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Conjugation and the periodic system of the elements

P P Shorygin, K Ya Burshtein
Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The knowledge of the characteristics and mechanisms of the interaction of the active centres of complex molecules is of primary importance for the development of theoretical and applied organic chemistry, promotes a more productive utilisation of the enormous amount of experimental data available, facilitates predictions and the search for new routes to and new varieties of the synthesis, industrial technology, and applications of organic compounds, and leads to more complete ideas about their functions in chemical, physical, and physiological processes. The studies in this field have been subjected to a critical survey and attention has been drawn to the possibility of distinguishing different forms of the mutual influence of atomic groups, the establishment of correlations between different parameters of conjugation and of the role of relativistic effects, the characteristics of conjugation systems incorporating heteroatoms from different groups in the Periodic System, and the study of the evolution of excited molecules.

The bibliography includes 188 references.

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I. Introduction

The properties and parameters of complex molecules made up of isotypical atomic groups are largely associated with the entire set of these groups; in the presence of heterogeneous fragments, a more or less marked relationship with individual fragments can be noted (examples: the colour of compounds with some kind of chromophoric centre; quasi-local vibration modes of the atoms; the dipole moment of a molecule containing a highly polar group). The application of mathematical methods makes it possible to obtain more detailed information (for example, the conversion of normal vibration frequencies of atoms into the force constants of individual chemical bonds) and leads to data for the distribution of electron density among the atoms, the interatomic distances, the structures of individual molecular orbitals having a bearing on the physical or chemical processes investigated, etc.

The more or less "local" characteristics of atomic groups or bonds obtained directly from experiment or by calculation make it possible to compare isotypical groups in various molecules. Slight variations in the corresponding parameters are usually attributed to the influence of adjacent and non-adjacent molecular fragments. Knowledge of the characteristic features of the mutual influence of atomic groups, to which the specific features of the physical and chemical properties of polyatomic (complex) molecules are in some way related, greatly expands the information afforded by the usual structural formulae and constitutes the most important problem in theoretical organic chemistry. However, one should note that the idea of mutual influence is based on comparisons with a selected initial basis, usually with a set of simpler molecules, simulating the fragments of a complex molecule, or with the classical structural formula. When there is an appreciable discrepancy between the real structures and such formulae, the choice of what one could describe as the "origin of coordinates" proves ambiguous and arbitrary. Difficulties of a similar kind and arbitrary features can arise also in other problems, for example, in the selection of a system of independent natural coordinates in the description of the force field (especially in cyclic molecules).

In order to expand and deepen our knowledge in the field under consideration, the constants and functions characterising reactivity (the Hammett, Taft, etc. constants), thermochemical properties, geometrical and electronic structures, the systems of electronic excitation levels, the force field in deformed molecules, optical and magnetic properties, various forms of relaxation, and biological activity have been resorted to. Computational quantum-chemical methods are being employed to an increasing extent. With their aid, it is possible to characterise the coordinates of chemical reactions and the transition states, to construct three-demensional electron density diagrams, to calculate (or if necessary to predict) the spectra of compounds of light and heavy elements, including electronic absorption spectra with identification of valence and Rydberg transitions, to assign the lines (bands) in the spectra and thus impart to them a much greater information content,[1–4] and to estimate the contribution of relativistic effects.[5,6] The latter are important for the chemical and phyiscal properties of molecules incorporating the atoms of heavy elements; it is sufficient to say that their contribution to the energy of the chemical bond reaches 50% in some cases.

Procedures for the productive employment of new physical methods for the investigation of molecular structures have been developed in the recent period. The electron-transmission spectroscopic technique[7,8] has been improved,[7–8] the use of

synchrotron emission has made absorption spectra in the range 1000–2000 Å accessible, and the technical possibilities of resonance Raman spectroscopy have been greatly expanded (the method has been extended to virtually all classes of organic compounds by employing excitations up to 1400 Å, the employment of recording times approaching the femtosecond range, and the measurement of spectra of microobjects, for example a *single* bacterium; the recording of the transformation of light by a single atom of molecule has been an outstanding achievement). Nuclear quadrupole resonance and binary (e, $2e$) spectroscopic data as well as non-linear optical methods have attracted attention. The formation of images of individual molecules with the aid of a scanning tunnel microscope has become realistic. The employment of light pulses with femtosecond durations (10^{-14}–10^{-15} s) has opened up new horizons; the determination of the characteristics of a chemical reaction of a molecule in a detailed time scan, eventually reflecting the evolution of the transition state and the possible rapid oscillations of the system within the limits of the coherence time ("femtochemistry",[9] reaction "vector dynamics",[10] attempts to analyse the photodissociation of a molecule by examining the dynamics of wave packets[11]) has become feasible.

Experimental and theoretical studies on numerous organic compounds have demonstrated the complexity of the entire pattern of intramolecular interactions. Here it is sufficient to draw attention to the multiplicity of (1) types of alternation of chemical bonds and heteroatoms in the chain, (2) three-dimensional forms of conjugated π-systems (quasi-linear systems—poly-ynes; two-dimensional systems—polyacenes, polyenes; three-dimensional, including spherical, systems—footballene), (3) couplings between different degrees of freedom, (4) degrees of stability (stable, and bistable, multistable, dynamic, unstable, non-rigid, and hypothetical systems), and (5) different versions of quantum states of the molecule.

The endeavour to make the enormous virtually non-encompassable accumulated data more readily available for practical use has led to numerous attempts to establish some kind of simple correlations between different properties of the molecule, on the one hand, and in series of structurally similar compounds, on the other (see, for example, Chau and McDowell[12] and Sacher[13]). The proposed relations with empirically selected constants are far from universal and have limited cognitive value; nevertheless many of them are extremely useful in practice.

The interaction between the active centres of a complex molecule† is reflected in one way or another in the energy and structure of the molecular orbitals, favouring their delocalisation, in the orders of chemical bonds and in the interatomic distances (promoting in most cases a certain degree of smoothing of the alternation), in the distribution of electron density, in the electronic and vibrational excitation energies, and in the possibilities of the evolution of the state of the system. These features can be greatly modified following the application of an external field as a result of association and solvation.

Henceforth, certain problems of conjugation and, in a broader sense, of the coupling between the active centres will be described in the text (see Sections II–IV and also Maier et al.[14] and Cook et al.[15]). Controversial problems, the limitations of the models employed, and contradictions in the estimates of the mutual influence of atomic groups will not be ignored.

† Depending on the way in which the molecule is acted upon, different fragments can become the active zone or the reaction centre. The term "active centre" has the designation of a more or less local subsystem and therefore a conventional significance; in optical studies, the chromophoric group is usually implied.

II. Coupling between the active centres of a complex molecule

The distribution of electron density (the distribution of excitation energy in other problems) in a polyatomic molecule, for example, in a molecule involving a simple π–π conjugation system, can be in principle determined as a characteristic of the "stationary state". However, in the case of molecules, complexes, or ions incorporating weakly bound active centres, for example, a conjugation system of the π–σ–π type, one cannot rule out the practical possibility of recording the evolution of the state of individual centres, for example, oscillations in electron density or beats in the populations of the orbitals of fragments, provided that the vibration period is greater than 10^{-14} s [9,16] (see Section III). Whether or not a weak or strong coupling is produced between the subsystems depends on the molecular structure; the principal trend is towards a weakening of the interaction with increase in the distance between the centres R and in the number of intermediate units.

Compounds with a very *weak* but stable coupling between the active centres, including conjugation systems of the π–σ–π type or others, are of exceptional interest in connection with problems of biophysics and of the functions of biological systems. On the other hand, fundamentally new possibilities arise here for the use of molecules as systems susceptible to reproduction, regulation, and control by changes in the state of atomic groups as a function of time. Nowadays the study of these problems has been acquiring increasing importance. An active search is being prosecuted for new molecular structures which enable one molecule to perform the functions of a specific element or block in microprocessor ("submicroprocessor") technology—memory, logic, signal amplification, etc. functions;[17–19] an exceptionally high "packing density" and a greatly increased speed of operation can be achieved, in principle, in this way.

Polyconjugated π–π systems with a very strong coupling between the subsystems are closer to the other limiting case and have aroused special interest as a possible basis for the preparation of organic semiconductors, superconductors, and materials in which migrating excitation zones of various types, described as wave packets, can be created. They are suitable for the solution of certain technical problems, including the creation of systems for the transformation of information.

It would perhaps not be an exaggeration to say that the majority of other organic compounds belong to systems of an intermediate type. The entire wide variety of different kinds of coupling between the active centres can be seen in such compounds and the mechanisms of their functioning can be investigated.

The coupling between the electron clouds of adjacent or close atomic groups can be characterised in a fairly convenient form within the framework of ideas about stationary states: in asymmetric molecules, in terms of the degree of delocalisation of the molecular orbitals formed from the orbitals of the fragments and in terms of their displacements on the energy scale; in symmetrical molecules, in terms of the splitting of the molecular orbitals, reaching frequently 2–4 eV. In any case, it is useful to determine the matrix elements of the operator V of the excitation energy associated with the interaction between the orbitals a and b, i.e. $V_{ab} = \langle \varphi_a | V | \varphi_b \rangle$, where φ are electronic wave functions.

However, these matrix elements cannot alone serve as a characteristic of the degree of mixing of the orbitals of the fragments (cf. Traven' and Stepanov[20]) or of the displacement of the molecular orbitals on the energy scale (ΔE), because data for the energy gap ΔE_0 between the initial orbitals are also necessary. We do not refer to the fact that in most cases one cannot make do with the "two level" approximations and data for only one element of the matrix $||V_{ab}||$; however, fairly simple relation (see Baidin et al.,[21] etc.)

$$\Delta E = 0.5\,[\sqrt{4V_{ab}^2 + \Delta E_0^2} - \Delta E_0]\ ,$$

should be used whenever possible. It is represented graphically in Fig. 1.

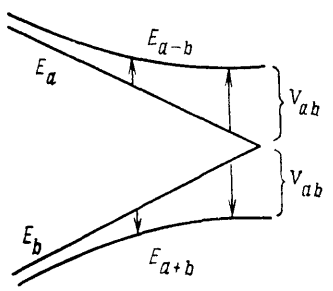


Figure 1. The shifts of the orbitals *a* and *b* on the energy scale induced by their interaction and the formation of orbitals of a mixed type with different initial splittings ($E_a - E_b$) but with a constant value of V_{ab}; the vertical arrows denote the shifts for two arbitrarily selected values of $E_a - E_b$.

Together with the molecular orbital energies, one can use also the set of ionisation potentials. The difference between these two variants is in most cases small and is determined by the contribution arising from the adaptation of the molecule to new conditions created as a result of the abstraction of an electron. The latter takes place very rapidly, approximately in 10^{-15} s, while the subsequent rearrangement of the molecule is slower and in principle one cannot rule out macroscopic time scales (the complete relaxation after a chemical reaction has taken place also requires a fairly appreciable time). In describing complex systems and processes to which correspond slight changes in electron density, it is more convenient to begin with molecular orbital energy data; otherwise, for example in the study of ionisation, it is best to resort to ionisation potentials and electron affinities (or to data derived from molecular orbital calculations with a parametrisation selected on the basis of photoelectron spectra[20]). There is no point in treating these variants as opposed procedures, since they are more likely to supplement one another.

If one is dealing with a coupling between remote active centres of the molecule, it is no longer possible to use the above criteria; in fact a splitting of the molecular orbital in terms of energy less than 0.1 eV is hardly susceptible to observation. However, under these conditions one still cannot rule out the possibility of the complete delocalisation of the molecular orbitals. On the other hand, among the manifestations of conjugation in different molecular properties, including reactivity, there may be some more sensitive to the interaction and even small differences in the structure of the interface can then prove of practical importance. As an example, one may refer to experiments[22] in which it has been shown that an increase in the number of units in the intervening polymethylene chain from 6 to 8 altered sharply the direction of a chemical reaction.

As regards the coupling between the vibrations of *atoms* in the subsystems under consideration, it is manifested by the establishment of delocalised modes and in the absence of interference can be readily observed in symmetrical molecules from the splitting of frequencies, which is associated, roughly speaking, with the rigidity of the entire intervening subsystem. The delocalisation of the vibrational modes has no direct bearing on the delocalisation of molecular orbitals and conjugation, which is unfortunately not always recognised (see, for example, Randhawa and Suri[23]); however, the contribution of non-diagonal force coeffcients has a bearing on the electronic interactions between different chemical bonds, manifested in the atomic vibration process.[24]

III. Comments on the mechanism of intramolecular interaction. What is the inductive effect?

The desirability of distinguishing different types of "electronic effects" (conjugation, the inductive effect, steric hindrance, etc.) and of the representation of their essential features has on the whole been evaluated in different ways in the literature; it has been noted that one is dealing not with physical phenomena but with a transition in describing the electronic structure of a molecule from the zeroth approximation to higher approximations. However, one should not go to extremes; the change in conditions in an intramolecular interaction and the appearance of definite specific features in properties, for example as a result of a transition from non-planar to planar diene systems, is entirely real. Avoiding the rather inappropriate but frequently resorted to references to "the delocalisation of electrons",[25–28] one can nevertheless speak of delocalisation of the molecular orbitals of conjugated systems. The presence of such molecular orbitals affects in one way or another the experimental data (see, however, the comments by Streitweiser and Vorpagel[29] and also Dewar[30] and Shaik et al.[31]). Speaking of conjugation, we have in mind the set of its manifestations in different properties of molecules, based on the overlap and mixing of the orbitals of the interacting fragments with a concomitant change in the orbital energies.[32] Deviations from a simple additive scheme, in which the property of a complex molecule is defined as the sum of the contributions of its fragments, are to some extent associated with conjugation. However, the specific features of the property or parameter investigated are then of primary importance and questions concerning "non-additivity" and its origin must be resolved separately for each property (see Section IV).

Among the possible manifestations of conjugation in chains with an alternation of chemical bond orders, for example, in polyenes and poly-ynes, one should mention the more or less pronounced smoothing of the differences in the alternating bond orders, lengths, and rigidities (it is frequently referred to as "delocalisation of bonds", which is in essence equivalent to "delocalisation of valence characteristics"). The set of distibine, diarsine, and certain others can serve as new interesting examples.[33,34] In such cases the

disposition of the Z–Z σ-bonds of a certain number of identical molecules on a single straight line favours the formation of delocalised orbitals, incorporating the entire chain of heteroatoms, or one may say the "conjugation of the σ-bonds of adjacent molecules". The molecules of diphosphine H_2P-PH_2 hardly interact with one another under such conditions (this is indicated by the symbol P–P P–P P–P). A very weak interaction with an insignificant smoothing of the bond alternation has been noted in diarsine (...As–As...As–As...); the molecules virtually retain their individuality, although, strictly speaking, delocalised orbitals must be used to describe the entire chain. The bonds between distibine molecules are more distinct; the large bathochromic shift of the absorption bands, which vanishes when the ordered arrangement of the molecules is lost, i.e. on breakdown of the conjugation chain, is striking.

