filled [with the minus sign before the root in Eqn. (3)], so that the gap is given by

$$\Delta E_{alt} = 2\,|\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(\pi\nu/N)|^{1/2} \simeq 2\,|\beta_1 - \beta_2|$$

for $N \to \infty$. Since the differences between the bond lengths are small ($R_2 - R_1 \simeq 0.04$ Å),[47,51] β_1 and β_2 can be expressed approximately in terms of the following expansions:

$$\beta_1 = \beta(R_1) = \beta_0 + \beta'\Delta R + \beta''\Delta R^2/2,$$
$$\beta_2 = \beta_0 - \beta'\Delta R + \beta''\Delta R^2/2,$$

where

$$\Delta R = R_2 - R_0 = R_0 - R_1, \quad \beta' = (\partial\beta/\partial R)_{R=R_0},$$
$$\beta'' = \left(\frac{\partial^2\beta}{\partial R^2}\right)_{R=R_0}$$

and R_0 is an average length equal to the C–C bond length in benzene. Then

$$\Delta E_{alt} = 2\,|\beta_1 - \beta_2| = 4\beta'\Delta R. \tag{4}$$

The main idea of the critical analysis of the scheme with alternation, carried out by the present authors[52-54], involved a test of the theory for the consistency of the semiempirical parameters. According to the alternation hypothesis (Eqns. (2) and (4)], ΔE_∞ is expressed in terms of β', i.e. it depends on the form of the function $\beta(R)$. In vibrational excitations of molecules, the bond lengths also change, so that the vibration frequencies of molecules with conjugated bonds depend on the form of the same function $\beta(R)$. In order to secure information about the real parameters, expressions were obtained[53] for six frequencies of the in-plane vibrations of benzene in terms of three parameters of the HLJ model. Comparison with the experimental frequencies makes it possible to find these three parameters quite reliably: two elastic constants—for the extension of the bond (k_1) and the changes in the angle between adjoining bonds (k_2)—and (the third constant) the ratio

$$\beta'^2/\beta_0 = -1.23 \cdot 10^5 CGSE = -7.7 \text{ eV Å}^{-2}.$$

For the generally accepted value $\beta_0 = 2.4$ eV, we obtain $\beta' = 4.3$ eV Å^{-1}. This value of β' agrees with X-ray diffraction data for bond lengths in conjugated molecules. Indeed, the following formula has been obtained[54] in terms of the same approximation for the C–C bond in a conjugated molecule:

$$R = R_0 - \frac{2\beta'}{k_0 + 2\beta''P} P, \tag{5}$$

where P is the π-electron bond order, R the bond length, k_0 the elastic constant of the σ bond, and R_0 a constant. This formula is virtually identical with the familiar Coulson formula[55]

$$R = 1.517 - 0.18P, \tag{6}$$

which has been used effectively in calculations on conjugated systems. The coefficient 0.18 in Eqn. (6) is obtained from Eqn. (5) for $P \simeq 2/3$, $\beta' \simeq 4.3$ eV Å^{-1}, and $k_1 = k_0 + 2\beta''P \simeq 47.5$ eV Å^{-2}.

As a result, we obtain from Eqn. (4) $\Delta E_{alt} \simeq 0.3$ eV, which is smaller by a factor of ~10 than the experimental value of ΔE_∞ for polyene. This result can be understood on the basis of simple qualitative considerations: the energies associated with the distortion of bond lengths with alternation must be comparable in order of magnitude to the vibration energies, i.e. must amount to a fraction of an electron-volt. The above analysis shows that the considerable magnitude of the gap in the spectra of polyenes ($\Delta E_\infty \simeq 2.2$ eV) cannot be associated with the interactions of electrons with atomic vibrations and rearrangements of atomic configurations. At the same time, the necessity arises for the employment of a self-consistent set of semiempirical parameters. All these factors make it possible to interpret correctly the results obtained by methods more rigorous than the HLJ approximations. For example, in calculations of the first transition energies in a polyene[56], the Pariser–Parr–Pople (PPP) approximation was used, while another study[57] involved a method taking into account a limited number of excited configurations. A satisfactory agreement with experiment for the $\Delta E - N$ relation for polyenes with alternating bond lengths was achieved in this case using parameters which had not been adjusted for consistency with experiments on vibrations and with structural data. The same inconsistency between the parameters is characteristic of studies[16,58] where a semiempirical version of the SCF method was used to calculate the band structure of polyenes. Here too the agreement between the calculated energy gap and experiment did not demonstrate the validity of the alternation hypothesis.

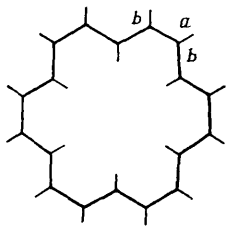


Figure 2. 18-Annulene. The group of three bonds *b*, *a*, *b* is repeated.

Analysis of experimental and calculated data for 18-annulene (Fig. 2) provided evidence against the alternation hypothesis. According to X-ray diffraction data[59], in this molecule 12 "inner" bonds have the length $b = 1.382 \pm 0.003$ Å and six outer bonds have the length $a = 1.419 \pm 0.004$ Å, i.e. a group of three bonds is repeated periodically and not a group of two, as in alternation. For such a structure, there is no gap in the spectrum, since among the three π-electron bands, the middle one is half-filled[52]. Nevertheless, the energy of the first transition in $C_{18}H_{18}$, which is $\Delta E = 2.77$ eV,[39,60] does not divide from the general relation (Fig. 1). Calculations by the PPP method, taking into account a large number of excited configurations, could not explain the observed absorption spectrum of 18-annulene; the energy of the first transition was much lower than the experimental value[60]. This did not naturally imply that the PPP method is inapplicable to many-electron molecules. Calculations on the spectra of coronene (24 π electrons) and ovalene (32 π electrons) by

the PPP method yielded excellent results[61]. It now became clear that the cause of the failure of the calculations on the spectrum of 18-annulene was that electron correlations are significant in one-dimensional chain molecules, and these are not taken into account in any way in the PPP method, where the ground state is described, as in the SCF or Hückel method, by a single configuration of π electrons. The example of 18-annulene also showed that structural factors (bond lengths) do not have a significant influence on the energies of electronic optical excitations.

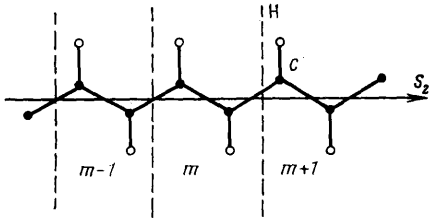


Figure 3. Schematic illustration of a polyene. The (...m – 1, m, m + 1,...) cells into which the polyene was divided in the calculation in Ref. 62 and the mirror-rotational twofold symmetry axis S_2 are shown.

In conclusion of this section, we shall discuss the unexpected result obtained by Andre and Leroy[62], who investigated the electronic structure of a polyene by the SCF method taking into account all the valence electrons (the *ab initio* method in terms of the Hartree–Fock approximation). For a given polyene chain with equal C–C bond lengths, two π electron bands were obtained (filled and vacant), separated by a gap of ~4 eV. This result, obtained *ab initio* from analytical basis functions in conjunction with computer calculations in accordance with a specified program, commanded respect and gave rise to the hope that latent causes exist for the appearance of ΔE_∞, which were overlooked in simpler semiempirical calculations. The authors[62] carried out calculations on a polyene with a structure close to the real structure taking into account hydrogen atoms (Fig. 3). The question arises if the cause involved the allowance for the interaction with the hydrogen atoms or the unusual structure of the real polyene. As frequently happens, numerical calculations did not provide an answer to such questions. The doubts were resolved in an elegant study by Ukrainskii [63], who analysed the method of calculation used by Andre and Leroy[62]. It was found that the latter workers artificially subdivided the polyene into CH–CH cells (Fig. 3) and, having specified the limiting distance for which the computer program no longer took into account the Coulombic interaction between the electrons, the computation was based on the number of neighbouring cells (in particular, it was restricted to three or five neighbouring cells). This condition artificially infringed the actual symmetry of the interaction and was equivalent to the superposition of an effective external field having a period with respect to the cells, which led to a pattern with two π-electron bands. The analysis showed[63] that the polyene illustrated in Fig. 3 possess a mirror-rotational twofold axis and that, in terms of the SCF approximation, the π bands (filled and vacant) in a long polyene should adjoin in this case. In order to obtain this result, the authors[62] should have taken into account in their calculation a much larger number of neighbouring cells, since the Coulombic interaction weakens very slowly over large distances.

III. THE INTERACTION BETWEEN ELECTRONS AND THE NATURE OF THE GROUND STATE OF CBP MACROMOLECULES

In a number of studies, an attempt was made to attribute the pronounced maximum in the absorption spectra of polyenes to the plasma vibrations of π electrons. A large system with a regular structure can be excited to a state with regular changes in electron density at the atoms, which are characterised by a spatial period (wavelength) and frequency (energy) of the vibrations, referred to as the plasma vibrations. From the standpoint of the methods of quantum chemistry, plasma excitations are not fundamentally new types of excitations: their energies may be calculated in terms of the PPP approximation. Since the latter is fairly cumbersome when applied to large systems, other methods are effective in this instance: the random phase approximation (RPA), methods involving density matrices or Green functions, etc. The considerable similarity of the PPP and RPA approximations was discovered in calculations on small molecules where both approximations led to virtually identical energies and oscillator strengths for the excited states[64]. The relation between the PPP method and the plasma or RPA approximation has been analysed by Mestechkin[65].

It has been found[66,67] that, in one-dimensional systems of the type of polyene, the plasma vibration frequencies start from zero (in a polyene with equal bond lengths) or from the gap ΔE_{alt} (in a polyene with alternation). The specific features of one-dimensional systems were manifested by the absence of distinct plasma vibration frequencies, in contrast to a three-dimensional metal, where the plasma vibration frequencies have energies of the order of several eV and can be distinguished from other excitations. The calculations[66,67] were based on the SCF approximation for the ground state, which predetermined the resulting spectrum of plasma excitations.

The study of spin excitations in a polyene, where the spin density changes regularly at the atoms (the π-electron density remains unity) revealed the instability of the SCF state of the system in relation to the transition to an energetically more favourable state with alternating spin densities at the atoms[68]. In order to describe such a state, it was necessary to go outside the framework of the SCF approximation or the Hartree–Fock approximation in which two electrons with opposite spins occupy the same molecular orbital. Quantum chemistry already had at its disposal the corresponding approximate methods, but these were used mainly for the calculation of spin densities in radicals[2]. We have in mind primarily the method of alternant molecular orbitals (AMO) proposed by Löwdin[69,70] for the calculation of the electronic structures of molecules and crystals. The ideas concerning the distribution of electrons with different spins in different molecular orbitals used by Löwdin were applied for the first time by Hyleraas[71] in calculations on the helium atom and by Weinbaum[72] in calculations on the hydrogen molecule. The AMO method is also known as the method of different orbitals for different spins (DODS).[73] The DODS and AMO methods have been used in various calculations of the

electronic structures of solids [74-78] and conjugated systems [2,79]. The relation between the AMO method and the method of geminals was analysed by Kapuy [80]. Certain aspects of these methods have been discussed by Larson [81,82]. In all methods of the AMO type, allowance for the Coulombic repulsion of two electrons with different spins in the same atom is important. As a result, electrons with different spins "avoid" one another, which reduces the energy and favours the appearance of a spin structure of the antiferromagnetic type.

