etc. All these problems are now being solved by investigators.

As Merrifield noted[4,5], the solid-phase method allows not only peptides to be constructed on a polymer, but also other oligomers, for example, nucleotides, the first papers about the synthesis of which have already appeared[40-43]. All this suggests that the solid-phase method has enormous prospects. It helps investigators to obtain compounds of the most varied degrees of complexity, having inestimable value not only for theory but also for practice.

Owing to the insufficient information it is at present difficult to state definitely the advantages of the liquid-phase method in comparison with the solid-phase. It must be noted that good results were obtained with this method in the synthesis of oligonucleotides[44,45]. Undoubtedly further investigations in this direction will bring new valuable results.

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The Structure of Conjugated Open-chain Hydrocarbons

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I. INTRODUCTION

One of the most important problems in theoretical organic chemistry is the study of the electron density distribution in molecules. Systems with conjugated carbon–carbon bonds occupy a unique position in this problem. Modern theoretical methods of organic chemistry have been their greatest successes when applied to such molecules as polyenes, poly-ynes, aromatic systems (benzenoid and non-benzenoid), organic dyes, and cumulenes. The

phenomenon of conjugation, discovered initially by organic chemists, obtained a theoretical basis with the development of electronic theories in organic chemistry (the Robinson–Ingold concepts[1,2]) and with the application of the quantitative methods of molecular quantum mechanics (quantum chemistry). The study of conjugated compounds by the methods of quantum chemistry always shows displacement of the π-electron density from the multiple bonds to the single bonds even in the ground electronic state of molecules, and the formation of multi-centre orbitals.

Since the nineteen-thirties it has been considered that the experimentally observed physical and chemical properties of conjugated compounds confirm the conclusions regarding π-electron delocalisation, reached on the basis of quantum-mechanical considerations. The concept of delocalisation has been severely criticised, however, particularly in recent years. This criticism is to be found in its most fully developed form in papers by Dewar and Schmeising[3-5] and others[6-12]. It has been shown that many of the experimental facts previously adduced as proof of the delocalisation of π-electrons can be no less successfully explained in terms of the concept of hybridisation, which assumes that the two-centre orbitals of the valency π-electrons are preserved in linear conjugated molecules in accordance with the classical structural formulae. The characteristic features of these compounds are attributed to the differences in the properties of the carbon atoms compared with those in saturated hydrocarbons and compounds with isolated multiple bonds. Attempts have also been made to explain the properties of organic compounds in terms of polar effects and the interaction of atoms which are not joined by valency forces.

It is at present expedient, and quite justified, to regard hybridisation, delocalisation, hyperconjugation, etc. as particular "electronic effects", but it should nevertheless be borne in mind that this separation is to some extent arbitrary and is due to the impossibility of obtaining a rigorous solution of the quantum-mechanical problem for a polyatomic molecule. The above structural concepts attribute a dominating influence on the properties of molecules to one of a number of possible electronic effects. As a result, each of the existing concepts is in principle restricted and in the best circumstances can be used to examine only a definite set of properties for a comparatively narrow range of compounds.

The present review examines theoretical and experimental studies of the structure of conjugated hydrocarbons. On the basis of an analysis of published data, the authors have tried firstly to provide a picture of the electron density distribution in linear polyenes, organic dyes, polyynes, and cumulenes, and secondly to define the limits of applicability of existing concepts of the structure of organic compounds, that is, to show the influence of π-electron delocalisation, the valency state of the carbon, and the interaction of atoms which are not joined by valency forces, on the interatomic distances, bond energies, force fields, and electrical fields of conjugated molecules.

II. BASIC CONCEPTS OF THE STRUCTURE OF ORGANIC COMPOUNDS

In the concept of delocalisation, to confirm the conclusion that the π-electron density is displaced, use is made primarily of the fact that the lengths of the single bonds in polyenes and poly-ynes are much less than the lengths of the C–C bonds in the molecules of saturated hydrocarbons. A basis for comparison was provided by the benzene molecule, in which, with complete delocalisation of the π-electrons, all the carbon–carbon bonds have a length of 1.397 Å, which is intermediate between the length of the C–C bond in ethane (1.54 Å) and the length of the bond in ethylene (1.334 Å). Pauling[13], Mulliken[14], and later Coulson[15] estimated the contribution made by π-electron delocalisation to the decrease in the length of the single bonds, on the assumption that the covalent radii of the carbon in the CC and CH bonds are additive. It was found that the decrease in the lengths of the single bonds in conjugated molecules is due both to the change in the hybridisation of the carbon atoms and to the π-electron delocalisation, to almost equal extents. Dewar and Schmeising[3-5], however, suggest that the additivity rule is not observed in this instance. The decrease in the radius of the tetrahedral carbon atom (C_{sp^3}) on changing to trigonal (C_{sp_2}) and digonal (C_{sp}) is greater in C–C bonds than in C–H bonds. Dewar and Schmeising therefore attributed the decrease in the lengths of the single bonds in conjugated molecules entirely to the hybridisation of the atoms, and not to π-electron delocalisation. On this basis, delocalisation was rejected even in such molecules as butadiene and diacetylene. According to Dewar and Schmeising[4], proof of the absence of delocalisation is provided by the fact that the lengths of the C–C bonds are constant within a given hybrid type (C_{sp^3}–C_{sp^3}, C_{sp^3}–C_{sp^2}, C_{sp^3}–C_{sp}, etc.), irrespective of the nature of the nearest substituents. The observed changes in the lengths of the C–C bonds on going from one hybrid type of single bond to another are strictly proportional to the fraction of "s-character" in the orbitals of the atoms forming the bond (Fig. 1).

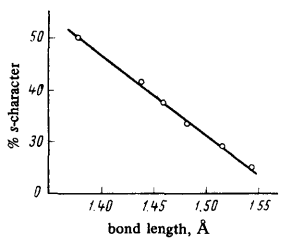


Figure 1. Dependence of bond length on the mean percentage of s-character for single C–C bonds.[4]

A remarkable feature is that the points corresponding to the central bonds of butadiene and diacetylene lie satisfactorily on the straight line. Dewar and Schmeising consider that a linear relationship would not have been expected if delocalisation had a significant influence on the lengths of single carbon bonds. Essentially analogous conclusions were reached as early as 1950 by Tatevskii[16,17], who classified carbon–carbon bonds and established that the bond lengths are constant for each type. A classification of carbon–carbon bonds according to type was also carried out by Herzberg and Stoicheff[18] using spectroscopic data. Later, linear relationships between the length of a bond of any multiplicity and the number of adjacent bonds were observed by Costain and Stoicheff[19] and Bernstein[20]. Moreover, the concept of π-electron delocalisation does not agree with a number of other familiar experimental facts, in particular the similar values found for the lengths

of central bonds with identical hybridisation in the non-planar molecules (in the vapour) of biphenyl and 4,4′-bipyridyl and the planar butadiene molecule[21,22]. Data on bond lengths in the cyclo-octatetraene molecule also do not agree with this concept. Work by Bastiansen and coworkers[23] has shown that in this molecule the single bonds are even slightly shorter than that in butadiene. Moreover, in cyclo-octatetraene (symmetry D_{2d}) the planes of the neighbouring double bonds lie at an angle of ~ 80°, so that the delocalisation of the π-electrons should be very slight, despite the fact that the molecule is an alternant hydrocarbon[24].

Mulliken[25] in his reply to Dewar and Schmeising, agrees that the additive approach to covalent radii is limited, but points out that the classification of carbon atoms in organic compounds as tetrahedral, trigonal, and digonal is also to a considerable extent arbitrary. As shown by Coulson's relationship[26], a condition for the preservation of hybridisation is that the valency angles of the carbon atom remain constant: 109°28′ for sp^3 hybridisation, 120° for sp^2, and 180° for sp. Since the valency angles often differ considerably from these values, a strict subdivision of the hybridisations of carbon into these three types is strictly speaking impossible. This feature was also pointed out by Lide[27].

According to Mulliken[25], the fact that the lengths of bonds with the same hybridisation are constant in conjugated and hyperconjugated molecules does not provide evidence against π-electron delocalisation. The observed facts contradict only the results of the quantum-chemical calculations carried out in the Hückel approximation, and they show complete agreement with the results of modern calculations carried out by various SCF MO LCAO methods[28-32]. The fact that the lengths of C–C bonds of the same hybridisation type are constant, in Mulliken's opinion, is due not to the absence of displacement of the π-electron density from the multiple bonds to the single bonds, but to the fact that the change in the degree of delocalisation in different molecules is small. Some supporters of the hybridisation concept[9-12] reject the existence of delocalisation on the basis of the fact that conjugated molecules do not show an increase in the lengths of the multiple bonds. Mulliken[25] points out that the increases in the lengths of multiple bonds on conjugation, predicted by SCF MO LCAO calculation, do not exceed the experimental errors of even the most precise measurements. Moreover, the lengths of the multiple bonds in conjugated molecules, despite electron delocalisation, may be even shorter than those in non-conjugated molecules. Calculations of overlap populations[33,34] show that the population in the C=C bonds in non-conjugated butadiene is greater than that in ethylene, and this leads to a decrease in the length of the bond; π-electron delocalisation operates in the opposite direction. Thus the double bonds in butadiene may be slightly shorter than the double bond in ethylene, slightly longer than this bond, or almost unchanged, as is in fact observed. Similar conclusions can evidently be reached for the triple bond. For cyclo-octatetraene, Mulliken[14] suggests that the length of the single bond in this molecule is determined not only by the sp^2-hybridisation of the carbon atoms, but also by first-order hyperconjugation.

These arguments are not sufficiently convincing, however. As before, it is difficult, on the basis of the concept of π-electron delocalisation, to explain at least two facts, namely, the linear dependence of the length of the C–C bond on the proportion of "s-character" and the similar values found for the lengths of C–C bonds with the same hybridisation in conjugated and non-conjugated molecules (butadiene, cyclo-octatetraene, biphenyl, etc.). On the other hand, as already noted, the hybridisation concept contradicts the data obtained in all quantum-mechanical studies of conjugated molecules. Dewar and Schmeising[3,4] doubt the reliability of the results of earlier calculations. In their opinion, the increased π-electron density on a single bond, for example in butadiene, is obtained because no allowance was made for the tendency of the electrons to lie on different sides of the nodal plane. A partial correlation related to this tendency is made in calculations by the Pariser–Parr method[35,36], and by Moffit's method[37,38] of atoms in a molecule, by the introduction of empirical corrections into the interelectronic repulsion integrals. The results of calculations for butadiene[28-31] by the methods of Pariser and Parr and Moffit[32,35-37], however, agree with the results of calculations for this molecule carried out by other methods[32-34], indicating that these effects play a secondary role. Moreover, direct calculation with allowance for vertical correlation, carried out by Dewar himself[39] by the split p-orbital method which he developed, gave bond orders for the bonds in butadiene which were very close to the values obtained by the SCF MO LCAO methods[28-31]. Calculations for butadiene by an improved valency bond method, carried out recently by Coulson and coworkers[40], also gave a similar result. Thus the various methods of quantum chemistry are unanimous regarding the problem of π-electron delocalisation in systems of the butadiene and diacetylene type. This however does not yet solve the problem of the lengths of carbon–carbon bonds in organic molecules.

In addition to these two views regarding the reasons for the changes in bond lengths, other ideas have been put forward. For example, Bartell[41-43], opposing both Mulliken and Dewar, considers that the concepts of π-electron delocalisation and hybridisation have no independent significance. In Bartell's opinion, the changes in bond lengths can be attributed to the interaction of atoms which are not joined by valency forces. Bartell considers that evidence in support of his view is provided by the existence of a linear relationship between the length of a C–C bond and the number of nearest substituents in accordance with the change in non-bonded repulsion[43]. The large amount of theoretical and experimental material which has now accumulated, however, shows that interaction between atoms which are not joined by valency forces is not the chief factor determining the lengths of carbon–carbon bonds. Here, reference must first be made to Kitaigorodskii's studies[44-48] of the conformation of organic molecules, carried out over many years. In the mechanical model used for conformational calculations, it is assumed that the optimal conformation is established as a result of a compromise between the tendencies of the molecule on the one hand to keep the values of the valency angles close to the ideal values (109°28′, 120°, and 180° for the sp^3, sp^2, and sp valency states of carbon respectively) and on the other hand to bring the atoms which are not joined by valency forces into equilibrium states. The lengths of the bonds are considered to be absolutely fixed. This approach leads to very good agreement between the calculated and real conformations for a large number of complex, chiefly aromatic, molecules in which the non-bonded repulsion is particularly large. The latest data on the calculation of the optimal conformations of organic molecules by Kitaigorodskii's method are given in papers by Dashevskii[49-51]. Studies[44-51] have shown that the inclusion, in the potential energy expression, of additional terms making allowance for the changes in bond length resulting from the interaction of atoms which are not joined by valency forces is

inappropriate, since the resulting corrections to the bond lengths are insignificant. The results of Coulson's calculations [52,53] of the conformations of "overcrowded" aromatic molecules agree with the conclusion that the bond lengths show little sensitivity to the interaction of atoms which are not joined by valency forces. The same conclusion was reached by Westheimer [54] from an analysis of structural data, and by Wilson [55] from an analysis of the barriers to internal rotation in ethane derivatives.

