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The electronic structure and reactivity of alkenes

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ABSTRACT. **The modern methods for the calculation of the electronic structures of alkenes are examined. The photoelectron spectra of alkenes are analysed and the relation between the properties of molecules and their orbital structure is discussed on the basis of experimental data and quantum-chemical calculations. The corresponding structural parameters of alkenes are systematically compared with their reactivities. The ionisation energies of alkenes are presented.**

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I. Introduction

The method for the investigation of the electronic structures of molecules which yields most information is nowadays photoelectron spectroscopy (PES). As it developed, it became possible to test experimentally the adequacy of quantum-chemical calculations within the framework of the molecular orbital (MO) theory. On the other hand, quantum-chemical calculations play an important role in the interpretation of photoelectron spectroscopy data.

The aim of the present review was to survey the studies on the electronic structures of alkenes with the aid of quantum-chemical calculations and photoelectron spectroscopy and to compare the parameters of the electronic structures of alkenes with their reactivities, which are determined mainly by the presence of the π-bond.

II. Approximations used in the analysis of the electronic structures of alkenes

1. Approximations of the molecular orbital method

Since exact quantum-chemical calculations of the electronic structures of polyatomic molecules are impossible, it is necessary to carry out significant simplifications and approximations depending on the complexity of the system investigated, the nature of the problem, and the possibilities of the computer technique. In the development of computational methods, one usually begins with the stationary Schrödinger equation for a polyatomic molecule. The fact that the mass of electrons is significantly smaller than the mass of nuclei while the forces acting on nuclei and electrons are of the same order of magnitude makes it possible to separate approximately the motions of the nuclei and electrons in the wave function (the Born–Oppenheimer approximation), while in the analysis of the photoelectron spectrum one can consider separately the positions of the bands in the spectrum (they are determined by the electronic subsystem) and the band contours (they are determined by the nuclear subsystem).[1,2]

The next approximation usually introduced involves allowance for the Coulombic interaction between electrons in the form of an effective potential acting on an isolated electron in the molecule. The set of eigenfunctions of the one-electron equation is usually referred to as molecular orbitals. The wave function of a many-electron system is represented in terms of this approximation by a linear combination of derivatives of one-electron wave functions.

A set of a finite number of basis functions, for which one usually selects functions centred on the atoms in the molecule, is used as an approximation to one-electron wave functions. The molecular orbitals are then represented by linear combinations of atomic orbitals (the LCAO-MO approximation). Only 1*s* atomic orbitals (AO) are used for hydrogen atoms, while *s*, p_x, p_y, and p_z atomic orbitals are used for carbon and other atoms.

For planar molecules, the molecular orbitals can be subdivided in accordance with the principle of their transformation on reflection in a plane. The π MO change sign on reflection in a plane, while σ MO do not. π MO are formed mainly from the p_z atomic orbitals, where the *z* axis is perpendicular to the symmetry plane of the molecule. Molecular orbitals of another type, frequently manifested in photoelectron spectra in the form of narrow bands, are the orbitals of the lone electron pairs of the heteroatoms. Such orbitals are mainly localised on heteroatoms and the removal of electrons from them does not lead to significant changes in the molecular geometry.

The molecular orbitals of the molecules are classified in accordance with the characteristics of the irreducible representations of the point group to which the equilibrium configurations of the molecule refer.[3] For example, in the ethylene molecule, which belongs to the D_{2h} symmetry group, eight types of symmetry of the molecular orbitals are distinguished: A_g, A_u, B_{1g}, B_{1u}, B_{2g}, B_{2u}, B_{3q}, and B_{3u}. In order to determine the symmetry type of a specific molecular orbital, it is essential to discover in terms of which irreducible representation the LCAO coefficients of the given molecular orbital are transformed for different symmetry operations. Here one uses standard tables of characters of irreducible representations.

The molecules of the class of alkenes can belong to the D_{2h}, C_{2h}, C_{2u}, C_2, and C_s symmetry groups. These groups contain only one-dimensional irreducible representations and in alkene molecules there is therefore no degeneracy of molecular orbitals in terms of symmetry. Doubly degenerate molecular orbitals are encountered only in cumulenes with an even number of double bonds (molecules of the type of allene $H_2C=C=CH_2$) which belong to the D_{2d} symmetry group incorporating a two-dimensional irreducible representation.

The knowledge of the LCAO coefficients for occupied molecular orbitals makes it possible to analyse the electronic populations of atoms and bonds, i.e. to discover the electronic structure of the molecule. The partial charges on atoms, calculated as the difference between the number of electrons in the isolated atom and its population in the molecule, are usually quoted. The total charges on atoms, as well as their σ and π components, are used as quantitative characteristics of the inductive and mesomeric effects of substituents in alkenes. Comparative analysis of the populations of bonds makes it possible to infer their relative strengths.

In discussing the effect of substituents in alkenes and also the reactivities of alkenes, use is frequently made of Fukui's theory of frontier orbitals (this theory has been most fully described by Hochstrasser[3] and Fukui[4]), in which only the interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecular fragments are considered. Here one analyses characteristics of frontier orbitals such as their energy, symmetry, bonding or antibonding character, and their overlap in space. For clarity, one frequently uses energy diagrams of orbital interactions for reacting systems. The approximation of frontier orbitals constitutes a simplified qualitative theory, which works successfully in alkenes, provided that the HOMO have energies appreciably different from those of the remaining molecular orbitals. In other cases, for example in HFC=C=CHF, where the HOMO and the occupied molecular orbital which follows it have the same energies,[5] it is essential to take into account several highest occupied or lowest unoccupied molecular orbitals. In those cases where the conclusions reached from the theory of frontier orbitals do not explain the experimental results, it is assumed that the given interaction is subject to charge and not orbital control.

In a qualitative description of alkenes with a complex structure, use is made in a number of instances of the model of group orbitals,[6–8] according to which the orbitals of individual fragments (methylene and methyl groups, amino-groups, etc.) can be transferred from molecule to molecule, and thus to construct the molecular orbitals of large molecules from the orbitals of these fragments. Here correlation diagrams for the orbital energies of the molecule and its fragments, referred to as Walsh diagrams, are widely used. The employment of the orbitals of fragments in discussing the effects of substituents proves to be extremely fruitful. For highly polar molecules, the predictions of this simple model may be of the usual kind.

In discussing the molecular orbital stabilisation or destabilisation effects under the influence of substituents, Dewar's theory of perturbations of molecular orbitals is sometimes invoked.[9] It makes it possible to estimate the contributions of the inductive and mesomeric effects of the substituents and also of hyperconjugation.

2. Non-empirical and semiempirical calculations within the framework of the molecular orbital method

In the theory of molecular orbitals, the orbitals are obtained as functions minimising the electronic energy of the molecule in terms of the fixed nuclei approximation. Here one solves a system of equations in which the interelectron repulsion is taken into account in the form of the interaction between the electron in the given orbital and the average field of the remaining electrons. This approach, known as the self-consistent field (SCF) method, leads to an unduly high electron repulsion energy because the electron in fact moves in the instantaneous and not the average field of the remaining electrons. The difference between the true energy of the molecule and the energy obtained in terms of the SCF approximation is called the correlation energy.

The overall estimate of the interelectron repulsion energy in the SCF method is approximately constant for each type of electron pairs and therefore has little effect in the study of processes where the number and type of electron pairs (bond electrons, lone pairs) are conserved. In processes accompanied by the separation of electron pairs (ionisation, dissociation), failure to take into account the correlation energy can lead to serious errors.

Both non-empirical (*ab initio*) and semiempirical methods are widely used in quantum-chemical calculations.

In non-empirical calculations, account is taken of all the electrons of the atoms and of all the molecular integrals encountered in the SCF equations. The accuracy of calculations of this type depends on the choice of the basis set of atomic orbitals for the construction of the molecular orbital. In calculations for alkenes, both minimal and extended sets are encountered. Minimal basis sets include only the Slater type orbitals (STO) which are necessary for the construction of the complete atomic shell. Each Slater atomic orbital is represented by the sum of several Gaussian functions (GF) the use of which simplifies the calculation of molecular integrals. The STO-3G minimal basis sets in which three Gaussian functions are used to represent each Slater atomic orbital has come to be most widely used. The minimal basis set, frequently employed for the optimisation of the molecular geometry, has the advantage that it requires relatively small amounts of computer time in the calculations. Non-empirical calculations for alkenes in terms of the STO-3G basis set have been carried out in a number of studies.[11–15] A significant deficiency of the minimal basis set consists in the absence of the possibility of altering the size of the atomic orbitals as a function of the molecular structure because the same set of atomic orbitals is used for all types of molecular orbitals. This deficiency is eliminated in the extended basis sets, such as 4-31GF, where the core orbitals are fitted by four Gaussian functions while the valence orbitals are divided into two components — the compact component comprising three Gaussian functions and the diffuse component represented by a single Gaussian function. The 4-31G basis set has been used in calculations for alkenes.[13,14,16] Further expansion of the basis set is achieved by including polarisation *d* orbitals for heavy atoms and *p* orbitals for hydrogen atoms, as is done in basis sets of type 6-31G (in calculations for haloethylenes[17]). Two-exponent function (double-zeta) basis sets have also been used in calculations for alkenes.[5,10,18–22] Other basis sets can also be encountered, for example, basis sets consisting of Hartree–Fock atomic orbitals (i.e. obtained for individual atoms by the SCF method).[22]

Non-empirical calculations by the SCF method, in which the electronic wave function of the molecule is represented by a single determinant made up of occupied molecular orbitals, do not permit allowance for the electronic correlation energy, as stated above. Therefore in a number of calculations for alkenes, the correlation correction is taken into account additionally using different methods — the configuration interaction,[10] perturbation theory,[5] and

many-particle Green's functions.[17,23] The number of such studies is relatively small, since allowance for the electronic correlation by the above methods constitutes a laborious computational procedure and requires the consumption of much computer time.

In non-empirical calculations, use is also made of the discrete-variational X_α method,[22] which, however, has not so far become quite so common in the quantum chemistry of alkenes as the molecular orbital method.

Together with non-empirical methods, semiempirical computational methods, in which account is taken only of the electrons of the valence shells of atoms, have found extensive application in calculations for alkenes. The use in these methods of the null differential overlap (NDO) approximation makes it possible to neglect all three- and four-centre two-electron integrals as well as most of the two-centre integrals encountered in SCF equations, which significantly accelerates the computational procedure. Such reduction in the accuracy of the treatment of the problem is compensated by the introduction of a series of empirical parameters for each type of atoms, the numerical values of which are calibrated against the experimental characteristics of the compounds, such as dipole moments, heats of formation, and ionisation energies.

The earliest semiempirical methods employing the NDO approximation, namely CNDO, INDO, and NDDO, were developed by Pople and co-workers.[24] In the simplest of these, the CNDO (complete neglect of differential overlap) method, all the two-electron integrals in which different atomic orbitals are encountered on a single centre are rejected. The INDO method (incomplete neglect of differential overlap) has an additional feature involving allowance for the exchange integrals between the atomic orbitals of the same atom. The most complete allowance for two-electron integrals is achieved in the NDDO method (neglect of diatomic differential overlap). There exist versions of these methods in spectroscopic parametrisation which are designed to reproduce the electronic absorption spectra (CNDO/S,[35] INDO/S [36]) or photoelectron spectra (SPINDO [25]). Subsequently Dewar proposed a modified version of the INDO method, namely MINDO/3,[26] in which one-centre repulsion integrals are not evaluated analytically (as in the initial INDO version) but are regarded as parameters. The MINDO/3 method has come to be widely used in the calculation of molecular geometries. However, it has been noted that the method greatly underestimates the repulsion of lone pairs. Subsequently, Dewar developed on the basis of the NDDO approximation the improved MNDO method,[27] which makes it possible to avoid a series of systematic errors of the MINDO/3 method and which yields more accurate values of the geometrical parameters, heats of formation, and ionisation energies of molecules. One of the important advantages of the MNDO method over MINDO/3 is that the former involves only the parameters of individual atoms, while the latter contains also the parameters of pair combinations of atoms (in recent years, Dewar also developed the AM1 (*Austun Model* 1) method,[28] which is based, like the MNDO method, on the NDDO approximation and which eliminates the inability of the MNDO and MINDO/3 methods to reproduce the properties of hydrogen bonds.

The simplest semiempirical valence approximation method, in which the interelectron repulsion is fully neglected, is the extended Hückel method (EHM),[29] which was used in earlier studies on alkenes[5,10,46] and was subsequently displaced by improved methods. A version of the NDO approximation, which takes into account only π electrons and which is applicable only in the case of systems with conjugated bonds, is used in the Pariser–Parr–Pople (PPP) method.[30]

In contrast to non-empirical methods, in semiempirical methods the problem of correlation energy has been partially solved as a result of the optimisation of parameters on the basis of experimental data. Therefore in many cases methods such as MINDO/3, MNDO, and AM1 yield more reliable results than non-empirical calculations even when extended basis sets are used in the latter. Nevertheless the MNDO/C method,[31] where correlation corrections are evaluated (and the parametrisation takes into account such corrections), is used in certain problems. When account is taken of correlation in semiempirical methods with the aid of configuration interaction, the relative values of the calculated energies in a series of similar compounds and not their absolute values are of interest.

Semiempirical methods require much less computer time than non-empirical methods and are therefore widely used in the study of alkenes having fairly complex structures.