A generalised Hartree–Fock method (GHFM), which is a version of the AMO method adjusted for self-consistency, has been proposed [83,84] for the investigation of the electronic structures of long molecules with conjugated bonds. The Hamiltonian of the system of π electrons for a cyclic polyene $(CH)_{2N}$ has the following form in terms of secondary quantisation†:

$$H_{\text{Hub}} = \alpha_0 \sum_{n\sigma} c^+_{n\sigma} c_{n\sigma} - \beta \sum_{n\sigma} (c^+_{n\sigma} c_{n+1,\sigma} + c^+_{n+1,\sigma} c_{n\sigma}) + \frac{\gamma}{2} \sum_{n\sigma} c^+_{n\sigma} c_{n\sigma} c^+_{n,-\sigma} c_{n,-\sigma}. \quad (7)$$

Here α_0 is the Coulombic integral in the Hückel method, $-\beta$ the resonance integral of the C–C bond ($\beta > 0$), $\gamma < 0$ the parameter of the Coulombic repulsion of two π electrons in a single carbon atom, and $c^+_{n\sigma}(c_{n\sigma})$ are the operators for the generation (annihilation) of an electron in the nth atom in the state with the $\varphi_n(r)$ basis function and the spin $\sigma = \pm 1/2$. The Hamiltonian defined by Eqn.(7) is called Hubbard's Hamiltonian [85] and differs from the PPP Hamiltonian defined by Eqn. (17) by the absence of terms with long-range Coulombic interaction. The use of Hubbard's Hamiltonian [Eqn. (7)] leads to a qualitatively correct description of the properties of polyene, although allowance for long-range Coulombic interaction may be important for other systems [86] (see Section VI below).

In terms of the GHFM approximation with the Hamiltonian defined by Eqn. (7), the variational wave function for the ground state of the polyene depends on the single variational parameter δ and has the following form:

$$|\Phi\rangle = \prod_{\sigma,|l|\leqslant\nu} f^+_{l\sigma} |0\rangle, \quad f^+_{l\sigma} = c^+_{l\sigma} \cos\theta_l + \lambda(\sigma)\, a^+_{l+N\sigma} \sin\theta_l, \quad (8)$$

where θ_l is defined by the formula

$$\sin 2\theta_l = \gamma\delta / [(\gamma\delta)^2 + 4\beta^2 \cos^2(\pi l/N)]^{1/2}.$$

The operators $f^+_{l\sigma}$ correspond to the generation of an electron in the molecular orbital specified by the GHFM and are expressed in terms of the operators $a^+_{l\sigma}$ for the generation of an electron in the molecular orbital specified in the SCF approximation, the latter orbitals having the following form:

$$\psi^l_\sigma(r) = \frac{1}{\sqrt{2N}} \sum_n \exp(i\pi l n/N)\, \varphi_n(r)\sigma,$$

where δ is the spin function. The operators $a_{l\sigma}$, $c_{n\sigma}$, and $f_{l\sigma}$ are related by the following expressions:

$$c_{n\sigma} = \frac{1}{\sqrt{2N}} \sum_l \exp(i\pi l n/N)\, a_{l\sigma},$$
$$c_{n\sigma} = \sum_{l=-\nu}^{\nu} c^l_{n\sigma} f_{l\sigma} + \sum_{l=-\nu}^{\nu} c^{l+N}_{n\sigma} f_{l+N,\sigma}, \quad (9)$$
$$\nu = \frac{N-1}{2}.$$

†There are a few explanatory comments on secondary quantisation in quantum chemistry in the present authors' previous review [1].

Here the coefficients $c^l_{n\sigma}$ and $c^{l+N}_{n\sigma}$ are defined by the formulae

$$c^l_{n\sigma} = \frac{1}{\sqrt{2N}} [\cos\theta_l \exp(i\pi l n/N) + \lambda(\sigma) \sin\theta_l \exp(i\pi n(l+N)/N)],$$
$$c^{l+N}_{n\sigma} = \frac{1}{\sqrt{2N}} [-\lambda(\sigma) \sin\theta_l \exp(i\pi n l/N) + \cos\theta_l \exp(i\pi n(l+N)/N)], \quad (10)$$

where $\lambda(\sigma) = 2\sigma$ ($\sigma = \pm 1/2$), which corresponds to the ground state with alternation of spin densities at the atoms; the spin density at the nth atom is

$$\langle\Phi| (c^+_{n,1/2} c_{n,1/2} - c^+_{n,-1/2} c_{n,-1/2}) |\Phi\rangle = -(-1)^n 2\delta. \quad (11)$$

This state will be conventionally referred to as the state with spin waves (SW). As will be shown below (Section III), in a long polyene this state has an antiferromagnetic spin structure, although the spin densities at the atoms disappear after the projection of the function (8) on the state with the total spin $S = 0$.

When $\lambda(\sigma) = 1$, Eqns. (8)–(10) define the state which we shall conventionally call the state with charge waves (CW). It may become the ground state for quasi-one-dimensional systems when account is taken in the Hamiltonian of terms with γ_{mn}, which will be described below (in Section VI).

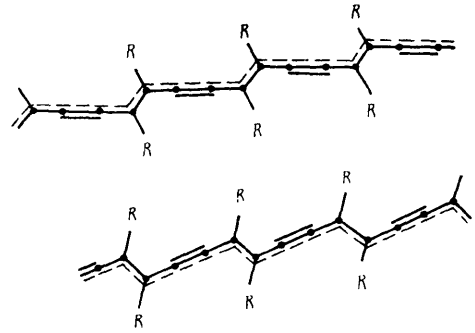


Figure 4. Schematic illustration of continuous conjugation (dashed lines) in the macromolecules of a polydiacetylene single crystal. The additional continuous lines indicate triple bonds.

The parameter δ for the polyene is determined from the equation

$$\frac{p}{2N} \sum_{l=-\nu}^{\nu} [(p\delta)^2 + \cos^2(\pi l/N)]^{-1/2} = 1, \quad p = \gamma/(2\beta), \quad (12)$$

which always has a solution $\delta \neq 0$. The molecular orbital energies are given by an expression of the type

$$E_{l\sigma} = \alpha_0 + \gamma/2 \pm [(\gamma\delta)^2 + 4\beta^2 \cos^2(\pi l/N)]^{1/2}. \quad (13)$$

In the ground state, all the levels are filled, which corresponds to the minus sign before the root in Eqn. (13), so that the energy of the first electronic transition assumes the following form in terms of the GHFM approximation:

$$\Delta E(N) = 2[(\gamma\delta)^2 + 4\beta^2 \cos^2(\pi\nu/N)]^{1/2}. \quad (14)$$

When $\beta = 2.4$ eV and $\gamma = 5.42$ eV, Eqn. (14) describes satisfactorily the energies of the first transitions in polyenes (Fig. 1). The value of γ adopted is smaller by a factor of ~2 than that of γ_{nn} in the PPP method, which is a consequence of the use of the approximation $\gamma_{mn} = 0$ (see Section VI). It follows from Eqn. (14) that $\Delta E_\infty = 2\gamma\delta$ when $N \to \infty$.

Recent experiments on the absorption of light by polydiacetylenes (PDA)[87] showed that $\Delta E_\infty \simeq 2$ eV for these polymers, which is in full agreement with the fact that the PDA macromolecule is in essence a polyene chain in which each fourth bond is somewhat shortened and close in properties to a triple bond (Fig. 4) owing to the presence in this bond of an additional pair of π electrons in a molecular orbital at right angles to the polyene π-electron system corresponding to continuous conjugation in the polymer. The shortening of the individual bonds does not affect the nature of the ground state and the CBP absorption spectra, which is confirmed yet again by the example of PDA.

The optical gap ΔE_∞ in the absorption spectrum is virtually identical with the activation energy or the semiconductor gap of the CBP. For polymers of the type of a polyene[88] and crystalline PDA[89], it was found that the electrical conductivity Ω has a temperature dependence typical for an intrinsic semiconductor:

$$\Omega = \Omega_0 \exp(-E_{act}/(2kT)),$$

with an activation energy $E_{act} \simeq \Delta E_\infty \simeq 2$ eV. The activation energy for photoconduction in PDA[89] is also close to ΔE_∞.

IV. THE SPIN STRUCTURE OF CBP MACROMOLECULES

In the discussion of the spin properties of CBP, we shall note in the first place that the function of the π electrons of the polyene $|\Phi\rangle$ [see Eqns. (8)–(10)] with $\lambda(\sigma) = \sigma$ is an eigenfunction of the operator of the z-component of the total spin $\hat{S}_z$ with the eigenvalue $S_z = 0$, but is not an eigenfunction of the operator of the square of the total spin $\hat{S}^2$. This is a deficiency of the approximation, because the ground state should have a definite spin and, as a rule, this spin is zero (the singlet state). The average values of the components of the total spin in the $|\Phi\rangle$ state are zero:

$$\langle\Phi|\hat{S}_x|\Phi\rangle = \langle\Phi|\hat{S}_y|\Phi\rangle = \langle\Phi|\hat{S}_z|\Phi\rangle = 0,$$

but the average value of the square of the total spin is not zero[90]:

$$\langle\Phi|\hat{S}^2|\Phi\rangle \sim N.$$

One can say that in this sense $|\Phi\rangle$ is a state isotropic with respect to spin but not a singlet state. The variational solution for $|\Phi\rangle$ is close to the exact state with respect to energy (see Section VIII) and, in order to make it close to the exact state with respect to spin properties, it is necessary to project $|\Phi\rangle$ on to the state with the spin $S = 0$ or to isolate from $|\Phi\rangle$ the component with the total spin $S = 0$. This can be done in various ways[90–92]. The function $|\Phi_0\rangle$, which depends on a single parameter δ_0 and has a more complex form than $|\Phi\rangle$, has been obtained[90,91]. It was found that in the $|\Phi_0\rangle$ singlet state the total energy, δ_0 and the gap in the spectrum ΔE_∞ differ from the corresponding values for the $|\Phi\rangle$ state only by an amount $\sim 1/N$ for high values of N. It is important to know this in calculations, which can be carried out much more simply with a function of the $|\Phi\rangle$ type. However, the spin properties of the $|\Phi_0\rangle$ and $|\Phi\rangle$ states differ to a greater extent. The spin densities at the atoms in the $|\Phi_0\rangle$ state are zero, so that we have instead of Eqn. (11)

$$\langle\Phi_0|(c^+_{n,1/2}c_{n,1/2} - c^+_{n,-1/2}c_{n,-1/2})|\Phi_0\rangle = 0.$$

Nevertheless the $|\Phi_0\rangle$ singlet state will have an antiferromagnetic spin structure. This is because the average value of the spin correlation operator

$$\hat{K}(m) = \frac{1}{N}\sum_{n=1}^{2N}(\hat{S}_n\hat{S}_{n+m}),$$

where $\hat{S}_n$ is the spin operator at the n^{th} atom, or the spin correlation function

$$K(m) = \langle\Phi_0|\hat{K}(m)|\Phi_0\rangle/\langle\Phi_0|\Phi_0\rangle$$

exhibit the following asymptotic behaviour when $m \to \infty$:

$$K(m) \simeq (-1)^m\delta^2.$$

This result indicates the presence of long-range antiferromagnetic spin order in a long polyene. We may note that the correlation function $K(m)$ has the same form for the $|\Phi\rangle$ and $|\Phi_0\rangle$ states[90,91].