In addition to data on bond lengths, to which we shall return, results of thermochemical measurements are usually adduced to prove π-electron delocalisation in organic molecules with alternating multiple and single bonds. As early as the nineteen-thirties, Pauling [56] suggested that the heat of formation of a compound can be used as a measure of the strength of the bonding in the molecule. The bond energy was taken as a criterion of bond strength; summation of the bond energies over all the bonds gives the heat of atomisation of the molecule [57]. In organic chemistry the concept of bond energy has been used to determine the additional stabilisation energy of conjugated molecules. The stabilisation or resonance energy was taken as the difference between the heat of atomisation of the real molecule and the additive sum of the bond energies in the corresponding non-conjugated model [14,58]. Another method for estimating the additional energy of conjugated molecules, proposed by Kistiakowsky [59], is based on data on heats of hydrogenation. The resonance energy is obtained by comparing the heats of hydrogenation of the conjugated molecule and a selected model compound, for example, butadiene and but-1-ene, or benzene and cyclohexene. Neither approach can now be considered satisfactory. For the first, the energies of the C–C and C–H bonds are not found to be constant, even in the alkanes [60], and for the second the resonance energy is not entirely an internal characteristic of the molecule, since its magnitude depends on the choice of model compound. The stabilisation energies calculated in this way include effects related not only to electron delocalisation but also to the effects of hybridisation, bond shortening, spatial interactions, etc. Nevertheless, it has been assumed that a predominant part is played by π-electron delocalisation.

In their discussion of resonance energies, as in their discussion of bond lengths, Dewar and Schmeising [3-5] attribute exclusive significance to hybridisation. From calculations based on empirical relationships between bond lengths and bond energies in diamond, methane, and other simple molecules, they concluded that for butadiene the delocalisation energy is equal to almost zero or in the extreme case does not exceed 2 kcal mole^{-1}, and that the total stabilisation energy for butadiene (8.6 kcal mole^{-1}) is due almost entirely to changes in the hybridisation of the carbon. From the same data it follows that the actual delocalisation energy for benzene amounts to not 36 kcal mole^{-1}, but only a quarter of this quantity. Dewar and Schmeising consider that earlier estimates of the delocalisation energy are too high since no allowance was made for the change in the valency state of the carbon atoms and the compression of the σ-bonds.

Mulliken and Parr [61] previously put forward a formula for calculating the heats of atomisation of organic molecules. For C–C and C–H bonds the formula contained empirical constants which did not take account of the changes in the hybridisation of the atoms. Soon after the publication of the paper by Dewar and Schmeising [3], Mulliken [25], introducing additional constants, extended the formula to molecules with C–C and C–H bonds showing different hybridisation. Mulliken's more general formula, like the formula given by Dewar and Schmeising, contains an additional term $E_h = (E'_{CC} - E_{CC}) - 2(E'_{CH} - E_{CH})$, where E and E' are the energies of the bonds formed by sp^3 and sp^2 carbon atoms. The energy E_h acquires a large relative weighting in the total stabilisation energy of the molecule only when the change in the energy of the carbon–carbon bonds with change in hybridisation is much more marked than that for the energy of the C–H bonds. The same assumption was made by Dewar and Schmeising when they suggested that the energies and lengths of the bonds are determined by hybridisation. In Mulliken's opinion, the validity of this assumption is not evident. Mulliken [25] agrees with Dewar and Schmeising that the difference between the heat of atomisation of conjugated molecules and the additive sum of constant bond energies, which is often taken as the resonance energy, is not a true characteristic of delocalisation. He also points out, however, that the approach adopted by Dewar and Schmeising is not rigorous enough to yield unambiguous conclusions regarding the absence of π-electron delocalisation. The same opinion was expressed by Skinner and Pither [62] in a review of thermochemical data for hydrocarbons. Mulliken considers that the theoretical approach to the determination of delocalisation energy appears promising. The calculated energy values can be verified by comparison with the experimental values obtained for the energy barriers to rotation. As an example, Mulliken [61] quotes butadiene, for which the calculated vertical resonance energy amounts to 6.5 kcal mole^{-1}. If this value is corrected for the hyperconjugation for a molecular shape in which the planes of the double bonds are perpendicular, and also for the decompression of the σ-bonds on rotation and the energy of rotation about the single bond in the absence of delocalisation, the calculated potential barrier to rotation amounts to $\sim$ 5 kcal mole^{-1}, which is close to the experimental value [63]. The values of the potential barriers show good agreement with the stability of the planar forms of conjugated systems, produced by π-electron delocalisation. Mulliken's remarks are general in character, however. The theoretical approach to the estimation of resonance energies, expressed, for example, in the LCAO-MO method in units of the resonance integral β, can give only the relative magnitude for different molecules in a series of compounds. As before, the absolute values of the resonance energies remain indeterminate [24]. Experiment shows that even in aromatic systems, steric interactions compete successfully with π-electron delocalisation [44-54]. The frequently encountered departure from coplanarity in aromatic molecules suggests that in linear conjugated systems also, the gain in energy resulting from electron delocalisation constitutes an insignificant fraction of the observed barriers to rotation. Under ordinary conditions, butadiene exists in the *s-trans*-form [64]; the concentration of the *s-cis*-conformation can correspond to only a very small percentage. Calculations by the self-consistency LCAO-MO method [31,32], however, show that the *s-cis*-form of butadiene has a greater stability (from the viewpoint of orbital overlap). Later calculations for this molecule by the SCF MO LCAO method [65] and with allowance for d-orbitals [66] indicate that the stabilities of the two conformations are approximately equal. The fact that butadiene exists chiefly in the *s-trans*-form indicates that a significant part is played by the interaction between atoms which are not joined by valency forces.

Recent papers on bond energies have put forward new calculation schemes, based either [67] on the work of Dewar and Schmeising or on correlations between bond energy and various molecular parameters: the overlap integrals of

the bonding orbitals[68], bond lengths, and bond orders[69,70]. Cox[71,72] extended the relationships obtained by Dewar and Schmeising to organic molecules containing hetero-atoms (O, N, S, and Hal). The data given in these papers, despite the differences in absolute values, change in the same sense as the changes in bond lengths and bond energies. In Table 1 we have compared the most self-consistent values for the energies of bonds of different types. It can be seen from Table 1 that the energy of the single bond in butadiene is almost the same as the energies of bonds of the same type in biphenyl, acetophenone, and biacetyl. The $C_{sp^2}-C_{sp^2}$ bonds in these molecules, however, are known to have significantly different π-orders, so that if a significant part were played by π-electron delocalisation, these bonds should have had different energies. Agreement is also observed between the values of the energies of single bonds of the type $C_{sp^2}-C_{sp}$ in the molecules of phenyl cyanide and vinylacetylene, for which the intermediate

Table 1. Hydrocarbon bond energies.

Type of bond	E, kcal mole^{-1}	References	Type of bond	E, kcal mole^{-1}	References
$C_{sp^3}-C_{sp^3}$	85.0	67	$C_{sp^2}=C_{sp^2}$	133	71
$C_{sp^3}-C_{sp^2}$	89.9	67	$C_{sp^2}=C_{sp}$	135.2*	75
$C_{sp^3}-C_{sp}$	102.4*	73	$C_{sp}=C_{sp}$	150	69
$C_{sp^2}-C_{sp^2}$	98.4* (biphenyl)	74	$C_{sp}\equiv C_{sp}$	167.2*	73
	99.4 (acetophenone)	71	C_{sp^2}—H	98.3 (mono-substituted)	
	97.1 (biacetyl)	71		97.5 (di-substituted)	
	98.0 (butadiene)	72			
$C_{sp^2}-C_{sp}$	108.6* (phenyl cyanide)	71		96.6 (tri-substituted)	71
	109.3* (vinylacetylene)	69			
$C_{sp}-C_{sp}$	126.6* (diacetylene)	69	C_{sp^3}—H	101.2 (mono-substituted)	72
				100.5 (di-substituted)	
C_{sp^2}⋯C_{sp^2}	113.0 (graphite)	69	C_{sp^2}—H	101.8 (benzene)	71
C_{sp^2}⋯C_{sp^2}	117.9 (benzene)	71	C_{sp}—H	112.3*	

*Bond energies calculated by the authors using the heats of formation of the compounds and the energies of the other bonds given in the Table. All the values of E relate to 25°C; the values $\Delta H^\circ_{\text{formation}}C(\text{gas}) = 170.9$ kcal g-atom^{-1} and $\Delta H^\circ_{\text{formation}}H(\text{gas}) = 52.09$ kcal g-atom^{-1} are assumed[57].

bonds also have different orders. This shows that the delocalisation energy in conjugated molecules makes up only an insignificant part of the so-called stabilisation energy. When the energies of bonds of the same type are used, the calculated heats of formation of linear conjugated systems almost agree with the experimental values. A different conclusion regarding the part played by π-electron delocalisation was reached on the basis of calculations of the conformation of biphenyl[76,77]. Here it was assumed that the angle of rotation of the benzene rings in the molecule (~ 41° in the vapour[22]) is determined by the competition between conjugation and the interaction between non-bonded atoms. According to Bartell[78], however, the minimum of the potential barrier for biphenyl shows little sensitivity to the potential associated with electron delocalisation. Change in the latter from 0 to 2 kcal mole^{-1} has almost no influence on the conformation of biphenyl, as can be seen from the published diagrams[76,77]. The non-planar structure of the molecule in the gaseous phase is thus evidently due chiefly to the mutual repulsion of the ortho-hydrogens. In the crystalline state, the planar form of biphenyl is favoured, because of the effects of packing (~ 3 kcal mole^{-1})[79,80]. Thus the height of the potential barrier to rotation cannot give information on π-electron delocalisation, since this effect is due to a considerable extent to the interaction of atoms which are not joined by valency forces[81-84].

Unlike that for linear conjugated compounds, the delocalisation energy for aromatic molecules, calculated with allowance for the type of bond hybridisation, constitutes a significant part of the stabilisation energy. The value obtained for benzene using the data in Table 1 (comparison with classical cyclohexatriene) amounts to ~ 22 kcal mole^{-1}. It is evidently this feature which makes necessary the introduction of additional terms making allowance for distortion of the aromatic rings in the calculations of optimal conformations by the methods of Kitaigorodskii[44-51] and Coulson[52,53].

The relationship between the energies of bonds of various types (values taken from Table 1) and interatomic distance (Fig. 2) is linear (this was noted earlier[67,71]). The points corresponding to the central single bonds in the molecules of butadiene, vinylacetylene, and diacetylene lie satisfactorily on the straight line. Thus these data on the

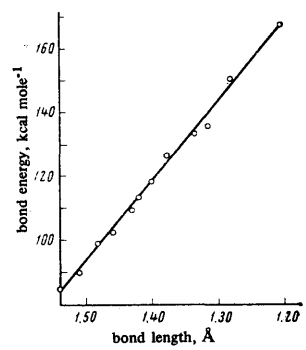


Figure 2. Dependence of the C–C bond energy on bond length.

lengths and energies of the bonds in linear conjugated molecules provide evidence in support of that part of Dewar and Schmeising's treatment which states that these parameters are independent of π-electron delocalisation and can be attributed to the change in the valency state of the carbon atoms. This conclusion does not relate to aromatic compounds. In these compounds, as will be shown below, the π-electron delocalisation is reflected to a marked extent in both the bond lengths and bond energies.

Published explanations of the polarity of conjugated and hyperconjugated molecules are contradictory. Supporters of the delocalisation concept consider that the existence of dipole moments in molecules such as propene and toluene

(~ 0.4 *D*) is due to the displacement of π-electron density. Dewar and Schmeising[3-5] attribute it to the fact that carbon atoms in the sp^3, sp^2, and *sp* states have different electronegativities, according to Walsh[85] and Coulson[86]. On the basis of similar considerations, Petro[87] put forward an additive scheme for calculating the dipole moments of hydrocarbons, in which the C–C and C–H moments were assumed to depend on the type of bond. The possibilities provided by the hybridisation concept in the interpretation of dipole moments are very limited, however. For example, according to this concept the dipole moments of azulene and fulvene should be equal to zero, since all the carbon atoms have the same sp^2-hybridisation, whereas the observed dipole moments are 1.0 *D* and 1.2 *D* respectively[24]. It is just as difficult to explain the polarity of these molecules on the basis of the hybridisation concept as it is to understand, for example, the decrease in the length of the single bonds in cyclo-octatetraene on the basis of the delocalisation concept. The concept of bond delocalisation does not encounter any fundamental difficulties, however, when applied to the dipole moments of non-alternant hydrocarbons (including azulene and fulvene). Hückel's simple MO method and the electron-gas method give very high values for azulene and fulvene (~ 6.5 *D* and 4.5 *D* respectively[88,89]), but the use of improved MO methods with self-consistency gives much better agreement between the calculated and experimental values[24].

Anomalies are observed in the optical properties of hydrocarbons with conjugated multiple bonds. In the electronic spectra this is revealed as a bathochromic shift and increase in the intensity of the absorption bands, and in the Raman spectra it is revealed as a sharp increase in the intensities of the lines due to the vibrations of the multiple bonds. Exaltation of molar refractions is also an optical sign of conjugation in organic compounds. Consideration of these phenomena lies outside the scope of the present review, however, since they are related not only to ground state but also to the excited electronic states of the molecule.