In non-empirical calculations, the geometry is usually optimised in terms of the STO-3G basis set, whilst in semiempirical calculations different methods can be used for this purpose. The procedure for the optimisation of the geometry of alkenes is sometimes carried out by methods of molecular mechanics (see, for example, Werstiuk and Timmins[32]). The standard values of bond lengths and bond angles are also frequently used to specify the geometries of large molecules.[22,33]

3. Koopmans' theorem

In the case of molecules with closed shells, where each molecular orbital in the one-determinant wave function is occupied by two electrons, the molecular orbital theory yields a simple method for the calculation of the ionisation energy (IE). According to Koopmans' theorem,[34] the ionisation energy is equal to the energy ε_i of the corresponding occupied molecular orbital with the sign reversed ($\varepsilon_i < 0$):

$$IE_i = E_{ion} - E_{mol} = -\varepsilon_i. \quad (1)$$

Koopmans' theorem was obtained subject to the condition that the molecular ion formed on ionisation has the same geometrical parameters as the initial molecule. Eqn. (1) is therefore used to estimate the vertical ionisation energies and is inapplicable to adiabatic ionisation energies. Furthermore, in the derivation of Koopmans' theorem, it was assumed that during the removal of an electron the molecular orbitals remain unaltered (the "frozen orbitals" approximation), i.e. that the electron shell of the molecular ion is described by the same orbitals as that of the initial molecule. Thus Eqn. (1) does not take into account the effect of the reorganisation (relaxation) of the electron shell of the molecular ion, which reduces the energy of the ion by $-\Delta E_{reorg}$ ($\Delta E_{reorg} > 0$).

Since the molecular orbital method does not take into account the electronic correlation effects, in Eqn. (1) account must be taken also of the correlation energy of both the molecule and the ion, the correlation correction reducing the energy of the molecule to a greater extent than that of the ion, which contains one electron less. Thus the difference between the correlation energies of the ion and the molecule ΔE_{cor} is positive. When account is taken of both corrections (ΔE_{reorg} and ΔE_{cor}), Eqn. (1) becomes

$$IE_i = -\varepsilon_i - \Delta E_{reorg} + \Delta E_{cor}. \quad (2)$$

Evidently the corrections taken into account enter Eqn. (2) with opposite signs. In the case of the ionisation of valence electrons, ΔE_{reorg} and ΔE_{cor} are similar in absolute magnitude and therefore partly cancel out, which justifies the application of Koopmans' theorem to valence electrons. In the case of the ionisation of inner

electrons, ΔE_{reorg} can exceed ΔE_{cor} by a factor amounting to several tens and in this case the Koopmans' theorem is inapplicable.

Attempts have been made in recent years to improve the accuracy of the estimation of the ionisation energies within the framework of Koopmans' theorem. Thus an approach has been developed[37] to take into account the correlation correction to the orbital energies of the molecule based on the use of natural molecular orbitals, which are obtained on diagonalisation of the density matrix. The applicability of this approach, which the authors called the extended Koopmans' method, has been demonstrated in the calculation of the ionisation energies for a series of atoms[38] and the accuracy of the extended Koopmans' method has been analysed.[39] However, this method has not so far found applications in calculations for organic molecules.

The approximations used in the derivation of Koopmans' theorem impose fundamental limitations on its applicability. Firstly, Eqn. (1) is valid only for molecules with closed electron shells where there are no unpaired electrons. In the case of open shells, where the ground state of the molecule has a radical character (a doublet or triplet state), molecular Coulombic and exchange integrals must be included in Eqns. (1) for the orbitals forming part of the open shell.[40] In alkenes, ground states with an open shell are not encountered. Secondly, Koopmans' theorem is valid only for one-electron ionisation and is inapplicable when the ionisation process is of a many-particle kind. Thirdly, Koopmans' theorem ceases to be applicable if the excited state formed on ionisation of the molecular ion cannot be described in terms of the orbital model of the ionisation and its description requires the mixing of several configurations of identical symmetry within the framework of configuration interaction.[17] Finally, Koopmans' theorem does not hold if there is a vibronic interaction between the states of the molecular ion manifested in the photoelectron spectra, which is observed, for example, in the case of fully deuteriated ethylene,[41] tetrafluorobutatriene,[10] and certain allenes,[11, 13, 42–44] One should also note that, in the SCF X_α method, Koopmans' theorem does not hold because direct comparison of the one-electron energies obtained in this method with photoelectron spectroscopic data lacks significance.[45]

The wide scale employment of Koopmans' theorem, despite its approximate nature, can be explained by its evident advantage: within the framework of one SCF calculation for the molecule, all the ionisation energies are obtained at once. At the same time, studies may be encountered where the ionisation energies of alkenes have been calculated as differences between the total energies of the ground state of the molecule and the radical cation states, for each of which its own SCF calculation is performed.[21] The geometry of the ground state of the molecule is then retained for the calculated states of the cation. This method of calculation of ionisation energies, called the ΔSCF method, includes, in contrast to Koopmans' theorem, allowance for the reorganisation energy of the electron shell of the cation. However, it has been noted that convergence of the iterative SCF procedure cannot be achieved for all the states of the cation considered.[21]

The agreement between the ionisation energies obtained within the framework of Koopmans' theory and experimental data depends on the chosen method of calculation. The difference between IE_{exp} and IE_{theor} can vary in different calculations from a few to several tens of electron-volts. In some investigations,[6,11] the results of calculations of ionisation energies by different methods have been compared and it has been noted that the greatest differences between the calculated and experimental ionisation energies are observed when the minimal STO-3G basis set and the semiempirical CNDO/2 methods are used. Linear relations between the experimental ionisation energies and the ionisation energies calculated by the Koopmans' theorem have been considered in a number of studies:[20,47,48]

$$IE_{exp} = K \times IE_{calc} + a, \quad (3)$$

and the correlation coefficients K for these relations have been determined. In comparing the results of the calculation with experiment, some workers[17,49] shift the spectrum of the calculated IE_{calc} in such a way that the ionisation energy of the HOMO agrees with the first ionisation energy.

III. Results of quantum-chemical calculations of the electronic structures and ionisation energies of alkenes

The simplest alkenes, ethylene and its derivatives with different substituents at the double bond, will be considered initially, then the homologues of the polyene series with different numbers of double bonds, and finally cumulenes of different structure.

1. Ethylenes

The electronic structure of the ethylene molecule has been studied in fair detail both experimentally and theoretically and the results of these investigations have been included in earlier reviews and monographs.[1,2] We shall therefore refer only to a study[50] in which the most complete and accurate non-empirical calculations have been carried out for the ethylene molecule and its cation taking into account the correlation corrections and the reorganisation energy of the electron shell. The calculation was performed using an extended two-exponent basis set supplemented by polarisation d functions and Rydberg s and p functions of carbon as well as diffuse d functions centred on the midpoint of the C–C bond (altogether 52 basis functions). The correlation energy of the ground state of the molecule was taken into account using the formalism of the cluster expansion of the wave function with subdivision in terms of symmetry. The ionised states of ethylene were calculated in terms of the configuration interaction approximation taking into account doubly, triply, and quadruply excited configurations. The vertical ionisation energies, calculated as differences between the energies of the cation and the molecule, were evaluated for the experimental geometry of ethylene in the ground state. The difference between the calculated and experimental ionisation energies does not exceed 0.3 eV and the calculated intensities of the bands in the photoelectron spectrum also agree well with experimental data. The study of high-energy ionised states of ethylene revealed the presence of a large number of low-intensity satellite peaks in the range 23–33.5 eV, the majority of which correspond to ionisation processes accompanied by excitation from the σ and π bonding molecular orbitals with $1b_{3u}$ symmetry to the antibonding π molecular orbital $2b_{2g}$. The results obtained by earlier non-empirical calculations for ethylene, carried out taking into account the electronic correlation, were also compiled in the above study.[50]

Among ethylene derivatives, fluoroethylenes have been studied in greatest detail.[51–53] According to ideas established at the present time, the influence of fluorine on the electronic properties of olefins can be explained by the inductive and mesomeric effects. The inductive effect is associated with the greater electronegativity of the fluorine atoms and consists in the strong polarisation of the σ skeleton of the olefin. The mesomeric effect reduces to the repulsive

interaction of the lone pair of fluorine with the π system arising as a result of $p-\pi$ conjugation. The competing influence of these two effects is manifested, in particular, by the fact that substitution by fluorine of one or several hydrogen atoms located in the nodal plane of the π system of the alkene does not lead to a significant shift of the ionisation energies of the π orbitals but does induce an appreciable shift (up to 4 eV) of the ionisation energies of the σ orbitals. This phenomenon, which has been called the perfluoro-effect, can be explained by the fact that the stabilisation of both σ and π orbitals by the inductive effect of fluorine is compensated in the case of π orbitals by the destabilising mesomeric effect.

The results of non-empirical and semiempirical calculations for fluoroethylene published up to 1986 have been discussed critically in detail in a monograph[52] and we shall therefore confine ourselves to listing the studies of this period, concentrating attention on later investigations.

Attempts at the interpretation of the photoelectron spectra of fluoroethylenes with the aid of non-empirical methods have been undertaken.[14,18,20,54] For this purpose, calculations have been performed in terms of a two-exponent basis set for monofluoro-ethylene[18] as well as tetrafluoroethylene without[20] and with[54] optimisation of the geometry. Calculations have also been performed for monofluoroethylene using the STO-3G and 4-31G basis sets.[14] The ionisation energies of fluoroethylenes have been calculated by semiempirical SCF methods in a number of studies.[19,49,55,56] The first ionisation energies have been calculated[19] by the PPP method for mono-, di-, and tri-fluoroethylenes, while for tetrafluoroethylene calculation by the CNDO/S method has been carried out.[49] The ionisation energies of all the fluoroethylenes have been calculated in terms of the CNDO and INDO approximations[55,56] and the CNDO/2 method has also been used in a study[57] where it was noted that this procedure yields a satisfactory agreement with experiment only for the first two ionisation energies of fluoroethylenes.

The most complete non-empirical calculation for the entire series of fluoroethylenes has been performed in a study[21] where a two-component basis set was used and a complete optimisation of the molecular geometry was carried out. The vertical ionisation energies have been determined in two ways—within the framework of Koopmans' theorem and by the SCF method, i.e. as the difference between the energies of the molecule and the cation adjusted for self-consistency. In the latter case, a separate SCF calculation was performed for the ground and each of the excited states of the cation (with retention of the molecular geometry) and thus account was taken of the reorganisation energy of the electron shell. The ionisation energies obtained by means of Koopmans' theorem are found to be higher and those calculated by the SCF method are lower than the corresponding experimental values. The final ionisation energies were therefore determined as arithmetical means of the above two theoretical values, whereby a better agreement with experiment was achieved. The bands in the photoelectron spectra of fluoroethylenes were reliably assigned[21] on the basis of the calculated results as well as the data obtained in a more detailed investigation of these compounds by photoelectron spectroscopy.[57]

The first band in the photoelectron spectra of fluoroethylene arises, according to both calculated and experimental data, as a result of the removal of an electron from the HOMO, which is a π(C=C) orbital with an antibonding contribution by fluorine atoms. In monofluoroethylene, IE_2 refers to the highest occupied σ MO, which is antibonding for the C−C and C−F bonds and bonding for the C−H bonds, while IE_3 refers to the bonding σ MO localised on the C−C and C−H bonds. This assignment agrees with the conclusions drawn from the analysis of the photoelectron spectrum of this compound.[57] According to calculated data, none of the molecular orbitals in $CHF=CH_2$ has the character of a pure lone electron pair of fluorine.

In 1,1-difluoroethylene, IE_2 corresponds to the bonding σ MO localised on C−H bonds. It was concluded that the third band, whose assignment gave rise to difficulties in early studies, arises from two molecular orbitals: the bonding σ(C−C) orbital a_1 and the orbital b_2, which can be regarded as a combination of the lone pairs of fluorine atoms. On the basis of calculated data, the fourth band was assigned to the π MO a_2, which represents the antibonding combination of p_π orbitals of fluorine atoms. The region of the fifth band includes two ionisation transitions, one of which corresponds to the σ MO a_1, which is antibonding for the C−C bond and bonding for the C−F and C−H bonds, while the second corresponds to the bonding π MO with a contribution by fluorine atoms.

The *cis*- and *trans*-isomers of 1,2-difluoroethylene are characterised by a close similarity of the photoelectron spectra (the ionisation energies obtained from these spectra agree within the limits of experimental error, except for the IE_3, which differ by 0.2 eV). Only the vibrational structure of the second band exhibits characteristic differences. As postulated by Cell and Kupperman,[57] it is formed in both isomers by two molecular orbitals. However, Heaton and El-Talbi[21] concluded that, whereas this band does indeed correspond to two σ MO a_1 and b_2 in the spectrum of the *cis*-isomer, in that of the *trans*-isomer it corresponds to only one σ MO a_g. With the aid of the analysis of the bond populations, which reveals the bonding or antibonding character of these molecular orbitals, it was then possible to account for the differences in the vibrational structure of the second band in the spectra of the isomers. According to calculated data, IE_2 and IE_3 correspond in both isomers to two σ MO involving respectively antibonding contributions by the C−F and C−C bonds. IE_4 in the *cis*-isomer and IE_5 in the *trans*-isomer correspond to the antibonding π(C=C) orbital with a bonding contribution from fluorine atoms, while IE_4 in the *trans*-isomer and IE_5 in the *cis*-isomer correspond to the σ MO, which is bonding for the C−F and C−H bonds and antibonding for the C−C bond; IE_6 corresponds in both isomers to the bonding π MO. As in the case of monofluoroethylene, none of the molecular orbitals of 1,2-difluoroethylene can be rigorously assigned to the lone pair of fluorine.

In the case of trifluoroethylene, the Koopmans' theorem and the ΔSCF method lead to different orbital assignments of the bands in the photoelectron spectrum (the ionisation energies obtained by the ΔSCF method agree better with experimental data). The nature of the bands is therefore not discussed and only the sequence of the molecular orbital energies is quoted, according to which IE_2 and IE_4 correspond to two σ MO—bonding in the case of IE_4 and with an antibonding contribution due to the C−F bonds in the case of IE_2. IE_3 corresponds to an antibonding combination of the lone pairs of the fluorine atoms of the CF_2 fragment; IE_5 and IE_6 correspond to π MO with main contributions by fluorine atoms.