A few other comments may be made concerning the unusual properties of antiferromagnetism in general and for organic molecules in particular. If we consider a small molecule (H_2, benzene, etc.), the corresponding correlation function $K(m)$ will be non-zero for any value of m and in any approximation (ranging from the SCF approximation to the exact solution). This demonstrates simply the presence of spin correlation in the molecules, if only as a consequence of the Pauli principle. However, whatever the form of $K(m)$, it would be incorrect to speak of antiferromagnetism in such small molecules, because antiferromagnetism is in essence a property of a large and even infinite system with a regular steric structure when the spin structure is characterised by an antiferromagnetic long-range order. For example, when $K(m) \simeq (-1)^m \times$ const. for $m \to \infty$ in a system as large as in our case, we have an antiferromagnetic long-range spin order. For $K(m) \simeq$ const. and $m \to \infty$, we would have a ferromagnetic long-range spin order. The case where $K(m) = 0$ for $m \to \infty$ corresponds to the state without a spin structure and without a long-range spin order.

It would be incorrect to assume that the antiferromagnetic spin structure in long polyenes and other CBP macromolecules appears as a result of the application of the AMO method for which such a structure is typical. The AMO method is not optimal for the description of any alternant system with conjugated bonds. The method leads to a decrease of energy only for small molecules (where the concept of antiferromagnetism has no significance) or for large quasi-one-dimensional systems of the type of polyene, polyacene, etc. (see Section VII below). For the two-dimensional network of graphite the AMO state is unfavourable as regards energy[93]. For two- and three-dimensional systems, the parameters of the Hamiltonian defined by Eqn. (7) must satisfy very rigorous requirements to make a state of the AMO type favourable. These conclusions are in full agreement with the finding that in nature antiferromagnetism is an exception rather than the rule and at the same time leads to the conclusion that antiferromagnetism is a property characteristic of quasi-one-dimensional systems.

For small molecules, the state with a function of the AMO type is energetically favourable mainly as a consequence of the spin projection procedure. For example, the AMO state for H_2 or for the ethylene π electrons is favourable only when special relations obtain between the parameters of the Hamiltonian, while the energy of the state with a singlet component of the AMO function for these molecules is always smaller than the energy of the state in the MO SCF approximation.

For large systems, the AMO energy also falls after spin projection. However, it has been shown[91] for a polyene that the energy of a large system decreases after spin projection by the constant $C_0 > 0$, which is independent of the number of electrons in the system N. As a result, it is found that, when the AMO method (without projection) is unfavourable compared with the MO SCF method, which is usually the case for two- and three-dimensional systems, then spin projection does not correct the situation. In fact, if we suppose that E(MO) and E(AMO) are the energies of a system of N electrons in the MO and AMO methods without spin projection and that

$$E\,(\mathrm{MO}) \equiv \varepsilon\,(\mathrm{MO}) \cdot N < E\,(\mathrm{AMO}) \equiv \varepsilon\,(\mathrm{AMO}) \cdot N,$$

where ϵ is the energy per particle in both methods, spin projection diminishes the right-hand side of the inequality by the constant $C_0 > 0$, but does not infringe the inequality. We always have

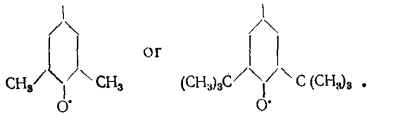
$$\varepsilon\,(\mathrm{MO}) \cdot N < \varepsilon\,(\mathrm{AMO}) \cdot N - C_0,$$

because

$$\varepsilon\,(\mathrm{MO}) < \varepsilon\,(\mathrm{AMO}) - C_0/N$$

for fairly large values of N.

The antiferromagnetic spin structure in CBP molecules is a consequence of the mutual repulsion of electrons with different spins in the same atom. If these two electrons did not repel one another (in conformity with the Coulomb law) and effectively attracted one another (which might be promoted by an electron–phonon interaction or some other interaction), we would obtain a superconductor and not an antiferromagnetic material. Since electron repulsion in the CBP marromolecules is considerable, the introduction of side groups with a high polarisability does not transform electron repulsion into attraction[94]. For this reason, the mechanism of superconduction proposed by Little[4] does not operate in CBP macromolecules. Antiferromagnetism in hydrocarbons is a fairly unexpected property, but unfortunately so far it has been found to be fairly useless. However, one cannot rule out the possibility that the spin structure may be "manifested" following the introduction of side groups into the polyene chain. These may be phenoxy-groups:



If, for example, phenyl substituents in polyphenylacetylene (PPA) are replaced, if only partially, by these groups so that the latter are linked to only even (or only odd) atoms of the polyene chain, then a macromolecule of this kind should become ferromagnetic, because all the unpaired spins of the phenoxy-groups are polarised in the same direction via the central chain. Organic ferromagnetic substances are discussed in greater detail in Section XII.

V. COMPETITION BETWEEN TWO TYPES OF STATES—WITH ALTERNATING BOND LENGTHS AND WITH SPIN WAVES

We may note that the nature of the ground state of a polyene depends significantly on semiempirical parameters. For self-consistent values of the parameters of the polyene, it was actually found that $\Delta E_{\mathrm{alt}} \ll \Delta E_\infty(\mathrm{GHFM}) \simeq \Delta E_\infty$. The state with spin waves was then found to be energetically more favourable as a result of taking into account the significant contribution of the correlation energy. Bearing in mind other quasi-one-dimensional systems, it is natural to formulate problems concerning the possibility of a situation in which the alternation of bond lengths is favourable and concerning the coexistence of states of two types. For the π electrons of a long polyene with Hubbard's Hamiltonian and an elastic σ-skeleton at the temperature $T = 0$, these problems have been solved by Popov[95] and Falikov and Harris[96] in terms of the GHFM approximation. It was found that the state with alternating bond lengths and a gap ΔE_{alt} is more favourable energetically when interactions between electrons and atomic vibrations predominate in the chain or when the inequality

$$\gamma/(2\beta) < 4\beta'^2/(\beta k_1). \tag{15}$$

holds. If Coulombic repulsion between electrons is more significant in the chain or

$$\gamma/(2\beta) > 4\beta'^2/(\beta k_1), \tag{16}$$

an antiferromagnetic state obtains with identical bond lengths and the gap ΔE_∞(GHFM). In infinitely long chains, either type of state may obtain depending on the relative values of the parameters: there is no coexistence between the states of the two types. Since formula (16) holds for conjugated hydrocarbons with a large store of energy,, the nature of the ground state will be determined by the electron interaction and, despite the appreciable differences between bond lengths, which usually alternate by virtue of boundary effects, mainly the state with spin waves arises in not unduly long polyenes; this can also be concluded in view of the similarity of the energy of the first electronic transition $\Delta E(N)$ to ΔE_∞ for not very large values of N (Fig. 1). These conclusions concerning the competition between the two types of states have been extended to non-zero temperatures[97].

VI. THE INFLUENCE OF THE LONG-RANGE COULOMBIC INTERACTION ON THE PROPERTIES OF CBP MACROMOLECULES

Fukutome[98] showed that the long-range Coulombic interaction in long CBP molecules can lead to a ground state with spin waves (SW) or with charge waves (CW). However, the energies of these two types of ground states were not calculated, so that it remained unknown which type actually obtains.

In order to investigate this problem, the present authors[86] used the variational function of the GHFM approximation (Eqn. (8)] for a cyclic polyene with a PPP Hamiltonian:

$$H_{\mathrm{PPP}} = H_{\mathrm{Hub}} + \frac{1}{2}\sum_{\substack{mn\\(m\neq n)}}\sum_{\sigma\sigma_1}\gamma_{mn}c^+_{m\sigma}c_{m\sigma}c^+_{n\sigma_1}c_{n\sigma_1} - \sum_{mn}\sum_{\sigma}\tilde{\gamma}_{mn}c^+_{n\sigma}c_{n\sigma} + \frac{1}{2}\sum_{\substack{mn\\(m\neq n)}}\tilde{\tilde{\gamma}}_{mn}, \tag{17}$$

where H_{Hub} is Hubbard's Hamiltonian [Eqn. (7)], γ_{mn} are the parameters of the Coulombic repulsion of the electrons in the m and n atoms, $\tilde{\gamma}_{mn}$ are the parameters of the attraction of an electron from the n atom to a positive m ion, and $\tilde{\tilde{\gamma}}_{mn}$ are the parameters of the repulsion of m and n ions. In terms of the PPP approximation, all the parameters with identical m and n are equal[99]:

$$\gamma_{mn} = \tilde{\gamma}_{mn} = \tilde{\tilde{\gamma}}_{mn}.$$

As noted above, function (8) depends only on the single parameter δ and describes a state of the SW type when $\lambda(\sigma)=2\sigma$ and a state of the CW type when $\lambda(\sigma)=1$. The total average energy of the ground state $E(\mathrm{PPP}, \delta)$ depends on δ and the parameters of the PPP Hamiltonian, only one term in the expression for the total energy depending on the choice of $\lambda(\sigma)$:

$$E(\mathrm{PPP}, \delta)=A_0-WB_0^2. \qquad (18)$$

where A_0 and B_0 are known functions and $W=1$ when $\lambda(\sigma)=2\sigma$ (SW type) or $W=4M-1$ when $\lambda(\sigma)=1$ (CW type), M being the Madelung sum for the chain:

$$M=-\sum_{t=1,2,\ldots}(-1)^t\gamma_{m+t,m}/\gamma>0.$$

Analysis of Eqn. (18) for the total energy yields the following criterion of the type of the ground state: the SW type obtains for $M<0.5$ and the CW type obtains for $M>0.5$. This criterion, which is independent of δ, can be understood: when M is fairly large ($M>0.5$), it is favourable for the systems to pass to a state with charge waves, since the gain in the Coulombic energy from the alternating charges, which is proportional to M, will be fairly large.

For Hubbard's Hamiltonian [Eqn. (7)], $M=0$ and the ground state is always of the SW type. For the PPP Hamiltonian [Eqn. (17)], which is closer to the real Hamiltonian, M depends both on the geometrical configuration of the chain and on the type of the semiempirical relation for γ_{mn}. It was found that, for many real configurations of the polyene chain and when the generally accepted formulae are used for γ_{mn},[100,101] $M<0.5$ is always obtained. This implies that the ground state of a long polyene has a structure with spin waves. Furthermore, the size of the gap in the spectrum of one-particle excitations proved to be[86] $\Delta E_\infty\simeq 2$ eV [in good agreement with experiment and with the results based on Hubbard's model (Section III)] when the Nishimoto–Mataga formula[101] is used:

$$\gamma_{mn}=1.2935\,\gamma/(1.2935+R_{mn}),\quad \gamma=11.13\,\mathrm{eV}.$$

Hence one may conclude that Hubbard's model with its parameters gives a correct qualitative description of the experimental situation in polyenes and apparently in other conjugated macromolecules.

We may also note that the dependence of the type of ground state on M makes it possible to formulate a hypothetical situation where the nature of the ground state and of its characteristic properties may change in a macromolecule following an alternation in its geometrical configuration (under the influence of external forces).