Considerable information on the detailed structure of molecules in the ground electronic state is provided by the radiofrequency spectra. Data on molecular structure recently obtained by NQR, EPR, and NMR methods indicate delocalisation of electrons not only in conjugated and hyperconjugated systems, but even in alkanes. Thus Semin[90], in an NQR study of compounds of the type $Cl-[CH_2]_n-Cl$ ($n = 1-10$) observed a characteristic interaction of the chlorine atoms through the chain of methylene groups. On the basis of calculations in the LCAO-MO approximation, the observed dependence of the NQR signal on the length of the chain was later attributed by Sokolov and Umanskii[91] to partial delocalisation of the σ-electrons of the C–C bond. Proof of delocalisation in hydrocarbons (including alkanes) has also been obtained by EPR[92-96] and NMR[97,98] methods.

In the light of these facts it is evident that none of the existing structural concepts can claim to explain all the varied properties of organic molecules. The non-equivalence of the concepts of hybridisation and π-electron delocalisation in their approach to the study of molecules should be noted, however. In this respect, the concept of delocalisation exhibits the greatest generality. Its conclusions are based on the theory and calculation methods of quantum chemistry. Its range of application is not restricted to individual classes of compound or to definite energy states of molecules. The concept of hybridisation (and the concept of non-bonded interactions), however, is based on a number of empirical relationships and is therefore more particular and simplified.

III. QUANTUM-MECHANICAL STUDIES OF CONJUGATED COMPOUNDS

The success of the application of quantum chemistry to conjugate compounds is due chiefly to the presence of π-electrons, which, in an approximation which is adequate in many instances, can be considered independently. In this section we shall deal with the results of quantum-mechanical studies of linear polyenes, organic dyes, polyynes, and cumulenes.

1. Linear Polyenes

A central problem in the structure of conjugated systems is the question of the change in π-electron delocalisation and the associated change in the lengths of the multiple and single bonds with increase in the length of the chain.

One of the first quantum-mechanical calculations for polyenes was carried out by Lennard-Jones[99,100] using the simple MO method. By using bond length data for ethylene and ethane and determining the resonance integrals for the double and single bonds in polyenes, Lennard-Jones found a decrease in the length of the central bond in butadiene. According to the calculation, the addition of new units to the conjugated chain should lead to gradual equalisation of the bonds. In an infinite polyene the double and single bonds are completely equalised, the length of each being 1.30 Å. Equalisation of the bonds in the central region of a polyene chain also followed from work published simultaneously by Penney[101], who used the valency bond (VB) method. Later, Coulson[102] studied linear polyene radicals $C_{2n+1}H_{2n+3}$ and concluded that as $n \to \infty$, the configurations with alternating bonds will be less stable than those with equalised bonds. In a subsequent paper Coulson[103] extended this conclusion essentially to polyene molecules $C_{2n}H_{2n+2}$, when he found that with increase in *n* for these molecules the orders of the double and single bonds are equalised from the ends of the chain to the centre. In the same paper Coulson for the first time introduced fractional bond orders within the framework of the MO method.

The inadmissibility of the model with equalised bonds for polyenes was soon demonstrated by Mulliken[104,105]. He showed by the simple MO method that for equalisation of the bonds the wavelength of the first absorption band should be proportional to the length of the chain for all conjugated systems, including linear polyenes. The same result was obtained by Kuhn[106] by the simple electron-gas method. It had been known even earlier[107-113], however, that the absorption bands in the spectra of polyenes converge with increase in chain length; with the addition of each unit the bands are displaced towards longer wavelengths by an ever-decreasing amount, tending towards a definite limit (Fig. 3). Kuhn[106,114,115] showed that in order to obtain satisfactory agreement between the experimental and calculated wavelengths in the ultraviolet spectra of polyenes it is necessary to assume strong alternation of the π-electron density in the polyene chain. In the electron-gas method this is achieved by introducing an alternating nuclear potential with maxima in the middle of the double bonds in the classical formula of the polyene. The calculations carried out by Kuhn and coworkers[116] for two- and three-dimensional models showed that the alternation of the electron density in long linear polyenes is the same as that in butadiene.

Dewar[117] studied the electronic structure of polyenes with long chains by the LCAO-MO method. He also showed that in the absence of alternation the calculated frequencies of the absorption bands should tend to zero as $n \to \infty$.

Agreement with experiment can be obtained by assuming that all the double and all the single bonds are equivalent and by assigning different values to the resonance integrals for both types of bond.

Platt[118] attributes the observed regular features in the absorption spectra of linear conjugated systems to the configurational interaction of several possible electronic states. Either the interaction is constant and the compounds have equalised bonds (cyanine dyes) or the interaction varies with chain length, leading to alternation of charge density and hence to alternation of bond lengths. In Platt's opinion, solution by the simple LCAO-MO method

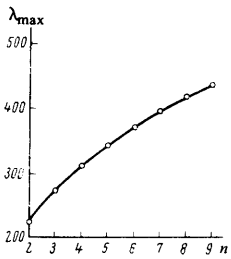


Figure 3. Dependence of λ_{max} (nm) on n for *trans*-polyenes $H_3C-[CH=CH]_n-CH_3$.[113]

leads to equalisation of the bonds in polyenes because no allowance is made for the configurational interaction between the ground and lower excited electronic states. A similar conclusion was reached by Labhart[119] using the free-electron method. He showed that when allowance is made for the compressional energy of σ-bonds the filled π-electron levels of polyenes with alternating bond lengths lie below the levels for polyenes with equal bond lengths. The conclusion that there is alternation of the π-electron charge density on the bonds also follows from the modified potential-box model examined by Bagdasar'yan[120]. Alternation is energetically favourable, since the energy of the electrostatic repulsion of the π-electrons on neighbouring bonds is then minimal.

Ooshika[121,122] was the first to use the semi-empirical Pariser–Parr–Pople SCF MO LCAO method[28,35,36] to solve the problem of the alternation of bond lengths in polyenes. For an infinite polyene chain the π-order of the C=C bond was found to be 0.938, and that of a C–C bond 0.249. These values are very close to the bond orders in butadiene, calculated by Mulliken[25]. Ooshika noted that strong alternation of the bond orders in polyenes leads to an absorption energy difference for an infinite number of double bonds equal to ~ 5.6 eV, although the experimental value is 2.5 eV.[118] Huzinaga and Hasino[123] carried out calculations for polyenes using a modified LCAO-MO method based on a united atom model[124], for which the Coulomb integral depends on the interatomic distance. The authors also obtained significant alternation of the lengths of the double and single bonds (~ 0.1 Å). Thus even in the late nineteen-fifties a large number of quantum-mechanical papers had shown that results agreeing with experiment can be obtained for polyenes only by assuming bond alternation, which is preserved with increase in chain length. Alternation of the bond orders and bond lengths decreases the total energy of the system, making it more stable relative to the system with equalised bonds.

In addition to quantum-mechanical calculations, classical models have been used in the interpretation of the electronic spectra of polyenes. Lewis and Calvin[125] used a model with non-coupled oscillators, but the relationship which they found between the wavelength of the absorption band of the polyene and the number of double bonds did not agree with experimental data[126]. Much better agreement with experiment was obtained by Kuhn[127] and Hirayama[128], who assumed coupled oscillators. In a series of papers by Simpson[129–132] the characteristic features of the structure of polyenes are attributed to the electrostatic interaction of the double bonds. In Simpson's opinion, a significant contribution to the ground state of these compounds is made by an ionic structure with alternating charges, for example, $-\dot{C}=\bar{C}-\dot{C}=\bar{C}$ for butadiene. Simpson's model is, however, extremely far from reality[133].

Among later quantum-mechanical studies of the structure of polyenes, mention must be made of work by Longuet-Higgins and Salem[134,135]. These authors used the simple LCAO-MO method, but they made allowance for the compressional energy of σ-bonds and introduced not the parabolic dependence of the resonance integral β on the interatomic distance, as Lennard-Jones had done[99,100], but an exponential dependence. It was found that with this approach, cyclic and linear polyenes with equalised bonds become dynamically unstable as $n \to \infty$. The theoretical analysis also led Longuet-Higgins and Salem to the conclusion that the molecular π-orbitals in the ground and excited states of an infinite polyene do not form a continuous bond, but are separated by a finite energy barrier. This means that an infinite polyene should behave not as a one-dimensional metal but as an insulator with a low electronic excitation energy. This conclusion is directly related to the chemical problem, examined below, of the mutual influence of atomic groups separated by a chain of conjugated bonds.

Pople and Walmsley[136] calculated the energy of the lower excited state for polyenes by the Pariser–Parr method[35,36] for weak and strong alternation of the bonds. They found that the limit of the long-wave absorption is 2.9 eV for the former, and 4.6 eV for the latter. Thus according to Pople and Walmsley, weak alternation of the bonds shows better agreement with the experimental value of 2.5 eV.[118] Dixon[137] examined the nature of the alternation of bonds in polyenes by the VB method. In contrast to the earlier calculations of Penney[101], the values of the Coulomb and resonance integrals were assumed to be different, depending on the interatomic distance (the method has been described in detail[138]). The lengths of the double and single bonds calculated by Dixon are almost independent of the dimensions of the polyene chain and show good agreement with the experimental bond lengths for butadiene[139,140]. Merz and coworkers[141] used the "molecules in molecules" method, developed by Longuet-Higgins and Murrell[142], to interpret the electronic spectra of conjugated compounds. They concluded that there is considerable localisation of the π-electrons on the bonds in linear polyenes, irrespective of the length of the chain.

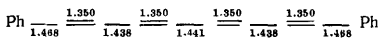
A recent paper by Dewar and Gleicher[143] (see also Refs. 5 and 144) described a study of the structure of polyene compounds by the Pariser–Parr–Pople SCF MO LCAO method and the split p-orbital method[145]. Both methods showed that with increase in the chain-length the alternation of the double and single bonds remains almost the same as that in the first members of the vinyl series. At the same time it was shown that the heats of formation of polyenes can be represented in the form of additive sums of the empirical energies of the C=C, C–C, and C–H bonds. In

the opinion of the authors cited, this indicates the absence of π-electron delocalisation and the inappropriateness of using the actual concept of bond delocalisation or resonance interaction to describe the collective properties of molecules, It is difficult to agree with this, however, since even the energies of aromatic hydrocarbons, in which the existence of resonance interactions cannot be doubted, can be described by additive schemes[146]. As will be shown below, bond energies, like bond lengths, cannot serve as reliable criteria of π-electron delocalisation in linear conjugated molecules.

Calculations of the absorption spectra, ionisation potentials, charges on the atoms, and bond orders in polyenes $H[CH=CH]_nH$ (n = 1–10) and in various condensed aromatic compounds have been described by Adams and Miller[147]. The calculations were carried out using a semi-empirical method in a π-electron approximation which differs from the generally adopted Pariser–Parr–Pople SCF MO LCAO method in that the atomic orbitals are expressed in terms of orthogonal orbitals of the Slater type (after Lowdin). The results obtained indicate that there is strong alternation of the π-electron density in polyenes and that the orders of the double and single bonds depend little on chain length.

Thus quantum-mechanical examination using all existing methods shows that polyenes in the ground electronic state form systems with alternating charge density. The problems of the degree of alternation and the change in bond orders with increase in chain length have been less fully investigated. The quantum-mechanical problem of the transfer of influence along a chain of conjugated bonds has been little studied, although there is an extremely widespread opinion that the polyene chain exhibits metallic conductivity[148].

The problem of the alternation of bonds in long polyenes might be solved unambiguously by experimental methods, but the amount of available material is extremely small. We know of only one X-ray diffraction study, by Dreuth and Wiebeng[149], in which the bond lengths in 1,8-diphenyl-1,3,5,7-octatetraene were determined. It was shown that the molecule has the *s-trans*-configuration with the following bond lengths in the chain:

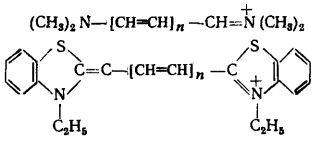


There is very little published information on the structure of excited states of polyenes. This problem was first examined in relation to polyenes by Bayliss[150] and later, in more detail, by Platt[118]. In the excited state of hexatriene according to Bayliss, migration of the charge takes place from the centre of the chain to its ends. The double-bond character of the central bond decreases, and that of the neighbouring single bonds increases. On excitation of the polyene, the alternation of the bonds is preserved, but its sign changes. In Platt's opinion[118], this explains various characteristic features of the absorption spectra of polyenes, in particular the existence of a distinct vibrational structure in the spectra at room temperature.

Recently, Hoffmann[151] carried out calculations on the geometry of polyenes in the first excited state. Using an extended version of Hückel's method which he developed, Hoffmann showed that in the excited state of butadiene the planes of the terminal CH_2 groups are mutually perpendicular. In the excited state of hexatriene, rotation about the central double bond takes place. Octatetraene and polyenes with higher molecular weight remain planar in the excited state.

2. Organic Dyes

From the work examined in the previous section, it follows that the convergence of the wavelengths of the absorption bands observed in the electronic spectra of polyenes with increasing chain length is due to the alternation of bond orders. There is an extensive class of compound, however, whose ultraviolet absorption bands do not show this tendency. These include the symmetrical polymethine (I) and cyanine (II) dyes:



With the addition of a new unit, the absorption band of (I) and (II) is displaced by a constant amount equal to 1000 ± 50 Å [152–162] (Fig. 4). The first attempts to use the methods of quantum chemistry (VB and MO) to interpret the electronic spectra of organic dyes are described in papers by Föster[163] and Herzfeld and Sklar[164–166]. Kuhn[114–116] was the first to show that the observed regular features in the spectra of compounds (I) and (II) can be described satisfactorily by the free-electron method using a model with equalised bonds. The application of the method of molecular orbitals to these compounds is described by Dewar[167].