In the photoelectron spectrum of tetrafluoroethylene, the experimental assignment is available only for the first band,[57] while the interpretation of the nature of the remaining bands without invoking calculations is made difficult by the presence of a large number of close ionisation transitions. For $CF_2=CF_2$, Koopmans' theorem and the ΔSCF calculation yield identical orbital assignments of the ionisation energies. According to these data, IE_2 corresponds

to the σ MO a_g with an antibonding contribution by the C–F bond and IE_3 and IE_4 have been assigned respectively to the σ MO b_{3g} and b_{2u}, which can be regarded, with some approximation, as a combination of the lone pairs of the fluorine atoms; IE_5 and IE_6 are associated with π MO consisting of the p_π orbitals of fluorine.

A semiempirical calculation for fluoroethylenes (except $CF_2=CH_2$) has been carried out in a study,[58] where the MRINDO/S method was used. This is a modified version of the INDO/S approximation, in which the one-centre exchange integrals are taken into account only in the valence atomic orbitals and are rejected for the Rydberg 3*s* and 3*p* atomic orbitals. The sequence of the π and σ MO obtained is the same as in the study of Heaton and El-Talbi.[21] The difference between the calculated and experimental first ionisation energies is 0.5–1.1 eV. The remaining ionisation energies were not discussed.

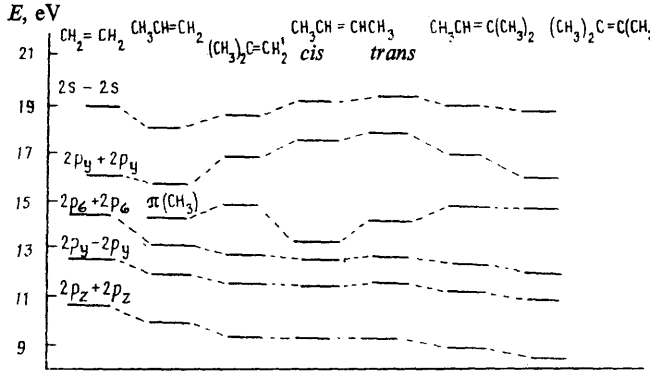


Figure 1. Correlation energy level diagram for the molecular orbitals of alkenes.

A theoretical study of the photoelectron spectra of chlorofluoroethylenes was undertaken in a study[17] where the 6-31G basis set, including the 4*s* and 4*p* atomic orbitals of Cl, the 3*s* and 3*p* atomic orbitals of C, and the 2*s* atomic orbital of H, was used in the non-empirical calculations for $CH_2=CFCl$, $CF_2=CHCl$, $CF_2=CFCl$, and $CF_2=CCl_2$. The experimental or optimised molecular geometry was employed. The ionisation energies were determined by means of Koopmans' theorem, the scale of the calculated ionisation energies being displaced for each molecule in such a way that the theoretical and experimental ionisation energies coincide. The ionisation energies thus obtained agree well with experiment. The ionisation energies of all the molecules for which calculations were made correspond to the highest occupied π MO having an antibonding contribution from the p_π atomic orbitals of chlorine atoms (the involvement of Cl in the formation of the HOMO has been confirmed by the analysis of the vibrational structure of the first band). IE_2 corresponds to the highest occupied σ MO localised on the C–C and CCl bonds, while IE_3 corresponds to a combination of the p_π atomic orbitals of chlorine atoms. An orbital assignment was given also for the remaining ionisation energies, calculated up to 22 eV. It was concluded that the ionisation of the inner electrons of haloethylenes in the range 20–75 eV cannot be described in terms of the orbital model.

The photoelectron spectra of mono-, di-, tri-, and tetra-methylethylenes have been compared in a study[7] where a quantum-chemical calculation by the method of group orbitals was carried out in order to assign the ionisation energies. The results of the calculation are presented in the form of a correlation energy level diagram for the molecular orbitals (Fig. 1), from which it is seen that the introduction of one methyl substituent into ethylene destabilises the ethylene molecular orbitals, which is associated with the transfer of electron density from the CH_3 group to these molecular orbitals.

A further increase in the number of substituting CH_3 groups intensifies this destabilising effect for the first three ionisation energies. In terms of the approximation of group orbitals, the fourth ionisation energy was assigned in all the methylethylenes to the π level of the CH_3 group. The nature of the change in the fifth and sixth ionisation energies under the influence of substitution was found to be more complex than for the first three ionisation energies.

The effect of the cyano-group on the first ionisation energy in ethylene has been examined in a study[46] where the Hückel approximation was used for the analysis of the nature of the HOMO of mono-, di-, tri-, and tetra-cyanoethylenes. The successive increase in the number of CN groups (*n*) induces an additive increase in the first ionisation energy, which is described satisfactorily by the relation

$$IE = 10.52 + 0.32n.$$

The effect of the cyano-group on IE_1 can be explained by the joint manifestation of both the inductive effect, where this group functions as an electron acceptor, and the conjugation effect, which has been shown to arise as a result of the mixing of the HOMO of ethylene with the π LUMO of the C≡N group. The mechanism of the joint effect of the methyl substituent and the cyano-group on IE_1, manifested by the fact that β-methylation of monocyanoethylene (acrylonitrile) causes a more marked decrease in IE_1 (by 0.69 eV) than α-methylation (0.55 eV), has also been explained. The point is that the orbitals of the CH_3 group interact more strongly with the π system in the β-position, since the HOMO coefficient is greater for the β-carbon atom than for the α-carbon atom. On the other hand, the effect of the introduction of the second cyano-group is greater in the α-position (0.46 eV) than in the β-position (0.23 eV), which can be explained by the smaller sensitivity of the inductive effect (compared with hyperconjugation) to the value of the HOMO coefficient at the substituted carbon atom. The destabilising effect of the acetyl group on the position of the HOMO has been demonstrated in relation to crotononitrile.

The influence of the mesomeric and inductive effects of substituents on the first ionisation energy of ethylene has been investigated[59] in relation to mono- and 1,2-di-substituted ethylenes with π-donor substituents [F, Cl, Br, I, OCH_3, SCH_3, $Si(CH_3)_2$] and monosubstituted ethylenes with π-acceptor substituents (CHO, $COCH_3$, CN, NO_2). The approximation of group (fragment) orbitals (LCFO-MO), in which the HOMO of the substituted ethylenes is represented by a linear combination of the HOMO of ethylene and either the π or *p* orbital of the substituent X, was used:

$$\Psi_{CH_2=CHX} = a_1\Psi_{CH_2=CH_2} + a_2\Psi_X.$$

The coefficients a_1 and a_2 characterise the contributions of the π MO of ethylene and the π MO of the substituent to the combined orbital. In this representation, the mesomeric effect (i.e. π conjugation) of the substituent is taken into account automatically. The inductive effect of the substituent X on the ionisation energy is

treated[59] as a result of the electrostatic interaction of the positive charge, delocalised over the π-system and arising when an electron is removed from the molecule, with the dipole of the C–X fragment. The vertical ionisation energy of the compound HX was used as the parameter characterising the inductive effect of the substituent X. The ionisation energies calculated in this way for mono- and di-substituted ethylenes differ from the experimental values by not more than 0.2 eV. It was concluded that the resonance effect of the nitro-group may be neglected because of the considerable difference between the HOMO and LUMO energies of this group and the HOMO energy of ethylene.

The influence of the σ–π conjugation, the inductive effect, and the $p_\pi - d_\pi$ interaction on the first ionisation energy in monosubstituted ethylenes with the organosilicon substituents SiH_3, $SiH(CH_3)_2$, $Si(CH_3)_3$, CH_2SiH_3, and $CH_2Si(CH_3)_3$ has been studied.[60] The ionisation energies were calculated in accordance with the Koopmans' theorem by the semiempirical CNDO/2 method using *sp* and *spd* basis sets. The contribution of the σ–π conjugation ($\delta IE_{\sigma,\pi}$) to the change in the ionisation energy of ethylene under the influence of the substituent (ΔEI) was estimated on the basis of the perturbation theory and the contribution of the $p_\pi - d_\pi$ interaction ($\delta IE_{p,d}$) was found from the difference between the HOMO energies of the substituted molecule calculated in terms of the *spd* and *sp* basis sets (in the calculation using the *sp* basis set, the influence of the *d* orbitals is not taken into account). The contribution of the inductive effect was determined from the residual, having subtracted $\delta IE_{\sigma,\pi}$ and $\delta IE_{p,d}$ from ΔIE. It was concluded that in the majority of ethylene derivatives σ–π conjugation predominates over other effects. The extent of the $p_\pi - d_\pi$ interaction diminishes in the sequence $SiH_3 > SiH(CH_3)_2 > Si(CH_3)_3$, i.e. with increase in the number of CH_3 groups at the silicon atom. The extent of the σ–π conjugation diminishes in the sequence $C(CH_3)_3 > Si(CH_3)_2 > CH_3 > SiH_3$, while the inductive effect diminishes in the sequence $Si(CH_3)_3 > SiH_3 > CH_3 > C(CH_3)_3$, which agrees with the concept of the electronegativity of the substituents.

A number of theoretical studies have been devoted to ethylenes with cyclic substituents.[33,61–64] The influence of the substituents F, Cl, CH_3, and OCH_3 in the *meta*- and *ortho*-positions on the ionisation energies of styrene has been studied[61] with the aid of photoelectron spectra and calculations by the CNDO/2 method. The calculations were performed using the standard bond lengths and bond angles. The photoelectron spectra of styrene and its derivatives exhibit in the range 8–11 eV three well resolved bands, which correspond, according to the calculated data, to the π MO arising as a result of the interaction of one of the two degenerate benzene molecular orbitals of the e_{1g} type and the π MO of the vinyl group (π_1 and π_3 MO) and to the second degenerate molecular orbital of benzene e_{1g}, which does not interact with the vinyl group (π_2 MO). The influence of the inductive effect of the substituents has been investigated on the basis of the change in IE_2 corresponding to the ionisation of π_2 MO, which is not involved in conjugation with the π-system of the vinyl group; the maximum inductive effect is manifested by the F atom; IE_1 and IE_3 are acted upon by both the inductive and resonance effects. The difference $IE_3 - IE_1$ varies about 1.93 eV, which indicates the similarity of the effects of substituents on the π_1 and π_3 MO. The resonance effect of substituents was estimated from the difference between IE_1 and IE_2. For *para*-substituted styrenes, this difference is greater than for the *meta*-substituted derivatives; the greatest resonance effect is observed for the OCH_3 substituent.

The effect of Cl, NH_2, and NO_2 on the ionisation energies of *trans*-2,2-disubstituted stilbenes has been studied.[62] Derivatives containing identical substituents in the *ortho*-positions of the phenyl fragment were examined. The presence of the NH_2 group leads to an appreciable decrease in all the ionisation energies of stilbene (by 1.0 eV for IE_1), while the presence of the NO_2 group entails an appreciable increase in all the ionisation energies (by 0.9 eV for IE_1), which can be explained by the strong inductive effect of these substituents. The presence of Cl leads to some decrease in the ionisation energies of stilbene (by 0.2 eV for IE_1). The assignment of the photoelectron spectra based on calculations of ionisation energies by the Hückel method made it possible, in particular, to identify bands referring to the ionisation of the lone pairs of the chlorine atoms in 2,2-dichlorostilbene (11.19 and 11.53 eV) and in 2-amino-2-chlorostilbene (11.03 and 11.52 eV).

The INDO/S semiempirical method has been used[33] to interpret the photoelectron spectra of stilbene, α-cyanostilbene, 2-styryl-thiophene, and α-cyanostyrylthiophene. An idealised geometry was specified for the phenyl fragment and the experimental geometry was used for the thienyl fragment. Calculation showed that the first five ionisation energies of these compounds are associated with molecular orbitals consisting of a combination of the π orbital $1e_{1g}$ of benzene, the π orbitals $1a_2$ and $2b_1$ of thiophene, and the π MO of ethylene with a perturbing effect of the cyano-group. The doubly degenerate π MO of the C≡N group have energies which are too low and they do not enter into this combination, so that the influence of the cyano-group reduces to the inductive and steric effects. The first band in the photoelectron spectra of the cyano-derivatives and 2-styrylthiophene is generated on ionisation of the delocalised π MO, which is an antibonding combination of the b_1 MO of benzene and π MO of ethylene. The second band corresponds to three molecular orbitals localised on benzene rings. The third band corresponds to the π MO of the ethylene bond. The calculation reproduces satisfactorily the difference between IE_1 and IE_2.

3-Methyl-3-vinylcyclopropene (I) as well as its α-methyl and β-methyl derivatives [compounds (II) and (III)] have been investigated[63] with the aid of the semiempirical AM1 method. The calculation was performed with complete optimisation of the geometrical parameters for different values of the dihedral angle θ between the planes of the ethylene and cyclopropene fragments (θ = 0°, 60°, 90°, 120°, and 128°). One minimum was observed on the potential curve as a function of θ for compound (III) and two minima were observed for compounds (I) and (II). According to the calculated data, the ionisation energy of compound (I) corresponds to the ionisation of the cyclopropene π(C=C) MO whereas the ionisation energies of compounds (II) and (III) correspond to the ionisation of the ethylene bond. The presence of the methyl substituent at the ethylene bond lowers IE_1, the effect of one CH_3 group introduced in the α-position proving to be stronger than the effect on IE_1 of two CH_3 groups introduced in the β-position.