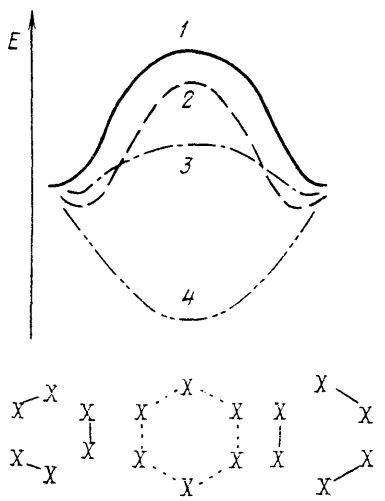
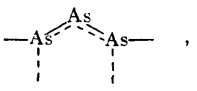


Figure 2. The energy of cyclic systems X_6. The extreme points of the curves on the right and on the left correspond to sets of three molecules X_2 (D_{3h} symmetry). Those in the middle correspond to systems in which all six X–X bonds are the same (D_{6h} symmetry). The H_6 system corresponds to curve *1*,[31] the benzene molecule corresponds to curve *4*,[31] molecules with only slight smoothing of bond alternation correspond to curve *2*, and the example of a structurally modulated (dynamic) system corresponds to curve *3*.

While there is an appreciable similarity in the manifestation of conjugation in distibines and poly-ynes, the forms of the bonds *between the fragments* of these structures differ greatly: in the former case, the overlap of the p_x orbitals of Sb, oriented along the chain, plays the main role, while in the latter case the main role is assumed by the overlap of the p_y and p_z orbitals oriented at right angles to the chain. In the first case, there is no rigid σ-skeleton ensuring the stability of the geometry and integrity of the system.

An almost complete equalisation of the bonds between the heteroatoms has been noted in dibismuthines (...Bi...Bi...Bi...Bi...).[34]

A symmetrical system, resembling the π-allyl system, i.e.

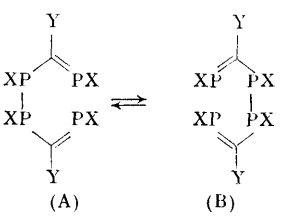


has been described.[35]

It is believed[31] that the equalisation of the carbon–carbon bonds in benzene is due to the σ-skeleton and that the π-subsystem is more likely to counteract this, the π-delocalisation being regarded merely as a concomitant factor. This interpretation is not convincing, but comparison of the six-membered C_6H_6 and X_6 systems is very appropriate. According to calculations,[31] the resonance energy in the H_6 system is insufficient to compensate for the energy expended on the deformation of the bonds and for the conversion of three H_2 molecules into the delocalised form H_6. However, in the Li_6 and C_6H_6 systems the energy is entirely sufficient (Fig. 2, curves *1* and *4*).

The smoothing of the bond alternation in the chain and certain other aspects of conjugation are frequently described[36] with the aid of a combination of resonance structures (to each of which the significance of a solution of the Schrödinger equation is attributed without due justification[37]); the use for this purpose of the symbolism of valence characteristics is unjustified, since one is dealing with the representation of wave functions and not their squares. The resonance structures do not by themselves provide an idea about the conjugation energy (and in general whether or not the proposed structures are suitable), the properties of molecules associated with the delocalisation of molecular orbitals, and the principal features of conjugation in chains of σ-bonds, for which intraatomic exchange integrals, etc. are important; the traditional description of the electronic structure of conjugated systems, for example, amides is not very satisfactory (see Sections VI, IX, and X), while in a more complete description one loses compactness (thus the description of one of the compounds mentioned in Section I requires the representation of more than 12000 (Kekulé structures). In any case, the data on the set of molecular orbitals provide much greater possibilities.

Among molecular systems with different forms of the potential, including those with two or several potential energy minima, it is easy to find examples of a high stability of *one* form, systems which readily isomerise (rearrange), structurally modulated (dynamic) rapidly oscillating systems, and, finally, "mesomeric" systems, where there is no justification for attributing their principal features to "oscillations". An interesting example[38] of a structurally modulated (dynamic) system can be represented by the following scheme:



On rapid oscillation (A)⇌(B) and for a relatively long recording time (τ_{rec}), we are able to observe a six-membered ring which is to a large extent equalised and in the absence of other information we can describe the system in terms of two resonance structures of types (A) and (B), which in a certain sense resemble Kekulé structures.

However, for a short τ_{rec} either structure (A) or (B) might be observed, which implies some similarity with the systems represented by curve *3* in Fig. 2.

The separation of the different forms of intramolecular interaction mentioned at the beginning of the Section is fairly problematical. These forms and simple summation of their contributions correspond to a fairly rough approximation. Thus the differentiation of the contribution by the inductive effect to the experimentally determined Hammett constants implies in essence a transition from reality to some kind of convention. Such a transition is justified if it facilitates to some extent the prediction of quantities (which are in principle observable); however, successes of this kind are fairly modest. The situation is complicated by the multiplicity of different versions of the interpretation of the very concept of the "inductive effect". This effect has been considered[39] as competition between acceptor ligands adjoining the atom, while in other studies[15,40–44] it has been regarded as the influence of a polar group on the σ-skeleton of the molecule, as a result of a change in the hybridisation of the atomic orbitals or of the involvement of unoccupied orbitals, etc. Some workers have calculated separately the contributions of the effects of the field of the polar group and of the inductive effect, while others assume that the latter in fact consists in the effect of the field; the use of this concept to account for the polarity of diatomic molecules has also not been ruled out. Such large discrepancies have created disadvantages but they can also have a humorous aspect.

In most studies the term "inductive effect" is understood as the polarisation of a molecular fragment induced by the static field of excess charges (+) or (–) on the atoms of other fragments, such polarisation not involving a redistribution of electron density between bonds[45] (cf. Cook et al.[15]); the latter is usually attributed to the donor–acceptor interaction as one of the aspects of conjugation with participation of unoccupied orbitals of the acceptor. Since in fact electron systems assigned to individual chemical bonds are not autonomous, the distinction between ideas concerning the distribution of electron density within the limits of bonds and between bonds can have no physical justification (see Section XI). The very differentiation of fragments and the corresponding part of the electron cloud (as well as the "electro-optical parameters" of chemical bonds) is fairly arbitrary. Thus the demarcation of conjugation and of the inductive effect is ambiguous and its possibilities should not be overestimated. It is not fortuitous that estimates of their relative roles based on the use of different criteria or schemes diverge appreciably. Thus the contribution of the inductive effect for nitrobenzene varies from zero to 100% according to the conclusions reached by different workers:[21,46–48]

The differentiation of the inductive effect has been of some interest as a route to the estimation of electron density from the form of the structural formula. Such estimates correspond to reality to some extent in certain simple molecules including a highly polar bond such as AlkF and AlkLi, but here too the involvement of hydrogen atoms and specific features of the cartesian component of the polarisability complicates the picture. In any case, the model with point charges on atoms and charge redistribution "along chemical bonds"[49] is clearly inadequate. As regards quantum-chemical calculations (see, for example, Topsom[50] and Shatkovskaya and Gineitite,[51] the latter yield more complete information but this is also by no means free of the influence of subjective factors associated with the choice of the method of separation. Under these conditions, the calculation of the resultant electron density on atoms without separating the contributions of the inductive effect on conjugation is entirely appropriate for the solution of the majority of problems without attributing great importance to the numerical estimates of these contributions obtained in different ways[21,44,52] (they have been frequently quoted with four significant figures), one can nevertheless assume that their qualitative comparisons are useful, particularly since they can differ sharply in terms of their conformational dependence (the orientation of specific orbitals is important for conjugation, while the orientation of the dipole is important for the inductive effect). However, judging from estimates,[52] the non-additivity of the influence of the effects considered can play a dominant role; if this is so, then the entire separation scheme is unjustified.

According to certain experimental and computational quantum-chemical data,[45,50–52] the influence of the inductive effect should diminish rapidly along the chain of C–C σ-bonds and more slowly along the chain of π-bonds. It is believed that the influence of conjugation diminishes more slowly (see the examples in Section X). However, one should not speak of conjugation "in general"—its different aspects (different manifestations) respond in different ways; thus one of the principal aspects is that the delocalisation of the molecular orbitals describing two identical active centres in a symmetrical molecule does not weaken at all with increase in the number of intermediate units, but its sensitivity to disturbances in molecular symmetry increases, while the conjugation energy actually diminishes rapidly. Examples of large differences between the coefficients of the transmission of influences on different parameters referring to the CHO group can be found in the paper of Yanovskaya et al.[52]

As the mechanism of the mutual influence of atomic groups was specified in further detail, the contributions of different channels leading to the interaction—through the intervening atoms or chemical bonds and through space—were considered.[53] The mixing of the electron wave functions of the above groups and the formation of delocalised molecular orbitals is possible as a result of the participation of the orbitals of the intervening bonds (an example is provided by the *n*,*n*-conjugation due to the slight involvement of the N–N σ orbital in the *trans*-conformer of hydrazine) or certain atomic orbitals of the intervening atoms (not necessarily the atomic orbitals which form the chemical bonds linking the active centres). Another channel is determined by the direct overlap of the orbitals of the active centres through space (for example, the overlap of two π orbitals in norbornadiene or the *n* orbitals in *cis*-hydrazine[54–56]). It is self-evident that the different forms of combination of these channels (leading to their enhancement or, on the contrary, to their weakening and even the disappearance of the observed signs of interaction) can be by no means ruled out (see Section XI).

The interaction between atoms or atomic groups of a complex molecule *through space* (TS) can be regarded, depending on how strong it is and what are the overlap populations of their orbitals, as an insignificant addition to the information yielded by classical structural formula, as a very weak chemical bond, or as a more important aspect of electronic structure which merits being reflected in the structural formula. Interaction through space is favoured by the diffuseness of atomic orbitals;[57] with increase in the distance between the centres, it diminishes faster than the interaction through the intervening subsystem. We have encountered this in the study of suitable conformers of non-rigid molecules as well as cyclic rigid structures in which the active centres approach one another in space (see Sections VII, VIII, X, and XI).

In this connection, the problem of the coupling between the active centres of molecules in close proximity has acquired great interest.[50,58] According to calculations,[59] the introduction of

extraneous molecules into the intervening region of space between two initial molecules (for a fixed distance R between them) promotes mixing, i.e. the delocalisation of orbitals within the limits of the entire system. One may add that the rate of electron transfer between the active centres of the molecule diminishes with increase in R, while the length of the intervening chain increases more slowly than the rate of transfer between two individual molecules.[60–62]

The question of the channel through which the influence of the inductive effect is transmitted[45] has been considered as a dilemma in which two variants are set in opposition (deliberate paraphrasing—the influence "through chemical bonds formed by intervening atoms" or "through space in which these atoms are located"). However, in reality, the atoms of a bridging group, side chains, the solvation shell, etc. are not always located in the particular part of the intervening space or near it. They influence in one way or another the strength of the field acting on the given object. Under these conditions, the presence of a continuous chain of intervening chemical bonds affects the "packing density", which is not by itself a decisive or essential apsect of the situation; among other things, one may mention that the polarisability of the butane molecule differs little from the polarisability of two ethane molecules and is described satisfactorily by the sum of atomic increments or, just as well, by the sum of bond increments. Under these conditions, the second variant (of the two quoted above in brackets) is less specific but more correct. It is not associated with limitations characteristic of the simple form of the LCBO (linear combination of bond orders) and the limitations in the multiplicity of the structures (cases) which actually exist.

In the estimation of the active field in practical studies, the intervening subsystem ("black box") was characterised by dielectric constants ε_{eff}; the values of ε_{eff} in the range from 1 to ∞(!) have been selected in different studies.[41,43,45,63] The arbitrary nature of the estimates of ε_{eff} naturally made the results worthless and made it evidently desirable to go over from macroscopic to "microscopic" characteristics and calculations at the LCAO level. We no longer speak of the inadmissibility (see Houk et al.[41] and many other studies) of the usual formula defining the Coulombic interaction between charges immersed in a medium for a model with an "intervening" medium (when the possibility of the intensification of the active field is not ruled out!).

A bridging group determines to some extent the distribution in space of the active centres and together with the latter can participate in the formation of delocalised molecular orbitals; the extent to which the subsystems are linked to one another and the possibility of the evolution of their state (the rate of energy or electron density transfer‡, the rate of even the direction of the chemical reaction) depend on its structure.

The possibility of an intramolecular energy transfer is associated with the overlap of parts of the emission spectrum of the emitter (excited chromophoric group) and the absorption spectrum of the receptor. The contribution of Forster's dipole mechanism then diminishes in proportion to R^{-6} and can be manifested for fairly long distances R between the π-subsystems (10–50 Å and more). The rate of energy transfer via Dexter's exchange mechanism, involving the overlap of the wave functions of the subsystem, diminshes exponentially and becomes insignificant for $R > 6$ Å; however, the participation of the σ-bonds of the intervening chain (for example, a polymethylene chain) in the $\pi-\sigma-\pi$ system can, according to some investigators,[59,60,62] alter the situation and enhance the role of the exchange mechanism. The rate of energy transfer $K_{en}(R)$ then diminishes with increase in R faster than the rate of electron transfer§ $K_{el}(R)$; in a series of studies[60–62] on compounds with $\pi_1-\sigma-\pi_2$ systems having different numbers of intervening units, $K_{en}(R)$ was found to be proportional to $K^2_{el}(R)$ and $K_{el} = 2.5 \times 10^{15}\ e^{-m}$, where m is the number of C–C σ-bonds in the intervening chain. Energy transfer along the receptor–polyene subsystem–emitter system has been considered by Maier et al.,[14] while the mechanism of the energy transfer as a result of the exchange of virtual photons (which is described by the non-diagonal elements of the decay matrix) has been examined by Morozov and Shorygin.[64]

We confined ourselves to brief remarks about the principal types of intramolecular interaction of atomic groups. Since even these principal forms are not clearly differentiated, it did not appear necessary (despite the inspiring terminology) to consider the numerous existing variants—homohyperconjugation and supra-annular, inductoelectromeric, and other effects.[56]

IV. Are correlations between different conjugation parameters possible?

The set of manifestations of conjugation in different properties of molecules includes numerous and varied parameters and naturally cannot be characterised by any one figure (provided that one does not postulate, contrary to facts, the existence of unambiguous correlations between all the properties investigated). The above parameters are by no means determined by identical factors. For example, the delocalisation of orbitals and the accompanying phenomena are favoured by the *similarity* in the disposition of the orbitals of the fragments on the energy scale, while the redistribution of electron density is favoured by *differences* between the latter.