VII. THE ELECTRONIC STRUCTURES OF CERTAIN CBP

The electronic structures of a number of quasi-one-dimensional systems of hydrocarbons and of the planar two-dimensional network of graphite have been calculated in terms of the GHFM approximation with Hubbard's Hamiltonian[90,102].

1. Polyacenes

The first members of the series of polyacenes in which the number of rings is $N=2$, 3, 4, 5, and 6 are respectively naphthalene, anthracene, tetracene, pentacene, and hexacene. The experimental spectra[103] appeared to indicate the existence of a finite limit to the first electronic transition energy. A group of four atoms a, b, c, and d is repeated periodically in the polyacene molecule (Fig. 5), so that the system is quasi-one-dimensional in the direction of an increase in the number of rings. In terms of Hückel's approximation, among the four π-electron bands two are filled and the third (vacant) adjoins the second closely. The alternation of the lengths of the outer bonds does not reduce the energy and does not lead to the appearance of a gap between the second and third bands[104]. However, transition to the state with spin waves is energetically favourable and in the ground state two bands of levels are filled:

$$E_l^{1,2}=\gamma/2-[(\gamma\delta)^2+[\beta_2\pm\sqrt{4FF^*+\beta_2^2}]^2/4]^{1/2},$$
$$F\equiv\beta_1(1+\exp(i2\pi l/N)),\quad l=1,2,\ldots N.$$

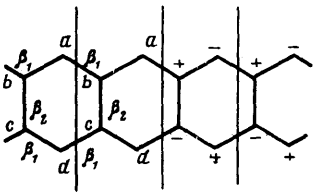


Figure 5. The polyacene cell with the designation of the opposite (+ and −) directions of the spin at carbon atoms and with an indication of the resonance integrals.

The third, vacant band is separated from the second (for $N\to\infty$) by a gap $\Delta E_\infty=2\gamma\delta$ where δ is determined from the corresponding self-consistency equation. According to estimates, $\Delta E_\infty\simeq 1$–2 eV in polyacenes, which does not conflict with experimental data[103]. The antiferromagnetic spin structure in very long polyacenes (the opposite directions of the spins in the atoms are indicated by the plus and minus signs for atoms belonging to two of the periodically repeated polyacene cells in Fig. 5) must be understood in the same sense as for polyenes (see Section IV). Polyacenes are an example of quasi-one-dimensional systems differing from a linear chain of atoms.

2. Graphite

When aromatic rings are added in different directions and not in a single direction as in polyacenes, we obtain the planar hexagonal network of two-dimensional graphite. The properties of two- and three-dimensional graphite have been examined in detail in a review[105]. Here we shall consider the example of two-dimensional graphite in order to show how the "dimensionality" of the system is manifested in the calculation of its properties. It has been shown[90,102] that the two-dimensional network of graphite ($2N^2$ atoms) may exist in a state of the SW type if the GHFM self-consistency equation

$$\frac{\gamma}{2N^2}\sum_{j,k}[(\gamma\delta)^2+|\varepsilon(jk)|^2]^{-1}=1,$$
$$\varepsilon(jk)=\beta(1+\exp(i2\pi k/N)+\exp(i2\pi j/N)),$$

has a solution $\delta \neq 0$. The function $|\epsilon(jk)|$ becomes zero in accordance with a linear law at two points in the region of variation of (j, k), so that for double summation (a two-dimensional integral) these points are non-singular when $\delta \to 0$. The existence of a solution $\delta \neq 0$ therefore requires the fulfilment of the condition

$$\frac{\gamma}{2N^2}\sum_{j,k}|\varepsilon(j,k)|^{-1} \geqslant 1.$$

Hence we find that transition to a state with a spin structure is possible only for parameters satisfying the condition

$$\gamma/(2\beta) > (\gamma/2\beta)_{\text{crit}} \simeq 1.13, \qquad (19)$$

while in quasi-one-dimensional systems such a transition is possible for any parameters $\gamma/\beta \neq 0$. The "dimensionality" of the system is manifested in this sense.

The parameters of graphite are close to those of polyenes, for which the approximate equation

$$\gamma/(2\beta) \simeq (\gamma/2\beta)_{\text{crit}}$$

holds. This leads to the following conclusions.

(1) The parameters of the electron interaction in graphite apparently do not satisfy inequality (19), so that the antiferromagnetic state does not occur (in agreement with experimental data).

(2) On the one hand, the closeness of the parameter $\gamma/(2\beta)$ to the critical value prevents conflict between the theory and experiment and, on the other, it indicates that graphite could make a transition to an antiferromagnetic state if it were possible, say, to extend somewhat all the bonds, to diminish β, and to satisfy inequality (19).

3. Cumulenes

Cumulenes are linear $=(C=C)_N=$ macromolecules consisting of carbon atoms and constituting in essence a third form of carbon (in addition to diamond and graphite [106-112]). In cumulene there are two mutually perpendicular subsystems of π electrons (coupled systems of $2p_x$ and $2p_y$ functions; z is the molecular axis). Each is analogous to the π-electron system of a polyene.

The electronic structure of cumulenes has been calculated [113] in terms of the SCF approximation on the hypothesis that the bond lengths alternate. However, as in polyenes, the effects of different bond lengths in cumulenes cannot play an appreciable role compared with the effects of electronic interactions. According to calculations in terms of the GHFM approximation [90,102], each of the π-electron subsystems of a long cumulene with identical bond lengths exists in a state with an antiferromagnetic spin structure and a gap in the spectrum of one-particle excitations, allowance for the Coulombic and exchange integrals $\gamma_{xy} = \langle xx|yy\rangle$ and $\tilde{\gamma}_{xy} = \langle xy|xy\rangle$ at each carbon atom leading to a correlation between the spin structures of these subsystems. As a result, the one-particle levels of each of the π-electron subsystems have the following form:

$$E_l = \gamma_{xy} \pm (\gamma - \tilde{\gamma}_{xy})/2 \pm [(\gamma \pm \tilde{\gamma}_{xy})^2\delta^2 \pm 4\beta^2\cos^2(\pi l/N)]^{1/2},$$

where the filled orbitals have the minus sign before the root and the vacant orbitals have the plus sign. The size of the gap in the spectrum of a long cumulene is

$$\Delta E_\infty = 2(\gamma \pm \tilde{\gamma}_{xy})\delta,$$

where δ is determined from the "polyene" Eqn. (12) but with another parameter: $p = (\gamma + \tilde{\gamma}_{xy})/(2\beta)$.

In order to estimate ΔE_∞, we shall assume that $\gamma = 5.42$ eV (as in polyenes), $\beta = k\beta_0$, where $k \simeq 1.5$, which corresponds, according to Streitwieser [114] to the C=C bond length in cumulene ($R = 1.28$ Å), [110,113] and $\beta_0 = 2.4$ eV. The value $\tilde{\gamma}_{xy} = 0.62$ eV was estimated from the formula $\tilde{\gamma}_{xy} = (\gamma_{xx} - \gamma_{xy})/2$, where the parameters γ_{xx} and γ_{xy} were found by analysing the spectra of atomic carbon and carbon ions [115,116]. We obtain as a result $\Delta E_\infty \simeq 1.2$ eV, in agreement with experiment [113] [ΔE_∞(exp) = 0.8–1.0 eV]. The state with spin waves ($\delta \neq 0$) is more favourable than the usual state ($\delta = 0$) for molecules with $N \geqslant 11$, i.e. for cumulene chains containing more than 22 carbon atoms.

In the crystalline phase, cumulene chains may contain several hundreds of atoms [110]. The results presented in Section V showed that the presence of an antiferromagnetic state in a long cumulene rules out the possibility of the alternation of bond lengths, since the bond lengths in long cumulenes are identical in the region remote from the ends of the chains.

It was convenient to use cumulenes for the investigation of the antiferromagnetic spin structure by the method of inelastic scattering of polarised neutrons, because they do not contain hydrogen atoms, whose nuclei interact strongly with neutrons. However, such studies are at present outside the scope of the available experimental technique.

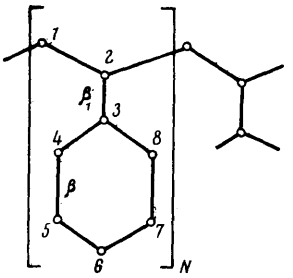


Figure 6. The elementary unit of polyphenylacetylene.

4. Polyphenylacetylene

The ground state of a long PPA molecule (Fig. 6) is characterised by an antiferromagnetic spin structure both in the central (polyene) conjugation chain of PPA, and in the benzene rings [117,118]. In conformity with the number of carbon atoms, there are in the elementary unit of PPA eight energy bands $E_{kl\sigma}$ ($k = 1,2,\ldots,8$), where $l = 1,2\ldots,N$ is the number of the level in the band and N is the number of PPA units. For electrons with different spins and different values of σ, the molecular orbital energies are different (there is no such difference in polyenes, cumulenes, and polyacenes). The bands of cyclic PPA with $N = 17$ are illustrated schematically in Fig. 7. In the ground state, the levels of the bands with $k = 1$, 2, 3, and 4 are filled. Depending on the degree of conjugation of the benzene rings with the continuous conjugation chain (or on the resonance integral β_1; see Fig. 6), the limiting energy of the first one-particle excitation in the PPA

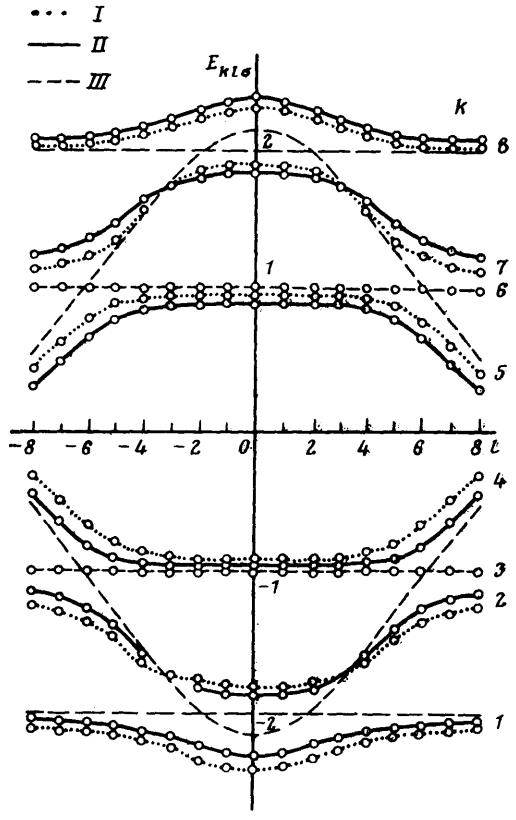


Figure 7. The one-electron energies (in units of β) $E_{kl\sigma}$ (circles) of cyclic PPA with $N = 17$ and $\beta_1/\beta = 0.875$ according to Refs. 117 and 118; $\sigma = -1/2$ (I) and $\sigma = 1/2$ (II); lines (III) correspond to $\beta_1 = 0$.

macromolecule changes from $\Delta E_{\infty}^{\min} = 1.6$ eV ($\beta_1 = \beta$, complete conjugation) to $\Delta E_{\infty}^{\max} = 2.2$ eV ($\beta_1 = 0$) when PPA is converted into a polyene with isolated benzene rings.