2. Polyenes

Numerous theoretical studies have been devoted to the electronic structure and the photoelectron spectra of polyenes. Some of them dealt with individual compounds—butadiene,[65,66] hexatriene,[66] and octatetraene,[12] whilst others were concerned with the general characteristics of the polyene series.[22,67] The influence of substituents has been traced in relation to monomethyl- and polymethylbutadienes[8,32,67] and decapentaene with different substituents at the C(5) and C(6) atoms.[68]

According to the results of a non-empirical calculation in terms of a grouped two-exponent basis set, the first band in the photoelectron spectrum of butadiene corresponds to the π HOMO b_g, whilst the second band corresponds to the second occupied π MO a_u.[66] The same result has been obtained in terms of a two exponent basis set supplemented by two diffuse *p* functions of carbon.[65] In both calculations, the first two ionisation energies agree with the experimental values to within 0.05–0.2 eV. The same assignment of the bands is given by the semiempirical SPINDO method.[67] The first three ionisation energies of hexatriene have also been calculated[66] (differing from the experimental values by −0.1 eV) and it was concluded that the first three bands in the photoelectron spectrum of this compound refer to π-type molecular orbitals, but, according to the calculation by the SPINDO method, the third band refers to σ-type molecular orbitals.[67] A comparative analysis of the orbital structures of the *cis*- and *trans*-isomers of hexatriene has been carried out (using the SPINDO method). The geometry of the *trans*-isomer (with C_{2h} symmetry) was specified on the basis of electron diffraction data, while in the *cis*-isomer (C_{2v}) the same bond lengths were used as in the *trans*-isomer. A satisfactory agreement with experiment was obtained for all the nine calculated ionisation energies. In the *cis–trans* transition, the energies of all three occupied π MO hardly change (like the experimental ionisation energies). A different picture is observed for this transition in the three highest occupied σ MO $9b_2$, $10a_1$, and $9a_1$, the energies of two of which ($10a_1$ and $9a_1$) increase, whilst that of the third ($9b_2$) falls, which leads to an appreciable narrowing of the energy range in which these orbitals are located in the *trans*-isomer. This result of the calculation made it possible to explain the differences in the shape of the photoelectron spectra of the hexatriene isomers in the region of 12 eV, where a broad gap is observed between the bands in the case of the *cis*-isomer (the σ MO lie within a wide range), being absent from the spectrum of the *trans*-isomer (the σ MO lie within a narrow range). It was concluded that the shift of the energies of the σ MO in hexatriene isomers is caused by the interaction through space between the C–H and C–C σ-bonds, which stabilises the orbitals with the a_1 symmetry and destabilises b_2 orbitals in the *cis*-isomer. Calculations by the non-empirical method using the minimal STO-3G basis set and by the SPINDO method led to the conclusion that the first three ionisation energies in octatetraene refer to π-type molecular orbitals.[12]

Calculations have been carried out for the polyenes $C_{2n}H_{2n+2}$ with $n = 1-6$ by the discrete-variational X_α method using a two-exponent basis set and a basis set comprising Hartree–Fock atomic orbitals.[22] The experimental geometry was used for the first members of the polyene series ($n = 1-3$), while for the remaining molecules the idealised geometry was employed. The first ionisation energies of butadiene, hexatriene, and octatriene, obtained in terms of a two-exponent basis set, differ from the experimental values by not more than 0.2 eV (photoelectron spectroscopic data are lacking for $C_{10}H_{12}$ and $C_{12}H_{14}$). The deviations of the remaining ionisation energies from the experimental values are on average ~0.5 eV for the two-exponent basis set and ~1 eV for the Hartree–Fock basis set. According to the calculations, the highest σ-type level (a_u or b_g) in all polyenes is close to the π-type level (a_u or b_u). It was suggested that for long polyene chains one may expect either a slight overlap of the σ and π zones in the photoelectron spectrum or these zones can be separated by a small gap amounting to several tens of electron-volts.[22,69]

For the theoretical study of the effect of methyl substituents on the π bands in the photoelectron spectra of polyenes, Beez et al.[67] used a model in which the π MO of the polyene is represented by a linear combination of the bonding orbitals (LCBO) of individual π-bonds (it was shown that the mixing of the bonding and antibonding orbitals of π-bonds leads to incorrect results in the calculation of ionisation energy), while the effect of the methyl substituent on the π-system of the polyene is considered as an inductive and hyperconjugation perturbation within the framework of the Hückel method. In this procedure, the CH_3 group is described by two degenerate pseudo-π orbitals made up of the σ orbitals of the C–H bonds. This simple and clear model makes it possible to reproduce the π-orbital ionisation energies with a satisfactory accuracy (to within not more than 0.1 eV for hexatriene, for example) and leads naturally to the sums rule, according to which the sum of the changes in all the π-orbital ionisation energies ($\sum_i \delta IE_i^\pi$) in the polyene under the influence of the CH_3 group is constant for the entire polyene series and is equal to δIE for ethylene (0.78 eV). The validity of the sum rule has been demonstrated in relation to monomethyl-substituted butadiene and hexatriene. Comparison of the experimental ionisation energies and the ionisation energies calculated within the framework of the LCBO model for mono-, di-, and tetra-methylbutadienes showed that the sums rule holds, provided that the substituting CH_3 groups are attached to different double bonds, i.e. the additivity of the effects of the CH_3 groups on the π ionisation energies holds in this case. On the other hand, if the substitution takes place at the same double bond, then the specific quantity $\sum_i \delta IE_i^\pi$, recalculated per CH_3 group, diminishes with increase in the degree of substitution—for example, we have the series $CH_2{=}CHCH_3$ (0.78 eV), $CH_3CH{=}CHCH_3$ (0.69 eV), $(CH_3)_2C{=}CH_2$ (0.64 eV), $(CH_3)_2C{=}CHCH_3$ (0.61 eV), and $(CH_3)_2C{=}C(CH_3)_2$ (0.55 eV). It has been shown that the terminal methyl substituents in the polyene do not alter the gap between IE_1 and IE_2. Substitution by CH_3 groups in the central positions leads to the mutual approach of IE_1 and IE_2, which can be explained, as demonstrated in relation to butadiene, by the interaction through space between the pseudo-π orbitals of the CH_3 group in the 2- or 3-position with the π orbital of the vicinal (unsubstituted) double bond. Allowance for this interaction in the LCBO model shows that it stabilises the HOMO in the polyene and destabilises the next occupied π MO. The same conclusion was reached in a study[8] where the investigation of the effect of methyl substituents was extended to non-planar cases when there is rotation about a single C–C bond in the polyene. Tetramethylbutadiene, containing one methyl group at each carbon atom, was investigated. This structure exists in the form of three isomers, namely (*E*, *E*), (*E*, *Z*), and (*Z*, *Z*), and can be regarded as two identical fragments interacting via the C(2)–C(3) single bond and rotated relative to this bond by an angle θ. Then, in terms of the first approximation of the perturbation theory, the gap $\Delta IE = IE_2 - IE_1$ depends on θ in accordance with the formula

$$\Delta IE = \Delta IE_0 - \cos\theta, \qquad (4)$$

where ΔIE_0 is the value of ΔIE for the planar case with θ = 0. This dependence of ΔIE on θ has been confirmed by a non-empirical calculation in terms of the minimal STO-3GF basis set in relation to unsubstituted butadiene. Using the ionisation energies found from the photoelectron spectra and Eqn. (4), the authors[8] obtained estimates of θ for the isomers; 0° ± 30° for (*E*, *E*), 80° ± 15° for (*E*, *Z*), and 80° ± 105° for (*Z*, *Z*). It has been shown[32] by calculations using the molecular mechanics method and the

semiempirical AM_1 method that the (*Z*)-conformer of the 1,3-disubstituted butadiene (2-methylpenta-1,3-diene) exists preferentially in the twisted form, while the (*E*)-conformer exists in a planar form. This made it possible to explain the differences between the photoelectron spectra of the (*Z*)- and (*E*)-conformers. It was noted that the AM_1 method overestimates the steric interaction between the CH_3 groups in the 1- and 3-positions and underestimates the stabilisation of the π-system due to the resonance effect.

The influence of electron-donating and electron-accepting substituents on the ionisation energies of polyenes has been studied theoretically[68] in relation to 5,6-disubstituted decapentaenes ($C_{10}H_{10}X_2$). The calculations were performed by the discrete-variational X_α method using a basis set of Hartree–Fock atomic orbitals. The idealised geometry was used for the hydrocarbon skeleton of the molecule. The geometrical parameters for the substituents and the C–X bond were selected on the basis of experimental data or the results of non-empirical calculations. In the unsubstituted polyene $C_{10}H_{12}$, the energies of the valence σ levels lie below those of the set of π levels. The introduction of lithium as a strong σ-donor does not destabilise the σ levels, which fall as a result into the region of the π levels. As a weaker σ-donor, BeH does not lead to the overlap of the σ and π sets of molecular orbitals and the energy IE_1 in the BeH-polyene is almost identical with IE_1 in $C_{10}H_{12}$. The introduction of F as a σ-acceptor lowers IE_1 by only 0.1 eV. The nature of the interaction of the NH_2 group, which is a π-donor, with the π-system of the polyene depends on its rotation relative to the plane of the polyene: the $2p_\pi$ atomic orbital of nitrogen is involved in conjugation with the π-system of $C_{10}H_{12}$ when the NH_2 group is in the plane of the polyene and interacts with the σ-system when the plane of the NH_2 group is perpendicular to that of the polyene. In the former case, the interaction indicated leads, as shown by the calculation, to a decrease in IE_1 by 1.2 eV, while in the latter IE_1 hardly changes. When BH_2, which acts as a π-acceptor, is introduced, IE_1 scarcely changes, provided that BH_2 is located in the plane of the polyene, and diminishes by 0.4 eV if the planes of BH_2 and the polyene are mutually perpendicular.

3. Cumulenes

The simplest representation of the cumulene series is allene $CH_2=C=CH_2$ where there are two mutually perpendicular π-systems between which there is no conjugation; the CH_2 groups are also located in mutually perpendicular planes. The allene molecule belongs to the D_{2d} symmetry group, which has a two-dimensional irreducible representation and gives rise to doubly degenerate molecular orbitals of the *e* type. In particular, in conformity with non-empirical[23,70] and semiempirical[15] calculations, the π HOMO 1*e* and the σ MO 2*e* which follows it are doubly degenerate in allene. The HOMO splits into two molecular orbitals, each of which is localised in one of the $CH_2=C$ fragments and represents an antibonding combination of the π orbital of the C=C bond with the pseudo-π orbital of the CH_2 group.[16] All the other homologues of the cumulene series with an even number of double bonds, for example, pentatetraene $CH_2=C=C=C=CH_2$, the π HOMO of which is likewise doubly degenerate, also belong to the D_{2d} symmetry group.[15] Analysis of the first band in the photoelectron spectra shows that the degeneracy is removed in the allene[23] and pentatetraene[15] radical-cations as a result of geometrical distortions arising in the ionisation of the molecule and reducing its symmetry (the Jahn–Teller effect). For example, the removal of the degeneracy of the HOMO in allene leads to the splitting of the first band in the photoelectron spectrum into two peaks with ionisation energies of 10.0 and 10.6 eV.[23] A simple molecular-orbital model shows that such splitting is a result of a twisting deformation which reduces the symmetry of the allene radical-cation from D_{2d} to D_2.[72] Cumulenes with an odd number of double bonds belong to the D_{2h} symmetry group and contain no molecular orbitals degenerate as regards symmetry. However, in this case ionisation may entail the appearance of a distortion in the molecule, which reduces its symmetry, as indicated, for example, by data obtained as a result of the optimisation of the geometry of the butatriene $CH_2=C=C=CH_2$ radical-cations in terms of the STO-3GF basis set.[75]

When the π-electronic structure of cumulenes is considered, the isolated ethylene-like π orbitals (2*e* in allene and $2b_{3u}$ in butatriene) and butadiene-like four-centre π MO, which are combinations of two ethylene orbitals—bonding ($1b_{2u}$ in butatriene and 2*e* in pentatetraene) and antibonding ($1b_{3g}$ in butatriene and 3*e* in pentatetraene)—are distinguished.[15] In the ethylene–allene–butadiene series, a gradual destabilisation of the isolated π MO (and a decrease in the corresponding ionisation energies) has been observed, which can be accounted for by the destabilising effect of the CH_2 group, which is in the nature of hyperconjugation.[15] This effect is manifested most strongly in butatriene, where the CH_2 groups are located in one plane and both interact with the π MO of the central C=C bond. On passing from butatriene to pentatetraene, where the isolated π MO are no longer encountered, the destabilising effect of the pseudo-π orbitals of the CH_2 group is weakened. In order to interpret the photoelectron spectra of allene, both non-empirical calculations, using the minimal STO-3GF basis set,[13,15] the 4-31GF basis set,[16] and a two-exponent basis set,[5,23] and semiempirical calculations by the SPINDO method,[15] have been resorted to. The most accurate calculation for the allene molecule using the experimental geometry, carried out in terms of a grouped two-exponent basis set with inclusion of polarisation *d* functions of carbon and taking into account the correlation corrections by the method of Green's functions, shows that the first band in the photoelectron spectrum (exhibiting Jahn–Teller splitting) corresponds to the π HOMO 1*e*. The second band (14–16 eV) is generated by the ionisation transition from two σ MO—2*e* and $2b_2$, while the third band corresponds to the σ MO $2a_1$.[23] A similar band assignment was obtained from calculations by the SPINDO method.[15]

Quantum-chemical calculations have shown[10,15,23,73] that the π-system of butatriene consists of two butadiene-like MO $1b_{2u}$ and $1b_{2g}$, the nodal plane of which coincides with the molecular plane, and the MO $2b_{3u}$ located on the central C=C bond in the molecular plane. When an attempt is made to interpret the photoelectron spectrum of butadiene with the aid of the ionisation energies obtained on the basis of Koopmans' theorem even in a very effective non-empirical calculation (two-exponent basis set with polarisation *d* functions as well as allowance for correlation corrections by the method of Green's functions),[23] a difficulty arises. It is associated with the fact that in the range 9–10 eV, where three bands are observed, there are only two ionisation processes, corresponding to the two highest π MO b_{3g} and b_{3u}. It has therefore been postulated that the middle band, with a maximum at 9.6 eV, is a satellite band. In order to elucidate the nature of the satellite band, the vibronic problem has been solved for butatriene with the aid of the formalism of Green's functions.[73] It was established that the band arises as a result of the vibronic interaction between the ground $^2B_{3g}$ state and the first electronically excited $^2B_{3u}$ state of the radical-cation, which are separated by a small gap (~0.7 eV). The intensities, calculated

taking into account the vibronic interaction, made it possible to reproduce closely the form of the first three bands in the photoelectron spectrum of butatriene. For an accurate prediction of the position of the above satellite band, the multiconfiguration SCF method has been used.[10] The geometry of the butatriene molecule was optimised in terms of the STO-3G basis set and the calculation for the molecule and the radical-cation was performed in terms of a grouped exponent basis set with inclusion of all the singly and doubly excited configurations (the excitations were considered only for π MO). It was concluded that non-empirical calculations of different types (SCF) in terms of the STO-3G and 4-31G basis sets, the method of Green's functions, and allowance for configuration interaction lead to the same conclusion, namely that the first three bands in the photoelectron spectrum of butatriene (not counting the satellite band) correspond to the ionisation of the highest π MO—b_{3g}, b_{3u}, and b_{2u} respectively.