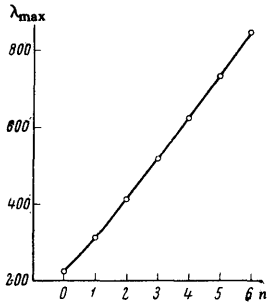


Figure 4. Dependence of λ_{max} (nm) on n for cyanines $(H_3C)_2\overset{+}{N}=CH-[CH=CH]_n-N(CH_3)_2$.[113]

Fukui and coworkers[168] concluded that in order to obtain better agreement with experiment in calculations for symmetrical polymethine dyes by the electron-gas method, it is necessary to assume a slightly modified potential, because of the influence of the terminal groups. A similar conclusion was later reached by Oldzewsky[169,170], who used the potential-box method and introduced barriers associated with the terminal effects of the nitrogen atoms. For a chain of carbon atoms, as in work by Kuhn[114–116], Bayliss[150], and Simpson[171], an equalised potential was used. McGlynn and Simpson[172] calculated the energies of electronic transitions by an improved LCAO-MO method in the Pariser–Parr approximation.

In recent years, new experimental data have been obtained on the electronic spectra of cyanines, oxonols $O=CH-[CH=CH]_n-O$, and merocyanines[173]

$$(CH_3)_2N-[CH=CH]_n-COH.$$

The dependence of λ_{max} on n for oxonols and merocyanines (Fig. 5) shows that these compounds have different structures. Leupold[174] obtained good agreement between the calculated and experimental positions of the long-wave absorption bands for symmetrical polymethines using a modified version of the simple LCAO-MO method (corrections were introduced for the hetero-atoms). The molecular diagrams obtained indicate almost complete equalisation of the bonds, the bond orders being close to the value obtained by the simple MO method for benzene (0.67). Leroy and Nys[175] carried out calculations for various types of cyanine dye by the Pariser–Parr SCF MO LCAO method. By assuming a linear relationship between bond length and bond order, they obtained values for the carbon–carbon bond lengths in cyanine dyes which almost coincided with the CC bond length in benzene (1.397 Å). Thus according to these authors[174,175], dyes of types (I) and (II) are linear analogues of benzene with respect to delocalisation of the bond lengths and bond orders.

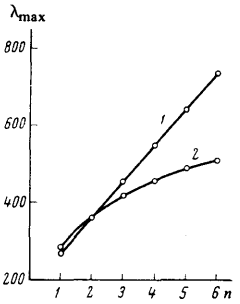


Figure 5. Dependence of λ_{max} (nm) on n for oxonols $O{=}CH{-}[CH{=}CH]_n{-}O^-$ (*1*) and merocyanines $(H_3C)_2N{-}[CH{=}CH]_n{-}CHO$ (*2*). [173]

In a subsequent paper, Leupold and Dähne[176] carried out calculations for oxonols and merocyanines by a method similar to that described earlier[174]. For oxonols, good agreement was obtained between the calculated and experimental bands in the electronic absorption spectra. The CC bond orders for oxonols were also found to be close to the carbon–carbon bond order for benzene. The absorption band maxima calculated for merocyanines[176] showed poor agreement with the experimental values. The experimental data for the electronic spectra of merocyanines[173] and various other unsymmetrical $\alpha\omega$-substituted polyenes[177] show a distinct tendency for the maxima of the long-wave band to approach a finite limit (Fig. 5). This is evidently due to incomplete delocalisation of the π-electrons. Recently, Klessinger[178] carried out calculations for cyanines and merocyanines using the Pariser–Parr–Pople SCF MO LCAO method and showed that these compounds belong to different classes. In the cyanines the bonds are equalised, the π-order approaching 0.67 (benzene) with increase in the chain length. The behaviour of the merocyanines is similar to that of polyenes—considerable alternation of the bonds, which remains almost unchanged with change in the length of the chain, is observed. Alternation of the bond orders in $\alpha\omega$-substituted polyenes is also indicated by dipole moment data[179] and the vibrational spectra (see below). Thus the characteristic features of the electronic structure of linear conjugated molecules in the ground state are clearly revealed in the ultraviolet absorption spectra. Compounds for which the absorption bands in the electronic spectra do not converge with increase in chain length form systems of equalised bonds (cyanines, polymethines, and oxonols). Compounds for which the absorption band maxima tend towards a definite limit with increase in the length of the chain show alternation of electron density (polyenes, merocyanines, and other $\alpha\omega$-substituted polyenes with paired electrons). The limiting wavelength in the electronic spectra is reached more rapidly, the more marked the alternation of the bond orders and hence the smaller the π-electron delocalisation. It is evidently for this reason that the absorption bands in the spectra of *p*-polyphenyls[128], for example, show rapid convergence towards a limit, compared with polyenes. The non-coplanarity of the benzene rings in *p*-polyphenyls, resulting from the interaction of the ortho-hydrogens, leads to greater localisation of the π-electrons within each unit of the chain.

Pouradier[180] analysed a large number of electronic spectra of cyanine dyes, and showed that the distance between the first and second components of the absorption band is approximately constant and amounts to ~ 1200 cm^{-1}, irrespective of the nature of the dye. The splitting was attributed to vibration of the chain in the excited state.

3. Poly-ynes and Cumulenes†

The first calculations for cumulenes were carried out by Pullman and Berthier[181] by the LCAO-MO method with allowance for hyperconjugation of the terminal bonds (after Mulliken[14]).

Quantitative data were obtained on the equalisation of the bonds in cumulenes with odd and even numbers of carbon atoms. It was noted that a bathochromic effect should be observed in the electronic spectra with increase in chain length. Later, again using the simple LCAO-MO method, Longuet-Higgins and Burkitt[182] carried out calculations for the lower polyalkynes (up to and including tetraacetylene) and cumulenes (as far as pentatetraene). The results showed that the poly-ynes and cumulenes show different behaviour with increase in chain length. The equalisation of the orders of the central bonds given by the method of molecular orbitals is slower for poly-ynes than for polyenes. For cumulenes, the bond orders change sharply on going from allene to butatriene, the orders of the terminal bonds decreasing, and the order of the central bond increasing. The bond orders for pentatetraene differ little from those for butatriene; only a slight decrease in the bond orders in the middle of the chain is observed.

The first experimental data on the electronic spectra of poly-ynes and cumulenes were obtained in the nineteen-fifties[183-187]. Comparison of the spectra enabled Krauch[188] to refute the extremely widespread opinion that the electron density distribution is the same for long poly-ynes and cumulenes[189]. If delocalisation of the π-electrons did in fact lead to complete equalisation of the bonds, so that an infinite poly-yne had the cumulene structure, the ultraviolet spectra should have shown a tendency for the absorption bands of molecules of the two classes to approach one another with gradual increase in the number of carbon bonds, but this is not observed. The differences between

† The structures of poly-ynes and cumulenes are considered in the same section of the present review merely for convenience of presentation and not for more significant reasons.

the spectra of these compounds increase with increase in the length of the conjugated chains (Fig. 6). The maxima of the absorption bands for cumulenes, like those of polymethines and cyanine dyes, are displaced regularly by the same amount with the addition of each new unit (for example by ~ 750 Å for tetraphenylcumulenes[187]), whereas the band maxima for poly-ynes, like those for linear polyenes, tend towards a definite limit[183,184].

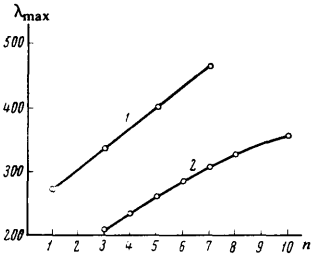
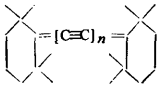


Figure 6. Dependence of λ_{max} (nm) on n for cumulenes



(1)

and poly-ynes $(H_3C)_3C-[C\equiv C]_n-C(CH_3)_3$ (2).[113]

Kuhn[116] examined the characteristic features of the electronic spectra of polyenes and poly-ynes by the free-electron method, using one-dimensional as well as two- and three-dimensional potentials. It was found that all the models give qualitatively similar results for the alternation of the multiple and single bonds in these systems, and that infinitely long polyenes and poly-ynes show approximately the same alternation of bonds as butadiene and diacetylene respectively. It was found that the absorption bands show more rapid convergence towards a limit for poly-ynes than for polyenes. This was reflected in the choice of a larger value for the amplitude of the alternating potential for poly-ynes (3.4 eV) compared with polyenes (2.4 eV). Thus the ultraviolet spectra indicate directly that the electron density distribution is different for poly-ynes and cumulenes. Marked bond alternation, changing little with change in the length of the poly-yne chain, was recently obtained by an SCF MO LCAO method[190] in calculations for the molecules of di-, tri-, and tetra-acetylenes[191,193]. Comparison of the molecular diagrams for these compounds and the molecular diagram for octatetraene[194], obtained by the same method of Julg[190], shows that the electron density distributions in poly-ynes and polyenes are similar.

The structures of cumulenes and poly-ynes have recently been studied by Shustorovich[195-203]. Using the simple LCAO MO method, improved by Longuet-Higgins and Salem[134], Shustorovich obtained data on the barriers to internal rotation in organic cumulenes[195,196], the ionisation potentials and electron affinities[197,198], and the alternation of bond lengths in cumulenes and poly-ynes[199,200]. Shustorovich also examined the electronic structures of cumulenes by the self-consistent π-MO method in the Pople approximation[201]. Despite the large amount of available published material on the electronic spectra of cumulenes, Shustorovich considered only preliminary data on carbene (a compound containing more than 1000 carbon atoms).

Shustorovich concludes that cumulenes and poly-ynes differ only in the structures of the terminal groups, whose influence becomes weaker with increase in the number of carbon bonds. When the chain is sufficiently long, organic cumulenes and poly-ynes are indistinguishable and consist of systems of weakly alternating conjugated bonds. This conclusion, however, does not agree with familiar experimental facts relating to the structures of cumulenes and poly-ynes. It was shown above that available experimental and calculated data on the electronic spectra indicate that there is equalisation of the bonds in long cumulenes on the one hand, and marked alternation of the bonds in poly-ynes on the other. Differences in the structures of these compounds are also indicated by structural data, although such data are at present available only for cumulenes and poly-ynes with a small number of bonds. The bond lengths in molecules of both classes show no tendency to converge (Table 2). If the structures of long cumulenes and poly-ynes were identical, however, the greatest changes in bond lengths with increase in their number should have been observed in these lower members of each series.

Table 2. Bond lengths in cumulenes and poly-ynes, Å.

Compound	References
$C \overset{1.309}{=\!=} C \overset{1.309}{=\!=} C$	204, 205
$C \overset{1.318}{=\!=} C \overset{1.284}{=\!=} C \overset{1.318}{=\!=} C$	206, 207
$C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C \overset{1.31}{=\!=} C$	208
$C \overset{1.205}{\equiv} C$	209
$C \overset{1.205}{\equiv} C \overset{1.378}{-} C \overset{1.205}{\equiv} C$	209
$C \overset{1.20}{\equiv} C \overset{1.38}{-} C \overset{1.20}{\equiv} C \overset{1.38}{-} C \overset{1.20}{\equiv} C$	210

The conclusion that the alternation of bonds in poly-ynes is weak follows inescapably when the version of the simple MO method due to Longuet-Higgins and Salem[134] is used. The simple MO method of Hückel is in general inapplicable to calculations for linear conjugated molecules, since it leads to equalisation of the bonds and to a linear dependence of λ_{max} on the number of multiple bonds[99,100,103], which does not agree with experiment. Longuet-Higgins and Salem, using a slightly improved version of Hückel's method, concluded that there is alternation of the bond orders in polyenes, although for an infinite polyene they also obtained a very small difference between the levels of the ground and excited states (ΔE = 0.25 eV, experimental value ΔE ~ 2.5 eV [116,118]). Shustorovich[199,200], using the same method, obtained for an infinite poly-yne the value ΔE = 0.05–0.4 eV (depending on the choice of initial parameters), which is also less than the experimental value (~ 3.4 eV [116]).

Hückel's simple MO method, however, describes effectively the electronic spectra of systems with equalised bonds, that is, the spectra of polymethines and cyanine dyes[167], oxonols[176], condensed aromatic systems[211,212], and cumulenes[182,183]. The fact that Hückel's method is applicable to one large group of compounds and is not applicable to another (polyenes, poly-ynes, and merocyanines) is not accidental. It is evidently related to the existence in the first instance, and the non-existence in the

second, of a correspondence between the actual relationship between the energy and the order of the π-bonding and the linear relationship which follows in Hückel's approximation[213]. As shown below, significantly different relationships between the energies and orders of the bonds are observed in these groups of compounds: for cumulenes, polymethines, etc. the relationship is approximately linear, whereas for polyenes and poly-ynes the relationship is more complex.