VIII. EXACT METHODS FOR THE INVESTIGATION AND SYSTEMATIC TREATMENT OF EXCITED STATES

Despite the advances achieved in the application of GHFM approximation in order to explain the properties of long conjugated molecules, justified doubts remain about the adequacy of this approximation. In fact, it was known that a quasi-one-dimensional system described by Hubbard's Hamiltonian [Eqn. (7)] has excitations whose energies are not separated by a gap ΔE_{∞} and approach the energy of the ground state for $\gamma/\beta \to \infty$, i.e. in the limiting case of isolated atoms. The energies of these states may be obtained by the diagonalisation of the effective Hamiltonian, which is called the Heisenberg spin Hamiltonian [119] and can be obtained from Hubbard's Hamiltonian [Eqn. (7)] for $\gamma/\beta \gg 1$, in the following form:

$$H_{\text{сп}} = \frac{4\beta^2}{\gamma} \sum_n \left(\hat{S}_n \hat{S}_{n+1} - \frac{1}{4} \right), \qquad (20)$$

where $\hat{S}_n$ is the spin operator at the n atom. The eigenfunctions (states) for this Hamiltonian are called homeopolar (for $\gamma/\beta \gg 1$) or quasi-homeopolar (for the real values of the parameters). The spin Hamiltonian method for the description of the excigations of conjugated molecules was proposed by Bulaevskii [120,121]. Kohn [122] and Bulaevskii [120,121] found that the optical transitions from the ground to the quasi-homeopolar states are forbidden or their intensity is low. The GHFM approximation does not yield states of this type; however, it is shown below (Section IX) how triplet states of this type can be obtained in terms of the GHFM approximation.

The reliability of the GHFM approximation, the spin Hamiltonian methods, and other approximate methods was finally elucidated after obtaining the exact solutions for a one-dimensional system with Hubbard's Hamiltonian [Eqn. (7)]. The unidimensionality of the system is important for the exact solutions. Examination of a one-dimensional classical gas consisting of identical solid spheres which can move in only one direction before and after elastic collisions may help to understand the cause of this. By virtue of the energy and momentum conservation laws, when two spheres collide in a single dimension, they can only exchange velocities but cannot alter the values. Consequently in such a system the set of velocities of the spheres does not vary with time, i.e. the distribution function for the spheres with respect to momenta is an integral of motion. The appearance in a one-dimensional system of an additional conservation law analogous to that discussed above ensures the possibility of an exact solution of our quantum problem.

Only a few words need be said about the exact solution; it has been described in greater detail in the review of Ovchinnikov et al. [123]. Using the ideas put forward by Bethe [9], who obtained an exact solution for the ground state spin Hamiltonian [Eqn. (20)], Gaudin [124], Yang [125], and Lieb and Wu [126] obtained an exact expression for the eigenfunction of Hubbard's Hamiltonian [Eqn. (7)]. It has the following form:

$$\Psi(n_1, n_2, \ldots n_N) = \sum_P [Q, P] \exp\left(i \sum_j k_{P_j} n_{Q_j} \right);$$
$$n_{Q_1} \leqslant n_{Q_2} \leqslant \ldots \leqslant n_{Q_N},$$

where n_Q are the coordinates of the electrons (the numbers of atoms in which the electrons are located), $k_{P_j} = k_1, k_2, \ldots, k_n$ is a set of quasi-momenta, which are the quantum numbers for the system, in conformity with the above comments on a one-dimensional gas, $Q = (Q_1, Q_2, \ldots, Q_n)$ and $P = (P_1, P_2, \ldots, P_n)$ are transpositions among the coordinates and quasi-momenta respectively. Furthermore, $[Q, P]$ are coefficients which depend on Q and P; they are determined from the Schrödinger equation and the symmetry requirements. The total energy of the system is very simply expressd in terms of the quasi-momenta k_j:

$$E = -2\beta \sum_{j=1}^{N} \cos k_j. \qquad (21)$$

However, the quasi-momenta are determined from the solution of a system of transcendental equations and depend on certain quantum numbers. By an appropriate choice of these numbers, it is possible to find sets of quasi-momenta k_j and to calculate the energies of the required states from Eqn. (21).

The exact energy of the ground state for an N-atom chain with Hubbard's Hamiltonian [Eqn. (7)] has been found by Lieb and Wu [126]:

$$E = -4N\beta \int_0^{\infty} \frac{\mathcal{J}_1(\omega) \cdot \mathcal{J}_0(\omega)\, d\omega}{\omega(1 + \exp(\omega p))}, \quad p = \frac{\gamma}{2\beta}, \quad N \gg 1,$$

where $\mathcal{J}_0(\omega)$ and $\mathcal{J}_1(\omega)$ are Bessel functions. The results of the exact calculation of the energy of the ground state are compared in Fig. 8 with the GHFM results for different ratios γ/β. We may note that, for real parameters $\gamma/\beta \simeq 2$, the energy gain (GHFM or exact) is small compared with the simple molecular orbital or Hartree–Fock approximation, but the rearrangement of the ground state is significant.

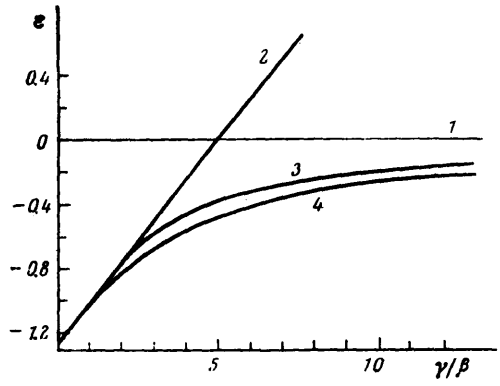


Figure 8. The energies of the ground state of the polyene $(CH)_{2N}$ π electrons per electron $\epsilon = E/(2N\beta)$ in Hubbard's model as a function of the γ/β ratio: 1) isolated atoms; 2) Hartree–Fock (MO SCF) method; 3) GHFM; 4) exact solution[127].

Hubbard's model, which is susceptible to an exact solution, makes it possible to carry out a complete qualitative investigation of the excitation spectrum of an N-atom model chain. All the states of the system with $\gamma/\beta \gg 1$, i.e. for large distances between the atoms, are subdivided into groups of states with similar energies. The first group consists of 2^N states of a quasi-homeopolar type, the energies of which, including the ground state, are also described by the spin Hamiltonian defined by Eqn. (20). For real parameters ($\gamma/\beta \simeq 2$), other approximations or exact methods are preferable. The exact spectrum of triplet excitations of the quasi-homeopolar type has been found by Ovchinnikov[128]. The first energy levels with the numbers $n = 1, 2, \ldots \ll N$ are equivalent:

$$\varepsilon_n^T = \frac{u}{N} n, \tag{22}$$

where

$$u = 4\pi\beta I_1(2\pi\beta/\gamma)/I_0(2\pi\beta/\gamma). \tag{23}$$

Here I_0 and I_1 are Bessel functions of an imaginary argument. The energy of each triplet excitation [Eqn. (22)] is inversely proportional to the number of atoms N in a continuous conjugation chain and therefore may be smaller than ΔE_∞, approaching zero with increase of N. If $\beta = 2.4$ eV and $\gamma = 5.42$ eV,[84] then $u = 24.5$ Ev. For β-carotene (in this molecule the light absorption is determined by a linear polyene chain with $N = 22$), experiment gives[129] ϵ_1^T(expt.) = 1.1 eV, while according to Eqns. (22) and (23) we have $\epsilon_1^T = 1.12$ eV. We shall describe below approximate methods for the calculation of u in CBP (Section IX) and the influence of triplet states on the properties of CBP (Sections X and XI).

Apart from triplet states, the first group includes singlet quasi-homeopolar states, whose spectrum resembles that of triplet states (Fig. 9). The energies of the first singlet and triplet excitations are similar:

$$\varepsilon_1^S - \varepsilon_1^T \simeq N^{-3}; \quad N \to \infty.$$

A weak long-wavelength absorption of CBP is associated with the excitation of these singlet states[130]. In estimating the absorption coefficient $k(\omega)$, account was taken of the fact that polymers possess a broad molecular-weight distribution (MWD) in which it is important to know $p(N)$ (the density of macromolecules with a large number of atoms N in a continuous conjugation chain) for the long-wavelength absorption:

$$p(N) = \frac{1}{\bar{N}} \exp(-N/\bar{N}), \tag{24}$$

where $\bar{N}$ is the MWD parameter. Assuming that only the first level $\epsilon_1^S = u/N$, to which corresponds an oscillator strength $f(N) \propto N$ and the line form parameter $\delta(\hbar\omega - \epsilon_1^S)$, is excited in each molecule and averaging with respect to MWD [Eqn. (24)], it is possible to derive the following formula for $k(\omega)$ [130]:

$$k(\omega) \simeq \int \hbar\omega \, f(N) \cdot \exp(-N/\bar{N}) \, \delta(\hbar\omega - u/N) \, dN. \tag{25}$$

The integration in Eqn. (25) is carried out with the aid of familiar rules for δ-functions. As a result, we obtain the following relation between the absorption coefficient (proportional to the extinction coefficient) and the wavelength λ of the absorbed radiation:

$$k(\lambda) = k_0 \lambda^2 \exp(-\lambda/\lambda_0), \qquad \frac{1}{\lambda_0} = \frac{u}{\bar{N}} \frac{1}{2\pi\hbar c}, \tag{26}$$

where c is the velocity of light and $\hbar$ Planck's constant.

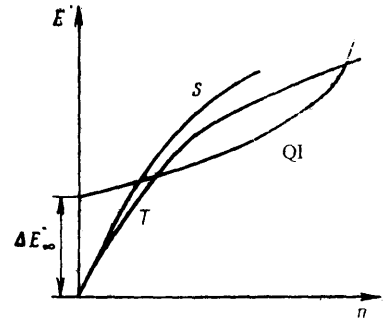


Figure 9. Schematic illustration of the energies E of the excited states of a quasi-one-dimensional system; quasi-homeopolar singlet (S) and triplet (T) levels of the first group; quasi-ionic (QI) levels of the second group; n is the number of the level.

The experimental absorption spectrum for PPA in the wavelength range from 700 to 1500 nm [131] is described with an adequate degree of approximation by Eqn. (26), whence it is possible to determine the ratio $u/\bar{N} \simeq 1.4$ eV. Thus the study of the long-wavelength absorption makes it possible to determine the MWD characteristics for CBP.[130] As will be seen below (Section X), the ratio $u/\bar{N}$ also

determines the paramagnetism of CBP at room temperature [130].