One may refer to examples of complex molecules in which the deviations from additivity in some properties are clearly pronounced, while in others they are absent and also to systems in which the opposite picture is observed. Examples of compounds, similar to benzamide, in which an anomalously large dipole moment is associated with the preferential conjugation of the carbonyl group with one subsystem (NH_2) while the long-wavelength UV absorption is associated with its conjugation with another system (Ph), are no less instructive. Furthermore, it is seen from experimental data that the π-donors and π-acceptors in aromatic compounds influence the electron density in the benzene ring, the reactivity characterised by the Hammett constants σ_{para}, and also the ionisation potentials P_1 in opposite directions, but their influence on a number of optical properties[65] (the positions of the benzene UV absorption bands, the electron polarisability, the intensities of many Raman lines) and certain geometrical parameters of the molecule is in the same direction. Yet another aspect may be noted by referring to the compound $I-\Phi-NO_2$, where iodine is a π-donor and influences the optical properties like other π-donors, but its influence on the

‡We have in mind the rate of change of the probability of recording the transfer and not the characteristic of the time scan of the process.

§The energy and electron density transfer processes, which can be regarded as transitions between quasi-degenerate states of the entire system should not generally speaking, be contrasted. Depending on the structure of the orbitals of the subsystems and their initial state, these processes can differ sharply or can be of a mixed character; here it is appropriate to mention the electronic transitions with "charge transfer" or with "elements of charge transfer".

frequency of the nitro-group $\omega(NO_2)$ (on the dissociation constant in *p*-iodobenzoic acid) is more like that of an acceptor¶ (see also Sections VII, IX, and X).

In practice we have an exceptionally wide range of variants and a complex picture of interactions between subsystems and relations between different manifestations of non-additivity. However, these relationships are susceptible to analysis and can be adequately explained by studying the modification of molecular orbitals induced by the influence of substituents, in particular, their delocalisation and the changes in their energy and involvement in the redistribution of electron density.

The differences between the influences of intramolecular interaction on different properties of molecules have frequently led to contradictory conclusions and in some studies have served as a basis for conclusions concerning the suitability or unsuitability of particular parameters for the quantitative estimations of conjugation; such conclusions are based on a subjective choice of the criterion used as a reference standard or as a "measure of the conjugation effect" (according to Randhawa and Suri[23] as the "percentage resonance"!). In this connection, one may say that the majority of parameters are associated with the response of the molecule to external influences and characterise the possibility or probability of a particular transformation or transition to a new state, which occurs, for example, as a result of a chemical reaction or as a result of the application of the measuring procedure itself. The final state of the molecule is then specific to the observed process and possibly the conditions under which it takes place. The correlations between the parameters characterising the transitions to different final states would imply also correlations between the latter, which is fortuitous rather than the rule.

Nevertheless, it is possible to identify certain groups of parameters which are related to a greater or lesser extent. For example, the relation between certain optical properties of molecules can be established on the basis of known physical laws and is entirely explicable. However, even in this case the picture is not simple. It is determined by the involvement of a large number of electronic excitation levels of the molecule. Both low-lying and high-lying excitation levels, including those which determine the absorption spectrum in the range 500–1000 Å, then contribute to the static polarisability of the molecule. The long-wavelength part of the absorption spectrum, including the near UV region (2000–4000 Å) is somewhat more important for the refractive index of visible light; the longest-wavelength intense absorption zone or band has a major or even decisive importance for the dispersion of the refractive index and even more so for the intensity of Raman lines (especially for overtones).[66]

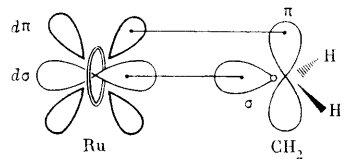
There is some chance of success in the search for correlations when different properties are considered in some specific electronic state of the molecule, for example, in the ground (unexcited) state. However, correlations with reactivity, which depends significantly on the presence of conjugation and its influence on the energy of the system in the transition and final states, are of greatest interest. The question what are the interrelations between the set of σ_{para} constants of the substituents X and the physicochemical characteristics of the compounds Y–Φ–X, for example R_2N–Φ–X, has been frequently dealt with in the literature. However, it is incorrect to formulate the question in this way. It is more logical to ask what are the correlations between the, by no means identical, sets of constants obtained from the corresponding types of initial data; it is even more appropriate to elucidate what relations exist between different kinds of initial data themselves (for example, between the basicity constants and the spectra). The establishment of certain relations of this kind would be extremely useful, but we are nevertheless faced by a complex set of conjugation parameters. Which of them will be usefully considered or adopted as the cornerstone depends on the aims of the investigator and perhaps on the ways in which he thinks.

¶ Here and henceforth the following notation is used: R = methyl group, Vy = vinyl group, All = allyl group, Φ = *para*-phenylene fragment, Π = π-bond system, and M = bridging group.

V. Chemical bonds and atomic groups incorporating heteroatoms

Before turning to complex systems, we shall note certain characteristic features of chemical bonds and atomic groups incorporating a heteroatom Z, which may constitute in certain combinations complex structures and conjugation systems. Comparison of the dissociation energies of the Z–Z and also Z–C, Z=C, and Z=Z chemical bonds formed by different atoms Z shows that the energy as a rule decreases on passing to bonds with heavier elements (as a result of the decrease in the overlap integrals of the more diffuse atomic orbitals) and in most cases with decrease in the atomic number of the element Z within the limits of the Period. This applies particularly to the π-component of double bonds. Thus, according to calculations,[67] the C=Al bond energy is smaller by a factor of 2 than the C=B bond energy, while the energy of the π-component (E_π) is correspondingly lower by a factor of 5; in the author's words, E_π for C=Z bonds decreases rapidly with decrease in the electronegativity of Z. According to calculations,[68] it amounts to 65, 35, 31, and 20 kcal mol^{-1} in the series C=C, C=Si, C=Ge, and C=Sn; estimates for the carbon–chromium bond yield a value less than 5 kcal mol^{-1}, so that the use of the double bond symbol is no longer necessary. The total energy ($E_\pi + E_\sigma$) of the C=Z double bond diminishes as Z varies in the sequence $0 \gg N > C > B \gg S > P \gg Ru, Al$.[67–70]

It is significant that the double bonds formed with participation of the atoms Z of different elements are by no means uniform in their nature. For example, whereas the C=Ti bond is described satisfactorily by two localised equivalent orbitals (with an appreciable participation of the 3*d* atomic orbital of titanium), the C=Mn bond represents a set of very different contributions of the σ- and π-components and involves a π-component which is very weak and markedly asymmetric as regards the contributions of the atomic orbitals of the manganese and carbon atoms.[69] According to calculations,[70] the $\rangle Ru=C\langle$ bond is covalent and is formed from 4*d* atomic orbitals of ruthenium:



The fragments must be arranged not as in ethylene but in mutually perpendicular planes. Judging from the arguments put forward by Zilm et al.,[71] the Sn=Sn bond can be regarded preferably as a mutually-dative linkage; the unoccupied *p* orbital of the adjoining atom participates in each of the two contributions to this bond.

Table 1. The compounds ZR_m.

Li	Be				B	C	N	O	F
7	10.5				10.9 —	11.4 6.0	12.5 4.8	13.4 6.0	17 6.5
0.8	(2)				3.9 162	4.5 157	5.0 199	5.2 184	6.2 132
0.9	1.8				2 —	2.2 —	2.7 —	3.1 —	4 —
50	(55)				88 —	86 —	75 —	87 —	110 —
Na	Mg				Al	Si	P	S	Cl
6	8.8				9.8 —	10.6 3.9	11.4 3.1	12.5 3.3	14.4 3.5
(0.7)	(1.6)				2.4 189	3.0 170	2.9 200	3.3 203	3.7 170
0.8	1.6				1.7 —	1.9 —	2.3 —	2.6 —	3 —
(45)	(45)				68 —	75 —	68 —	72 —	84 —
Ti	V^V	Cr^{VI}	Cu^I	Zn	Ga	Ge	As	Se	Br
9.4	—	—	(9.5)	9.4 —	9.6 —	10.2 3.7	10.7 2.7	12 —	13.5 —
2.2	—	—	(1.8)	2.4 202	2.35 195	2.7 180	2.6 200	2.7 235	3 180
1.6	2.0	2.2	1.8	1.4 —	1.7 —	1.8 —	2.1 —	2.4 —	2.7 —
65	(35)	(25)	55	45 —	60 —	60 —	57 —	59 —	70 —
Zr	Nb^V	Mo^{VI}	Ag^I	Cd	In	Sn	Sb	Te	I
9.4	9)	—	(9)	8.8 —	8.9 —	9.7 2.9	10.3 —	11.3 —	12.5 0.2
1.9	(2)	(2)	(1.6)	2.0 215	1.95 212	2.2 186	2.25 210	2.4 250	2.4 196
1.5	1.9	2.2	1.8	1.4 —	1.6	1.8 —	2.0 —	2.1 —	2.4 —
75	(52)	(32)	40	36 —	40	54 —	53 —	51 —	56 —
Hf	Ta^V	W^{VI}	Au^I	Hg	Tl	Pb	Bi		
9.7	8.8	8.6	—	9.3 —	— —	9.3 —	9.8 —		
2.0	2.3	2.05	(2.8)	2.45 202	1.8 220	1.9 205	1.9 (220)		
1.4	1.8	2.1	2	1.5 —	1.6 —	1.75 —	1.9 —		
80	62	38	(60)	31 —	32 —	37 —	35 —		

In general, double bonds with participation of a heteroatom Z in most cases bear little resemblance to the C=C bond; in conformity with their specific features, the manifestations of conjugation with adjoining fragments can differ greatly (see Section VI).

The available data suitable for a comprehensive characterisation of simple compounds ZR_m and their Z–C bonds are compiled in Table 1. These compounds imitate in a certain sense the fragments of complex conjugate systems incorporating groups of the type ZR_n. Each box in Table 1 indicates the heteroatom Z and its valence state if it is not the usual one; the following data are presented in the form of a column or two columns: (1) the vertical ionisation potential (eV) (the first of those corresponding to the Z–C bonds);[39,72–77] (2) the force constant of the Z–C bond (mdyn $Å^{-1}$) (indicated in bold type);[78–84] (3) the electronegativity of the $-ZR_n$ group;[85,86] (4) the *average* Z–R bond dissociation energy (kcal mol^{-1}).[87–89] In the second column we have (1) the electron affinity of the ZR_m molecule (eV) [90–92] and (2) the intense long-wavelength UV absorption band (in most cases the $\sigma \rightarrow \sigma^*$ band; gas phase, nm).[73,93–100] Approximate estimates based on analogies and comparisons with molecules having similar structures are indicated in brackets. The arrangement of the data in Table 1 was dictated by the need for compactness.

The principal trends noted when compounds ZR_m are compared are as follows: as Z varies across the Periodic System from right to left and from above downwards, the force constant K(Z–C) and the ionisation potential decrease; the electronic polarisability per Z–C bond increases; there is a sharp increase in the intensity of the Raman lines[32,66] and the Z → C electron density shift becomes more pronounced (in LiR, it corresponds to a transfer of a charge amounting to ~0.6 e); the electronic excitation energy decreases, at least within the limits of a particular Group in the Periodic System (comparisons along Periods are difficult because of the lack of uniformity as regards symmetry types and the unreliability of the assignments of the absorption bands). Similar trends have been noted also on comparing data for Z–Z bonds as well as Z=C and Z=Z bonds. However, all the foregoing features cannot be fully extended to compounds of the heaviest elements such as Au, Pt, and Hg, which is associated to a large extent with the contribution of relativistic effects and the corresponding contraction of the valence shells.

We have presented data for molecules with fairly simple structures. One may note that *almost any increase in the complexity* of the molecule (attachment of additional atomic groups) *reduces* the electronic excitation energy and in many cases (excluding the addition of active acceptors) also the ionisation potential. Naturally, in individual instances the appearance of steric hindrance can lead to the breakdown of conjugation as a result of a change in conformation, but one cannot rule out also the converse possibility where the real conformation which is relatively unfavourable for conjugation (say in hydrazine) is converted into a more favourable conformation as the structure becomes more complex or when the bond angles are greatly distorted (for example, in cubene compared with alkenes).

The assignment of molecules of the type ZR_m to the class of comparatively simple ones does not imply that they do not exhibit the non-additivity and mutual influence of fragments. In relation to the $H_3C-Zn-CH_3$ molecule, one may note an appreciable splitting (~2.2 eV) of the delocalised σ molecular orbitals of the Zn–C bonds, the non-zero value of the non-diagonal Zn–C/Zn–C force coefficient, etc. However, these aspects will not be considered here.

VI. π−π conjugation

The principal types of conjugated systems (π−π, σ−π, *n*−*n*, etc.) and the characteristics of their reactivity were at one time examined in detail.[101] At the present time compounds with conjugated π-bonds have been most thoroughly investigated by physical and chemical methods. Almost all the most important features of the physical, chemical, and technical properties of polyenes, poly-ynes, polyphenylenes, and other similar systems are related directly or indirectly to π−π conjugation; the functions of polyconjugated systems constitute the basis of many most important physiological processes; the photochemical reactions of π-conjugated systems can be seen among chemical processes which occur in the interstellar space, for example, on dust particles.[102,103]

It is know that the C−C central bond in the molecules of butadiene, diacetylene, and dicyanogen is shortened and its rigidity has increased more than might have been expected judging from the C−C bonds in propene, propyne, and acetonitrile; the specific features of the π-bonds are much less marked. According to new data,[104] the alternation of bonds in *trans*-polyenes is slightly smoothed out and to a greater extent in the centre of the chain where the rigidity of the double bonds (compared with the terminal ones) is reduced by 5−10% and the bond lengths are greater by approximately 1%. The changes in interatomic distances as the conformations are varied can be demonstrated in relation to glyoxal, whose conjugation energy (~3 kcal mol^{-1}) is close to that of butadiene. According to calculated data,[105] presented in Fig. 3, in the planar conformers there is a small amount of double bond character in the region of the central C−C bond (which according to R Bader's calculations should be accompanied by the breakdown of axial symmetry, i.e. by some ellipticity of the distribution of electron density). In *gauche*-conformers, all the manifestations of π−π conjugation, including effects in the bond lengths, are reduced to a minimum.