As examples of two accumulated π-systems linked by a single bond,[6] 1,2,4,5-hexatetraene $CH_2=C=CH-CH=C=CH_2$ (I) (C_{2h} symmetry) and 1,3,4-pentatriene $CH_2=CH-CH=C=CH_2$ (II) have been investigated. Calculation of the ionisation energies in accordance with Koopmans' theorem with the aid of various semiempirical methods—EHM, CNDO/2, MINDO/3, and SPINDO—leads to the same sequence of the highest occupied π MO, namely $\pi_z - \pi'_z$ (b_g), $\pi_x - \pi'_x$ (a_g), $\pi_x + \pi'_x$ (b_u), and $\pi_z + \pi'_z$ (a_u), which are involved in the generation of the first four bands in the photoelectron spectrum of compound (I). It follows from the experimental ionisation energies that the energy splitting of the bonding and antibonding combinations for the $\pi_z - \pi'_z$ and $\pi_z + \pi'_z$ pair (π_z and π'_z are the orbitals of the allenyl fragments whose nodal plane coincides with the molecular plane) is much greater than for the $\pi_x - \pi'_x$ and $\pi_x + \pi'_x$ pair (π_x and π'_x are the orbitals of the allenyl fragments located in the molecular plane). It was noted that the best agreement between the calculated and experimental ionisation energies is afforded by the SPINDO method. In the photoelectron spectrum of compound (II), the first three bands correspond to the ionisation of the three highest occupied molecular orbitals. The study of the photoelectron spectrum and calculation of the ionisation energies of the 3-methyl derivative of compound (I) showed that the introduction of the CH_3 group has only a slight effect on the π_x type orbitals but causes an appreciable shift of the π_z-type orbitals. The effect of various substituents on the electronic structures and ionisation energies of cumulenes has been studied in a number of investigations.[5,10,11,16,57,74,75] Mono-, di-, tri-, and tetrafluoroallenes have been investigated in a study,[5] where the molecular geometry was optimised in terms of a biexponential basis set with polarisation *d* functions of carbon, which yields a correct description of the C—F bond; the ionisation energies were calculated in terms of the same basis set supplemented by the *d* functions of fluorine and the *p* functions of hydrogen, taking into account the correlation corrections by the method of perturbation theory. The high quality of the calculation is confirmed by the fact that the calculated dipole moments of the molecules reproduce satisfactorily the experimental values (the differences are on average 15%). According to the calculated data, as carbon atoms are substituted by fluorine, the negative charge on the central carbon atom increases, varying from +0.12 in allene to −0.43 in perfluoroallene; this effect is attributed to the π-donor capacity of fluorine. The calculation predicts a gradual increase in the first ionisation energy with increase in the number of substituting fluorine atoms, which agrees with photoelectron spectroscopic data (available only for some fluoroallenes). A large difference between the values of IE_1 (0.5 eV) of the difluoroallene isomers $H_2C=C=CF_2$ and $HFC=C=CHF$ has been noted. The random degeneracy in the latter compound, where the HOMO and the molecular orbital which follows it have the same energies, is striking.

The results of the non-empirical calculation in terms of the 4-31G basis set for 1,1-difluoroallene and tetrafluoroallene have been published.[16] Calculation showed that IE_1 for 1,1-difluoroallene corresponds to the π[C(1)=C(2)] orbital with an antibonding contribution by the electron pair of fluorine, while IE_2 corresponds to the π[C(2)=C(3)] orbital with a hyperconjugation contribution by the σ orbitals of the C—F bonds. The fluorine atom has only a weak effect on the energy of the π[C(1)=C(2)] HOMO, since in this case the stabilising inductive effect of fluorine is compensated by the destabilising resonance effect and lowers markedly the energy of the π[C(2)=C(3)] MO, where there is also a stabilising influence of the inductive effect and of the effect of the hyperconjugation of the CF_2 group.

The non-empirical calculation for perfluorobutatriene, carried out using a two-exponent basis set and the standard geometry of the molecule, may serve as an example of the study of the perfluoro-effect in cumulenes.[10] According to the calculated data, the first three bands in the photoelectron spectrum of this compound correspond to the ionisation of the highest occupied π MO b_{3g}, b_{3u}, and b_{2u}, while the fourth band (whose position and shape are similar to those of the corresponding band in the spectrum of tetrafluoroallene) is due to a linear combination of the unshared pairs of the fluorine atoms. All the fluorine atoms are located in the nodal plane of the HOMO b_{3g} and the orbital b_{2u}, corresponding to IE_3, and for this reason they give rise to only a slight change in the energies of these molecular orbitals compared with unsubstituted butatriene: IE_1 does not change at all, while IE_3 changes by 0.4 eV. A strong stabilising effect of fluorine is observed in the case of the molecular orbital b_{3u}, which lies in the same plane as the fluorine atoms: IE_2, corresponding to this molecular orbital, shifts by 2.6 eV on perfluorination.

Monosubstituted allenes have been investigated by Sinegovskaya et al.[74] (with substituents OAlk, where Alk = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, and t-C_4H_9) and by Kamphuis et al.[11] with the substituents t-C_4H_9, OCH_3, OC_2H_5, OC_4H_9-t, $N(CH_3)_2$, SCH_3, SC_2H_5, and SC_4H_9-t). Sinegovskaya et al.[74] calculated the ionisation energy of alkyl allenyl ethers by the MNDO method with complete optimisation of the geometry. IE_1 and IE_3 for allenyl methyl ether correspond to a linear combination of the π[C(1)=C(2)] orbitals with the *p* atomic orbitals of ether oxygen (in the case of IE_1, the contribution of the *p* atomic orbitals of oxygen is antibonding, while in the case of IE_3 it is bonding), IE_2 corresponds to the unperturbed π[C(2)=C(3)] orbital, and IE_4 corresponds to the almost pure *n* orbital of oxygen (n_O). It was shown that this sequence of the four highest occupied molecular orbitals in allenyl methyl ether can be readily obtained from the consideration of the Walsh correlation diagram constructed from the two highest molecular orbitals of allene and of the $(CH_3)_2O$ molecule. Successive substitution of CH_3 by C_2H_5, n-C_3H_7, and iso-C_3H_7 in allenyl methyl ether leads to a shift of IE_1 and IE_2 by 0.1—0.3 eV and of IE_3 and IE_4 by 0.3—0.8 eV towards lower values. Calculation shows that, with increase in chain length and in the degree of branching of the alkyl substituent, the efficiency of the mixing of the n_O orbital and the σ_{CC} orbitals of the substituent increases.

It has been established[11] that the effect of bulky electron-donating substituents containing alkyl groups on the photoelectron spectra of allenes is determined not only by electronic effects (inductive,

conjugation, and hyperconjugation effects) but also by conformational effects. Calculations by the MINDO/3 method with complete optimisation of the geometry showed that the radical-cations in the ground state can have a geometry differing markedly from that of the corresponding molecules. For example, in allenes with the $N(CH_3)_2$ and t-C_4H_9 substituents, the C=C=C fragment in the cations has a bent structure. For the radical-cations where the substituting OAlk or SAlk group includes CH_3 and C_2H_5, the *S-cis*-form is preferred, while in the case of OC_4H_9-t and SC_4H_9-t the *S-trans*-form is preferred. The non-planar *gauche*-form, in which there is strong $\sigma-\pi$ mixing, is preferred for the $N(CH_3)_2$ group and the effect of the substituents can no longer be interpreted in terms of separate π and σ interactions.

The influence of the CF_3 group on the ionisation energies in cumulated systems was investigated separately in a study[75] where calculations were performed by the MINDO/3 method for tetrasubstituted allenes with the CF_3, OCH_3, and OC_2H_5 substituents. It was shown that the inductive effect predominates when the CF_3 group is introduced. It is additive and stabilises the HOMO to the extent of 0.5 eV per CF_3 group.

The effect of methylation on the photoelectron spectra of more complex cumulenes was investigated in relation to mono- and dimethyl-derivatives of penta-1,2,4-triene (vinylallene).[47] The CNDO/S method used for the calculation reproduced satisfactorily the dependence of the ionisation energies on the position of the CH_3 group. The methyl group at the terminal atom of the allene fragment affects appreciably the energy of the orbital localised on the terminal allene bond and corresponding to IE_2. The methyl group bound to the central carbon atoms C(3) and C(4) interacts through space with the orbitals of the vicinal C=C bonds. This interaction stabilises the HOMO and destabilises the molecular orbital corresponding to IE_3.

IV. The reactivities of alkenes

In the study of the reactivities of alkenes in relation to electrophiles, the first ionisation energy may serve as a measure of the electron-donating capacity. The electron-accepting capacity of the alkene in reactions with nucleophiles can be characterised by the electron affinity (EA). The correlation between the rate of reaction and the ionisation energy or the electron affinity, observed in series of related alkenes, makes it possible to predict fairly accurately the reactivity on the basis of the ionisation energies or electron affinities obtained experimentally or from quantum-chemical calculations. The quantum-chemical calculations, performed within the framework of the molecular orbitals model, not only yield the numerical values of the ionisation energy and the electron affinity, determined respectively as the HOMO and LUMO energies, but also make it possible to determine the nature of the location of these frontier orbitals on individual atoms and bonds, which makes it possible in its turn to explain the regioselectivity of the electrophilic or nucleophilic reaction. The calculation also enables one to model the intermediate state generated by the reacting species in the rate-limiting stage of the reaction.

The study of the relation between the first ionisation energies and the relative rates of electrophilic addition enabled Nelson et al.[48] to separate the electronic and steric factors in alkene bromination, hydroxymercuration, and hydroboration reactions. Olefins with sterically unlike electron-donating and electron-accepting groups Alk, OAlk, SCH_3, SC_6H_5, $Si(CH_3)_3$, Cl, Br, I, CN, and OAc, which were present both at the double bond and in the alkyl chain of the olefin (altogether 21 compounds) were investigated. In the bromination reaction, the dependence of $\lg k_{rel}$ (k_{rel} is the relative reaction rate constant) on the ionisation energy is described by one linear relation (with a correlation coefficient of 0.96), embracing the compounds of the entire series, the rate of reaction being independent of the degree of substitution at the double bond. On the other hand, in the case of hydroxymercuration and hydroboration it is not possible to obtain a single linear relation with the ionisation energy: for each reaction, there are two groups of alkenes, each of which is described by its own linear relation. One group includes alkenes substituted only at one of the atoms involved in the double bond, whilst the other comprises alkenes with substituents at both atoms of this bond, i.e. each group combines sterically similar compounds, the alkenes with smaller steric hindrance reacting faster. Thus it has been possible to show that the rate of bromination of the alkene is independent of the steric factor and is determined solely by the electronic effect of the substituent, i.e. by the ionisation energy of the alkene, while in hydroxymercuration and hydroboration the steric factors predominate over the electronic factors. However, satisfactory linear correlations have been obtained between the ionisation energies and relative reactivities for both experimental ionisation energies and ionisation energies calculated by the MNDO method on the basis of Koopmans' theorem, which justifies the prediction of the reactivities of alkenes by a computational procedure. The overall rule is that the rate of electrophilic addition falls with increase in ionisation energy. Analysis of the nature of the HOMO on the basis of data obtained by the MNDO calculation makes it possible to explain the regioselectivity of the hydroxymercuration and hydroboration reactions, where Hg and B atoms add preferentially to the unsubstituted carbon atom involved in the double bond. This has been demonstrated for the compounds $H_2C=CHCH_2X$ with different substituents X. In the hydroboration reaction of these compounds, the addition of boron to the unsubstituted carbon atom of the double bond is more preferred the greater the coefficient of the HOMO at this atom compared with the substituted carbon atom. The MNDO calculation also made it possible to establish that the transition states in the rate-limiting stages of the hydroxymercuration and hydroboration reactions are similar and both differ from the transition state in the bromination reaction. The transition state was modelled by a three-centre intermediate, for which the calculation was performed with complete optimisation of the geometry.