The second group of levels of the Hamiltonian defined by Eqn. (7), which becomes separated for $\gamma/\beta \gg 1$, consists of $N \times 2^N$ quasi-ionic states with excitation energies $\sim\gamma$. For the formation of such states, an electron of one atom must be transferred to another, where an electron is already present, which requires the expenditure of energy $\sim\gamma$ (γ is exactly equal to the energy of repulsion of two electrons in the same atom). The resulting pair of charges (+ and −) on different atoms ensures the appearance of conduction, as a result of such excitations and justifies the term "quasi-ionic". This group of levels includes optically active excited states. Single-particle excitations, associated with electron transfer from a filled to a vacant GHFM band, describe very acuurately optically allowed excitations of states in the second group. The exact spectrum of quasi-ionic excitations has been found [132]. It was discovered that the latter have a gap in the spectrum (for $N \to \infty$):

$$\Delta E_\infty(\text{exact}) = \gamma - 4\beta + 8\beta \int_0^\infty \frac{\mathcal{J}_1(\omega)}{\omega} \frac{d\omega}{1+\exp(p\omega)}. \qquad (27)$$

This implies that the GHFM approximation reproduces correctly the situation with a gap in the spectrum of optically allowed excitations of long conjugated molecules. It has been found [128] that, for $\gamma/\beta \to 0$, we have

$$\Delta E_\infty(\text{exact}) \simeq \frac{8(\gamma\beta)^{1/2}}{\pi} \exp\left(-\frac{2\pi\beta}{\gamma}\right), \qquad (28)$$

whereas the GHFM approximation yields for the same limiting case

$$\Delta E_\infty(\text{GHFM}) \simeq 16\beta \exp\left(-\frac{2\pi\beta}{\gamma}\right).$$

The experimental value $\Delta E_\infty \simeq 2.2$ eV for polyenes is satisfactorily reproduced by Eqns. (27) and (28) with the parameters $\beta = 2.4$ eV and $\gamma = 8.5$ eV, which do not differ very greatly from the optimum GHFM parameters.

The third group of levels of the Hamiltonian defined by Eqn. (7), which becomes isolated for $\gamma/\beta \gg 1$, consists of $N(N-1) \times 2^{N-1}$ states with energies $\sim 2\gamma$ and a wave function having doubly ionic structures (with two pairs of + and − charges). The levels of this group (and all other groups) can occur in the visible and ultraviolet parts of the spectrum for real values of the parameters regardless of the number of the group.

We shall examine from the standpoint of this systematic treatment the excited states of the benzene molecule, paying attention to the covalent-ionic structure of the wave function, which were found by the exact numerical solution of the problem of benzene in the π-electron approximation (a six-atom chain) with the PPP Hamiltonian [68,133]. The ground state $^1A_{1g}$, the triplet state $^3B_{1u}$ (3.7 eV) and the singlet state $^1B_{2u}$ (4.8 eV) are quasi-homeopolar because the wave function of these states includes a contribution of covalent structures. The wave functions of the $^1B_{1u}$ (6.1 eV) and $^1E_{1u}$ (6.8 eV) states include no contributions of covalent structures and are therefore quasi-ionic [68,133]. The experimental excitation energies are indicated in brackets.

IX. AN APPROXIMATE METHOD FOR THE CALCULATION OF THE SPECTRUM OF TRIPLET EXCITATIONS

The exact methods for the calculation of excitation energies are too complex to be applied to systems more complicated than polyene. Because of this, various approximations are as a rule used for real molecules. An approximate method, based on the calculation of the structure of CBP macromolecule in terms of the GHFM approximation and employing the technique of Green functions in a minimum volume, has been proposed [117,118,134] and applied to PPA and polyene chains (linear and closed). The fact that the Hartree–Fock equation for the Green function of a system of π electrons has solutions for both the ground and excited states is used in essence in this method. The proposed method of calculation is equivalent to the random phase approximation, which was shown by the identity of the secular equations for the excitation spectrum of a one-dimensional chain obtained by the two methods [74,75,117,134]. The study of the secular equations of the method of Misurkin and coworkers [117,134], which are not quoted here because of their cumbersome nature and the large number of new symbols, showed that they make it possible to find the energies of the singlet and triplet excitations of the system.

The energies of singlet excitation $\epsilon_i^S \geqslant E_\infty$. Transitions to these singlet states involve changes in electron density at the atoms and are responsible for the strong absorption in the optical region ($\hbar\omega \geqslant \Delta E_\infty$). The energies ϵ_i^S can be calculated with satisfactory accuracy in terms of the GHFM approximation as the difference between the energies of the corresponding molecular orbitals. However, the singlet excitations with energies $\epsilon_n^S < \Delta E_\infty$ are not described by this approximate method, so that in practice the only available information about these states has been obtained by exact methods for simple chains of the polyene type [128,132].

The spectrum of low-energy triplet excitations, obtained by the approximate method, is of the same form as that produced by the exact method [see Eqn. (22)]:

$$\epsilon_n^T = \frac{u}{N} n, \quad n = 1, 2, \ldots \ll N,$$

where u is found by the numerical solution of the corresponding secular equations. These equations have been obtained and solved for cyclic and linear polyenes and for a cyclic model of the PPA macromolecule [117,118,134]. As an illustration, we quote below the secular equation for cyclic PPA with N elementary units:

$$\sum_{m=1}^{8} A(mn \mid u) \cdot f(m) = f(n), \quad n = 1, 2, \ldots 8.$$

This system of linear equations has a non-trivial solution for $f(n)$, i.e. $f(n) \neq 0$, when one eigenvalue of the $A(mn|u)$ matrix is unity. From this condition, it is possible to find u by means of a computer. The $A(mn|u)$ matrix has the following form:

$$A(mn \mid u) = A_1(mn \mid u) + \Delta(mn) \cdot A_2(mn \mid u),$$

$$A_1(mn \mid u) = -\frac{\gamma}{N} \sum_l \sum_{k=1}^{4} \sum_{p=5}^{8} \left[\frac{c_{m\eta}^{k,l+1} c_{m\mu}^{pl} c_{n\eta}^{k,l+1} c_{n\mu}^{pl}}{E_{k,l+1,\eta} - E_{pl\mu} - u/2N} + \frac{c_{m\eta}^{p,l+1} c_{m\mu}^{kl} c_{n\eta}^{p,l+1} c_{n\mu}^{kl}}{E_{kl\mu} - E_{p,l+1,\eta} + u/2N} \right],$$

$$A_2(mn \mid u) = -\frac{\gamma}{N} \sum_{k=1}^{4} \sum_{p=5}^{8} \left[\frac{c_{m\eta}^{k,-\nu} c_{m\mu}^{pv} c_{n\eta}^{k,-\nu} c_{n\mu}^{pv}}{E_{k,-\nu,\eta} - E_{pv\mu} - u/2N} + \frac{c_{m\eta}^{p,-\nu} c_{m\mu}^{kv} c_{n\eta}^{p,-\nu} c_{n\mu}^{kv}}{E_{kv\mu} - E_{p,-\nu,\eta} + u/2N} \right],$$

$$\eta = 1/2, \quad \mu = -1/2,$$

$$\Delta(mn) = 1 - 2(\delta_{n1} + \delta_{m1} - 2\delta_{m1}\delta_{n1}), \quad -\nu \leqslant l \leqslant \nu - 1, \quad \nu = (N-1)/2.$$

Here m and n are the numbers of atoms in the PPA unit ($m, n = 1, 2, \ldots, 8$), k and p are the numbers of filled and vacant MO bands, l is the number of the molecular orbital in the band, and $c_{n\mu}^{pl}$ is the LCAO-MO coefficient for an electron with the spin $\mu = -1/2$ in a molecular orbital with the energy $E_{pl\mu}$. The remaining details and symbols are

described in the relevant papers [117,118]. Similar equations can be obtained and solved for any systems, both periodic and non-periodic: linear CBP, CBP with various defects, etc. The possibility of determining the energies of triplet excitations in long CBP molecules is particularly important, because properties of CBP such as paramagnetism at room temperature and catalytic properties are associated with these triplet states. Comparison of the results of the approximate and exact methods for a polyene with real values of the parameters [117,134] showed that they yield virtually the same values of ϵ_n^T (to within 6%).

X. THE NATURE OF THE PARAMAGNETISM IN CBP

The presence of the electron spin (paramagnetic) resonance (ESR) signal is one of the characteristic properties of CBP. [135] The fairly complex dependence of the electronic structure of CBP on the conformation of macromolecules determines the complex nature of the dependence of the ESR signal on many external factors and makes it difficult to describe fully the paramagnetic properties of these polymers. A typical temperature dependence of the paramagnetic susceptibility χ, measured by the ESR method for a PPA specimen, is illustrated in Fig. 10 (curve *1*) [136].

The paramagnetism of CBP is usually attributed to the presence of structural defects in the macromolecular chain [137-139], the presence of charge-transfer complexes (CTC), [140,141] and excitations to biradicals (triplet) states [142]. However, all these paramagnetic states have a formation energy which is too high (1–2 eV) and this precludes an explanation of the sharp increase of the ESR signal intensity on moderate heating in the region of room temperature. In fact, for the formation of biradical states the fragment of the macromolecule must be rotated about the conjugated bond by ~90°, which requires more than 1 eV [143] and leads to a triplet state with an odd number of π electrons in each of the resulting fragments. In the condensed phase, this energy expenditure increases owing to steric hindrance. On formation of CTC, an electron is transferred from the highest occupied molecular orbital of one macromolecule to the lowest vacant molecular orbital of another, which requires the same energy expenditure as in the one-particle excitation, i.e. 1.5–2 eV (see Sections III and VII above). Nevertheless, stable paramagnetic defects of this type [137-142] can be formed in the synthesis of CBP and can contribute significantly to paramagnetism at low temperatures.

We may also note that, with increase of temperature, relaxation effects appear in the ESR signal of CBP, which cannot be explained, for example, by the recombination of paramagnetic centres. When the temperature is varied in the range 275–350 K, the ESR signal intensity varies in parallel with temperature, assuming initially an intermediate value, which continues to change slowly as the specimen is maintained at a given temperature. The ESR signal intensity or $\chi(T)$ reaches its limiting value (curve *1* in Fig. 10) after a time of the order of tens of minutes or hours, which depends strongly on temperature.

It has been suggested [144,145] that the thermal population of triplet states [with energies of the type defined by Eqn. (22)] in CBP macromolecules is responsible for a significant contribution to the paramagnetism of CBP at room temperature. A formula for the static paramagnetic susceptibility $\chi_N(T)$ per π electron was obtained in the same investigations for a molecule with N atoms in a continuous conjugation chain:

$$\chi_N(T) = \frac{2\mu_B^2 g^2}{kT} \exp\left(-\frac{u}{kTN}\right), \quad \frac{u}{kTN} \gg 1, \tag{29}$$

where $\mu_B = e\hbar/2mc$ is the Bohr magneton, $g = 2$, and e and m are the charge and mass of an electron. In the derivation of Eqn. (29), only the form of the triplet excitation spectrum [Eqn. (22)] was significant. The calculation of u was described above (Section IX). For PPA, u varies from 5.7 β for $\beta_1 = \beta$ to 9.65 β for $\beta_1 = 0$ (see Fig. 6 and Section VII above) [117,118]. CBP with a long continuous conjugation chain, for which triplet energies are smallest and their populations and contributions to paramagnetism are greatest, are important under the conditions of the thermal population of triplet states. Averaging of the quantity defined by Eqn. (29) with respect to the MWD [Eqn. (24)] for macromolecules with a large number of atoms leads to the following formula for the contribution of thermally excited triplet states to the static paramagnetic susceptibility [144,145]:

$$\chi(T) = \frac{2\mu_B^2 g^2}{kT} n_\pi \left(\pi^2 \frac{u}{\bar{N}kT}\right)^{1/4} \exp\left[-2\left(\frac{u}{\bar{N}kT}\right)^{1/2}\right], \tag{30}$$

where n_π is the number of π electrons in the CBP conjugation chain per gram.