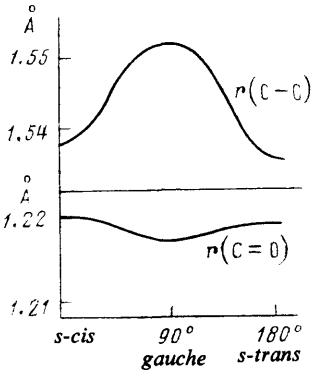


Figure 3. The C−C and C=O bond lengths in the OHC−CHO molecule in different conformations (θ = 180° for the *s-trans*-conformer).[105]

The conditions governing the conjugation of the C=C double bonds with the C=Z and Z=Z bonds can vary within wide limits. The transition for systems incorporating heavy atoms Z should be accompanied by the mutual approach of the frontier orbitals (which in general favours an increase in conjugation energy) and by a tendency towards an increase in the contribution of the C=Z fragment to the long-wavelength region of the electronic absorption spectrum. According to calculations,[106] the conjugation energy in the C=C−C=Ti system should be somewhat greater than in butadiene; in other cases, there is a possibility of its decrease and of the weakening of other manifestations of conjugation, which is partly associated with the contribution of relativistic effects.[57,107]

VII. Does the methylene bridge break the conjugation chain?

This question has been discussed for a long time in the literature but hitherto contradictory views have been expressed; the interest in this question has increased in connection with new problems, in particular the search for the possibility of creating organic conductors on the basis of polyconjugated systems, for example, polyacetylenes (see Section II). In a recently published study,[108] the authors confirmed the version stating that conjugation and π-electron delocalisation are retained in the presence of a methylene bridge but in another study[109] this version was rejected; semiempirical calculations of the interatomic distances and carbon−carbon bond orders led to the conclusion that in polyacetylenes there is no conjugation of the π-subsystems through the methylene group. A more complete idea about this problem is provided by calculations of the energies and structures of molecular orbitals.[110,111] The reasons for the contradictions are associated partly with the choice of different criteria (see Section IV) and with the differences in terminology. By invoking the delocalisation of π orbitals as the criterion, one must bear in mind that, when the π-subsystems are identical, such delocalisation should, generally speaking, be complete not only in molecules such as those of butadiene but even in the presence of a very weak bond between the subsystems (say between two ethylene molecules separated by a distance of 5−10 Å). However, under the conditions of a weak bond, a slight difference between the structures of the π-subsystems is sufficient to cause a breakdown in delocalisation; furthermore, the defects in the π−π conjugation chain in real polyacetylene specimens are not arranged regularly, the defect-free conjugation zones are not identical and, furthermore, they are not uniform as regards conformations at the locations of bridging groups. The question stated in the heading can therefore be answered in the given instance only by taking into account statistics and, naturally, the specific features of the criteria employed.

We shall consider in greater detail the simplest dienes with a symmetrical structure. Here the π orbitals of two vinyl groups, π_1 and π_2, can be mixed and can form two delocalised molecular orbitals, in one of which π_1 and π_2 are incorporated with the same signs (π_+) while in the other they have different signs (π_-). The energies of the new orbitals differ by Δπ. In the case where the interaction of the π-bonds through space predominates, π_- lies higher on the energy scale than π_+ and, when interactions through a bridge predominate, the opposite arrangement is possible.[54–56] The mixing of the unoccupied π* orbitals leads to a splitting Δπ*, which frequently differs greatly from Δπ. The mechanisms of the mixing (see Section III) of the occupied and unoccupied orbitals may not in fact be the same.

Henceforth in the text the deviations from the Koopmans theorem, the allowance for which in many problems is absolutely essential[56] and merits consideration in a special review, will not be discussed; we shall therefore retain the conventional designations of

the type $\Delta\pi$ and $\Delta\pi^*$ in the analysis of experimental ionisation potentials, etc.

According to experimental data, $\Delta\pi$ = 2.4 eV and $\Delta\pi^*$ = 2.2 eV in the planar *s-trans*-butadiene molecule. The values of $\Delta\pi$ and $\Delta\pi^*$ diminish rapidly in the series of compounds butadiene, penta-1,4-diene, hexa-1,5-diene, etc.; this can also be said about diynes, dinitriles, and diketones. However, in compounds containing a chain of methylene groups $-(CH_2)_n$ there are too many conformational possibilities† and this makes a simple comparison of experimental data relatively unproductive—the conformation is in this instance one of the decisive factors on which depend the degree of overlap of the orbitals of the fragments and the values of $\Delta\pi$ and $\Delta\pi^*$. One can also mention that, for a large chain length, one cannot rule out the possibility of the mutual approach the appreciable interaction of the terminal C=C bonds through space, i.e. the occurrence of a conformation resembling a ring.[112]

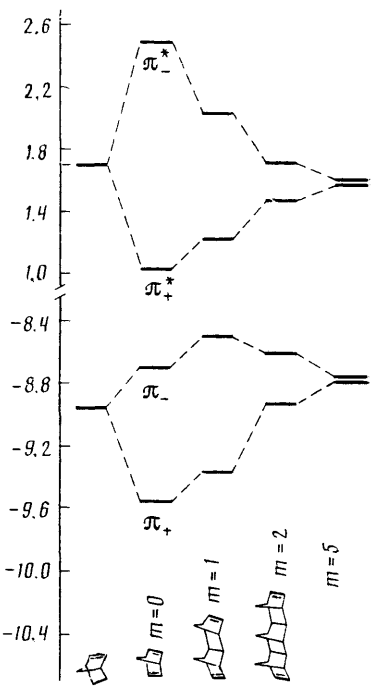
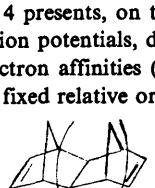


Figure 4. The energies of the π orbitals of type I diene hydrocarbons with an increasing number of intervening C–C σ-bonds.[55]

Fig. 4 presents, on the basis of the data of Balaji et al.,[55] the first ionisation potentials, designated by the indices π_+ and π_-, as well as the electron affinities (indices π_+^* and p_-^*) of symmetrical dienes (I) with a fixed relative orientation of the C=C bonds.



(I)

† The relative distribution of the double bonds in space can be described taking into account six degrees of freedom.

Fig. 4 presents experimental data for compounds with m = 0, 1, and 2, and the results of an approximate extrapolation for compounds with $m > 2$; the extrapolation for m = 7 (16 intervening C–C σ-bonds) yields $\Delta\pi \simeq 0.003$ eV.[55] Such a low value of $\Delta\pi$ is naturally not susceptible to detection by photoelectron spectroscopy, but, under suitable conditions, the possibility of investigating the interaction by other methods is not as yet ruled out. In particular, the study may be based on the rate of the photoinduced electron transfer, which was found to be in the subnano-second range in experiments[113] in the presence of ten intervening C–C bonds and was an order of magnitude lower in the presence of twelve C–C bonds. If the "conductivity" of the interface is still smaller, the transition time may run to seconds, i.e. may correspond to the possibility of clear representations.

With increase in m and hence in the distance R between the double bonds in dienes (I), the direct overlap of the π orbitals through space (TS) diminishes rapidly. Whereas in norbornadiene (m = 0, R = 2.4 Å) such overlap largely determines the real splitting ($\Delta\pi$ and $\Delta\pi^*$), for m = 1 and R = 4.8 Å it becomes very small and less significant than the interaction through the intervening C–C bonds (TB), which weakens much more slowly—by a factor of 2–3 when m increases by unity.[55]

In connection with these comparisons, one may mention that the influence of the inductive effect of the polar groups on the dissociation constants of carboxylic acids weakens by a factor of 2–3 with increase in the length of the intervening chain by one additional C–C bond,[45] while the induced charges on the C atoms of the alkyl group should diminish along the chain even faster according to calculations.[50,51]

Quantum-chemical studies of $\pi-\sigma-\pi$ systems have shown that the weakening of the interaction with increase in the number of intervening σ-bonds is not an immutable rule; under suitable conditions, one cannot exclude the possibility of the introduction of an additional unit such that the bond between the terminal active centres would be enhanced.

In norbornadiene, the dihedral angle θ between the planes of the two "ethylene" fragments is 116°. In other dienes with a similar structure but with a larger angle θ, the direct overlap of the π orbitals is less marked; in the almost planar cyclohexa-1,4-diene it becomes very small whereas the interaction through bridging groups (TB) is to a large extent retained and thus comes to the fore; accordingly, the π_+ orbital is located higher on the energy scale than the π_- orbital. Signs of non-additivity in the UV and Raman spectra of norbornadiene have been noted.[114]

If the two π-subsystems are arranged at right angles to one another, then, without the involvement of suitable intervening units, we have $\Delta\pi$ = 0; this is the case with the spiropentadiene



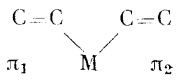
We shall designate such a system by the symbol ||=. Without going into specific structural details, one can say, in principle, that the introduction of an intervening double bond, oriented at a certain angle in such a way that there is a possibility of its interaction with each of the initial bonds (symbol ||⁄=), gives rise to the possibility of the formation of delocalised molecular orbitals with an appreciable energy splitting. A structurally suitable combination of σ-bonds can also serve as an active intervening unit; thus the

involvement of the orbitals of the intervening ring in the tricyclododecatetraene molecule



promotes the mixing of the highest occupied orbitals of the two diene fragments and the splitting of the HOMO reaches 1.5 eV.[115]

The question arises how the bond between the π-subsystems depends on the nature of the bridging group. Some information about this can be drawn from the results of studies on divinyl compounds.[116]



The coupling between the orbitals π_1 and π_2 is determined by the fact that they both overlap simultaneously with a suitable orbital of the bridging group M and thus (even for a very small contribution of the latter) form a conjugation system with delocalised orbitals of the type π_+ and π_- (see above).

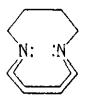
The difference between the energies $\Delta\pi$ of the new molecular orbitals is greater the closer is the energy of the orbital of M to that of the $\pi_{1,2}$ orbitals and the greater the overlap population in the M–C bonds. The difference $\Delta\pi$ is a maximum for planar conformers and reaches 3.5 eV for M = C=C, i.e. in the case of hexatriene. In the series of dienes with M=NH, O, CH_2, SiH_2, SnH_2, and $-CH_2-CH_2-$ the quantity $\Delta\pi$ diminishes and approaches zero but the orbital π_+ nevertheless lies higher than π_-, which is consistent with the conditions under which the bond through the bridge predominates (TB > TS). However, when M = CF_2 or CCl_2, the energy of the atomic orbitals of the bridging carbon atom is reduced under the influence of the electronegative ligands and the overlap population in the C–C bond of the $C-CHal_2-C$ fragment diminishes appreciably; the conjugation of the π-bonds through the bridge is therefore weakened so much that even their slight interaction through space predominates and the delocalised orbitals π_+ and π_- are arranged on the energy scale in the opposite order characteristic of this type of interaction.[116]

VIII. $n-n$ and $\sigma-\sigma$ conjugation

Turning now to examples of $n-n$ conjugation, we may note that the interaction of the n orbitals of adjoining atoms is unimportant for the formation of a chemical bond between fragments; however, the wave functions of the lone pairs (LP) in the Z–Z systems are mixed and their (+) and (–) combinations are split as regards energy for suitable molecular conformations with the accompanying destabilisation of the highest occupied molecular orbital (HOMO).

The difference (Δn) between the first two ionisation potentials, which corresponds approximately to the splitting of the above combinations of the atomic orbitals forming the two highest occupied orbitals, is illustrated by several examples in Table 2. The data for the first two compounds refer to the *s-trans*-conformations (the angle of rotation θ about the central σ-bond is 180°) corresponding to the maximum splitting; they were obtained on the basis of calculations and using analogies. The table also includes experimental data for the n orbitals of the oxygen atoms and certain dicarbonyl compounds, more precisely for those where the maximum splitting has been noted owing to a more favourable conformation (by no means in all cases optimal) for conjugation.[117]

Table 2. The gap between the first and second ionisation potentials corresponding to the delocalised n_+ and n_- orbitals.[54,72,77,117,118]

No.	Compound	Δn, eV	No.	Compound	Δn, eV
1	R_2N-NR_2	2.5	9		2.1
2	$R_2As-AsR_2$	1.6			
3	Cl—Cl	2.5			
4	I—I	1.8			
5	Diketones: α	2.6			
6	β	0.9	10		1.1
7	γ	0.5			
8	δ	0.3			

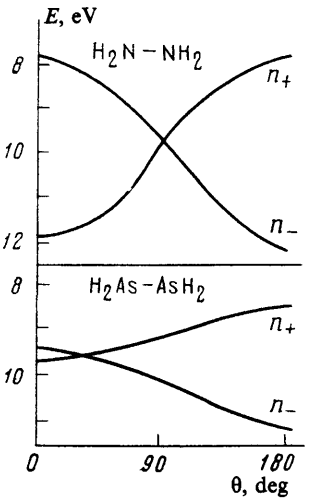


Figure 5. The energies of the delocalised n orbitals of N_2H_4 and As_2H_4, designated by the symbols n^+ and n^-, for different conformations including the *s-cis*-conformation (θ = 0°) and the *s-trans*-conformation (θ = 180°) (data obtained in Galasso's non-empirical calculations[54]).

Fig. 5 shows how the energies of the n_+ and n_- orbitals of H_2N-NH_2 and $H_2As-AsH_2$ should change as the conformations are varied according to calculations.[54] The splitting Δn in the *cis*-conformers is determined by the direct overlap of the n atomic orbitals of the heteroatom "through space". In the *trans*-conformers, it takes place as a result of the mixing of the low-lying σ orbitals of the central Z–Z bonds; despite the fact that the energies of these σ orbitals in the compounds of heavier atoms approach those of the n orbitals of the heteroatoms, the splitting diminishes, which is apparently associated with the change in the

nature of the lone pair and the decrease in their overlap with the molecular orbital σ_{Z-Z}. The lengthening of the Z–Z bond also has an effect in the *cis*-conformer.