The relation between the electron affinities and reactivities of alkenes with an electron-deficient double bond, which function as electrophiles in the Diels–Alder cycloaddition reaction as well as other reactions involving the addition of nucleophilic species, has been traced.[46] The electron affinity was regarded as a measure of the electrophilic reactivity of the alkene. Mono-, di-, tri-, and tetracyanoethylenes as well as ethylenes containing, together with the cyano-group, also another electron-accepting substituent (CF_3, OAc, CO_2, CH_3, and certain others) have been investigated. Since the experimental electron affinities are available only for a small number of the test compounds, those of alkenes were estimated from the known ionisation energies. The method used for such estimations is based on the fact that, according to data calculated by the CNDO/2 method, the HOMO and LUMO energies (characterising the ionisation energy and the electron affinity respectively) in cyanoethylenes are linearly related: an increase in the HOMO energy under the influence of the cyano-groups is accompanied by a

proportional decrease in the LUMO energy. The following linear relation then holds:

$$EA = 3.3IE - 36 \text{ (eV)},$$

from which the electron affinities were in fact determined. The reliability of the electron affinities obtained is confirmed by their correlations with the polarographic potentials for the reduction of cyanoalkenes. For the cycloaddition reaction, where the alkene and the nucleophile (for example, NH_2 of OH) form only one bond with the alkene in the intermediate, the electron affinity (or the LUMO energy) is the controlling factor only for a nucleophile with a low ionisation energy ($\leqslant 8$ eV). The reactivity of the cyanoalkene in relation to a nucleophile with a high ionisation energy ($\geqslant 12$ eV) is controlled by the maximum orbital coefficient of the LUMO, which always corresponds to the least substituted carbon atom involved in the double bond and which in fact proves to be most susceptible to nucleophilic attack. By analysing the nature of the interactions between the frontier orbitals of the alkene and the nucleophile (interactions of the type alkene HOMO–nucleophile LUMO), the authors were able to differentiate pairs of frontier orbitals which determine both the relative rate and the regioselectivity of the reaction between the alkene and the nucleophile as a function of the type of nucleophile.

It has been suggested,[61] in relation to *meta*- and *para*-substituted styrenes with the F, Cl, CH_3, and OCH_3 substituents, that the ionisation energy be used as a measure of the gas-phase affinity of an alkene for a proton or a hydrogen atom (in hydrogenation reactions). The numerical values of the ionisation energies were determined from the photoelectron spectra and by calculations in terms of the CNDO approximation.

Substituted derivatives of allene, whose molecule contains two mutually perpendicular π-systems, are interesting objects for the study of reactivity.

In order to investigate the effects of the substituent on the reactivity of the allene fragment, Taber et al.[71] carried out calculations by the EHM method for monosubstituted allenes $H_2C=C=CRX$ as well as $H_2C=C=CF_2$. The results of the calculations showed that the ionisation energy, determined on the basis of the Koopmans' theorem from the HOMO energy, decreases in the following sequence of substituents X: H > CN > F > Cl > F_2 > Br > CH_3, while the electron affinity, estimated as the LUMO energy decreases in the following sequence: CN > F > F_2 > H > NH_2 > Cl > CHO > CH_3 > Br. Analysis of the composition of the frontier molecular orbitals showed that, when X = CH_3, F, Cl, Br, and NH_2, the HOMO is to a large extent localised on the substituted double bond while the LUMO is localised on the unsubstituted double bond. In the case where X = CN and CHO, the opposite situation is observed: the HOMO and the LUMO are localised on the unsubstituted and substituted double bonds respectively. Therefore, the reaction, accompanied either by the loss of an electron (with participation of the HOMO) or the acquisition of an electron (with participation of the LUMO), can proceed, depending on the nature of the substituent, via both the substituted and the unsubstituted double bond of the allene.

In the [4 + 2]cycloaddition reaction (diene synthesis), which takes place as a result of the interaction of the HOMO of the diene (the electron-donating agent) with the LUMO of the dienophile (the electron-accepting agent), the substituted allene can function both as a diene and as a dienophile depending on the substituent and the nature of the other reactant. A number of studies have been devoted to this reaction of fluoroallenes.[5,16] Dommelsmith et al.[16] studied mono- and 1,1-difluoroallenes, for which calculations were made by the non-empirical method in terms of the 4-31G basis set. For the asymmetric substitution of hydrogen by fluorine in the allene, the degeneracy of the HOMO is removed because the fluorine atoms act differently on the two π MO, one of which is localised on the substituted C(1)=C(2) bond, while the other is localised on the unsubstituted C(2)=C(3) bond. As a result, the HOMO in the $CH_2=C=CHF$ and $CH_2=C=CF_2$ molecules is localised on the fluorinated π bond and is influenced little by the fluorine atom located in the same nodal plane. Therefore the C(1)=C(2) bond can be characterised, as in the unsubstituted allene, as an electron-enriched double bond.

The next occupied molecular orbital as well as the LUMO are localised on the non-fluorinated C(2)=C(3) bond and are strongly stabilised as a result of the inductive effect of fluorine. Thus this bond can be regarded as electron deficient. The concerted [4 + 2]cycloaddition reaction involving the enrichment of the species in electrons proceeds therefore with participation of a non-fluorinated bond in fluoroethylenes, while the non-concerted [2 + 2]cycloaddition involves the fluorinated bond. Dixon and Smart,[5] who used an expanded two-exponent basis set for the non-empirical calculation and studied mono- and 1,1-difluoroallenes as well as trifluoroallene, arrived at similar conclusions about the nature of the HOMO and LUMO in fluoroallenes and about the influence of these frontier molecular orbitals on the regioselectivity of the cycloaddition reactions.

Table 1 presents a compilation of the ionisation energies of 243 compounds with a C=C bond. The first column lists the empirical formulae of the compounds, which are arranged in order of increasing numbers of C, H, N, O, F, Si, S, Cl, Br, Sn, and I atoms. The second column presents the structural formulae (conventional representations of the carbon skeleton for complex hydrocarbons) and in some cases the names of the compounds. The third column lists the first two vertical and adiabatic (in brackets) ionisation energies. In addition, the symmetry and the nature of the corresponding ionisation energy are also indicated in brackets.

Table 1.

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_2H_4	$H_2C=CH_2$	10.55(10.51) ($1b_{2u}$)	12.85(12.45) ($1b_{2g}$)	[76]
C_2D_4	$C_2D=CD_2$	10.53($1b_{2u}$)	12.47($1b_{2g}$)	[77]
C_3H_4	$H_2C=C=CH_2$	9.62(2e)	10.2	[78]
C_3H_6		10.01(9.74) (a'', $\pi_{C=C}$)	12.4(11.82) (σ_1)	[76]
C_4H_4	$H_2C=C=C=CH_2$	9.15($1b_{3g}$)	9.98($2b_{3u}$)	[78]
C_4H_4		9.58(9.58) ($2a''$, π)	10.58(10.58) ($12a'$, π)	[78, 80]
C_4H_6		9.33($3a''$)	10.06($12a'$)	[78]
C_4H_6		9.20(9.03) ($1b_g$)	11.5($1a_u$)	[79]

Table 1 (contd.).

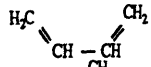
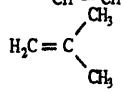
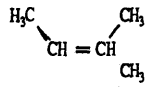
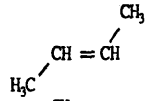
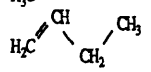
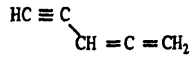
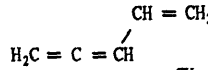
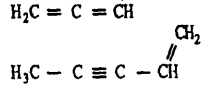
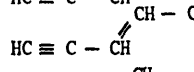
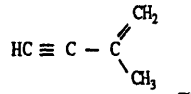
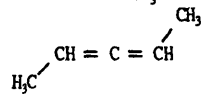
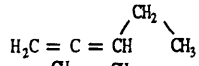
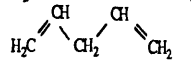
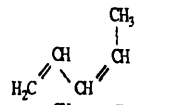
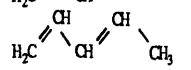
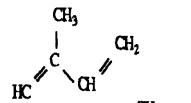
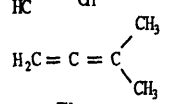
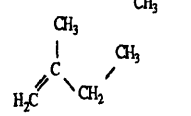
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry) IE$_1$	IE$_2$	Refs.
C_4H_6		9.06(9.06) ($1b_g$, π)	11.47(11.22) ($1a_u$, π)	[77]
C_4H_8		9.44(9.21) (a'', $\pi_{C=C}$)	11.59(11.35) (a')	[76]
C_4H_8		9.12(9.07) ($2b_1$)	11.7(11.27) ($6b_2$)	[7, 78]
C_4H_8		9.37(9.09) (a'', $\pi_{C=C}$)	11.96(a')	[76]
C_4H_8		9.72(9.59) ($3a''$, $\pi_{C=C}$)	11.75(11.30) ($9a'$)	[76]
C_5H_4		9.65 (a'', π)	10.30 (a', π)	[6]
C_5H_4	$H_2C{=}C{=}C{=}C{=}CH_2$	8.67 ($3e$)	9.2	[78]
C_5H_6		8.88 (a'', π)	10.04 (a', π)	[6, 78]
C_5H_6		8.94(8.94) ($6a''$, π)	9.51(9.51) (a', π')	[80]
C_5H_6		9.17 ($3a''$)	10.44 ($15a'$)	[78]
C_5H_6		9.11 ($3a''$)	10.38	[78]
C_5H_6		9.27 ($3a''$)	10.43 ($15a'$)	[78]
C_5H_8		9.13	9.65	[78]
C_5H_8		9.25	10.0	[78]
C_5H_8		9.62 ($2a_u$)	10.12 ($1b_g$)	[78]
C_5H_8		8.67 ($3a''$)	11.1 ($2a''$)	[78]
C_5H_8		8.61(8.61) ($3a''$, π)	11.10 ($2a''$, π)	[8, 77, 78]
C_5H_8		8.89(8.89) ($3a''$, π)	10.9 ($2a''$, π)	[77]
C_5H_8		8.95	9.9	[77]
C_5H_{10}		9.15 ($4a''$)	—	[78]

Table 1 (contd.).

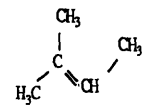
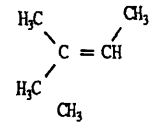
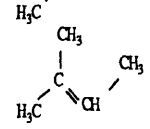
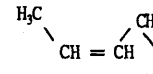
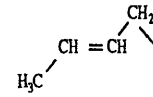
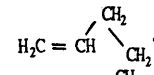
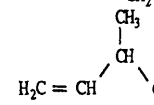
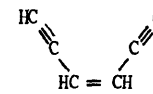
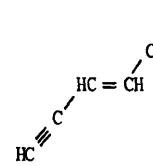
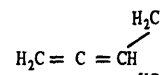
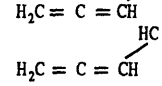
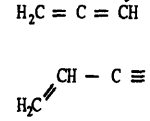
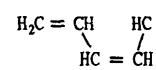
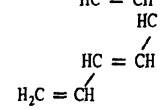
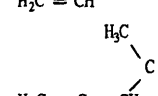
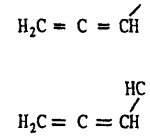
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry) IE$_1$	IE$_2$	Refs.
C_5H_{10}		8.68 ($4a''$)	11.3 ($16a'$)	[78]
C_5H_{10}		8.92(8.72) ($\pi_{C=C}$)	11.23(11.08)	[8, 76]
C_5H_{10}		9.15	—	[76]
C_5H_{10}		9.04 ($4a''$)	—	[78]
C_5H_{10}		9.04 ($4a''$)	—	[78]
C_5H_{10}		9.52 ($4a''$)		[78]
C_5H_{10}		9.7(9.52) (π_1)	11.2(11.0) (σ)	[76, 77]
C_6H_4		9.10(9.10) ($2b_1$, π)	10.54 ($9a_1$, π')	[80]
C_6H_4		9.07(9.07) ($2a_u$, π)	10.55(10.55) ($9a_g$, π')	[78, 80]
C_6H_6		9.65 (a'')	10.3 (a')	[78]
C_6H_6		8.53 (b_g, π)	9.78 (a_g, π)	[6]
C_6H_6		8.71(8.50) ($2a_u$, π)	9.97 ($9b_u$, π')	[80]
C_6H_8	$H_3C{-}CH{=}C{=}C{=}CH{-}CH_3$	8.09(8.09) ($2b_g$, π)	10.6 ($2a_u$, π)	[77]
C_6H_8		8.32(8.32) ($2b_1$, π)	10.27(10.27) ($1a_2$, π)	[67, 77]
C_6H_8		8.29(8.29) ($2a_u$, π)	10.26(10.26) ($1b_g$, π)	[67, 77]
C_6H_8		8.54(8.54) (π_1)	9.79 (π_2)	[47]
C_6H_8		8.32 (π_1)	9.73 (π_2)	[47]

Table 1 (contd.).