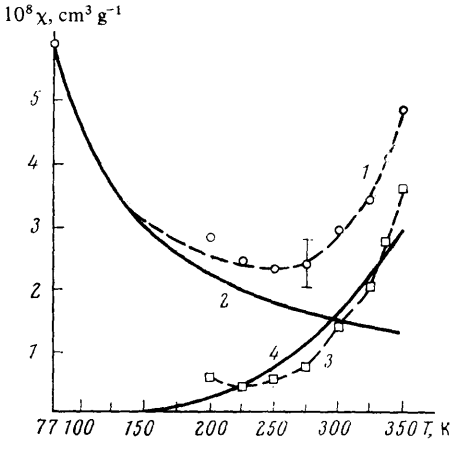


Figure 10. Dependence of the static paramagnetic susceptibility χ of PPA on the temperature T: 1) $\chi^{exp}(T)$ with an indication of the typical experimental error; 2) contribution of paramagnetic defects, $\chi_D = aT^{-1}$; 3) contribution of thermally excited triplet states, $\chi^{exp}(T) - aT^{-1}$; 4) theoretical dependence of the contribution of thermally excited triplet states according to Eqn. (30) with $n_\pi = 1.2 \times 10^{22}$ g^{-1} and $u/\bar{N} = 0.76$ eV.

Since $\chi^{exp} \propto 1/T$ at low temperatures and χ^{exp} increases with increasing temperature when $T \geqslant 250$ K, $\chi^{exp}(T)$ has been represented [136] by the sum of two contributions with different temperature dependences:

$$\chi^{exp}(T) = aT^{-1} + bT^{-3/4} \exp(-cT^{-1/3}). \tag{31}$$

The first contribution, which obeys the Curie law, is due to different types of stable paramagnetic defects, CTC,

etc., which were discussed above. The contribution defined by the second term of Eqn. (31) is determined by the population of the triplet states and corresponds to Eqn. (30). The Curie constant a was determined from the ESR signal intensity at 77 K where the contribution of the thermally excited paramagnetism is negligible: $a = 4.5 \times 10^{-6}$ cm^3 K g^{-1}. If the Langevin formula

$$a = n_D g^2 \mu_B^2 S(S+1)/3k$$

is used for a and it is assumed that the paramagnetic defects have the spin $S = 1/2$, then the concentration of defects is $n_D = 6 \times 10^{18}$ g^{-1}. This implies that one defect corresponds to ~1000 PPA units.

Analysis showed that the experimental temperature dependence of the contribution of thermally excited triplets $\chi^{exp}(T) - aT^{-1}$ (Fig. 10, curve *3*) is described satisfactorily by the second term of Eqn. (31) (Fig. 10, curve *4*), provided that the theoretical expressions derived by identifying Eqn. (30) with the second term of Eqn. (31) are used to calculate the coefficients b and c.[136] It has been found that $b = 1.03$ and $c = 187.7$ for the theoretical value $n = 1.2 \times 10^{22}$ g^{-1} and the ratio $u/\bar{N} = 0.76$ eV, obtained for the values $u \simeq 14$ eV and $\bar{N} \simeq 18$, which are typical for PPA.[117,118,130]

Different types of paramagnetic centres should be reflected in the shape of the ESR signal. For PPA at room temperature, the signal consists of a superposition of at least two lines with $g = 2$ and having comparable intensities: one line has the width $\Delta H_1 = 5$–8 G and the other has $\Delta H_2 = 2$–3 G.[146] The hyperfine structure (HFS) of the first line resembles that of the PPA radical-anions arising following electron transfer from alkali metal atoms to PPA molecules[147]. The first line is apparently associated with stable paramagnetic defects or CTC and the second with thermally excited triplets, its small width being due to the considerable delocalisation of the triplet excitation over the macromolecule.

The problem of the relaxation of the ESR signal intensity in CBP is of interest and its investigation can yield useful information. The observed relaxation with characteristic times of the order of tens of minutes or hours is hardly associated with the intrinsic lifetimes of the excited triplet states, as has been suggested[144,145], because there are at present no adequate grounds for believing that these lifetimes are quite so long. The relaxation of the ESR signal can be explained more realistically by slow configurational distortions of the macromolecular skeleton, which partly alter the degree of bond conjugation.

In order to investigate this problem, a study was made[136] of a polyene chain with randomly distorted bonds, which have the resonance integrals

$$\beta_i = \beta_0 (1 - 0.1 q x_i), \quad i = 1, 2, \ldots 2N,$$

where x_i are random numbers ($0 \leqslant x_i \leqslant 1$) and $q > 0$ is the disorder parameter. Calculations by the method described in Section IX showed that the parameter u, determining the extent of triplet excitation [Eqn. (22)], decreases almost linearly with increasing q at a rate $\Delta u/\Delta q \simeq -\beta_0 < 0$. Using the dependence of β_i on ΔR_i (increase in the length of the ith bond) or on $\Delta\varphi_i$ (the angle of rotation about the ith bond), estimates were made of the chain deformation energies using familiar semiempirical formulae[54,143]. It was found that the thermal energy at 300–350 K is in principle sufficient for deformations of macromolecules which lead to a change in the ESR signal intensity by 15–30%.

The deformation energy may be transmitted to the macromolecule from its environment and, according to the change in the ESR signal, only the deformations of very long molecules are appreciable, since only they contribute appreciably to the paramagnetism. The observed relaxation time is therefore the time during which very long molecules receive sufficient thermal energy and reach thermodynamic equilibrium with the molecules of the environment. The higher the temperature, the greater should be the number of small defects in the continuous conjugation chain. In other words, an increase of temperature entails an increase of the degree of disorder q and hence a decrease of u, since the contribution of thermally excited triplet states to $\chi(T)$ should increase with T faster than predicted by Eqn. (30) with a constant value of u. The systematic discrepancies between curves *3* and *4* in Fig. 10 for $T > 250$ K appear to confirm this view.

XI. CATALYTIC ACTIVITY AND REACTIVITY OF CBP

The existence of triplet states with low excitation energies makes it possible to re-examine the known facts about the catalytic activity of CBP.[148–152] The catalytic activity of small amounts of added CBP in the *cis–trans* isomerisation of dimethyl maleate[149] has been examined theoretically[153]. During isomerisation, rotation about the central double bond results in an increase of the energy of the singlet state of the molecule and, in the vicinity of the angles of rotation $\varphi \simeq 70°$ and 110°, the singlet state intersects the triplet state, which has a significantly lower energy in the vicinity of $\varphi \simeq 90°$. A transition to the triplet state is therefore natural and this is interfered with only by the strong prohibition as regards multiplicity. When a long PCB molecule adjoins the molecule involved in the *cis–trans* transformation, the overall multiplicity of the complex may be conserved, provided that, simultaneously with the transition to the triplet state in the first molecule, there is also a transition to the triplet state in the CBP molecule[153]. As a result of the removal of prohibition of change in multiplicity, there is a significant increase (by a factor of 10^7) in the pre-exponential factor in the expression for the rate of reaction, while the activation energy of the complex hardly changes and is given by

$$E_a = E_a^0 + \eta \frac{u}{N} - V_{13},$$

where E_a^0 is the activation energy for the non-catalytic reaction, u/N the energy of the first triplet excitation [Eqn. (22)], $V_{13} = 0.1$–0.3 eV the exchange energy of the interaction of two molecules of the complex, and $\eta \simeq 0.5$ a coefficient which depends on the form of the intersection of the energy surfaces. The following expression has been obtained for the coefficient of the acceleration of the reaction κ_N or the reaction rates in the presence of the catalyst (W_{cat}) and in its absence (W_0):

$$\kappa_N = W_{cat}/W_0 = 10^7 \exp(V_{13}/kT) \cdot \exp(-u/2NkT). \qquad (32)$$

At $T = 400$ K with the chosen values of the parameters V_{13}, η, and u (Section X), we obtain $\kappa_N \simeq 10^{10} \times 10^{-160/N}$. Molecules with $N \geqslant 20$ can therefore catalyse the reaction at an appreciable rate. After averaging the quantity defined

by Eqn. (32) with respect to MWD [Eqn. (24)], we obtain the final expression for the acceleration coefficient [153]:

$$\varkappa = 10^7 \exp(V_{19}/kT) \cdot \left(\frac{u\pi^2}{2\bar{N}kT}\right)^{1/4} \cdot \exp\left[-2\left(\frac{u}{2kT\bar{N}}\right)^{1/2}\right]. \qquad (33)$$

For the chosen values of the parameters, $\kappa \simeq 10^5$.

CBP molecules with high values of N catalyse the reaction either by the mechanism described above, without the involvement of a paramagnetic steady state, or as a result of the removal of prohibition of change in multiplicity in the presence of triplet species. The known examples of catalysis on graphite and with participation of CBP may be associated with both mechanisms. In terms of the ideas which have been developed, the correlation between the catalytic activity of CBP and their paramagnetic properties is understandable. One can also postulate that, in the presence of such correlation, the catalytic reaction requires the removal of prohibition of change in multiplicity. As an example, one may consider the reaction

$$CH_3CHOHCH_3 \rightarrow \begin{cases} CH_3{-}CH{=}CH_2 + H_2O \\ CH_3COCH_3 + H_2, \end{cases}$$

which is catalysed by CBP activated by charcoal and graphite [150]. The reaction apparently proceeds via a triplet state.

In conclusion, we shall consider the problem of the reactivity of CBP in addition reactions. According to a general postulate [154], the reactivity of π systems in such reactions increases with increasing degree of conjugation. However, deviations from this rule are known, for example in reactions of the Diels–Alder type, where conjugation with the dienophile does not increase the reactivity [155]. It has also been suggested that the reactivity of polyenes longer than butadiene in addition reactions diminishes [156], despite the general postulate. Nevertheless, calculation on the model reaction involving the addition of the methyl radical to a polyene confirmed the validity of the general rule [157]. It was found that the stabilisation energy, which constitutes an effective reactivity index in this reaction decreases monotonically, tending to a definite limit as the length of the polyene increases. The activation energy U also diminishes monotonically. According to the experimental data, $U_2 = 8$ kcal mole^{-1} for the addition of the methyl radical to ethylene and $U_4 = 4.1$ kcal mole^{-1} for its addition to butadiene. For a polyene with 20 carbon atoms, $U_{20} = 1.8$ kcal mole^{-1}, [157] which is virtually equal to the limiting value for the infinite polyene. One should note that the Hückel approximation was used in the calculation [157], because the activation energy is related to the differences between the total energies and the contribution of the correlation energy to this difference is insignificant.

XII. THE MULTIPLICITY OF THE GROUND STATES OF LARGE ALTERNANT ORGANIC MOLECULES WITH CONJUGATED BONDS. ORGANIC FERROMAGNETIC SUBSTANCES [158]

In the first place, we shall specify more exactly what is understood by an alternant system. If the conjugated system is alternant, all its atoms can be divided into two groups, A^0 and A^*, in such a way that any A^0 atom has only A^* atoms as neighbours and any A^* atom has only A^0 neighbouring atoms. We assume that A^0 (or A^*) atoms may include chemically different atoms (C, N, O, etc.), so that our definition of alternant conjugated systems is wider than the generally accepted definition in which only conjugated hydrocarbons are considered.