The characteristic features of the structures of cumulenes and poly-ynes in the ground and excited electronic states were recently studied in detail by Hoffmann[151] using an extended MO method with allowance for σ-electrons. Hoffmann obtained data on the geometry of cumulenes with odd and even numbers of carbon atoms (n) in the ground and excited states. For both states, oscillation of the barriers to rotation (ΔE) depending on n were observed, and it was found that $\Delta E \to 0$ as $n \to \infty$. It was shown that the difference between the energies of the higher filled and lower vacant molecular orbitals (E) is greater for cumulenes with odd values of n than for those with even values; in both instances the value of E approaches zero with increase in n. Hoffmann's calculations agree with experimental data on the excitation energies and electronic spectra of cumulenes. The known experimental values of E decrease regularly in the order: ethylene, allene, butatriene, and pentatriene[214,215]; a linear relationship is also observed between λ_{max} and the number of double bonds[183,187,216]. Hoffmann studied the electron density distribution using the total charges on the atoms and the overlap populations (n_{ij}). The data which he obtained indicate equalisation of the bonds in cumulenes. For decanonaene ($C_{10}H_4$) Hoffmann obtained the following values of n_{ij} (from the end of the chain to the middle): 1.27, 1.37, 1.32, 1.35, and 1.33. Hoffmann concluded that the poly-ynes show appreciable alternation of bond orders, changing little with increase in chain length. Thus for the poly-yne $C_{16}H_2$ he obtained the following values for the overlap populations n_{ij} (from the end of the chain to the middle): 1.86, 1.01, 1.78, 1.03, 1.76, 1.03, 1.76, 1.03. Hoffmann's calculations showed that in the excited state, unlike acetylene which has the *trans*-form[217-219], diacetylene remains linear, contrary to Pontrelli's conclusion[220].

The structures of butatriene, vinylacetylene, and divinylacetylene were recently studied by Julg and Pellegatti[221] using an improved MO method[190]. For the π-orders for butatriene they obtained the values 0.91 for the terminal bonds and 1.38 for the central bond.

In addition to the literature cited, further references to early work on the electronic spectra of conjugated hydrocarbons can be found in a detailed review by Mason[113]; extensive references on the chemistry of poly-ynes are given in a review by Sladkov and Kudryavtsev[222], and similar references on the chemistry of cumulenes are given in a review by Cadiot, Chodkiewicz, and Rauss-Godineau[223].

IV. THE VIBRATIONAL SPECTRA OF CONJUGATED COMPOUNDS

Isolated attempts have been made to obtain force constants for molecules by quantum-mechanical calculation. The first attempts were made by Coulson and Longuet-Higgins[224] as early as 1948 for the molecules of benzene and butadiene. Calculations within the framework of the simple MO method gave qualitative agreement between the force constants for benzene and the constants determined from the vibrational spectra. Later, Longuet-Higgins and Burkitt[182] used a method developed earlier[224] to calculate the force constants of the carbon–carbon bonds in the molecules of poly-ynes and cumulenes. They noted that the values of the force constants of the bonds are highly sensitive to the π-order, and that the values of the interaction constants are highly sensitive to the mutual polarisability of the bonds. Misurkin and Ovchinnikov[225] recently calculated the vibrational frequencies of the benzene ring using constants found by the MO method. The discrepancies between the calculated and experimental values amounted to several hundred cm^{-1}. This and other work[226-234] indicates that quantum-mechanical methods cannot yet be used to obtain reliable information on the force field of a molecule. As yet, the only real basis for the interpretation of frequencies is the classical semi-empirical theory of vibrations.

The present chapter examines work on the study of the vibrational spectra of conjugated organic compounds. Its aim is to examine the picture of the electronic structure of the molecules revealed by the existing methods of vibrational spectroscopy, that is methods based on experimental data and theoretical concepts which are different from those of the methods of quantum chemistry.

1. Elastic Properties of Conjugated Chains

A large amount of experimental material[139,140,235-237] has been published on the structure of butadiene. Most authors assume that the butadiene molecule can exist in two isomeric forms, the *s*-trans and the *s*-cis. Although the existence of the *s*-trans-form of butadiene is not now doubted, the question of the realisation of the second isomeric form has not yet been completely resolved. The fact that usually only the *s*-trans-form of butadiene exists under normal conditions has been confirmed directly by studies of electron diffraction[139] and the rotational structure of the bands in the vibrational spectra[140].

The normal vibrations of butadiene were first calculated by Sverdlov and Tarasova[238] using the force constants for propene. The marked discrepancy between the observed and calculated frequencies in this and later work by Sverdlov and Tarasova[239] indicates that the force field of butadiene cannot be represented by the additive combination of the force fields of simpler molecules. Recently, Tatevskii and coworkers[240] tried to describe the vibrational spectrum of butadiene by assuming that the elastic properties of the double bonds are the same in the C=C–C=C system and in ethylene. Earlier, Ferigle and Weber[241,242] made an analogous assumption regarding the properties of the triple bond in the C≡C–C≡C system and in acetylene in a calculation of the vibrations of diacetylene and dimethyldiacetylene. To obtain satisfactory agreement with the experimental frequencies of butadiene, Tatevskii and coworkers[240] had to alter significantly the values of a large number of bond–angle interaction constants and increase the constant for the central bond. For diacetylene and dimethyldiacetylene, however, with this assumption, it was necessary to introduce anomalously high values for the constants for the interaction of the triple bonds with adjoining single bonds and also to increase the constant for the central bond. The assumption that the force constants of multiple bonds are the same in conjugated and non-conjugated molecules is unjustified for a number of reasons, including the fact that the constants obtained by Tatevskii and coworkers[240] for butadiene and by Ferigle and Weber[241,242] for diacetylene do not show the continuity required by actual sets of force constants in the description

of the properties of the molecules of a homologous series. The vibrational frequencies for polyenes and poly-ynes calculated using these constants not only show poor agreement with the observed frequencies but also show regular features which are different from those found for the observed frequencies with increase in the length of the chain[243,244]. Sufficiently reliable data on the force fields of compounds with alternating multiple and single carbon–carbon bonds evidently cannot be obtained on the basis of even a correct study of single molecules.

In a study of the structure of conjugated hydrocarbons, the authors of the present review carried out an analysis of the vibrational spectra of a large number of conjugated molecules of various classes: linear polyenes, poly-ynes, vinylacetylenes, cumulenes, and conjugated nitriles. The vibrational spectra of molecules with known structures were calculated for comparison.

The spectra of C_6H_6 and C_4D_6 were used in a study of butadiene[245,246]. In the calculation of the force constants, allowance was made for the characteristic frequency and form for individual atomic groups of many of the vibrations of butadiene. The set of force constants obtained for butadiene was subsequently tested for the molecules of polyenes with higher molecular weight. The constants were also further verified by calculating the electro-optical parameters and integral intensities of the absorption bands in the infrared spectra of C_4H_6, C_4D_6, and other polyenes.

The set of force constants found for the C=C–C=C system[245] indicates that there is appreciable interaction between the carbon–carbon bonds in the ground electronic state of butadiene. The force constants of the C=C bonds were found to be significantly lower than the analogous constants for ethylene[247], propene[248], and 2-methylpropene[249] (12.00 compared with 14.20‡) whereas the constant for the central C–C bond was found to be greater than that for propene and 2-methylpropene (10.40 compared with 7.02); higher values were obtained for the constants for the interaction of the double bonds (–1.50) and the interaction of the double and single bonds (0.40).

The force constants of butadiene were used to describe the vibrational spectrum of 1,3,5-hexatriene[245]. The frequencies of hexatriene calculated on this basis show satisfactory agreement with the experimental values. Complete agreement with the observed vibrational frequencies for the chain of carbon atoms in hexatriene was obtained by correcting slightly the force constant for the interaction of neighbouring double bonds and by making allowance for the weak interaction of the terminal carbon–carbon bonds. Hence the differences in the frequencies of butadiene and hexatriene are due not to a change in the force field resulting from the greater delocalisation of the π-electrons with increase in the length of the chain, as claimed by Lippincott and coworkers[250], but to the purely kinematic factor.

The problem of the equalisation of the bonds in polyenes containing a large number of units was examined by Ivanova and the authors[243] by analysing the vibrations of molecules of the type $X-[CH=CH]_n-X$, where $X = COOC_2H_5$, and $n = 2-8$. Studies of the chemical properties[244] and electronic and vibrational spectra[177,251–253] indicate that these compounds are linear polyenes with transoid arrangement of the bonds. The vibrations of molecules with two to eight units were calculated[243] using three different types of sets of force constants for the polyene chain: those of butadiene[245], propene[248], and benzene[254]. It was found that the calculation reproduces the characteristic features of the experimentally observed infrared[252,253] and Raman[251,252] spectra only when the force constants of butadiene are used. Thus increase in the length of the polyene chain does not lead to significant redistribution of the force field of the molecule.

The force fields of poly-ynes were studied by Popov and Lubuzh[255]. Attempts to describe the vibrational spectra of diacetylene and a number of other poly-ynes containing up to six triple bonds in the chain, using the constants for simple molecules, did not give satisfactory results, as in the case of the polyenes. The force field of the butadiene system C≡C–C≡C was found by simultaneous solution of the secular equations for diacetylene and dimethyldiacetylene. The values obtained differ significantly from the corresponding constants for saturated hydrocarbons and molecules with an isolated triple bond. Thus the force constant of the C≡C bond in diacetylene was found to be less than the constant for acetylene and methylacetylene (22.20 compared with 24.50 [256,257]), and the constant for the central C–C bond was found to be significantly greater than that for the single bond in methylacetylene (11.80 compared with 8.00 [257]). Significant values were obtained for the constants for the interaction of the triple bonds (–1.50) and the interaction of the triple and single bonds (0.50).

The vibrations of the poly-yne chain in the compounds $R-[C\equiv C]_n-R$, where R = Alk and $n = 2-6$, can be described[225] using force constants whose values are extremely close to those for diacetylene and are independent of chain length. This indicates that in the poly-yne chain, as in the polyene chain, equalisation of the orders of the multiple and single bonds does not take place with increase in chain length. This conclusion regarding the structures of linear polyenes and poly-ynes, based on an examination of their vibrational spectra, agrees with the results of most quantum-mechanical calculations and also with the available experimental data on the electronic spectra (the convergence of λ_{max} with increase in n) and bond lengths (the fact that the lengths of the multiple and single bonds are independent of chain length) for these compounds. It should be noted that the differences in the values of the force constants for the C=C bonds in ethylene and polyenes and for the C≡C bonds in acetylene and poly-ynes are not incompatible with the equality of the lengths of the multiple bonds in the corresponding molecules (with the significant interaction constants in conjugated molecules)[258].

Thus analysis of the vibrational spectra of butadiene[245] and diacetylene[255] and of polyenes[243] and poly-ynes[255] with higher molecular weight showed that molecules with alternating multiple and single carbon–carbon bonds have a characteristic type of force field. The force field of vinylacetylene[259] also belongs to this type. Let us consider the factors which may be responsible for the specific features of the force fields of these compounds. Table 3, taken from our paper[266], compares the most important characteristics of the force field for the chains of carbon atoms in butadiene and diacetylene with the analogous characteristics of molecules for which significant electron delocalisation is not expected (compounds *1–7*) and compounds for which delocalisation has been assumed (compounds *8* and *9*). The data show that change in the valency state of the carbon atoms does not lead to a significant change in the force constants for the single and multiple bonds. The force constants for the multiple bonds remain almost unchanged when an H atom is replaced by a methyl group. The constants for the interaction of even adjacent bonds are very small for compounds *1–7*. Quite different relationships between the force constants are observed in the benzene molecule and in the pentadienyl

‡ Here and subsequently the force constants are given in units $\times 10^6$ cm^{-2}.

ring of ferrocene, that is, with complete delocalisation. In this instance there is a change in the constants for the carbon–carbon bonds and a sharp increase in the constants for the interaction of adjacent bonds, and significant values are observed for the constants for the interaction of bonds without a common atom.

Table 3. Force constants of carbon–carbon bonds (in units $\times 10^6$ cm^{-2})*.

No.	Compound	Group	K_i	K_j	K_{ij}	K_{ik}	Type of force field	Refs.
1	ethane	C—C	7.0	—	—	—		260
2	propane	C—C—C	7.0	7.0	<0.1	—		261
3	ethylene	C=C	14.2	—	—	—	non-conjugated	247
4	propene	C=C—C	14.2	7.0	0.1	—		248
5	acetylene	C≡C	24.5	—	—	—		256
6	methylacetylene	C≡C—C	24.5	8.0	0.1	—		257
7	allene	C=C=C	15.0	15.0	0.2	—		262
8	benzene	C⋯C⋯C⋯C	11.4	11.4	1.0	—0.9	aromatic	254
9	pentadienyl ring of ferrocene	C⋯C⋯C⋯C	10.2	10.2	1.0	—0.8		263
10	butadiene	C=C—C=C	12.0	10.4	0.4	—1.5	mesomeric	245
11	diacetylene	C≡C—C≡C	22.2	11.8	0.5	—1.5		255
12	acrylonitrile	C=C—C≡N	13.8	9.5	0.5	—0.1	inductive	264
13	cyanoacetylene	C≡C—C≡N	24.3	10.2	0.7	—0.3		265

* K_{ij} is the adjacent bond interaction constant, and K_{ik} the interaction constants for bonds without a common atom.

Comparison of the elastic characteristics of simple molecules leads to the conclusion that the force constants of carbon–carbon bonds are parameters which are extremely sensitive to π-electron delocalisation but which have a comparatively low sensitivity to change in the hybrid type of the bond. It is therefore natural to relate the specific features of the force field of butadiene and diacetylene not to the hybridisation of the carbon but to partial π-electron delocalisation.