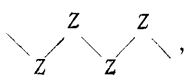
The principal conclusions drawn from ionisation potential data are as follows: (1) the manifestations of $n-n$ conjugation are associated with the interaction both through the intervening chemical bonds and through space; the relative roles of these channels depend on the molecular conformation; (2) with increase in the atomic weight of the heteroatom, Δn diminishes, which can be assessed as the weakening of conjugation as a result of the decrease in the contributions of both channels; (3) the difference Δn diminishes with increase in the distance R between the active centres; (4) in the molecules of compound (IX), which appears in Table 2 ($R \simeq 2.5$ Å), the interaction through the C–C σ-bond predominates, while in compound (X) ($R = 2.6$ Å) the interaction through space is dominant, which is favoured by the orientation of the n orbitals of the two nitrogen atoms "towards one another".[118] If the orientation and the distance R are kept constant, then in the bimolecular system $R_3N \ldots NR_3$ one may expect approximately the same value of Δn.

The molecular orbitals of σ–σ conjugation systems, consisting of isotypical units, are delocalised. With increase in chain length, the number of occupied molecular orbitals and their maximum splitting on the energy scale increase, while the energy gap between the frontier orbitals, the first ionisation potential, and the electronic excitation energy diminish.[77,119,120] In this respect, there is no fundamental difference between the σ–σ conjugation chains (including those in *n*-paraffins) and polyenes, but the linkage between the electron clouds of the fragments and the features of non-additivity enumerated above depend on the nature of the atoms Z and become more explicit[119] in the series of chains formed by the following groups:

$$CR_2 < SiR_2 < SnR_2 < CH{=}CH.$$

The coupling between the orbitals of the atoms in a chain of σ-bonds was described on the basis of estimated intraatomic [interatomic? (Ed. of Translation)] exchange integrals $\langle \varphi_1 | V | \varphi_2 \rangle$ and also the weak overlap of the atomic orbitals of non-adjacent atoms;[42] the overlap and order of the bonds between non-adjacent atoms cannot, however, be regarded (contrary to what has been stated by Gineityte and Shatkovskaya[121]) as "criteria of the delocalisation of electrons".

We may note that, in systems involving "conjugation of the σ-bonds of adjacent molecules" $\cdots Z-Z\cdots Z-Z\cdots$ (Section III), the optimum geometry is attained more readily than in the chains



noted above, where the α-skeleton imposes certain limitations. Accordingly, among the entire wide variety of systems (chemical compounds), we have in the first case a wider range of possible interaction conditions.

IX. The donor–acceptor interaction of atomic groups

Considering a wide range of X–Y and X–M–Y systems in their *stationary* states, one may say that conjugation or, more precisely, the mixing of the orbitals of molecular fragments may not be accompanied (as happens, for example, in the C=C–C=C–C=C system) or may be accompanied (for X ≠ Y) by a redistribution of electron density between the groups X and Y– which is slight or appreciable depending on the structure of these groups. If it is appreciable and can be described as the electron transfer X → Y, then in the majority of problems it is more practical to employ another terminology and to begin with another procedure for the differentiation of the initial "fragments" with the corresponding excess charges; in this case, it may not be necessary to introduce the terms "redistribution", "interaction", etc. in describing the system.

In any case, the contribution of the donor–acceptor interaction can be estimated approximately *a priori* on the basis of empirical rules and approaches and can be determined from experimental data (from the molecular dipole moment μ, from IR absorption band intensities, etc.) or from information about the systems of unoccupied and occupied molecular orbitals, whose analysis provides a more detailed picture and fairly understandable explanations.

The electronegativities of the atomic groups χ tabulated in the literature are attractive because of the possibility of inferring directly the donor–acceptor capacities of the substituents in which we are interested. However, in fact we have a set of extremely heterogeneous data obtained in different ways, frequently without information about the type of atomic partner-groups and about the molecular conformations, although such information is of primary importance (as well as the information about the influence of the medium and especially the solvation of the active centres, which may greatly modify the donor–acceptor properties and the conditions governing the mutual influence of the atomic groups). For this reason, the values of χ quoted in the text below can be used only for qualitative comparisons.

In view of the multiplicity of methods proposed for the determination of χ, this constant has come to be adopted as an independent property inherent in the atomic group; there is no need for comments and it is sufficient to quote some of the large number (more than 30) of the published values of χ for the amino-group: 1.361, 2.992, and 3.63 (quoted after Vereshchagin[86]).

A step towards a more correct analysis consisted in the differentiation of two types of donor–acceptor interaction—with increase or decrease in the order of the bond connecting the molecular fragments under consideration.[122] Thus combinations of atomic groups favouring a redistribution of electron density between them and accompanied by manifestations of non-additivity in other properties have been noted. The designations "π-donor + π-acceptor" and "σ-donor + σ-acceptor" began to be used widely subsequently for the designation of such combinations. This problem was reflected indirectly much earlier by the introduction of the Hammett constants σ^+ and σ^-.

Even after the more concrete specification indicated, the designations "donor" (D) and "acceptor" (A) should not be treated as a classification of the atomic groups. Depending on the "partners" and the molecular conformation, the latter can behave differently. Thus the systems of carbon–carbon π-bonds (Π) can be π-acceptors in Π–D molecules, for example in aniline, and π-donors in Π–A molecules, for example in nitrobenzene.

The dipole moment of nitrobenzene is known to be greater than that of nitromethane by 0.8 D, which corresponds by convention to a $Ph \rightarrow NO_2$ charge transfer of the order of (1/20)e. When the nitro-group is displaced from the plane of the benzene ring up to an angle of rotation of approximately 90°, the contribution of the π–π conjugation is virtually ruled out and the difference from nitromethane diminishes by a factor greater than 4 and, according

to quantum-chemical calculations,[46] by a factor of 1.5 (see also Baidin et al.[21]); according to the generally accepted view, only the contribution of the inductive effect then remains and the nitro-group becomes a σ-acceptor. The appreciable $H_2N \rightarrow Ph$ charge transfer in aniline molecules justifies the usual classification of NH_2 as a π-donor, but in an unfavourable conformation the amino-group (as well as the SR group) becomes a σ-acceptor.

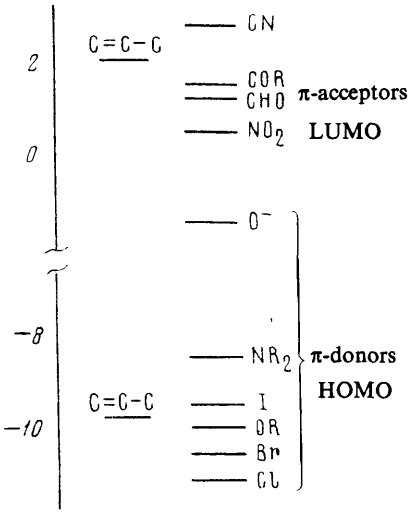


Figure 6. The positions on the energy scale of the HOMO of the π-donors and LUMO of the π-acceptors (simulated by the D−R and A−R molecules);[123] the possibility of the involvement of the groups D and A in the donor−acceptor interaction is related to them (however, cf. the data for PR_2 and AsR_2!).

The π-donor → π-acceptor redistribution of electron density depends significantly on the energy gap between the occupied orbital of the donor and the unoccupied π-orbital of the acceptor (Fig. 6) and also on the structure of the interface. It is self-evident that the electronic excitation of the molecule can alter radically the donor−acceptor properties of the substituents.

Table 3 provides data on the first vertical ionisation potentials (P_1) corresponding to molecular orbitals with an appreciable contribution of the *n* orbital (the lone electron pair) of the amino-nitrogen for compounds containing an active π-donor (amino-group) and intervening units of various types.[72,77,124] The values of ΔP_1 quoted denote the changes in P_1 on passing from simpler amines (X = H) to derivatives incorporating other groups X. Thus, whereas P_1 = 8.95 eV and ΔP_1 = 0 for R_2NH, the corresponding values for R_2N-NO_2 are P_1 = 9.75 eV and ΔP_1 = 0.8 eV. The influence of substituents on the amino-group can be inferred also from other data.[125–128] These include the experimental and calculated relative proton affinities (PA) of the amino-group in the compounds H_2N-CH_2-X (seventh column in Table 1—PA, kcal mol^{-1} [125]); the results of the calculation of the changes, induced by the influence of the group X, in the extremum of the electrostatic potential (EPE) generated by the lone pair,[128] which indicates the degree of involvement of the lone pair in conjugation (the fourth, eight, and twelfth columns—EPE, kcal mol^{-1}; the values for X = H were adopted as zero). The tenth column lists the Hammett constants σ_{para} [127] which are suitable for the investigation of the influence of X on reactions in electron-donating groups.

Some idea about the way that the amino-group influences in its turn the group X is provided by the changes induced by it in the stretching vibration frequency of the π-bond in the group X ($\Delta\omega_X$, cm^{-1}) (the fifth, ninth, and fifteenth columns).[32] For comparison, Table 3 includes electronegativity (χ) data for all the substituents X [85,86] in the form of the difference $\chi - 2.3 = \Delta\chi$.

Table 3. Signs of the mutual influence of the substituents in the D−A and D−M−A* systems.

Group X	Δχ for group X	R_2N-X (*a*)			R_2N-CH_2-X (*b*)				σ_{para} for group X	$R_2N-\Phi-X$ (*c*)				
		ΔP_1, eV	EPE, kcal mol^{-1}	$\Delta\omega_X$, cm^{-1}	ΔP_1, eV	PA, kcal mol^{-1}	EPE, kcal mol^{-1}	$\Delta\omega_X$, cm^{-1}		ΔP_1, eV	EPE, kcal mol^{-1}	Δμ, D	Δλ, nm	$\Delta\omega_X$, cm^{-1}
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
NO_2	1.4	0.8	50	−70	[0.8]	[−25]	16	[−30]	1.0	0.6	30	1.5	100	−17
CN	1.0	0.6	40	−40	0.7	−16	15	−24	0.9	0.5	—	1.2	35	−11
COR	0.4	0.3	25	−50	0.2	[−10]	—	−4	0.7	0.2	—	1.0	65	−13
Cl	0.7	[0.1]	30	—	[0.2]	[−10]	15	—	0.2	0.2	—	0.3	8	—
C=C	0.25	−1.0	17	−15	−0.1	2	—	0	0.1	−0.4	—	0.4	40	0
H	0	0	0	—	0	0	0	—	0	0	0	0	0	—
R	0	−0.4	4	—	−0.1	3	0	0	−0.1	−0.2	—	0	3	—
NR_2	0.35	[−1]	15	—	[−0.3]	[3]	[−2]	—	−0.3	−0.6	[−3]	0.1	10	—

* Approximate estimates are indicated in brackets.

The values of $\Delta\mu$ characterised the redistribution of electron density in the direction $R_2N \rightarrow X$, or, more precisely, the deviations of the dipole moment of $R_2N-\Phi-X$ from the vector sum of the moments of PhX and $PhNR_2$.[65] In the fourteenth column, $\Delta\lambda$ denotes the bathochromic shifts of the intense absorption band, which is in the region of 250 nm for $PhNR_2$ and corresponds to an element of charge transfer.

All the figures in brackets in Table 3 were obtained by quantum-chemical calculations or are approximate estimates based on analogies.

We shall consider in greater detail compounds of the type H_2N-A with $n-\pi$ conjugation systems in which the $D \rightarrow A$ shift of electron density has been noted. The formamide molecule can serve as the simplest example. In order to describe its large dipole moment, one usually refers[128] to the contribution of the structure $H_2N^+=CH-\overline{O}$, which reflects qualitatively also the shortening of the N–C bond, the coplanarity of the molecule, and the large energy barrier (18 kcal mol^{-1}), which prevents the rotation of the amino-group. According to calculations,[129] on rotation about the C–N bond with transition from a non-planar to a planar conformation, favouring $n-\pi$ conjugation, the electron density on the O atom increases slightly (cf. Refs. 49 and 130), while the C–N bond is shortened by 0.1 Å and its rigidity increases significantly.[131] However, certain other data do not correspond to the above methods of describing the structure of amides. Thus the length and force constant of the carbonyl bond, $R(C=O)$ and $K(C=O)$, differ little from those of simple aldehydes and the redistribution of electron density concerns, according to Wiberg and Laidig,[129] mainly the C–N region. One may add that the available data for the R_2N-NO_2 [132,133] and R_2N-CN molecules (but not for the just as polar R_2N-SO_2R group in which many features of conjugation are manifested weakly or are absent[134,135]) are in broad outline of the same kind.

The manifestations of $n-\pi$ conjugation in $PhNR_2$ molecules are well known. The energies of the p orbital in the PR_2, AsR_2, SbR_2, and BiR_2 groups differ little from that of the orbital in NR_2 (± 0.1 eV), but, as shown by the dipole moments of the compounds $PhZR_2$ and the Hammett constants σ_{para} which are close to zero,[127] are not active π-donors. The neutral character of the AsR_2 group ($\sigma \simeq 0$) has been treated[136] as a result of the annihilation of the contributions of the inductive effect (+0.28) and conjugation (–0.28), but in all the ZR_n substituents investigated, NR_2 and OR, the constants σ_{para} are close to zero despite the large differences between polarities! At the same time, the characteristic features of conformational equilibria were not considered by Gel'fond et al.[136]

Studies on specific $PhZR_2$ conformers yielded more information. According to calculations,[137] in the $PhPR_2$ conformer, where the two groups R are located on one side of the plane of the benzene ring, the PR_2 group behaves as a weak π-donor, while in the conformer with the symmetrical disposition of the methyl groups on either side of the plane of the benzene ring, the above group behaves more as a weak acceptor; a more significant bathochromic shift of the UV bands and appreciable intensification of the 1600 cm^{-1} Raman line of the benzene ring—almost the same as in $PhNR_2$—are characteristic of the first conformer. In $PhAsR_2$, which consists mainly of the conformer of the second type, the substituent exhibits stronger electron-accepting properties, which are usually attributed to the participation of the unoccupied d orbital of the As atom. The energy of the $n-\pi$ conjugation in the $PhNR_2$ molecule reaches 8 kcal mol^{-1}; for comparable conformations, it should be smaller by a factor of 1.5–2 in the $PhPR_2$ molecules.[138]

Judging from the data presented and also from the results of calculations,[20] NMR spectra,[139] and other data,[39,140,141] one can assume that the features of $n-\pi$ conjugation weaken in the series of compounds $PhZR_2$, where Z = N, P, As, Sb, and Bi, and in the PhZR series, where Z = O, S, Se, or Te. This applies particularly to the π-overlap and the $C_{arom}-Z$ bond length,[142] to the mixing of the n and π orbitals,[20] to the deviations from additivity in the dipole moments,[140] to the electron density on the carbon atoms of the benzene ring and the σ_{para} constants, to the conjugation energy[141] and the tendency by the molecule to assume the planar conformation favouring conjugation, and to the HOMO energy and the sensitivity of all the above parameters to changes in the angle of rotation θ of the ZR_n group about the $C_{arom}-Z$ bond. However, the above principal trends do not occur in the compounds PhX (X = halogen) and also in the compounds $O_2N-\Phi-ZR$,[65,140] where transition to heavier atoms Z entails the intensification of many manifestations of non-additivity; one of the causes is associated with the absence of the "problem of conformations" in the compounds PhX (X = halogen).