When the problem of the multiplicity of the ground states of alternant conjugated systems is examined, a significant factor is, as shown by Bulaevskii [159], that the description of conjugated hydrocarbons by the spin Hamiltonian method is very exact when the ground state of the system and the quasi-homeopolar excited states with the lowest energies are considered. In order to determine the energies of all these states, it is necessary to find the spectrum of the Heisenberg Hamiltonian of the molecule:

$$H = \sum_{ll'} I_{ll'}\left(\hat{S}_l\hat{S}_{l'} - \frac{1}{4}\right), \qquad (34)$$

where $\hat{S}_l = (\hat{S}_l^x, \hat{S}_l^y, \hat{S}_l^z)$ is the spin operator ($S = 1/2$) of the carbon atom with the index l, the summation is carried out with respect to the neighbours l and l',

$$I_{12} = \frac{1}{2}\{((\gamma_{11} - \gamma_{12})^2 + 16\beta_{12}^2)^{1/2} - (\gamma_{11} - \gamma_{12})\};$$

and γ_{11}, γ_{12}, and β_{12} are the usual parameters of the PPP Hamiltonian. We may note that, for large distances between atoms, we have $\gamma_{12} \ll \gamma_{11}$ and $\beta_{12} \ll \gamma_{11}$ and in this limiting state we obtain

$$I_{12} \simeq 4\beta_{12}^2/\gamma_{11},$$

so that the Hamiltonian defined by Eqn. (34) assumes the form defined by Eqn. (20). For the real parameters $\gamma_{ll'}$, and $\beta_{ll'}$, the Hamiltonian defined by Eqn. (34) yields, for example, an energy of the first triplet excitation of benzene which differs by only 10% from the experimental value or the energy calculated in terms of the PPP approximation. This is in fact the accuracy of the spin Hamiltonian method which we postulated.

For an alternant conjugated system with the Hamiltonian defined by Eqn. (34), it is possible to prove the theorem that the ground state of such a system is non-degenerate [158]. In the derivation of this proof, which is not described here, the Hamiltonian defined by Eqn. (34) is expressed in the form

$$H = \frac{1}{2}\sum_{ll'} I_{ll'}^{(1)}(S_l^+S_{l'}^- + S_l^-S_{l'}^+) + \sum_{ll'} I_{ll'}^{(2)}\hat{S}_l^z\hat{S}_{l'}^z, \qquad (35)$$

$$S_l^{\pm} \equiv \hat{S}_l^x \pm i\hat{S}_l^y,$$

where

$$I_{ll'}^{(1)} = I_{ll'}^{(2)} = I_{ll'} > 0,$$

and use is made of the ideas put forward by Lieb et al. [160] and the fact that the system is alternant.

If $I_{ll'}^{(1)}$ and $I_{ll'}^{(2)}$ are now treated as independent parameters and it is assumed that $I_{ll'}^{(1)} = 0$, we obtain from Eqn. (35) the so called Ising Hamiltonian for which the ground state is one with spins directed upwards in A^0 atoms and downwards in A^* atoms. If the number of A^0 atoms is not equal to the number of A^* atoms, then z — the projection of the total spin of the system in the Ising limit for the Hamiltonian defined by Eqn. (35) with $I_{ll'}^{(1)} = 0$ — will be non-zero and defined by the expression

$$S_z = \frac{|n_{A^0} - n_{A^*}|}{2},$$

so that the total spin is

$$S \geqslant \frac{|n_{A^0} - n_{A^*}|}{2},$$

where n_A is the number of A atoms. Since according to the above theorem the ground state is non-degenerate, the

spin of the ground state will be the same whatever the value of $I_{ll'}^{(1)}$ and $I_{ll'}^{(2)}$. Hence it follows that, for the real spin Hamiltonian defined by Eqn. (35) or (34), the ground state will have the following total spin;

$$S \geqslant \frac{|n_{A^0} - n_{A^*}|}{2}, \qquad (36)$$

as for the Ising Hamiltonian. Examination of different examples showed that the following equality holds:

$$S = \frac{|n_{A^0} - n_{A^*}|}{2}. \qquad (37)$$

Thus, in order to determine the spin of the ground state of an alternant conjugated system, it is necessary to compute the numbers n_{A^0} and n_{A^*} and to use Eqn. (37).

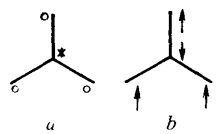


Figure 11. The trimethylmethylene molecule: *a*) atoms belonging to two groups, A* and A^0; *b*) the arrangement of spins in the atoms in the ground state in the Ising limit.

We shall now analyse several examples. In the Ising limit, trimethylmethylene (Fig. 11*a*) has the configuration in the ground state with the arrangement of spins illustrated in Fig. 11*b*. Hence we have $S = 1$ for this molecule [in conformity with Eqn. (37)] and not $S = 2$, because the molecule can be obtained from an allyl radical ($S = 1/2$) and a carbon atom ($S = 1/2$) [carbyne radical (Ed. of Translation)] and, according to the moment addition rules, the combined spin can be either zero or one. The only possibility compatible with inequality (36) is $S = 1$.

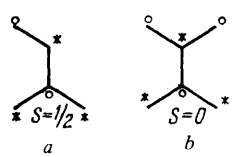


Figure 12. Hydrocarbon molecules having the total spins $S = 1/2$ (*a*) and $S = 0$ (*b*) in the ground state.

The molecules illustrated in Fig. 12 have the spins $S = 1/2$ and $S = 0$. The latter molecule is diamagnetic despite the fact that it has no Kekulé structure. Consequently an alternant molecule may not have a Kekulé structure and may be diamagnetic in the ground state.

Fig. 13 illustrates three isomeric hydrocarbons: (a) Chichibabin's hydrocarbon which Syrkin and Dyatkina[161] showed both experimentally and theoretically to be diamagnetic in the ground state but which has a small energy of excitation to the triplet state; (b) the Schlenk–Brauns hydrocarbon, which is firmly believed (according to the literature) to be a biradical, i.e. it has $S = 1$ in the ground state. This conflicts with our prediction, according to which this molecule should have $S = 0$ in the ground state. Hydrocarbons (a) and (b) have planes of symmetry with respect to the replacement of A* atoms by A^0 atoms, like the hydrocarbon illustrated in Fig. 12*b*. In the presence of such symmetry, the ground state always has $S = 0$. The third hydrocarbon (Fig. 13*c*), which does not have such symmetry, should have $S = 1$ in the ground state according to Eqn. (37).

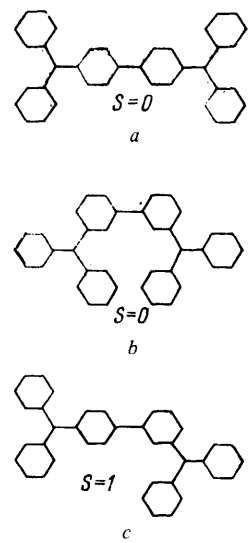


Figure 13. Large isomeric molecules: a) Chichibabin's hydrocarbon; b) Schlenk–Brauns hydrocarbon; c) hydrocarbon in which the number of atoms in one group is not equal to that in the other.

Next, Leo's triradical (Fig. 14) should have $S = 3/2$ in the ground state according to Eqn. (37). The condensed aromatic system illustrated in Fig. 15 has a total spin $S = (L - 1)/2$ which depends on the number of rows L (with increasing number of rings in each succeeding row) (the fragment illustrated in Fig. 15 has $L = 5$ and $S = 2$). Other examples of polyradicals can be found in Buchachenko's book[162].

We shall now consider polymeric systems the total spin of which is proportional to their size. If these systems are synthesised, they will prove to be organic ferromagnetic substances. This can be seen from the preceding examples, one of which is discussed in Section IV; an unusual feature of these ferromagnetic substances is that the spins at neighbouring atoms are opposed, so that the spin order is the same as in an antiferromagnetic substance. However, the total number of atoms with the spins directed upwards is not equal to the number of atoms with the spins directed downwards and the difference between these numbers increases monotonically with increase in the size of the system; the total spin of the system is therefore proportional to its size. Fig. 16 illustrates several polymeric systems of

this kind. Either bivalent O, S, etc. atoms or some other stabilising groups can be selected as the substituent R. These systems are not hydrocarbons, but the above claims are valid also for alternant systems with heteroatoms.

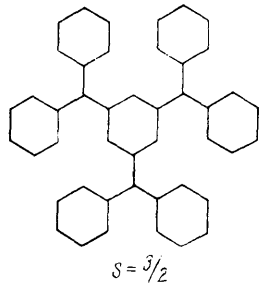


Figure 14. Leo's triradical.

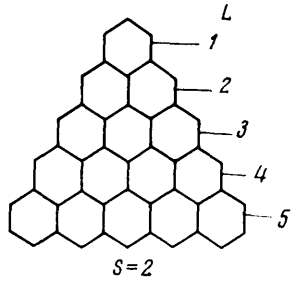


Figure 15. A triangular condensed aromatic system containing L rows of rings ($L = 5$).

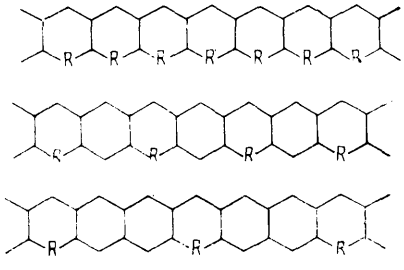


Figure 16. Macromolecules of hydrocarbons with periodically inserted heteroatoms (R = O or S).

Fig. 17 presents examples of two-dimensional infinite systems in which the total spin in the ground state is infinite: these are also ferromagnetic substances. The above systems can be constructed from the graphite network having replaced some of the carbon atoms by boron or nitrogen atoms. We may note that the graphite networks with boron atoms inserted at random have been known for a long time. The synthesis of all the structures of the above type will give rise to organic ferromagnetic substances.

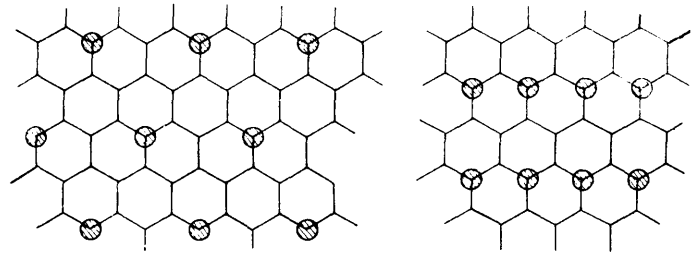


Figure 17. Two-dimensional structures obtained from the graphite structure by the replacement of the designated carbons atoms by boron or nitrogen atoms.

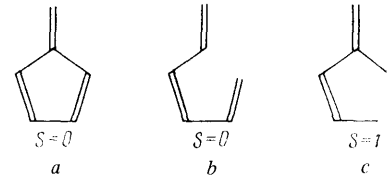


Figure 18. The fulvene molecule (a) and two alternant molecules obtained from the latter on dissociation of different bonds of the five-membered ring with $S = 0$ (b) and $S = 1$ (c).

The above theorems are invalid for non-alternant systems. However, some conclusions can be reached about them also. Consider, for example, the fulvene molecule (Fig. 18a). Its ground state has the spin $S = 0$, which has been demonstrated experimentally and by calculations. On opening the ring (Fig. 18b), the molecule is converted into a linear alternant system where the spin in the ground state is $S = 0$, while for another mode of ring opening (Fig. 18c) fulvene is converted into an alternant system with $S = 1$ in the ground state. Thus, using the ideas developed above, one may predict that the ring opening reaction in the b molecule may occur under thermal conditions, while that in the c molecule may occur with excitation to the triplet state, i.e. photochemically.

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