Relationships between the bond order and force constant (Fig. 7) and between the bond hybrid type (or length) and force constant (Fig. 8) have been obtained for single and multiple carbon–carbon bonds[265]. Curve *2* in Fig. 7, based on the relationship between force constant and hybridisation for a single C–C bond, shows the contribution of the σ-components to the values of the constants for multiple bonds (in the harmonic approximation and assuming additivity of the σ- and π-electrons). Comparison of curves *1* and *2* shows that the increased rigidity of the bond with increase in its order is due chiefly to the π-electrons. The values of the π-orders of the bonds, found from the curves in Figs. 7 and 8, amounted to 0.40 and 0.80 for butadiene, 0.45 and 1.88 for diacetylene, and 0.45, 0.80, and 1.88 for vinylacetylene. A noteworthy feature revealed by comparison of these data is the similarity in the values for the orders of the single bonds in butadiene, diacetylene, and vinylacetylene. This indicates that the multiplicities of the central bonds in these molecules are approximately the same. If the decrease in the lengths of single bonds situated between double and triple carbon–carbon bonds were determined to a significant extent by the values of their π-orders (in accordance with the delocalisation concept) we would expect only a very slight difference in the lengths of the C–C bonds in butadiene, diacetylene, and vinylacetylene (not more than 0.03 Å, if we calculate the covalent radius of carbon from data on the lengths of CH bonds). This is not the case, however. On going from butadiene to diacetylene, the length of the single bond decreases by 0.11 Å, which is almost twice that observed on going from ethane to butadiene (~ 0.06 Å).

Conjugated nitriles, such as cyanogen, cyanoacetylene, and cyanoethylenes, which have a formal resemblance to the corresponding conjugated hydrocarbons, are of considerable interest in the further study of this problem.

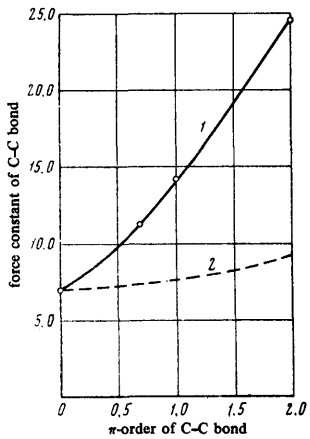


Figure 7. Plot of bond order against force constant for C–C bonds.

Qunatum-mechanical calculations which have been carried out for these molecules do not yet permit an unambiguous conclusion to be reached regarding the electron density distributions. McLean and Clementi[267,268], using the SCF MO LCAO method with allowance for all the electrons, obtained molecular wave functions for hydrogen cyanide (HCN) and cyanogen (C_2N_2). The bond orders for cyanogen calculated on the basis of these results by Mulliken[269] indicate that the delocalisation of the π-electrons in this molecule is as extensive as that in diacetylene. A different

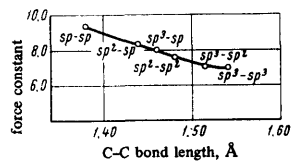


Figure 8. Plot of bond length against force constant for C–C single bonds.

conclusion was reached by Burnelle[270], who also applied the wave functions of McLean and Clementi to the HCN and C_2N_2 molecules. Burnelle concluded that the electron density curves for the HCN and C_2N_2 molecules are almost identical in the region of the nucleus of the nitrogen atom and in the region of the unshared pairs, and also in the zone of the C≡N bonds. Moffat[271] used the LCAO MO method with self-consistency to calculate the orders of the

C=C, C≡C, C–C, and C≡N bonds for an extensive series of nitriles. By assuming that the Coulomb and resonance integrals of the molecules studied are proportional to the corresponding integrals for benzene, Moffat obtained high π-orders for the C–C bonds in acrylonitrile (0.45), cyanoacetylene (0.36), and cyanogen (0.31). Shvarts[272] studied cyanoethylenes by the LCAO MO method and concluded that with increase in the number of nitrile groups attached to the double bond there is a decrease in the π-order of the latter and an increase in the conjugation energy.

The authors of the present review recently carried out an analysis of the vibrational spectra of cyanogen, cyanoacetylene[265], and mono-, *trans*-di-, *cis*-di-, tri-, and tetra-cyanoethylenes[264]. The observed values of the constants show that the force fields of conjugated nitriles differ qualitatively from the force fields of conjugated hydrocarbons. The constants for the bonds in cyanogen, cyanoacetylene, and cyanoethylenes were found to be much closer to the values of the corresponding constants for simple molecules than is the case for butadiene, diacetylene, and vinylacetylene. The values of the constants for the interaction of the multiple bonds are also much smaller. The orders of the central C–C bonds in the above nitriles are smaller by a factor of 3–4 than those for conjugated hydrocarbons. Thus the analysis of the vibrational spectra indicates that the π-electron delocalisation resulting from the intramolecular mutual influence of the nitrile groups and the double (or triple) bonds is not as extensive as that in analogous systems with alternating multiple and single carbon–carbon bonds. In spite of this marked difference in the π-electron delocalisation, the lengths of the single bonds with the same hybridisation in nitriles and in hydrocarbons show almost no differences. Thus here, as in butadiene, diacetylene, and vinylacetylene, we reach the conclusion that the interatomic distances are determined chiefly by the valency state of the carbon atoms, and not by π-electron delocalisation. This is also in accordance with a number of other experimental facts already mentioned. Data on the bond lengths for cyclo-octatetraene, in which the conditions necessary for conjugation are absent, are of particular interest. Our calculation of the force constants for the cyclo-octatetraene molecule[266] confirm that there is very little π-electron delocalisation.

The conclusion that the length of a carbon–carbon bond in linear conjugated systems shows little sensitivity to change in the bond order is not always correct, however. Studies of organic dyes[174,175,178], cumulenes[204,205], and condensed aromatic hydrocarbons[211,212] have shown that the bond orders in these molecules serve as an accurate indication of bond lengths. For example, for ovalene, which has twelve types of non-equivalent carbon–carbon bond, Buzeman[273] obtained excellent agreement between all the experimental and calculated bond lengths. The latter were determined using the π-orders calculated by the simple MO method. It is evident that here, as in many other instances, the agreement is not accidental. Thus at first sight there appear to be contradictory facts, some of which indicate that there is a relationship between bond order and bond length (aromatic compounds, polymethines, cyanines, and cumulenes), whereas others indicate that the bond length is not determined by the bond order (linear polyenes and poly-ynes). The authors of the present review[265] showed that this is due to the specific values of the π-orders of the bonds in the molecule and to the nature of the relationship between the order of a carbon–carbon bond and the change in its length due to π-electrons. The relationship observed[265] is given by curve *II* in Fig. 9. In the construction of curve *II* it was assumed that the lengths of pure σ-bonds of the types C_{sp^2}–C_{sp^2} and C_{sp}–C_{sp} are equal to the lengths of the central bonds in butadiene (1.483 Å) and diacetylene (1.379 Å). The length of a σ-bond of the type C_{sp^3}–C_{sp^3} is equal to the length of the C–C bond in ethane (1.54 Å). The vertical axis on the right gives the differences in the lengths of the multiple and single bonds formed by carbon atoms with the same hybridisation, and the horizontal axis gives the bond orders. As starting compounds we took acetylene, ethylene, benzene, graphite, and ethane, for which the hybridisation, orders,

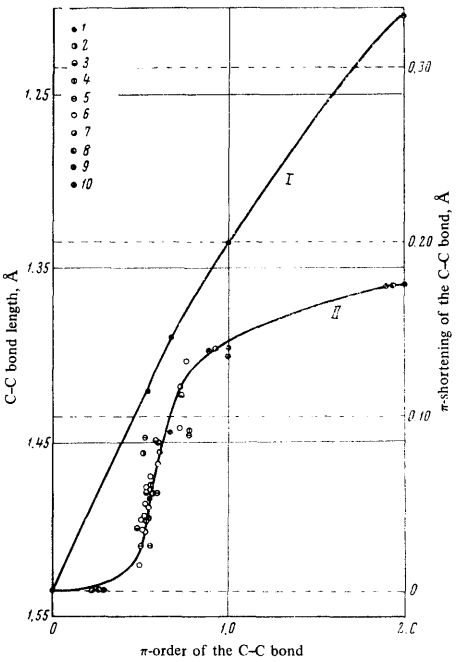


Figure 9. Plot of bond order against bond length (*I*) and bond order against π-shortening of the bond (*II*):
1) Ethane, graphite, benzene, ethylene, acetylene; *2*) naphthalene; *3*) anthracene; *4*) coronene; *5*) pyrene; *6*) ovalene; *7*) butadiene; *8*) diacetylene; *9*) vinylacetylene; *10*) allene.

and lengths of the bonds are known. Thus curve *II* gives the change in the length of the carbon–carbon bond due entirely to the π-electrons. The total change in bond length on going from ethane to acetylene is shown by curve *I* (the familiar Pauling curve). The fact that curve *II* is S-shaped indicates that the lengths of the carbon–carbon bond are not equally sensitive to bond order. The changes in bond order from 0 to 0.4 and in the regions around 1.0 and in around 2.0 lead to small changes in bond length, within the limits of experimental error. It is evidently for this reason that the bond lengths in butadiene, diacetylene, and vinylacetylene (whose bond orders lie in these ranges) differ little from the lengths of the carbon–carbon bonds of the same hybridisation type in molecules in which there is no π-electron delocalisation.

The bond length is most sensitive to change in bond order in the range 0.4–0.9, that is, in the range corresponding to aromatic compounds and organic dyes. Since all the carbon–carbon bonds in these molecules have a

hybridisation close to sp^2–sp^2, the interatomic distances depend almost exclusively on the bond orders, the relationship being almost linear. Curve *II* in Fig. 9 passes through the points corresponding to the molecules of naphthalene, anthracene, coronene, pyrene, and ovalene, and also the points corresponding to the molecules of butadiene, diacetylene (and hence other linear polyenes and poly-ynes), vinylacetylene, and allene.

The observed relationship between bond length and bond order shows that π-electron delocalisation and the associated changes in the orders of the single and multiple bonds in linear polyenes and poly-ynes does not lead to a significant change in bond length. The decrease in the length of the single bonds in these molecules with isolated multiple bonds is determined chiefly by the valency state of the carbon atoms. At the same time, preservation of the lengths of the bonds of a given hybrid type in the molecules of organic compounds cannot be taken as a sufficient basis for rejecting π-electron delocalisation.

This conclusion is equally applicable to bond energies. It can be seen from Fig. 10 that the relationships between bond order and total bond energy (curve *1*) and between bond order and the energy introduced into the carbon–carbon bond by the π-electrons (curve *2*) are analogous to the corresponding relationships between bond length and bond order (Fig. 9). The construction of the curves in Fig. 10 is analogous to that of the curves in Fig. 9; the values of the bond energies are taken from Table 1. The

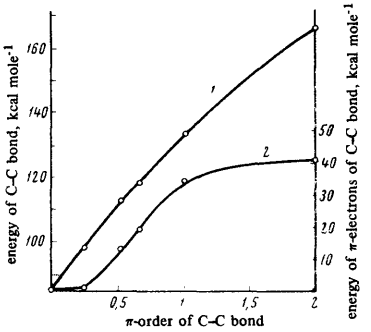


Figure 10. Plot of bond energy against bond order (*1*) and π-bond energy against bond order (*2*).

fact that the bond energy and bond length show identical behaviour with change in bond order is not surprising, since there is a linear relationship between them (Fig. 2). Fig. 10 shows that in conjugated hydrocarbons with open chains the energy of the π-bond is not proportional to the bond order, as follows from the simple Hückel method[213]. This feature evidently explains the overestimation of the part played by π-electron delocalisation in the interpretation of the properties of polyenes and poly-ynes by the Hückel method.

2. Polar Properties of Conjugated Chains

To obtain a more detailed picture of the electron density distribution along a chain of conjugated bonds, it is of considerable interest to study the intensities of infrared absorption bands and Raman lines. According to the modern semi-empirical theory of intensities[274], the electro-optical parameters characterising directly the electronic structure of a molecule are the dipole moments and polarisabilities of the individual bonds and their derivatives with respect to the vibrational coordinates.

The specific form of the electric field of butadiene was determined by the authors of the present review[275] by analysing the intensities of the infrared spectra of the C_6H_6 and C_4D_6 molecules. It was shown that the double bonds in butadiene have dipole moments of ~ 1.3 D, whose positive ends are the $C_{(2)}$ and $C_{(3)}$ central atoms. The parameter which characterises the change in the C=C moment on elongation of the double bonds was also found to have an appreciable magnitude. Since all the carbon atoms in the molecule are in the same valency state (sp^2), the results indicating non-equivalence of the electron density distribution in the C=C–C=C system contradict the views of Dewar and Schmeising[3-5] regarding the structure of butadiene. The observed electro-optical parameters of the terminal $=CH_2$ groups of butadiene (like the $=CH_2$ force constants) differ from the corresponding quantities in non-conjugated molecules (ethylene and propene) to a much smaller extent than the parameters of the central =CH bonds. This suggests that partial delocalisation of the electrons in butadiene and the production of an excess of negative charge on the $C_{(1)}$ and $C_{(4)}$ atoms relative to $C_{(2)}$ and $C_{(3)}$ take place chiefly as a result of the overlap of the π-orbitals of the $C_{(2)}$ and $C_{(3)}$ central atoms. An analogous conclusion regarding the polarity of the multiple bonds and the nature of the electron density distribution was reached by studying the intensities of the infrared absorption bands of other simple conjugated molecules—diacetylene and vinylacetylene[276].