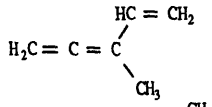
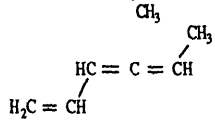
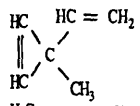
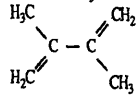
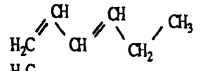
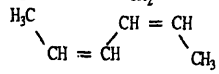
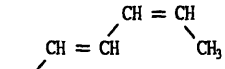
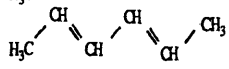
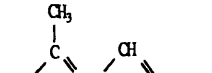
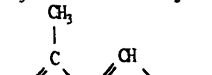
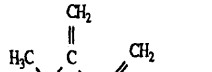
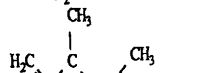
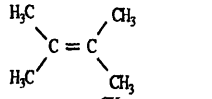
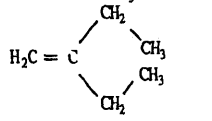
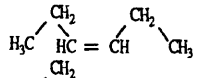
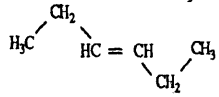
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_6H_8		8.54 (π_1)	9.73 (π_2)	[47]
C_6H_8		8.56 (π_1)	9.47 (π_2)	[47]
C_6H_8		8.29	—	[63]
C_6H_{10}		8.62(8.62) ($2b_g$, π)	10.18 ($2a_u$, π)	[8, 77]
C_6H_{10}		8.63 ($3a''$)	11.1 ($2a''$)	[78]
C_6H_{10}		8.18 ($2b_g$)	10.7 ($2a_u$)	[78]
C_6H_{10}		8.25 ($4a''$)	10.7 ($3a''$)	[78]
C_6H_{10}		8.22 ($2b_g$)	10.7 ($2a_u$)	[8, 78]
C_6H_{10}		8.28 ($4a''$)	10.8 ($3a''$)	[78]
C_6H_{10}		8.47 ($4a''$)	10.5 ($3a''$)	[78]
C_6H_{10}		8.79 ($4a''$)	10.8 ($3a''$)	[78]
C_6H_{10}		8.39 ($4a''$)	10.6 ($3a''$)	[78]
C_6H_{12}		8.41(8.26) (b_{3u})	10.83(10.69) (b_{3g})	[76, 78]
C_6H_{12}		9.06	—	[76]
C_6H_{12}		8.95	—	[48]
C_6H_{12}		8.97	—	[48]

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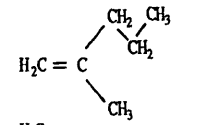
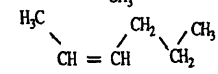
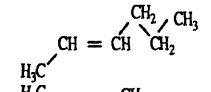
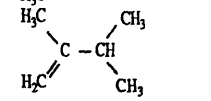
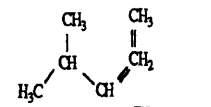
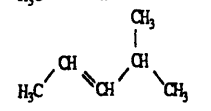
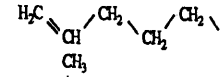
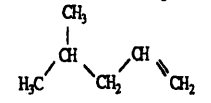
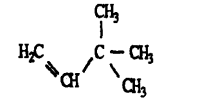
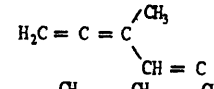
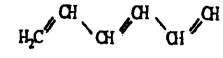
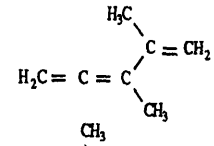
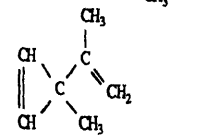
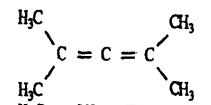
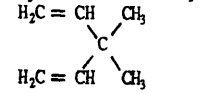
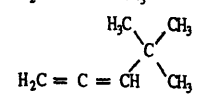
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_6H_{12}		9.08	—	[48]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		9.07	—	[76, 78]
C_6H_{12}		8.98	—	[76, 78]
C_6H_{12}		8.97	—	[76]
C_6H_{12}		9.48	—	[76]
C_6H_{12}		9.45	—	[76, 78]
C_6H_{12}		9.7 (π_1)	11.1 (σ_1, C(CH$_3$)$_3$—C)	[76]
C_7H_8		8.39 (a'', π)	9.59 (a', π)	[6]
C_7H_{10}		8.07(8.07) (π)	10.07(10.07) (π)	[77]
C_7H_{10}		8.10 (π_1)	9.56 (π_2)	[47]
C_7H_{10}		7.84	—	[63]
C_7H_{12}		8.53(8.53)	—	[81]
C_7H_{12}		9.55 (b_1, π)	9.95 (a_2, π)	[77]
C_7H_{12}		9.32	—	[11]

Table 1 (contd.).

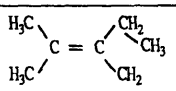
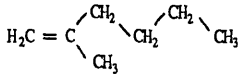
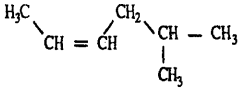
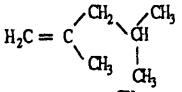
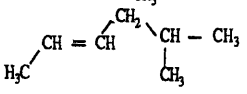
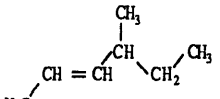
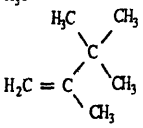
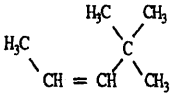
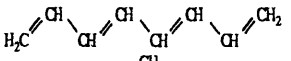
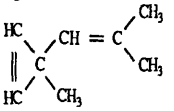
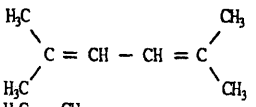
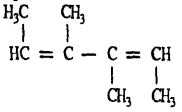
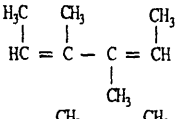
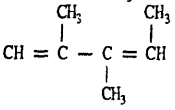
Empirical formula	Name, structural formula	IE(IE_{ad})(symmetry)		Refs.
		IE_1	IE_2	
C_7H_{14}		8.21	—	[76]
C_7H_{14}		9.04	—	[76]
C_7H_{14}		8.92	—	[76]
C_7H_{14}		9.03	—	[76]
C_7H_{14}		8.92	—	[76]
C_7H_{14}		8.91	—	[76]
C_7H_{14}		9.02	—	[76]
C_7H_{14}		8.92	—	[76]
C_8H_8	Styrene $C_6H_5CH=CH_2$	8.48(8.42) (b_1, π)	9.28(9.13) (a_2, π)	[33, 77]
C_8H_{10}		7.79(7.79) (b_g)	9.61(9.45) (a_u)	[12]
C_8H_{12}		8.08	—	[63]
C_8H_{14}		7.83(7.65) ($3b_g, \pi$)	10.12 ($3a, \pi$)	[8, 77]
C_8H_{14}		8.1 (*E*, *E*)	—	[8]
C_8H_{14}		8.6(*E*, *Z*)	—	[8]
C_8H_{14}		8.7(*Z*, *Z*)	—	[8]
C_9H_{10}	Allylbenzene $C_6H_5CH_2CH=CH_2$	8.65(8.60) (b_1)	9.27 (a_2)	[77]

Table 1 (contd.).

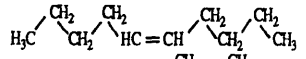
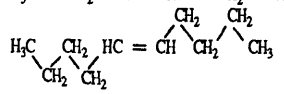
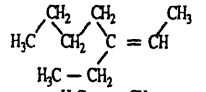
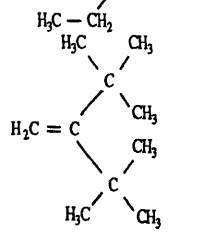
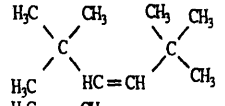
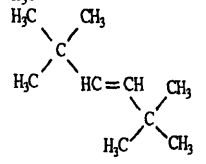
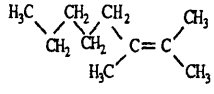
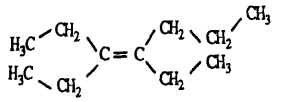
Empirical formula	Name, structural formula	IE(IE_{ad})(symmetry)		Refs.
		IE_1	IE_2	
C_9H_{10}	α-Methylstyrene $C_6H_5C(CH_3)=CH_2$	8.50(8.20) (b_1, π)	9.13 (a_2, π)	[77]
C_9H_{10}	*trans*-β-methylstyrene $C_6H_5CH=CHCH_3$	8.37(8.20) (b_1, π)	9.14 (a_2, π)	[77]
C_9H_{10}	*o*-Methylstyrene $CH_3C_6H_4CH=CH_2$	8.50(8.20)	9.00 (a_2, π)	[77]
C_9H_{10}	*m*-Methylstyrene $CH_3C_6H_4CH=CH_2$	8.36(8.15)	8.97 (a_2)	[77]
C_9H_{10}	$C_6H_5CH=CHCH_3$	8.48	—	[82]
C_9H_{12}	—	9.52–10.06 (e, π)	9.67 (a_2, π)	[77]
$C_{10}H_{10}$	1-Phenylbutadiene $C_6H_5CH=CHCH=CH_2$	8.16(7.95) ($\pi_{C=C}$)	9.27 (a_2)	[77]
$C_{10}H_{10}$	2-Phenylbutadiene $H_2C=C(C_6H_5)CH=CH_2$	8.77(8.57) ($\pi_{C=C}$)	9.3 ($a_2 + b_1$)	[77]
$C_{10}H_{12}$	*cis*-β-Ethylstyrene $C_6H_5CH=CH_2H_5$	8.54	—	[82]
$C_{10}H_{12}$	*trans*-β-Ethylstyrene $C_6H_5CH=CHC_2H_5$	8.30	—	[82]
$C_{10}H_{12}$	*o*,*m*-Dimethylstyrene $(CH_3)_2C_6H_3CH=CH_2$	8.30(8.00)	8.76 (a_2)	[77]
$C_{10}H_{20}$		8.77	—	[76]
$C_{10}H_{20}$		8.76	—	[76]
$C_{10}H_{20}$		8.10	—	[76]
$C_{10}H_{20}$		8.98	—	[76]
$C_{10}H_{20}$		8.69	—	[76]
$C_{10}H_{20}$		8.74	—	[76]
$C_{10}H_{20}$		8.13	—	[76]
$C_{11}H_{22}$		8.04	—	[76]

Table 1 (contd.).

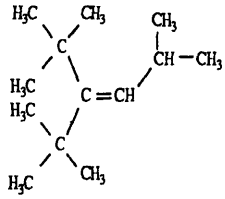
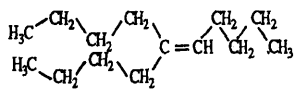
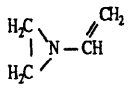
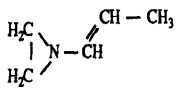
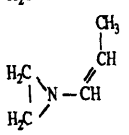
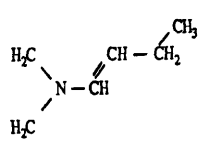
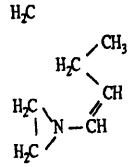
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_{12}H_{16}$	*cis*-t-Butylstyrene $C_6H_5CH=CHC(CH_3)_2$	8.85	—	[82]
$C_{12}H_{16}$	*trans*-β-t-Butylstyrene $C_6H_5CH=CHC(CH_3)_3$	8.18	—	[82]
$C_{13}H_{26}$		8.31	—	[76]
$C_{14}H_{12}$	*trans*-Stilbene $C_6H_5CH=CHC_6H_5$	8.00(7.70) (b_1, π)	9.25—9.75 ($b_1 + 2a_2$)	[77]
$C_{14}H_{12}$	*cis*-Stilbene $C_6H_5CH=CHCH_5$	8.20(7.80) (b_1, π)	9.08—9.40 ($b_1 + 2a_2$)	[77]
$C_{14}H_{12}$	α-Phenylstyrene $(C_6H_5)_2C=CH_2$	8.25(8.20) (b_1)	9.05—9.20 ($b_1 + 2a_2$)	[77]
$C_{14}H_{28}$		8.17	—	[76]
C_6N_4	Tetracyanoethylene $(NC)_2C=C(CN)_2$	11.79 ($2b_{3u}, \pi''_{C=C}$)	13.45	[83]
C_3H_3N	Acrylonitrile $H_2C=CHCH$	11.1(10.84)	12.35(12.28)	[83]
C_3H_3N	Allylamine $H_2C=CHCH_2NH_2$	9.44(8.76) (a'', n)	10.04 (a'', π)	[76, 77]
C_4H_5N	$H_2C=C(CH_3)CN$	10.37	—	[46]
C_4H_5N	$H_2C=CCH_2CN$	10.18	—	[48]
C_4H_5N	$H_3CC(H)=C(H)CN$	10.23	—	[46]
C_4H_7N		8.75		[64]
C_5HN	Tricyanoethylene $(NC)_2C=C(H)CN$	11.55	—	[46]
C_5H_9N		8.34	—	[64]
C_5H_9N		8.39	—	[64]
$C_5H_{11}N$	$H_2C=HCCH_2N(CH_3)_2$	8.47(7.84) (n)	(9.37) ($\pi_{C=C}$)	[76]
$C_6H_{11}N$		8.26	—	[64]
$C_6H_{11}N$		8.26	—	[64]

Table 1 (contd.).