Allowance for the difference between the width of the energy gap ΔE between the n and π orbitals (which is smallest for PhI) is clearly insufficient to account for the entire observed picture; thus, one may turn ones attention to the appreciable decrease in the degree of $n-\pi$ mixing for almost identical values of ΔE in the series of compounds N ··· Bi. The latter is usually explained by the enhancement of the s character of the n orbitals, although this is not easy to test because of the lack of experimental data for the conformations being compared.

The sequences of Z based on the changes in the UV spectra of PhZr ($\Delta\lambda$) differ appreciably from those presented above. Within the limits of Group V elements, only nitrogen is outstanding. In the PhOR ··· PhTeR series and also in VyOR ··· VyTeR, a gradual shift of the region of intense absorption towards longer wavelengths is observed[143,144] (in conformity with this, a tendency towards an increase in the intensity of the Raman lines can be seen[143,145]); these data do not constitute an incontrovertible sign of the enhancement of any particular aspects of conjugation but it appears that the orbitals of heavy atoms are much more involved in the long-wavelength absorption (here one can turn ones attention to the energy of the n, σ, σ^*, and Rydberg orbitals and the UV spectra of the SR_2 and SeR_2 molecules and even more so TeR_2 molecules (see Table 1 and Refs. 73, 146, 147). Unfortunately, the interpretation of the PhX absorption bands is unreliable and incomplete, which applies particularly to the Rydberg transitions.

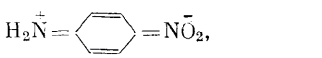
The overall pattern appears fairly complex and does not fit within the framework of a simple scheme; however, quantum-chemical calculations make it entirely possible to achieve qualitative explanations.

X. Donor–acceptor interaction in systems with a D–M–A bridging group

The question arises how the conditions governing the donor–acceptor interaction change on passing from D–A systems to D–M–A systems, where M is a bridging group. We shall consider initially the special case where the intervening unit is a system of carbon–carbon π-bonds. The degree of charge transfer in the $D-\Phi-NO_2$ molecules is smaller by a factor of $\sim 2-3$ than in $D-NO_2$. However, in the presence of the most active π-donors

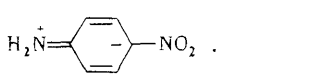
($-CH_2^-$, $-O^-$, $-NH^-$, $-S^-$), it is nevertheless extremely pronounced‡ and reaches 0.1 ... 0.2 e within the framework of the conventional D → A scheme according to calculations.[148]

The charge transfer in the *p*-nitroaniline molecule can be estimated as approximately 0.03 e; here the interatomic distances[149] correspond to an approximation to the quinonoid structure



and the C–NO_2 bond is shorter than in nitrobenzene by 0.03 Å. This led to the conclusion that conjugation involves the participation of both substituents; according to Furukawa et al.,[150] the conjugation energy, the amount in excess of the energy yielded by the interaction with each substituent separately (this is ~5 kcal mol^{-1} for $PhNO_2$ and ~8 kcal mol^{-1} for $PhNH_2$), is approximately 2 kcal mol^{-1}.

This interpretation has been rejected in a number of investigations;[46,151,152] it is believed[151] that the nitro-group is subjected to the inductive influence by the excess negative charge (about 0.06) generated on an adjacent carbon atom as a result of the influence of the amino-group, i. e. as a result of $n-\pi$ conjugation:



In certain other studies, the decrease in the basicity of the amino-group was considered and it was attributed to the interaction of the substituents in the cation, and not in the initial nitroaniline molecule, or to the influence of solvation.

The set of experimental data is not fully consistent with these conclusions. It is sufficient to state that the displacement of the nitro-group (as well as R_2N-) from the molecular plane weakens the signs of the interaction of the substituents.[32] These signs include the high intensity of the long-wavelength and charge-transfer absorption bands (~3000 Å), the shortening of the $C_{arom}-N$ bonds,[149,152] the fairly appreciable energy barrier hindering the free rotation of the nitro-group, the predominant influence of the amino-group on the frequencies ω_{as} of the antisymmetric vibration of the nitro-group (more local, with small involvement of the C–NO_2 bond), the influence of the latter on the NH_2 frequencies, the anomalously large molecular dipole moment, the high intensity of the IR bands due to the symmetrical vibrations of NO_2 and NH_2 (much greater than for the monosubstituted benzene derivatives), which can be interpreted as an indication of the migration of electron density during the atomic vibrations to the region of the conjugation system, and the fairly high absorption intensity due to the antisymmetric vibration, indicating an appreciably greater polarity of the N–O bonds[153] (whereas in the $H_2N-\Phi-CH=CH_2$ and similar molecules the substituents hardly influence one another). As regards solvation, its influence on different signs of conjugation and on the electron-donating capacity of the amino-group is very appreciable (for example, see Refs. 154 and 155), but is nevertheless of secondary importance; the clear non-additivity of the influence of the substituents on the spectra of isolated molecules has been established experimentally (see Table 3 and also Refs. 154, 156, and many others).

‡ The symbol D → A should not be accepted literally; the redistribution of electron density involves to some extent also the atoms of the intervening chain.

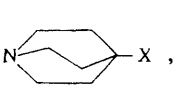
Whereas in the case of *p*-nitroaniline there are still some grounds for considering the structure of the quinonoid type (see above), in the presence of a longer intervening chain of π-bonds this becomes completely unjustified; the smoothing of the bond alternation induced by the substituents in the intervening poly-yne or polyene system is known to be observed only in the vicinity of substituents.

As the intervening subsystem lengthens, the D → A transfer of electron density diminishes, but, despite this the deviations from additivity in the dipole moments ($\Delta\mu$) increase owing to the increase in the effective length of the dipole. Thus $\Delta\mu$ = 0.6 D for R_2N-CHO, while in $R_2N-(CH=CH)_4CHO$ $\Delta\mu$ reaches 5 D.[52]

The changes in the force constant *K* (rigidity) of the π-bond in the group A can be traced in relation to nitro-compounds. According to experimental data, *K*(N–O) is reduced owing to the influence of the amino-group by more than 8% in the R_2N-NO_2 molecule, by approximately 3% in the $R_2N-\Phi-NO_2$ molecule, and by less than 0.5% in a system of the type $R_2N-\Phi-C=C-\Phi-NO_2$.

In the presence of even longer chains of carbon–carbon π-bonds, the influence on the rigidity of the N–O bonds (and also the changes in the basicity of the amino-group itself under the influence of the nitro-group) are no longer susceptible to observation, but the non-additivity of the influence of substituents on certain optical properties actually becomes even more explicit. This is apparently associated with the fact that the absorption bands (electronic transitions) appear in the long-wavelength region, which is readily accessible to observation; they affect the colour and make a particularly large contribution to the electronic polarisability of the molecule (and also to the intensity of the Raman lines — some of them are more intense by a factor of 100–1000 than for nitrobenzene). However, the additional bathochromic shifts of the UV absorption bands following the increase in the length of the intervening chain by one unit gradually diminish. Thus the different properties respond in different ways to the lengthening of the chain, but these differences have a completely definite physical basis.

We shall now turn our attention to compounds of the type $D-CH_2-A$ and the entire set of data in Table 3. Despite the heterogeneity of the parameters listed there, which in general bear little relation to one another, one may note certain features common to them. Thus, the non-additivity in the influence of heterotypical atomic groups, where the electron-donating amino-group is coupled to the electron-accepting group X in one way or another, is most marked in almost all cases. Among electron-accepting groups, the nitro-group is outstanding, which can be accounted for by the lower position of its π* orbital (Fig. 6). On the other hand, a qualitative similarity may be seen in many aspects of the influence of the substituent X in the series of compounds R_2NX, R_2N-CH_2X, $R_2N-\Phi-X$, and 4-X-quinuclidine. Such similarity apparently extends to a significant degree also to systems consisting of D–Y and A–Y molecules in close proximity. Contrary to expectation, some of these parameters differ little in the above series (ΔP_1), others are weakened (EPE, PA, $\Delta\omega_X$), while some parameters are actually strengthened ($\Delta\mu$). Furthermore, in compounds of types *a*, *b*, and *c* the π-acceptor and π-donor substituents X influence the parameters associated with the amino-group — P_1 and the rigidity of the N–H bonds[126] — (as well as the dissociation constants of the acids $X-\Phi-COOH$) in opposite directions, while in the quinuclidine derivatives



they exert their influence in the same direction; this agrees with the fact that the values of $\Delta\chi$, which are very close to the characteristics of the σ-donor–acceptor capacities of the substituents, have the same sign for all the groups X considered (cf. the values of σ_{para}).

The similarity in the manifestations of the intramolecular interaction in the R_2N-CH_2-A and $R_2N-\Phi-A$ molecules does not imply identity of the mechanisms; one may say that the group A = CN, NO_2, Cl, or F (but not COR [157,158]) in the compounds R_2N-CH_2-A acts as a σ-acceptor, while in aromatic nitriles and nitro-compounds it acts as a π-acceptor:

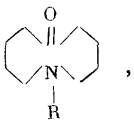


The influence of the σ-acceptor properties of the above groups has been described as a tendency to assume an electronic structure of the type $R_2\overset{+}{N}=CH_2A^-$.[128,157] The shortening of the bond with the amino-group and the lengthening of the $C-NO_2$ bond, which follows from non-empirical calculations[159] for $H_2N-CH_2-NO_2$, is consistent with this; similar results have been obtained for H_2N-CH_2-Cl.[128]

The similarity noted above does not extend to UV spectra. The point is that in aromatic compounds the combination of the groups D and A promotes an intense absorption in the long-wavelength region where the band involving an element of the D → A charge transfer but also with an appreciable participation of the benzene ring is located (see the molecular orbital in Fig. 6 of Ref. 160). In the observed long-wavelength part of the absorption spectrum of R_2N-CH_2-CN, the contribution of the amino-group predominates; the electron-acceptor group promotes the stabilisation of the lone pair orbital and the zone of intense absorption moves away into the region of 1800 Å (see Figs. 1 and 2 in Ref. 157). This example indicates the necessity to study and to interpret fully the bands over a wider region in the spectrum.

The quantitative conclusions which might be drawn from the entire data obtained require more detailed calculations. One has to bear in mind that in reality the structures of the molecular orbitals, for brevity referred to as lone pair orbitals, differ greatly in the compounds being compared; the description of the principal trends depends to a considerable extent on the choice of the reference standard (in Table 3, this is X = H); there is no certainty that the dominant conformations in compounds R_2N-CH_2-X are isotypical. Finally, the data for diamines, and in the first place for hydrazines, are not treated unambiguously. The question arises how the group $X=NR_2$ in these compounds influences the other amino-group. Here $\Delta P_1 = -0.65$ eV, while $\Delta P_2 = -0.15$ eV, but both P_1 and P_2 characterise not one amino-group but the set of two such groups and, in considering the processes involving one-amino-group, it is therefore better to employ the average (−0.4 eV). In this case, both variants yield a negative sign but in diazaadamantane with the N–C–N system analogous variants give rise to different signs; thus, in describing different processes, even qualitative differences may appear in estimates of the influence of intramolecular interaction.

Table 3 may be supplemented by data for molecules in which the groups A and D are located in such a way that they can interact appreciably through the intervening free space; the transannular interaction in atranes and in various cyclic and polycyclic bifunctional compounds in which the active centres are fixed at a comparatively short distance from one another by a rigid skeleton of chemical bonds which does not itself participate in the conjugation has long been known. The aminoketone



may serve as an example.

Despite its unusual structure, in terms of the value of ΔP_1 it differs little from other ketones included in Table 3, while in terms of $\Delta\omega_{C-O}$ it is actually superior to some of them.

It is even more useful to compare a molecule of the type D–M–A with a set of two molecules one of which includes the group A and the other the group D. In an experiment, it is possible to immobilise an AX + DY pair of this kind by a solid inert matrix (for example, argon). It is easy to imagine that, after the formation of the AX + DY system, there is a possibility of its further evolution involving several stages with the modification of the wave functions and hence of the electronic structure. Under suitable conditions, one of the stages may be the electron transfer D → A. The knowledge of the characteristic features of the generation of the potential within the limits of the entire system (AX + DY or D–M–A) and of the parameters of all types of relaxation facilitates the selection of the molecular structure of a compound or complex to be used in "submicroelectronic" devices. The symbolic representation of one of the simplest elements of such a device, incorporating one molecule of the type D–M–A, is presented in Fig. 7; the possibility of creating controllable elements has been described.[17,18,161]

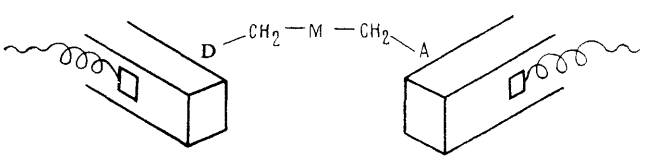


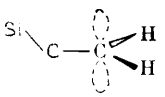
Figure 7. Model of an element in the microprocessor technique incorporating one molecule of the D–M–A type.

The study of the functions of D–M–A systems is of fundamental importance for the understanding of the mechanisms of many most important chemical, physical, and physiological processes.