Let us consider briefly the picture of charges on atoms following from quantum-mechanical calculations. Coulson and Rushbrooke[277] previously showed that the π-electron charges on all the carbon atoms in polyenes are the same and equal to 1. Later, McWeeny[278] showed that the formal charge on carbon can be represented as the sum of the local charge of the atom and the charge of the bond. It was concluded that two carbon atoms with equal formal charges can have different local charges, so that the distribution of the charges in alternant hydrocarbons may be unsymmetrical. Maslen and Coulson[279] calculated the charges of the atoms and bonds in linear polyenes (without allowance for the distribution of electrons in the σ-bonds). The following values were obtained for butadiene:

$$\overset{0.82}{C}\overset{0.75}{=}\underset{0.35}{C}\overset{0.75}{-}\underset{0.14}{C}\overset{0.75}{=}\underset{0.35}{C}\overset{0.82}{.}$$

Thus the values of the π-electron charges on the $C_{(1)}$ and $C_{(4)}$ atoms are greater than those on the $C_{(2)}$ and $C_{(3)}$ central atoms. An interesting feature is that the charges on the $C_{(1)}$ and $C_{(4)}$ atoms almost coincide with the values of the charges on the carbon atoms in ethylene, calculated by the same authors[279]. The magnitude of the C=C moment, determined by Maslen and Coulson only on the basis of the non-equivalent distribution of the π-electron density along the bond, amounts to ~ 0.45 D.

Fukui and coworkers[280] used the LCAO MO-method to calculate the σ-electronic charges of the atoms in butadiene. The calculations gave the following σ-electron density distribution:

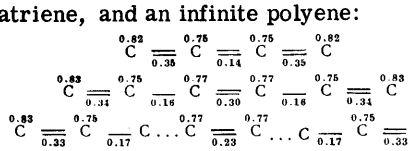
$$\overset{0.18}{C}=\overset{0.11}{C}-\overset{0.11}{C}=\overset{0.18}{C}.$$

The dipole moment of the C=C bond due to the non-equivalent distribution of the σ-electrons of butadiene amounts to ~ 0.45 D and is directed in the same direction.

Thus the data on the electron density distribution in butadiene obtained from quantum-mechanical calculations and analysis of the intensities of the infrared spectra show qualitative agreement.

The polar properties of conjugated compounds containing a larger number of units in the chain were studied by Ivanova, Lubuzh, and the present authors[252,253,255] using the intensities of the infrared absorption bands of $\alpha\omega$-substituted polyenes of the type $X-[CH=CH]_n-X$, where $X = COOC_2H_5$ and $n = 2-7$, and poly-ynes of the type $R-[C\equiv C]_n-R$, where R = Alk and $n = 2-4$. The experimental data on the intensities of the absorption bands of the polyenes at about 1600 cm^{-1} and of the poly-ynes at about 2200 cm^{-1}, and an analysis of the forms of the vibrations, indicate that the observed proportionate increases in the integral intensities of absorption for the polyenes and poly-ynes are due chiefly to the increase in the number of bonds taking part in the vibrations, and not to changes in the polar properties of the chains. Calculations of the intensities of the absorption bands of polyenes led to the conclusion that the values of the polarisation of both single and double bonds depend little on the position of the bonds in the chain. Good agreement between the experimental and calculated values of the relative intensities of the infrared absorption bands of the polyenes at about 1600 cm^{-1} was obtained with the assumption that the polarisation of a single bond is equal to half the polarisation of a double bond and of opposite sign. Thus studies of the frequencies of the normal vibrations and the intensities of the infrared absorption bands show that in molecules with alternating multiple and single carbon–carbon bonds there is alternation of both bond orders and charges on the carbon atoms along the chain, the degree of alternation in both instances being independent of chain length. Thus the frequencies and intensities of alternant hydrocarbons can be explained within the framework of a single model with partly delocalised bonds. Moreover, the data obtained cannot be explained using the hybridisation concept.

The conclusion, which follows from the analysis of the infrared spectra, that there is alternation of the charges on the carbon atoms in a polyene chain, agrees with the results of quantum-mechanical calculations by Maslen and Coulson[279]. The following results were obtained for butadiene, hexatriene, and an infinite polyene:



These data show that the charges on the atoms of the terminal bonds are independent of the dimensions of the polyene chain. The charges on the atoms of the central bonds in the polyenes also remain unchanged with increase in the number of units. The dipole moments of the double and single bonds have opposite directions. It may be noted that quantum-mechanical calculations and analysis of the infrared spectra lead to a polyene model in which the central bond has no dipole. Other data also point to a model in which the central bond exhibits unique properties. Even in long polyenes, the central bond exhibits specific chemical and stereochemical properties[148]. For example, of the large number of possible *cis–trans* isomers of a polyene chain, the one most readily realised is that with the central double bond in the *cis*-configuration. Ease of isomerisation at the central double bond is observed in the molecules of lycopene and the α-, β-, and γ-carotenes. The molecules undergo relatively easy rupture at this point[148].

As already noted, the force fields of conjugated nitriles differ qualitatively from the force fields of conjugated hydrocarbons. In particular, the force constants of the C=C, C≡C, and C≡N bonds and the intermediate C–C bonds in cyanoethylenes and cyanoacetylene (Table 3) have values which are close to the corresponding constants for the isolated multiple bonds and the simple σ-bond. Study of the intensities of the infrared absorption bands of acrylonitrile[281] showed that the mutual influence of the multiple carbon–carbon bonds and the nitrile group produces an electron density distribution which differs significantly both from that for simple molecules and from that for alternant hydrocarbons without leading to appreciable π-electron delocalisation. Calculation of the electro-optical parameters gives a dipole moment of ~ 1.0 D for the double bond in acrylonitrile with the negative charge on the $C_{(2)}$ atom, that is, the direction of the double bond moment in acrylonitrile is the opposite of that for butadiene and vinylacetylene. The double bonds in the C=C–C≡N and C=C–C≡C (or C=C–C=C) systems differ in the values of the π-orders, in the nature of the electron density distribution along the bond, in the ability of the charge to migrate during the vibration (this is much smaller for acrylonitrile than for vinylacetylene and butadiene). In these conjugated nitriles, the displacement of the electron density towards C≡N takes place chiefly within individual bonds. There may be instances when the inductive effect causes the electrons to leave the limits of their "own" bonds. This requires a relationship between the donor and acceptor properties of the interacting atomic groups which is different from that in acrylonitrile and cyanoacetylene. These conditions are satisfied, for example, in the cyanamide molecule, in which the inductive effect leads to delocalisation of the electrons of the unshared pairs of the nitrogen and a change in its valency state[282].

The electron density distribution in acrylonitrile was recently studied by Halper and coworkers[283] using the simple Hückel method with allowance for overlap. The results obtained show good agreement with the results of the analysis of the intensities of the infrared absorption bands. The dipole moment of the C=C bond, determined on the basis of the π-charges on the atoms found by Halper and coworkers[283], amounted to ~ 0.7 D, compared with the value of ~ 1.0 D obtained from the infrared spectra[281].

Study of the electron density distribution in butadiene, diacetylene, vinylacetylene, and polyenes and poly-ynes with higher molecular weights showed that the delocalisation of the electrons in these molecules leads to polarisation of the bonds. In molecules known to contain polarised bonds (cyanogen, cyanoacetylene, and cyanoethylenes), however, the delocalisation of the π-electrons is significantly smaller, and is probably due to different factors. As already noted, the direction of the displacement of the electron density of multiple bonds in these molecules under the influence of the inductive effect of the acceptor nitrile group is the opposite of that for the analogous bonds in compounds with purely carbon–carbon conjugation. Thus the effect of delocalisation and the inductive effect have opposite influences on the π-electron density distribution. It is probably because of this feature, and also because of the polarisation of the bonds on delocalisation and the production of an inductive interaction, that the alternation of the bonds is preserved in linear polyenes and poly-ynes. The degree of alternation, that is, the orders of the multiple and single bonds, is determined by the competition between the two effects. In aromatic compounds, for example, in benzene, the complete equalisation of the bonds is due to

the fact that π-electron delocalisation is possible whereas polarisation is impossible, that is, only one effect operates.

Let us now consider the Raman spectra of conjugated systems. The Raman spectra of the esters of polyene $\alpha\omega$-dicarboxylic acids $C_2H_5OOC[CH=CH]_nCOOC_2H_5$, where $n = 2-8$, and diphenylpolyenes $C_6H_5[CH=CH]_nC_6H_5$, where $n = 5$ or 6, were studied in detail by Shorygin and Ivanova[251,284,285]. It was found that with increase in n, the intensities of the various Raman lines of the polyenes do not increase to the same extent. In the spectra of short polyenes ($n = 2-4$) the number of observed lines assigned to the vibrations of the chain corresponds exactly to that predicted by theory for centrosymmetric molecules. With increase in n, the frequency of the exciting light approaches the range corresponding to the characteristic frequencies of the electronic transitions, and when the frequencies coincide, that is, with excitation in or close to the resonance range, not all of the Raman-active vibrations of the polyene chain are observed, but only two normal vibrations ($\sim$ 1600 cm^{-1} and 1140 cm^{-1}) and their overtones and combination frequencies (as far as the fourth order). An interesting feature is that the maximal deviations of the frequencies of higher order from the multiple fundamental tones, due to anharmonicity, are small and amount to $\sim$ 30 cm^{-1}. The lines at $\sim$ 1600 cm^{-1} and 1140 cm^{-1} are characterised by unusually high absolute intensities. Approximately the same frequencies are observed in the vibrational structure of the first absorption bands and fluorescence bands in a number of other polyenes[286]. These lines are also present in the Raman spectra of polyenes with various substituents in the α- and ω-positions[287]. With increase in the number of double bonds, the frequency in the region of 1600 cm^{-1} decreases regularly, approaching a definite limit, whereas the 1140 cm^{-1} frequency is independent of chain length. Calculations for polyenes[243,245] showed that this behaviour of the Raman frequencies is not due to equalisation of the bonds. The reason for the unique activity of the symmetric vibrations at $\sim$ 1600 cm^{-1} and 1140 cm^{-1} compared with the other vibrations permitted by symmetry for a system of conjugated double bonds is that only these vibrations involve the entire polyene chain, so that they are accompanied by the maximal change in the polarisability of the molecule.

The reason for the marked decrease in the frequencies at $\sim$ 1600 cm^{-1} with increase in the length of the chain ($\sim$ 100 cm^{-1} on going from $n = 2$ to $n = 8$) without change in the nature of the bonds and with preservation of the 1140 cm^{-1} frequency under the same conditions was investigated[281] by comparing the zeroth amplitudes of the double ($\bar{Q}$) and single ($\bar{q}$) bonds. It was found that the ratio $\bar{Q}/\bar{q}$ for the vibrations at $\sim$ 1600 cm^{-1} decreases with increase in the length of the chain, the decrease being greater for the first terms of the vinyl series, but remains almost constant for the vibrations at 1140 cm^{-1}. Since the overall change in the double and single bonds in these vibrations depends little on chain length, the decrease, with increase in n, in the relative participation of the more rigid double bonds in the $\sim$ 1600 cm^{-1} vibration leads to a decrease in the frequency without change in the nature of the bonds. With the condition that the ratio $\bar{Q}/\bar{q}$ is constant, the frequency at 1140 cm^{-1} can remain unchanged in the spectra of various polyenes only if the elastic properties of the bonds are preserved irrespective of chain length[288].