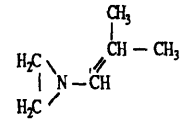
Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_6H_{11}N$		8.2		[64]
$C_6H_{11}N$	$NH(CH_2CH=CH_2)$	8.79 (n, N)	9.82 (π_-)	[76]
$C_9H_{15}N$	$N(CH_2CH=CH_2)_3$	8.30 (n, N)	9.70 (π_+)	[76]
C_4H_2N	*cis*-1.2-Dicyanoethylene *cis*-NCCH=CHCN	11.3(11.15) ($2b_1, \pi''_{CC}$)	(12.77) ($8b_2, \pi''_{CN}$)	[77, 83] [39]
$C_{15}H_{11}N$	$C_6H_5—CH=C(CN)C_6H_5$	8.22	—	[39]
$C_4H_2N_2$	*trans*-1.2-Dicyanoethylene *trans*-NCCH=CHCN	11.3(11.15) (π_2)	12.9(12.78) ($\pi_{x,y}$)	[77]
$C_4H_2N_2$	1.1-Dicyanoethylene	13.35 ($2b_1, \pi''_{CC}$)	12.90 ($7b_{2g}, \pi''_{CN}$)	[83]
$C_6H_{14}N_2$	$H_2C=C[N(CH_3)_2]_2$	7.5 (π)	8.2 (N_-)	[76]
C_3H_4O	*trans*-Acroleine $H_2C=CHCHO$	10.13(10.13) (a', n)	10.95 ($a'', \pi_{C=C}$)	[77]
C_3H_6O	Allyl alcohol $H_2C=CHCH_2OH$	10.16(9.63) (π)	10.93 (n)	[84]
C_3H_6O	Methyl vinyl ether $H_2C=CHOCH_3$	9.14(8.96) ($3a'', \pi$)	12.10 ($13a', n\sigma$)	[76]
C_4H_6O	Crotonaldehyde $CH_3CH=CHCHO$	9.86(9.77)	10.36(10.21)	[77, 84]
C_4H_6O	$H_2C=C=CHOCH_3$	8.73	—	[77]
C_4H_8O	$H_2C=C(H)OC_2H_5$	9.15	11.68	[76]
C_4H_8O	$H_2C=CHCH_2OCH_3$	9.44	—	[48]
C_5H_8O	2-Methoxybutadiene $H_2C=CHC(OCH_3)=CH_2$	8.62(8.43)	10.1	[77]
C_5H_8O	1-Methoxybutadiene $H_2C=CHCH=CHOCH_3$	8.21(8.03)	10.7	[77]
C_5H_8O	$H_2C=C=CHOC_2H_5$	8.47	—	[11]
$C_5H_{10}O$	$CH_3CH=C(CH_3)OCH_3$	8.25	11.25	[76]
$C_5H_{10}O$	$H_2C=C(H)OCH(CH_3)_2$	8.84	11.34	[76]
$C_6H_{12}O$	$H_2C=C(H)O(CH_2)_3CH_3$	8.77	11.02	[76]
$C_6H_{12}O$	$H_2C=C(OC_2H_5)_2$	8.3	10.3	[76]
$C_7H_{12}O$	$H_2C=C=CH(OC(CH_3)_3)$	8.31		[11]
$C_3H_4O_2$	Acrylic acid $H_2C=CHCOOH$	10.77(10.60) (a', n)	10.91 (a'', π)	[77]
$C_4H_6O_2$	Methyl acrylate $H_2C=CHCOOCH_3$	10.72	11.12	[77]
$C_5H_8O_2$	$H_2C=C(CH_3)COOCH_3$	10.28	11.05	[77]
$C_6H_{10}O_2$	Ethyl *trans*-crotonate *trans*-$CH_3CH=CHOOC_2H_5$	10.11	10.71	[77]
$C_6H_8O_4$	Dimethyl maleate $H_3COOCCH=CHCOOCH_3$	10.47	11.0	[77]
$C_6H_{12}O_4$	Diethyl fumarate $H_5C_2OOCCH=CHCOOC_2H_5$	10.7	11.23	[77]
$C_{11}H_{20}O_4$	$(C_2H_5O)_2C=C=C(OC_2H_5)_2$	8.13	—	[75]
C_2F_4	$F_2C=CF_2$	10.54(10.11) (b_{3u})	15.93	[76, 85]
C_3F_4	$F_2C=C=CF_2$	(10.88)	—	[5, 16]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
C_3F_6	$F_2C=CFCF_3$	11.29	14.57	[76]
C_4F_8	*cis*-$CCF=CFCF_3$	11.49	—	[76]
C_4F_8	*trans*-$F_3CCF=CFCF_3$	11.55	—	[76]
C_6F_{12}	$(CF_3)_2C=C(CF_3)_2$	12.61	—	[76]
C_7F_{12}	$(CF_3)_2C=C=C(CF_3)_2$	12.28	—	[75]
C_2H_3F	$H_2C=CHF$	10.58(10.37) (π)	13.79 (σ)	[77]
C_3H_5F	$H_2C=CHCH_2F$	10.60(10.11) ($\pi_{C=C}$)	12.43	[76]
$C_2H_2F_2$	1,1-Difluoroethylene	10.72(10.31) (π)	14.79(14.06) (σ)	[77]
$C_2H_2F_2$	*cis*-Difluoroethylene	10.43 (π)	13.97 ($\sigma_{C=C}$)	[77]
$C_2H_2F_2$	*trans*-Difluoroethylene	10.38 (π)	13.90 ($\sigma_{C=C}$)	[77]
$C_3H_2F_2$	$H_2C=C=CF_2$	10.1(9.79)	—	[16]
C_2HF_3	$F_2C=CHF$	10.54(10.14) (a'', π)	14.65 (σ)	[76]
$C_3H_3F_3$	$H_2C=CHCF_3$	(10.9)	—	[16]
$C_8H_3F_3$	Pentafluorostyrene $C_6H_5CH=CH_2$	9.36(9.18) (b_1)	9.73 (a_2)	[77]
$C_9H_{10}O_2F_6$	$(CF_3)_2C=C=C(OC_2H_5)_2$	8.93	—	[75]
C_2H_6Si	$H_2C=CHSiH_3$	10.04 (a'', π)	11.5 (a'', σ_1)	[77, 86]
C_3H_8Si	$H_2C=CHCH_2SiH_3$	9.49 ($3a''$, π)	11.72 ($9a'$, σ_{Si-C})	[86]
$C_5H_{12}Si$	Trimethylvinylsilane $H_2C=CHSi(CH_3)3$	9.8 (π_1)	10.3 (σ_1)	[77, 86]
C_6H_{12}	Divinylsilane $(CH_2=CH)_2Si(CH_3)_2$	9.8 (b_1, π)	10.0 (a_2, π_2)	[77, 86]
$C_6H_{14}Si$	Allyltrimethylsilane $H_2C=CHCH_2Si(C_3)_3$	9.0 (π)	10.5 (σ_{Si-C})	[76, 77]
$C_8H_{12}Si$	$(CH_2=CH)_4Si$	9.8 (e, π_1)	10.1 (a_2, π_2)	[76, 77
$C_6H_{12}Si_2$	$(CH_2=CHSiCH_3)_2$	8.63	—	[86]
$C_7H_{18}Si_2$	$H_2C=CHSi_2(CH_3)_5$	8.56	—	[86]
$C_8H_{10}Si_2$	$(CH_3)_3SiHC=CHSi(CH_3)_3$	9.19 ($6a_u$, π_1)	9.45 ($10a_g$, σ_{Si-C})	[86]
$C_5H_{12}O_3Si$	$H_2C=CHSi(OCH_3)_3$	11.0 (π)	11.74	[86]
$C_{18}H_{18}O_3Si$	$H_2C=CHSi(OC_2H_5)_3$	10.16	10.7	[86]
C_3H_6S	$H_2C=CHSCH_3$	8.51(8.44) ($3a''$, π)	11.00 ($17a'$, $n\sigma$)	[76]
C_3H_6S	Allylmercaptan $H_2C=CHCH_2SH$	9.25(9.25) (a'', nS)	10.05 (a'', $\pi_{C=C}$)	[76, 77]
C_4H_6S	$H_2C=C=CHSCH_3$	8.24	—	[11]
C_4H_8S	$H_2C=CCH_2SCH_3$	9.95	—	[48]
C_5H_8S	$H_2C=C=CH(SC_2H_5)$	8.09	—	[11]
$C_6H_{10}S$	Diallyl sulphide $(CH_2=CHCH_2)_2S$	8.60(8.43) (n)	9.82—10.02 (9.5) ($\pi_1+\pi_2$)	[77]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{ad}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_7H_{12}S$	$H_2C=C=C(H)SC(CH_3)_3$	8.26	—	[11]
C_8H_8S	$H_2C=CHSC_6H_5$	10.5	—	[48]
$C_9H_{10}S$	Methyl styryl sulphide $C_6H_5CH=CHSCH_3$	7.75 (π_5)	9.13 (π_4)	[77]
$C_4H_8S_2$	$H_2C=C(SCH_3)_2$	8.12 (π)	8.74 (nS)	[76]
$C_4H_8S_2$	*cis*-$CH_3SCH=CHSCH_3$	7.80	9.15	[76]
$C_4H_8S_2$	*trans*-$CH_3SCH=CHSCH_3$	7.85 (π_u)	8.67 (nS)	[76]
$C_6H_{12}S_4$	$(CH_3S)_2C=C(SCH_3)_2$	7.75	8.58	[76]
$C_5H_{11}NS$	$H_2C=C(SCH_3)N(CH_3)_2$	7.8	8.6	[76]
C_2Cl_4	$Cl_2C=CCl_2$	9.5(9.34) ($2b_{3u}$, π)	11.4 ($3b_{3g}$, nCl)	[76]
C_2H_3Cl	$H_2C=CHCl$	10.2(10.0) ($2a''$, π)	11.7 ($7a'$, nCl)	[87]
C_3H_5Cl	Allyl chloride $H_2C=CHCH_2Cl$	10.34 ($\pi_{C=C}$)	11.3 (nCl)	[48, 83]
C_4H_7Cl	$ClCH=CHC_2H_5$	10.00	—	[48]
$C_2H_2Cl_2$	$H_2C=CCl_2$	10.0(9.83) ($2b_1$, π)	11.7 ($4b_2$, nCl)	[87]
$C_2H_2Cl_2$	*cis*-$ClHC=CHCl$	9.8(9.65) ($2b_1$, π)	11.9 ($4b_2$, nCl)	[87]
$C_2H_2Cl_2$	*trans*-$ClHC=CHCl$	9.8(9.64) ($2a_u$, π)	11.9 ($5a_g$, nCl)	[87]
$C_8H_6Cl_2$	*o,o*-Dichlorostyrene $C_6H_3Cl_2CH=CH_2$	9.05(8.70) (b_1)	9.30 (a_2)	[77]
C_2HCl_3	$Cl_2C=CHCl$	9.6(9.48) ($4a''$)	11.7 ($11a'$)	[87]
C_2F_3Cl	$F_2C=CFCl$	10.24	13.01	[76]
C_2HF_2Cl	$F_2C=CHCl$	10.04	12.15	[76]
C_2H_2FCl	$H_2C=CFCl$	10.21	—	[17]
$C_2F_2Cl_2$	$F_2C=CCl_2$	9.82	12.13	[76]
$C_4F_6Cl_2$	*trans*-$F_3CClC=CClCF_3$	10.55	12.05	[76]
$C_4H_6SiCl_2$	$(CH_2=CH)_2SiCl_2$	10.8	—	[86]
$C_8H_{18}Si_2Cl_2$	$(CH_3)_3SiClC=CClSi(CH_3)_3$	8.96 ($7a_u$)	9.75 (12_{ag})	[86]
$C_2H_3SiCl_3$	$H_2C=CHSiCl_3$	10.7	11.3	[86]
C_2Br_4	$Br_2C=CBr_2$	9.264(9.105) ($2b_{3u}$)	—	[88]
C_2H_3Br	$H_2C=CHBr$	9.83(9.83) (a'', π)	10.93(10.93) (a', nBr)	[76]
C_3H_5Br	$H_2C=CHCH_2Br$	10.01 ($\pi_{C=C}$)	10.20	[76]
C_3H_5Br	$H_2C=C(Br)CH_3$	9.58 ($\pi_{C=C}$)	10.63(10.51) (nBr)	[76]
C_4H_7Br	$BrHC=CHC_2H_5$	9.82	—	[48]
C_2F_3Br	$F_2C=CFBr$	10.11	11.94	[76]
C_2H_2FBr	*cis*-$FCH=CHBr$	9.75	11.05	[76]
$C_2H_2Br_2$	$Br_2C=CH_2$	9.78 (π)	10.73 (nBr)	[76]
C_2H_2Br	*cis*-$CHBr=CHBr$	9.44(9.32) (b_1, π)	10.74 (b_2, nBr)	[76]
$C_2H_2Br_2$	*trans*-$CHBr=CHBr$	9.44(9.30) (a_u, π)	11.05 (a_g, b_g, nBr)	[76]

Table 1 (contd.).

Empirical formula	Name, structural formula	IE(IE$_{adi}$)(symmetry)		Refs.
		IE$_1$	IE$_2$	
$C_6H_{14}Sn$	Allyltrimethyltin $(CH_3)_3SnCH_2CH=CH_2$	8.70 (σ/π)	—	[89]
$C_{15}H_{32}Sn$	Allyltributyltin $(C_4H_9)_3SnCH_2CH=CH_2$	8.40 (σ/π)	—	[89]
$C_{21}H_{20}Sn$	Allyltriphenyltin $(C_6H_5)_3SnCH_2CH=CH_2$	8.33 (σ/π)	—	[89]
			—	[89]
$C_5H_{11}ClSn$	Allyldimethyltin chloride $(CH_3)_2ClSnCH_2CH=CH_2$	8.95 (σ/π)	—	[89]
$C_{11}H_{23}ClSn$	Allyldibutyltin chloride $(C_4H_9)_2ClSnCH_2CH=CH_2$	8.63 (σ/π)	—	[89]
$C_4H_8Cl_2Sn$	Allylmethyltin dichloride $CH_3Cl_2SnCH_2=CH_2$	9.33 (σ/π)	—	[89]
$C_7H_{14}Cl_2Sn$	Allylbutyltin dichloride $C_4H_9Cl_2SnCH_2CH=CH_2$	9.24 (σ/π)	—	[89]
C_2H_3I	H_2C=CHI	9.33(9.33) (a', π)	10.10(10.10) (a'', n)	[76]
C_3H_5I	H_2C=CHCH$_2$I	9.75	—	[48]
$C_2H_2I_2$	*cis*-IHC=CIH	8.92 (n)	9.86 (π_1)	[76]
C_2H_2I	*trans*-IHC=CHI	8.94 (n)	9.60 (π_1)	[76]
$C_3H_2I_3$	I_2C=ClCH$_2$I	9.30 (n)	9.75 (n)	[76]

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