XI. Conjugation in molecules of allylic compounds

The bond systems separated by the methylene bridge have been attracting increasing attention recently. It has become evident that the usual ideas about the weakness of the interaction between the subsystems cannot be extended to all molecules with a methylene

bridge; the manifestations of non-additivity are much more striking in certain cases than, say, in butadiene. We may refer to the examples of the solvolysis of derivatives of pentacyclononyl nitrobenzoate: under the influence of certain hydrocarbon substituents of low polarity, extending through two–three C–C σ-bonds, the rate of reaction increases by a factor of $10^{12}-10^{14}$.[162] Even more interesting examples may be quoted if one turns to ions, radicals, and electronically excited molecules, while the conjugation energy may prove to be an order of magnitude higher than in dienes. Thus such energy in the 3-silapropyl cation in the optimum conformation



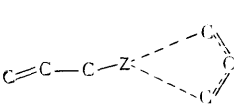
exceeds 25 kcal mol^{-1}.[163]

Allylic, benzyl, and similar compounds of heavy elements have attracted attention.[53,101,107,164–169] It was necessary to establish the principal features of their structure and, as far as possible, to find answers to the following questions:

1. What determines the tendency towards the formation of π-complexes or σ-structures?
2. How do the manifestations of conjugation in σ-structures depend on the nature of the heteroatom and of its valence state and also on the conformation of the molecule?
3. What is the mechanism of this interaction?
4. How are relativistic effects reflected in the signs of conjugation?
5. Do the unshared electron pairs of the heteroatom contribute to conjugation?
6. How are the manifestations of conjugation in the electronic and vibrational spectra and the redistribution of electron density between the fragments of the molecule interrelated?

As regards the first question, one should note in the first place that in allylic compounds different structural variants may occur depending on the nature of the heteroatom and the types and positions of the substituents. These variants include symmetrical π-complexes (characteristic of transition metal and alkali metal compounds), slightly or appreciably asymmetric systems, and, finally, typical σ-allylic structures which will in fact be the subject of our attention.

In contrast to π-complexes, in the σ-allylic structures there is a fairly strong σ-bond between the heteroatom and one of the terminal carbon atoms and only weak or negligible overlap of the atomic orbitals of the heteroatom and other carbon atoms. In individual instances, it has been suggested that there is an equilibrium between the σ-allylic form and the π-complex.[170–172] In complex molecules, one cannot rule out the participation of one heteroatom simultaneously in bonds of two types—characteristic of π- and σ-structures:



The study of the reactivity of a series of σ-allylic systems led to the concept of σ–π conjugation,[101] which can be described, in terms of LCBO, as the mixing of orbitals localised on bonds—the C–Z σ orbitals and the C=C π orbitals. Subsequently spectroscopic studies on the compounds $\Pi-CH_2-ZY_n$ with the atoms Z belonging to different Groups in the Periodic System led to the conclusion that compounds of heavy elements and the elements in the first Groups have specific features.[53,107,164] Manifestations of conjugation clearly occur in these compounds. These include, in particular, the deepening of the colour,[160,164] an increase in electronic polarisability, a sharp increase in the intensity of the Raman lines of the π-bonds,[32,53,165] and specific changes in reactivity;[21,101,173,174] a decrease in the heat of hydrogenation of the double bond (by 1–10 kcal mol^{-1}), a decrease in the vibration frequency and rigidity of the C=C bond, and, in certain cases, a slight smoothing of the differences between the C–C and C=C bond lengths (complete equalisation occurs in symmetrical π-complexes).

The mixing of the above π and σ orbitals (with the corresponding delocalisation) leads to the expansion of the energy gap between them and to the destabilisation of the highest occupied molecular orbital (HOMO). These features are more marked the closer are the energies of the initial orbitals and the greater their overlap or, more aptly, the greater the integral $<\sigma|V|\pi>$ (see the formula in Section II). The overlap depends comparatively little (±30%) on the type of heteroatom Z, but depends greatly on the conformation, being a maximum for the *gauche*-conformers. In planar forms, the mixing is minimal and the sets of frontier molecular orbitals of the compounds $AllZR_n$ can be regarded, without stretching things too much, as a set of several modified molecular orbitals of propene (π and π*) and the compounds ZR_m (σ orbitals, including the C–Z bond, the *n* orbitals of the Z atom, etc.).

Several examples in Fig. 8 provide a qualitative idea about the possibilities in the mixing of the orbitals of fragments adjoining the methylene bridge and combination of various substituent groups ZR_n and the simplest π-subsystems. Each column indicates the corresponding Z atom. The continuous sections of the horizontal straight lines represent the position on the energy scale of the π molecular orbitals of propene and $R_3C-CO-R$ and the σ molecular orbitals of the ZR_m molecules, which simulate the molecular fragments of $All-ZR_n$ and $R_3C-CO-CH_2-ZR_n$ in the absence of conjugation. The divided sections correspond to the orbitals of some of the compounds $R-ZH_3$; their positions explain the causes of the possible differences between the conjugation conditions in the $AllZR_n$ and $AllZH_n$ molecules. The divided sections of the horizontal straight lines correspond to tentative estimates. The dotted lines join isotypical molecular orbitals. The wavy lines correspond to orbitals of the model in which the contribution of the relativistic effects is not included.[57]

In setting up a molecular orbital scheme, photoelectron and electron-transmission spectroscopic data[72,77,90–92] as well as the results of MNDO calculations[57,175,176] were resorted to. Unfortunately, this method does not take into account the Rydberg atomic orbitals and yields incomplete and insufficiently reliable data for the unoccupied orbitals. Nevertheless the major role of Rydberg transitions has been noted in the UV spectra of many organic compounds;[73,98,100,147] thus the long-wavelength electronic transition in SnR_4 is associated with the involvement of the 6*s* and 6*p* atomic orbitals of tin.

The vertical arrows in Fig. 8 show in relation to Si, Sn, P, and As compounds how the positions of the molecular orbitals change on passing from non-interacting fragments to the *gauche*-conformers of C=C–C–Z and O=C–C–Z. To a first approximation, these changes can be identified with the shift in the *trans* → *gauche* transition induced mainly by conjugation (although delocalisation of the orbitals and small shifts on the energy scale occur also in planar

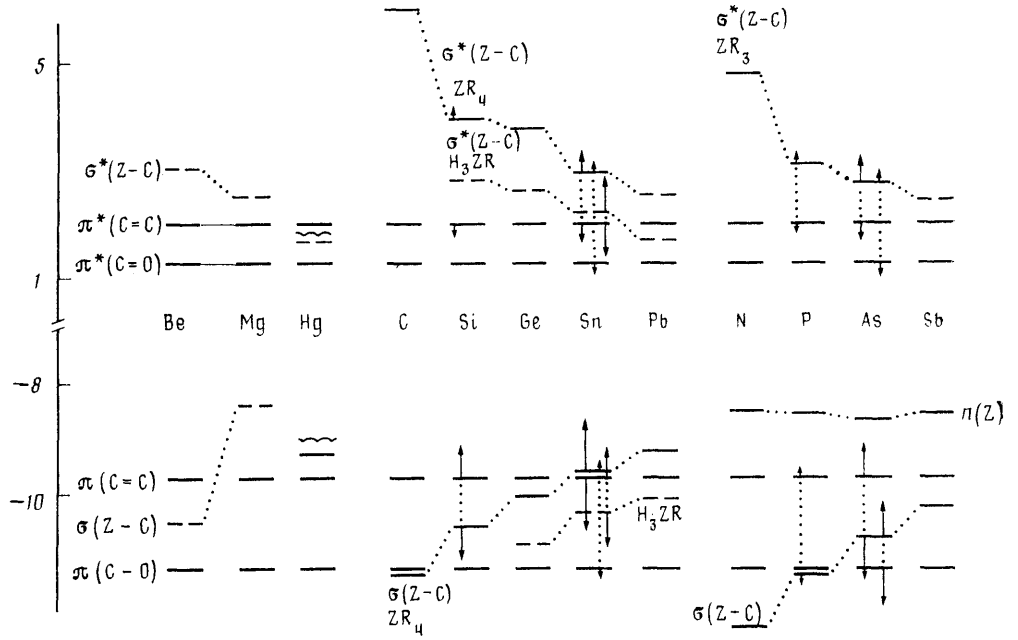


Figure 8. Schematic arrangement of the C=C and C=O π orbitals as well as orbitals associated primarily with the Z−C bonds in the ZR_m molecules; the proximity of the σ and π orbitals favours their mixing in the *gauche*-conformers of the $\Pi-CH_2-ZR_n$ molecules.

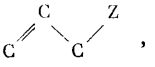
conformers). Changes of this kind in the B, C, N, and O compounds are slight but in allylic compounds of heavy elements, where the $E_\pi - E_\sigma$ energy gap is smaller, they become more significant.[57,107,175] They are accompanied by explicit changes in the UV absorption spectra;[160,164] the delocalisation of the occupied molecular orbitals in the non-planar conformers is then responsible for the intensification and the mutual approach of the frontier orbitals gives rise to the bathochromic shift of the absorption bands conventionally designated as $\pi \rightarrow \sigma^*$ bands, which can thus come to the fore.

More comprehensive information about allylic compounds is provided by Table 4. The figures quoted there show how much the following quantities *diminish* on passing from propene and ZR_m to the compounds $All-ZR_n$: (1) the first ionisation potential P_1 (which refers in addition to the lone pair of the Z atom):[39,72,77] (2) the wavelength λ of the first intense UV absorption band of the solutions in heptane (bold type):[32,73,92,164] (3) the stretching vibration frequency $\omega_{C=C}$.[32,78,160] The initial data for propene are as follows: $P_1 = 9.8$ eV, $\Delta P_1 = 0$, $\lambda = 180$ nm, $\Delta\lambda = 0$, $\omega = 1645$ cm^{-1}, and $\Delta\omega = 0$. Under the experimental conditions, the *gauche*-conformer predominated in most cases, which intensified the signs of conjugation. Approximate estimates based on analogies or on approximate quantum-chemical calculations, which are suitable only for qualitative inferences, are given in Table 4 in brackets; they correspond to the *gauche*-conformations.

The decrease in the ionisation potential (ΔP_1) characterises the destabilisation of the HOMO on passing from non-interacting fragments (simulated by the ZR_m and propene molecules) to the real $C=C-C-ZR_n$ system with orbitals of the mixed π/σ type. In those cases where the σ molecular orbital of ZR_m lies above the π molecular orbital of propene and makes a dominant contribution to the HOMO of $AllZR_n$, the ΔP_1 readings are begun from this orbital; the corresponding numbers in Table 4 are designated by the letter σ. In one way or another, the quantity ΔP_1 reflects the dominant influence of conjugation; in the majority of compounds, it is very close to the value which would have been observed in the conformational *trans* → *gauche* transition. The latter has been confirmed indirectly by the approximate constancy of E_π for the *trans*-conformer. However, among the compounds of certain elements (especially Li, F, and Cl), there is no such constancy; here the influence of the differences between the potential fields in the region of the heteroatom, which is usually regarded as the inductive effect, operates.

The shift of the UV band ($\Delta\lambda$) is in all cases determined relative to propene. In compounds of the Second Period *p* elements, this is a $\pi \rightarrow \pi^*$ transition, while in compounds of heavy elements it is a transition with participation of a molecular orbital to which the atomic orbitals of the heteroatom make an appreciable contribution; the involvement of the Rydberg states is then entirely probable (see above).

In interpreting the values of $\Delta\omega$ quoted above, one should bear in mind that in other structures, where the subsystem



is coplanar and there is no conjugation-induced decrease in the rigidity of the double bond but the influence of the greater mass of the heteroatom remains, the difference $\Delta\omega$ proved to be smaller by a factor of 2−3,[165] i. e. is relatively insignificant.

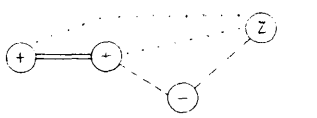
Table 4. The decrease in the first ionisation potential (ΔP_1, eV), the wavelength of the UV absorption band ($\Delta\lambda$, nm), and the C=C stretching vibration frequency ($\Delta\omega_{C=C}$, cm^{-1}) on transition from C=C−C to C=C−C−ZR_n.*

				Be (0.5) — —	B 0.1 5 9	C 0.2 0 0	N −0.2 2 3	O −0.2 5 2	F −0.7 0 −6
				Mg (0.4σ) — (60)	Al (1.0σ) — 15	Si 0.8 15 13	P 0.2 — 8	S −0.2 20 5	Cl −0.6 6 2
Ti (0.9σ) — 47	V — — —	Mn — — 25	Ni — — (40)	Zn 0.9σ — 25	Ga (1.0σ) — (20)	Ge 0.9 20 13	As 0.5 25 10	Se −0.1 20 8	Br −0.4 12 7
Zr — — 50	Nb — — (37)	Tc — — —	Pd — — (50)	Cd — — (30)	In (0.4σ) — —	Sn 1.2σ 30 18	Sb (0.7) — 15	Te 0 40 17	I 0 20 15
Hf 1.1σ — 42	Ta^V — — (30)	Re — — 27	Pt — — (32)	Hg 0.9σ 50 20	Tl — — —	Pb (0.8σ) — —			

* Under the symbol of each element, the first, second, and third rows indicate ΔP_1, $\Delta\lambda$, and $\Delta\omega_{C=C}$ respectively.

It is seen from Tables 1 and 4 and Fig. 8 that there is some correspondence between the spectra of the compounds ZR_m and $AllZR_n$; when Z is varied along the Periodic System from above downwards and from right to left, the above signs of conjugation in allylic compounds in general become more marked (cf. the data in Section V). In compounds of the heaviest elements, this tendency becomes less marked partly owing to the contribution of the relativistic effects.[57,177] The energy of the σ orbitals is then very important. Fig. 8 shows that, when Z varies within one subgroup of the elements from above downwards, the σ molecular orbitals of the compounds ZR_m are located in an increasingly higher position and thus the energy gap $E_\pi - E_\sigma$ narrows (which favours the π/σ mixing), but subsequently, when the σ molecular orbital lies above the π molecular orbital and the gap actually begins to widen, the π/σ mixing should weaken (but with a further increase in the bathochromic shift of the UV absorption band). Such changes in the occupied and unoccupied molecular orbitals are by no means "synchronous". The mixing of the *n* and π orbitals is in this case very slight (in contrast to the $\Pi-ZR_n$ system where there is no bridging group).