3. Transfer of Influence Along a Chain of Conjugated Bonds

The concept of molecules with alternating multiple and single carbon–carbon bonds as systems transferring the influence of substituents without significant weakening (vinylogy) is widely encountered in the literature. Analysis of the available data on the physical and chemical properties of conjugated compounds, however, indicates that there is little justification for these views. Thus calculations of the vibrations of linear polyenes and poly-ynes[243,245,255] showed that significant interaction takes place only between the closest multiple bonds. With increase in the number of intermediate units, the interaction rapidly becomes weaker and is almost imperceptible for multiple bonds separated by more than two carbon atoms. It is natural to assume that the mutual influence of substituents in the α- and ω-positions will decrease to the same extent. The problem of the transfer of influence through a system of conjugated bonds was examined by Ivanova and the present authors[243,253] in an analysis of the vibrational spectra of the esters of polyene $\alpha\omega$-dicarboxylic acids ($n = 2-8$), unsymmetrical polyenes $X-[CH=CH]_nCOOC_2H_5$ ($X = CH_3$, NO_2, and CHO, $n = 2-4$) and $\alpha\omega$-dinitriles $NC-[CH=CH]_n-CN$ ($n = 4$ or 5). The study showed that the values of the frequencies and intensities of the C=O stretching vibrations in the infrared spectra of the esters $C_2H_6OOC[CH=CH]_nCOOC_2H_5$ are independent of chain length and agree with the corresponding values for the $\alpha\beta$-unsaturated esters of carboxylic acids (RCH=CHCOOR, R = Alk[289]). Change in X and n in $X-[CH=CH]_nCOOC_2H_5$ did not lead to marked changes in the frequencies and intensities of the absorption bands of the carbonyl group in the spectra. This indicates that a conjugated system of carbon–carbon bonds in the ground electronic state of the molecule does not effectively transfer the influence of substituents. This conclusion is confirmed by the agreement shown by the ν_s and ν_{as} frequencies of the C=O vibrations in the spectra of polyene diesters and the C≡N vibrations in the spectra of polyene dinitriles. The absence of splitting of the frequencies of the symmetric and antisymmetric vibrations of equivalent atomic groups in the spectra of symmetrical molecules indicates the absence of mechanical and electronic interaction between the groups[290,291]. The conclusion that substituents at the ends of a polyene chain have an extremely restricted sphere of influence agrees with data obtained by Hutchinson and Sutton[179] on the dipole moments of the series of polyenes $(H_3C)_2N-[CH=CH]_n-CHO$ ($n = 0-4$) and data obtained by Yanovskaya[292] on the ionisation constants of polyene mono- and di-carboxylic acids. The nature of the changes in both dipole moments and ionisation constants with increase in chain length shows that the mutual influence of substituents separated by a conjugated chain weakens very rapidly. It can hardly be detected by dielectric or potentiometric measurements or by vibrational spectroscopy even for polyenes with $n \geqslant 3$. Quenching of the influence of substituents was also observed by Shorygin and Ivanova[293,294] from the Raman spectra of various other classes of conjugated compound. A long system of conjugated bonds does not transfer the influence effectively even when one end of the chain carries a substituent with clearly defined electron-donating properties (for example, R_2N-) and the other carries a substituent with clearly defined electron-accepting properties ($-NO_2$).

4. Classification of the Force Fields and Electric Fields of Organic Compounds

A considerable amount of material on the force fields of various classes of organic compound has now accumulated. Its analysis has enabled the present authors[266] to classify

force fields (initially on the basis of purely external characteristics) into several types, arbitrarily described as non-conjugated, aromatic, mesomeric, and inductive. It was found that this classification corresponds to the electronic structures of the molecules. Each type of force field is determined by a definite form of electron density distribution. The force constants of bonds and their interaction constants for simple molecules are given in Table 3.

We have already noted the characteristic features of the force fields of saturated hydrocarbons, compounds with isolated multiple bonds, aromatic compounds, and linear polyenes and poly-ynes. The force fields of conjugated molecules containing electron-accepting groups exhibit certain specific features. The data given above for the molecules of acrylonitrile and cyanoacetylene show that the polarisation of multiple carbon–carbon bonds has little influence on the values of the diagonal elements, but leads to an increase in the non-diagonal elements of the interaction of the bonds.

The sets of force constants of each type describe the vibrational spectra of a large number of molecules with the corresponding electron density distribution. The force constants of the non-conjugated type describe the spectra of alkanes, alkenes, and alkynes; those of the aromatic type describe the spectra of benzene derivatives and condensed aromatic compounds; those of the mesomeric type describe the spectra of polyenes, poly-ynes, and vinylacetylenes; and those of the inductive type describe the spectra of a large number of nitriles[295,264,265]. Each type of force field is characterised by definite values of the force constants of the bonds and values of the bond interaction constants. Changes in the constants are mutually related. Thus decrease in the constants of the multiple bonds in linear polyenes and poly-ynes (as a result of π-electron delocalisation) is accompanied by an increase in the constants of the single bonds and the bond interaction constants (as a result of the formation of multi-centre orbitals). Change in the nature of the electron density distribution leads to a change in the complete set of force constants. Within a given type of force field, however, the values of the constants are transferable.

The classification of force fields facilitates the solution of two problems. When the force field is known, its classification in a given type immediately gives information on the electronic structure of the molecule. On the other hand, a knowledge of merely the nature of the electron density distribution in a molecule increases considerably the reliability of the determination of force constants. The existence of a correlation between the structure and force field of a molecule imposes a number of additional conditions on the solution of the reverse spectroscopic problem. An example is provided by the study of the molecules of cyclo-octatetraene (C_8H_8) and butatriene (C_4H_4).[266] The frequencies of the vibrations of these extremely complex molecules were determined using force fields compiled on the basis of data on their electron density distributions. Calculations of the normal vibrations for C_8H_8 and C_8D_8, in agreement with quantum-mechanical calculations[24], confirmed that there is no significant π-electron delocalisation in cyclo-octatetraene, despite the formal resemblance to the molecules of alternant hydrocarbons. In the calculation for butatriene it was assumed that the nature of the electron distribution in one of the planes of the molecule is similar to that in butadiene, and in the other (perpendicular to the first) is similar to that in an isolated double bond. In accordance with this assumption, the force field of butadiene was compiled by superimposing fields of two types—mesomeric and non-conjugated. In the determination of the numerical values of the force constants, the values of the orders of cumulative bonds for butatriene obtained by the MO method[221] were assumed, and use was made of the relationship between the force constant, hybridisation type, and bond order (Figs. 7 and 8). The frequencies of the vibrations of butatriene calculated for these conditions showed good agreement with the observed values. Recently, an attempt was made to calculate, on the basis of the proposed classification of force fields, the frequencies of the vibrations of vinylacetylene and the four methyl derivatives of vinylacetylene using constants selected on the basis of definite assumptions regarding the electron density distribution in the C=C–C≡C system[259]. Agreement between all the calculated and experimental frequencies (more than 120) was obtained only when a force field of the mesomeric type was used. It should be borne in mind, however, that the proposed classification[266] of force fields is to some extent arbitrary. A sharp distinction cannot be made between the force fields of organic molecules, particularly molecules containing hetero-atoms. When there is strong intramolecular interaction between individual atomic groups, the force field of the molecule may appear in a new form or exhibit the features of several types simultaneously. Examples are provided by the molecules of $\alpha\beta$-unsaturated ketones[296] and the cyanamide molecule[282]. Nevertheless, a knowledge of the force fields of the limiting structures is also necessary in complicated cases.

A much more complete picture of the electronic structure of a molecule in the ground state can be obtained by simultaneous analysis of the force field and the electric field. Data are now available on the electric fields of a comparatively large number of molecules of organic compounds of various classes[256,275,281,297-304]. These values were obtained with the same approximation and within the framework of a single calculation scheme by Gribov[274]. Calculations showed that the electro-optical parameters characterise the properties of only the electron cloud of the molecule and in this sense they resemble force constants. A paper by one of the present authors[305] classified the electric fields of organic molecules and established a correlation between the specific features of the electronic structure and the characteristic features of the electric field.

Calculation of the intensities of the infrared absorption bands of saturated hydrocarbons and compounds with isolated multiple bonds[256,298-301] showed that the electro-optical parameters of the $-CH_3$, $=CH_2$, and $\equiv CH$ groups, found for simple molecules, can be used to describe satisfactorily the intensities for more complex alkane, alkene, and alkyne molecules. Thus within a series of these compounds, the electro-optical parameters of the above groups, like their force constants, are transferable. The mechanical and polar properties of the $-CH_3$, $=CH_2$, and $\equiv CH$ groups in the molecules of a given series remain to a considerable extent unchanged, that is, the electron density distribution remains approximately the same. The electric fields of alkanes, alkenes, and alkynes are also characterised by low values for the dipole moments and polarisations of the carbon–carbon bonds. The participation of purely carbon-carbon bonds in the vibrations of the molecules does not make a significant contribution to the intensities of the infrared absorption bands. This leads to the at first sight paradoxical conclusion that the infrared spectra of compounds of these classes are due chiefly to the electro-optical properties of the CH bonds.

The electric fields of linear conjugated molecules belong to a different type. Butadiene[275], diacetylene[276], and vinylacetylene[276], as well as polyenes[252] and poly-ynes[255]

with higher molecular weights are characterised by appreciable dipole moments and polarisations of the carbon–carbon bonds. In the C=C–C=C, C=C–C≡C, and C≡C–C≡C systems the excess of negative charge is found on the $C_{(1)}$ and $C_{(4)}$ atoms. The electro-optical parameters of identical atomic groups in the molecules of conjugated hydrocarbons have similar values. Thus the electric field of vinylacetylene can be made up almost entirely of the parameters of the corresponding atomic groups of butadiene and diacetylene[276,305], and the electric fields of polyenes can be made up of the parameters of butadiene[252]. In this sense the electro-optical parameters of butadiene and diacetylene are transferable and can be used to compile the electric fields of more complex linear molecules with alternating multiple and single carbon–carbon bonds. It was noted above that in the same series of compounds an analogous property is shown by the force constants of butadiene and diacetylene. Thus for conjugated molecules, as for non-conjugated molecules, the transferability of some parameters is accompanied by the transferability of others. A correlation between electric fields and force fields is also observed for the molecules of other classes of organic compound. In all cases each type of electric field corresponds to a definite type of force field.

The results of experimental and theoretical studies of conjugated hydrocarbons enable the following conclusions to be reached regarding their structures and certain other properties.

1. Linear polyenes and poly-ynes consist of systems of conjugated alternating bonds. Increase in the length of the chain does not lead to appreciable equalisation of the carbon–carbon bonds. The lengths and orders of the multiple and single bonds in polyenes and poly-ynes with high molecular weights are approximately the same as those for butadiene and diacetylene respectively.

2. Organic dyes (polymethines, cyanines, and oxonols) contain equalised bonds. With increase in the length of the chain, the lengths and orders of the bonds approach those of the bonds in benzene.

3. Cumulenes consist of systems of double bonds conjugated in two mutually perpendicular planes; increase in the length of the chain does not lead to a change in the lengths and orders of the bonds. In a cumulene with a long chain, all the bonds except the terminal bonds have the same lengths and orders. As for other compounds with equalised bonds, λ_{max} in the ultraviolet spectra of the cumulenes is displaced by a constant amount with the addition of each new unit.

4. The lengths and energies of carbon–carbon bonds are not equally sensitive to bond order throughout the entire range of possible change in this quantity. Preservation of the lengths and energies of the bonds of a given hybridisation type in the molecules of organic compounds cannot be taken as a basis for rejecting π-electron delocalisation.

5. Delocalisation of π-electrons and the associated changes in the orders of multiple and single bonds does not lead to a significant change in the lengths and energies of the bonds in polyenes and poly-ynes. The increase in the energy and the decrease in the length of the single bonds in alternant hydrocarbons are determined chiefly by the valency state of the carbon atoms.

6. The lengths and energies of the bonds in polymethines, cyanines, oxonols, and aromatic compounds depend almost exclusively on the bond orders, the corresponding relationships being almost linear.

7. Delocalisation of π-electrons in polyenes and poly-ynes leads to a non-equivalent distribution of electron density along each bond, with the exception of the central bond. In butadiene, vinylacetylene, and diacetylene, the positive ends of the dipoles of the multiple bonds are the central carbon atoms. With increase in the length of the chain, alternation of the bond orders, and also alternation of the charges on the atoms, are preserved.

8. The mutual influence of atomic groups separated by a chain of conjugated carbon–carbon bonds rapidly becomes weaker with increase in the number of intermediate units.

9. The characteristic features of the force fields and electric fields of conjugated hydrocarbons are determined chiefly by π-electron delocalisation.

10. The methods of quantum chemistry and vibrational spectroscopy lead to the same picture of the structure of conjugated hydrocarbons.

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A number of interesting experimental and theoretical papers on the structures of conjugated hydrocarbons appeared after the present manuscript had been submitted for publication. We can now only mention briefly some of these papers, most directly related to the topics discussed above.

Page 121. Traetteberg[306] has made a new study of the structure of cyclo-octatetraene. The value which he obtained for the C–C bond length in this molecule (1.475 Å) is greater than the value found earlier (1.460 Å)[23]; there is now almost no difference between the length of this bond and the length of the single carbon–carbon bond in butadiene.

Page 126. Studies confirming the alternation of the charges on the atoms and the bond orders in polyenes now include the following: calculations by Flurry and Bell[307] using the SCF MO LCAO method in the Pariser–Parr–Pople approximation, including resonance integrals characterising non-neighbouring interactions; calculations by Misurkin and Ovchinnikov[308] using the Hartree–Fock generalised self-consistent field method; calculations for $\alpha\omega$-diphenylpolyenes using Pariser–Parr–Pople method; calculations for polyenes by Adams and Miller[310] using a modified method with self-consistency; calculations for dienes and hexatriene by Allinger and coworkers[311] using the Pariser–Parr method; and calculations for polyenes by Kutzelnigg[312] within the framework of the simple Hückel approximation using a perturbation method.

Alternation of bond lengths was obtained by Haugen and Traetteberg[313] in an electron-diffraction study of 1,3-butadiene ($L_{C=C}$ = 1.343 Å and L_{C-C} = 1.467 Å) and *trans*-1,3,5-hexatriene ($L_{C=C}$ = 1.345 Å and L_{C-C} = 1.450 Å).

Page 127. Dähne and Leupold[314] published a review on the calculation of the electronic spectra of dyes of various classes.

Page 132. Cherniak and Costain[315] showed by microwave spectroscopy that the lengths of the C–C bonds in *trans*-acrolein and 1,3-butadiene are approximately equal (1.470 Å).

Page 134. Data indicating non-equivalent distribution of the π-electron density along the carbon framework of 1,3-butadiene were obtained by Hobgood and Goldstein[316] in an analysis of the NMR spectra.

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