The mechanism of conjugation in σ-allylic compounds can be elucidated by using a scheme simplified to the maximum extent:

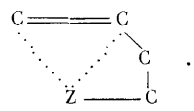


Here the four carbon atoms of the main chain $C_\gamma=C_\beta-C_\alpha-Z$ are represented by circles; the lines between the circles symbolise the interaction of the atomic orbitals in pairs. The symbols (+) and (−) denote the signs of the contribution of the $2p_x$ atomic orbitals of the three carbon atoms to the HOMO, whose structure is close to the π orbital of ethylene§ but which includes in addition a small contribution by the $2p_x$ atomic orbital of the bridging C_α atom. If this atomic orbital has in addition a non-zero population of the overlap with the orbitals of the heteroatom Z (which happens in non-planar conformers), then conditions are created for the formation of delocalised molecular orbitals incorporating the entire C=C−C−Z system. One may say that the conformation of the system determines the overlap population mentioned above and transition to compounds of heavy elements implies a higher (and close to the π orbital) position on the energy scale of the σ orbital of the C−Z type, which favours the π/σ mixing. In conformity with the above (by no means complete) scheme, the atomic orbitals of the heteroatom Z can, at least in non-planar conformers, become mixed with the π molecular orbital as a result of overlap (1) with the $2p_x$ atomic orbitals of C_β and C_γ (interaction through space denoted by dotted lines) and (2) with the $2p_x$ atomic orbital of C_α (interaction through a bridge or, in other words, there is a bond between the fragments formed as a result of the simultaneous overlap of the $2p_x$ atomic orbitals of the bridging C_α atom with the orbitals of X and C=C). Generally speaking, each of these two channels separately might promote the destabilisation of the HOMO and a decrease in the first ionisation potential; in the case considered, the contributions of these channels have different signs and one cannot therefore rule out the possibility of their "annihilation" (as in certain dienes[178]). Which of these two channels predominates depends, generally speaking, on the nature of the heteroatom, the bridging group, and the π- bond and also on the molecular conformation and on the structure of specific orbitals. The mixing of different orbitals of the two active centres can be determined by different channels; thus one cannot rule out the possibility that the highest occupied orbitals of the fragments are mixed via one channel, while the unoccupied one are mixed via another.

According to calculations,[57,107,176] the interaction through a bridge predominates markedly in the majority of σ-allylic compounds of *p* elements; it in fact determines the destabilisation of the HOMO (by as much as 1−1.5 eV). The specific features of the conformation then have an effect mainly through the overlap population of the $2p_x$ atomic orbital of the C_α atom and the orbitals of the Z atom (although the latter makes only a small contribution to the formation of the C−Z chemical bond). The interaction through space in such molecules is altogether insignificant. However, the more diffuse atomic orbitals of the heteroatom, for example, the *s* atomic orbitals of the alkali metals can, like the *d* orbitals of transition metals, overlap effectively with the atomic orbitals of all three carbon atoms; under these conditions, π complexes are formed readily and in relation to such complexes it is more appropriate to speak not of interaction through space but of chemical bonds with the heteroatom. The involvement of the $d-\pi$ overlap the σ-allylic compound of rhenium is represented in Fig. 9 after Bodner et al.[179] In any case, the presence of two−three methylene groups instead of one weakens the interaction through the bridge system and facilitates the mutual approach of the heteroatom

§ The cartesian *x* axis is perpendicular to the  plane; the Z atom lies outside this plane.

and the double bond in space, creating additional possibilities for interaction through space:



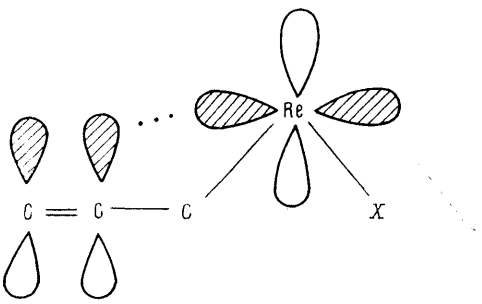


Figure 9. Involvement of the *d* atomic orbitals of rhenium in conjugation.[179]

The question arises of the correspondence between the above conclusions concerning the conjugation mechanism, based on the consideration of delocalised molecular orbitals, and the known ideas about $\sigma-\pi$ conjugation as a consequence of the overlap of the C=C π orbital and the C–Z σ orbital constructed from hybridised atomic orbitals and located in bonds. The electron density on the localised σ orbital is generated by several delocalised σ molecular orbitals, but in our case only one of them (the highest occupied σ molecular orbital) interacts with the π orbital, since the energies of the remaining orbitals differ markedly from that of the π orbital. Thus "conjugation with the σ-bond" can be interpreted as the participation of this particular "component" (by no means localised in the one σ-bond considered and not playing the principal role in the formation of the $C_\alpha-Z$ chemical bond). On the other hand, one may say that, for the description of the influence of conjugation on the parameters of an individual chemical bond (for example, on the force constant), the system of localised orbitals is more or less suitable but for the description of the electronic absorption spectra and various "one-electron" properties it is more convenient to resort to delocalised molecular orbitals.

By virtue of the influence of steric factors and conjugation, the *gauche*-conformation is more favourable on energy grounds for the majority of σ-allylic compounds (in contrast to $\pi-\pi$ conjugation systems). The conjugation energy, which is related to the weak interaction of the frontier orbitals having markedly different energies, is then low in the electronic ground state (<3 kcal mol^{-1}).[166,180] It proves to be somewhat greater for compounds of heavy elements, although the changes in the energy of the electrons occupying the π and σ molecular orbitals occurring under these conditions in the *s-trans* → *gauche* transition to some extent cancel out; however, after the transition of the molecule to the first electronically excited ($\pi \rightarrow \sigma^*$) or ionised state, such cancelling does not occur and the dependence of the energy of the molecule on the conformation should be appreciable[174] (see Fig. 10 and also Fig. 3 in the paper of Shorygin et al.[164]). The results of changes in the energies of the HOMO and LUMO not only do not cancel out but are actually added together if one considers the shift of the long-wavelength absorption band. Thus conjugation has little effect on the energy of an unexcited neutral molecule, has a greater effect on the ionisation potentials and electron affinities, and has a strong effect on the UV absorption spectrum.

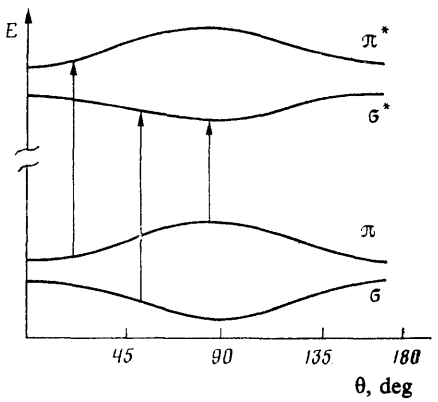


Figure 10. The energies of the σ and π orbitals of $XHg-CH_2-CH=CH_2$ for different conformations;[175] the arrows denote the types of allowed electronic transitions.

According to calculations,[166,167,175,176] the redistribution of electron density between the heteroatom and the vinyl group in the allylic compounds of the majority of *p* elements is insignificant and is almost independent of the conformations; the influence of the heteroatom on the charge of the C_γ atom, which varies within the range ± 0.03 e, is more instructive in this instance.

The redistribution of electron density on the atoms of the main chain in allyl fluoride and the hypothetical model of σ-allyl-lithium is more appreciable and can be represented by the following symbolic scheme for the *gauche*-conformers:[57,176]

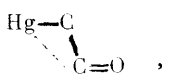
$$\overset{0.05}{C}=\overset{0.25}{C}-C-F, \quad \overset{0.1}{C}=\overset{0.4}{C}-C-Li \;(0.1), \quad \overset{0.2}{C}=\overset{0.1}{C}-\overset{0.5}{C}-Li.$$

In precisely these two extreme cases, the results resemble the situation which may be expected on the basis of ideas concerning the inductive influence of strongly polar C–Z bonds. However, the inclusion in the scheme of two equally important variants (out of the multiplicity of the possible ones) for allyl-lithium is sufficient to draw ones attention to the ambiguity of the treatment. The latter appears even less satisfactory in view of the considerable decrease in the redistribution of charges in the planar conformers of both compounds. In any case, the estimation of the involvement of individual molecular orbitals and of the distribution of electron density in space in different conformers leads to a completely valid description of the entire picture.

On considering a wider range of allylic compounds, one may say that the low electronegativity of the $-ZR_n$ group in general favours the transfer of electron density—predominantly to the bridging carbon atom in the σ-allylic forms and to the terminal carbon atoms in π-complexes. If such a group is called a σ-donor, then the $-CH_2-ZR_n$ group can be regarded as a π-donor. Accordingly, the σ_{para} Hammett constant, for example of the $-CH_2-SnR_3$ group, is −0.35 whereas that for the $-SnR_3$ group is close to zero;[127] the data are even more striking for the mercury and lead compounds.

Most of the conclusions about allylic compounds can be extended by benzyl, indenyl, and other systems of a similar type. The question arises whether they can be extended also to the compounds R_nZ-CH_2-A incorporating a π-acceptor A, for example, CN, COR, and NO_2. The data for the amines R_2N-CH_2-A have already been considered in Section X. Heavy atoms Z with a low electronegativity promote in this instance to a somewhat greater extent than in allylic compounds a decrease in the rigidity of the π-bond, the enhancement of other signs of σ−π conjugation, and the "metal atom → terminal atom of the π-bond" charge transfer (see the spectra of carbonyl compounds[44,124,158,160,164,165,181] and nitriles[124,157,182]).

We shall consider as an example the XHg−C−C=O bond system. According to approximate quantum-chemical calculations,[183] the Hg → O charge transfer in the planar conformer should be approximately 0.02; when coplanarity breaks down, an additional conjugation-related change in the atomic charges (up to 0.02) and bond orders (up to 1−2%) and very weak bonding



(designated by dashed lines) are observed. However, the description of these small changes as a certain trend towards the structure $X-\overset{+}{H}gC=C-\overline{O}$ (similar to that in the paper of Guerrero et al.[44]) can be resorted to only in a qualitative consideration. Conjugation favours in this instance the predominance of the *gauche*-conformers and accordingly a more explicit non-additivity in the generation of the UV absorption spectrum (Fig. 11) and a decrease in the C=O frequency.[181]

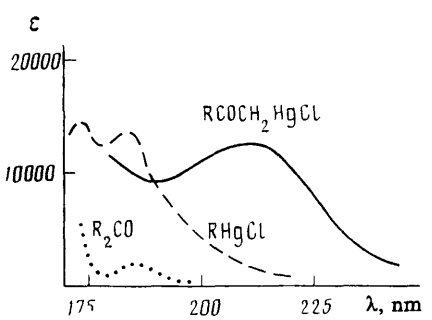


Figure 11. Signs of non-additivity in the UV absorption spectrum of $RCOCH_2HgCl$; the absorption band type is close to $\pi \rightarrow \sigma^*$.[180]

In compounds with the oxygen bridge, X−O−COR, the C=O frequency is much more sensitive to changes in the structure of X than in compounds with the CH_2, NH, S, and Φ bridges. Thus in the series of compounds $R_nZ-O-COR$ it varies within the range from 1785 cm^{-1} for Z = O to 1645 for Z = Sb^{III}, 1620 cm^{-1} for Z = Pb, and 1560 cm^{-1} for the anion $(OCOR)^-$.[181] Here we have a combination of $n-\pi$ conjugation in the O−COR subsystem, which is promoted by coplanarity, and σ−π conjugation, which is promoted by the breakdown of coplanarity. The correspondence between the electronegativity of the group ZR_n and the influence of the latter on ω_{C-O} is by no means always complete under these conditions.[184] It has also not been noted on comparing the A−M−Sb^{III} and A−M−Sb^V subsystems: judging from the data of Epstein et al.,[185] the M−Sb^V fragment is much more active as part of the conjugation system and a π-donor (while the −M−Au subsystem is more active than −M−Hg [186]). Interesting data for aromatic compounds with −O− and −NH− bridges can also be found in the communications of Chuvashev et al.[187] and Pozdnyakov et al.[188]

As already noted in Sections X and XI, the entire set of data obtained creates a basis for the interpretation of the characteristic features and the mechanism of the mutual influence of atomic groups separated by a bridging group (X−M−Y); it gives rise to additional possibilities for inferences about conjugation in electronically excited ionised states and the relative stabilities of σ-structures and π-complexes. The influence of substituents through a bridging group is of primary importance for the physical and chemical properties of many organic compounds; in many cases, it proves to be even greater than in the X−Y systems.

XII. Conclusion

The determination of the mechanism and of the characteristic features of the mutual influence of atomic groups forms part of the range of fundamental problems of organic chemistry. It leads ultimately to a more compact description of the enormous, almost unencompassable experimental data and hence to an improvement of its employment and to an increase in the productivity of the work of investigators endeavouring to obtain compounds with the required properties.

The mutual influence of functional groups is manifested by a complex set of heterogeneous signs of non-additivity; these signs are not linked by simple and universal correlations; it is sufficient to say that a change in the structure of the interface sometimes enhances and sometimes weakens other signs of conjugation. Under these conditions, the determination of at least the general trends, wherever this is possible, is already a useful step and facilitates further research.

The schemes for the differentiation of different forms of intramolecular interaction, including conjugation and the inductive effect, used in the literature are conventional in character and at the same time far from uniform, which very greatly complicates comparison of the conclusions of different workers. Calculations of the contribution by the inductive effect in the study of the interaction of the active centres of molecules is frequently based on estimates of the dielectric constant ε of the intervening medium, which is regarded as a kind of "black box". The adjustment or selection of ε in the range from 1 to ∞ and the use of the simple Coulomb law reveal the lack of validity of the method.

Almost all the most important features of the physical, chemical, and technical properties of organic compounds, including the possibility of the evolution of the state of the molecule in time (migration of the excitation energy or of the electron along the chain of chemical bonds) are associated directly or indirectly with conjugation and other forms of the mutual influence of atomic groups.

All forms of conjugation merit constant attention. The signs of the conjugation of σ-bonds are not an exception in this respect. They are significant even in the molecules of n-alkanes and in certain systems they actually prove more appreciable than in molecules with conjugated π-bonds. However, in view of the exceptionally great variety of the practical applications of organic compounds, it is not surprising that in some cases a strong interaction between the active centres plays an important or decisive role, while in others a weak interaction between such centres assumes this role. The latter factor has come to attract increasing attention in connection with the development of certain new types of study, including the study of the possibilities of using "submicroelectronic" systems for the transformation of information with an exceptionally high packing density, because in this instance one molecule with several active centres can in principle perform the function of a whole unit.

Advances in the experimental technique and in quantum-chemical calculations, the synthesis and study of new previously inaccessible model compounds, and the experience gained in logical analysis and generalisations, have made possible an appreciable advance in the understanding of the most important problems of theoretical organic chemistry, in particular, they have made it possible to characterise the principal aspects of conjugation with participation of heteroatoms from all the Groups of the Periodic System and to estimate at the same time the role of relativistic effects. Despite certain disappointments and a series of difficulties which have arisen at this new level of research, one can undoubtedly count on further rapid progress and the transformation of the science of molecular structure into an active research instrument designed to solve problems in practical chemistry.

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