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THE ELECTRONIC STRUCTURE AND PROPERTIES OF THE σ-BONDS IN THE MOLECULES OF ORGANIC COMPOUNDS

N. D. Sokolov

1. INTRODUCTION

The importance of σ-bonds in organic chemistry lies not only in the fact that most organic compounds do not contain other types of bond but also in the fact that σ-bonds form the framework of all molecules in general. Approximately 80% of the energy of formation of aromatic molecules corresponds to σ-bonds, their elastic properties are determined to a considerable extent by σ-electrons, most chemical reactions are accompanied by the rupture and formation of σ-bonds, in many instances the sign of the dipole moments is determined by the σ-electrons, etc.

It is often assumed that the σ-bonds in polyatomic molecules are localised and that their interaction can be neglected. This view is refuted by a large number of experimental facts, for example the dependence of the ionisation potential of alkanes on the length of the chain of σ-bonds, the dependence of the position of the electronic absorption bands in the optical spectra on the length of this chain, the non-additivity of the dipole moments of halogenated alkanes, the hyperfine structure of their nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) spectra, and many others.

From the viewpoint of quantum mechanics, strictly speaking, it cannot be assumed that the electronic wave functions in a molecule are localised on individual bonds or groups of bonds. Since the molecule is a single unit, the electronic wave functions should characterise the molecule as a whole. When the LCAO-MO† method is used, this means that the one-electron wave functions of the molecule ψ_i should be made up of linear combinations of the atomic orbitals φ_k of *all* the atoms in the molecule:

$$\psi_i = \sum_k c_{ik} \varphi_k. \qquad (1)$$

According to this formula generally speaking in the stationary state each electron has a finite probability of being found close to each atom in the molecule. The need to represent the molecular orbital in form (1) for molecules with saturated bonds was demonstrated by Walsh[1] in his interpretation of the electronic spectra of a number of simple molecules AB_2, ABC, AB_3, HAAH, H_2AB, etc. Starting from the delocalised molecular-orbital model, Walsh developed a method by which it was possible not only to interpret the spectrum but also to predict the geometry of the molecule in the ground and excited states and also the vibrational structure of the spectrum, to determine the selection rules and polarisation of the bands, etc. The need to use delocalised molecular orbitals of type (1) can be seen particularly clearly for symmetrical molecules.

† LCAO-MO = molecular orbital approximated by a linear combination of atomic orbitals.

The necessary requirement that the molecular wave function should exhibit the same symmetry elements as the molecule can in general be satisfied within the framework of the LCAO-MO method only by means of a linear combination containing the atomic orbitals of all the atoms‡.

The delocalised character of the molecular orbital does not in itself mean that changes or perturbations taking place in one part of the molecule will necessarily influence all other parts of the molecule. The transfer of an effect depends on the magnitude of the interatomic and (for saturated molecules) intra-atomic interactions. Within the framework of the LCAO-MO method, the interatomic interaction is characterised by the resonance integral between neighbouring atomic orbitals, which depends on their degree of overlap. For a conjugated chain of π-bonds, one atomic orbital from each atom appears in formula (1), and all the resonance integrals β are the same; each atom (except the end members) interacts to the same extent with two neighbours (Fig. 1*a*). For an unbranched chain of C–C σ-bonds (if for simplicity we neglect the C–H bonds), formula (1) contains two atomic orbitals from each atom (one from the terminal atoms); each atomic orbital "interacts" with two neighbouring atomic orbitals, but these interactions are different. For example, let us consider atomic orbital *2* (Fig. 1*b*). It interacts with atomic orbital *1* of the neighbouring atom; as before, we denote the corresponding resonance integral by the symbol β. On the other hand, atomic orbital *2* interacts with atomic orbital *3* belonging to the same atom; the corresponding resonance integral can be denoted by β', whose absolute magnitude is less than that of β.

If the ratio $m = \beta'/\beta$ were zero, the C–C bonds in the molecule would be strictly localised. All its properties would be additive; the influence of each atom would be transmitted only to neighbouring atoms. In actual fact $m \neq 0$, so that, strictly speaking, additivity of properties should not be observed in saturated chains. The magnitude of β' is approximately proportional to the splitting of the *s* and *p*-levels of the carbon atom (i.e. the energy of the transition $s^2p^2 \rightarrow sp^3$). From experimental data for alkane molecules it follows that $m = 0.34$ (see for example Klopman[3])§. The interaction of the σ-bonds, which is taken into account by the integral β', is called the inductive effect.

The interaction of σ-bonds depends not only on the intra-atomic integral β', but also on the resonance integral β'', characterising the overlap of two even or two odd atomic orbitals of the chain e.g. atomic orbitals *2–4* or *1–3* (Fig. 1). This integral is of the same order of magnitude as β'; for simplicity, however, the integral β'' is neglected.

The fact that $|\beta'| < |\beta|$ is one of the factors which makes σ-systems differ from π-conjugated systems. Another reason for this difference, as will be seen later, is that in an unbranched chain of σ-bonds there are two atomic orbitals for each atom, and not one, as in π-conjugated systems.

‡ A systematic treatment of molecules by the LCAO-MO method, taking account of all the atomic orbitals, was proposed by Hoffmann[2]. See also papers by Clementi[21]—cf. footnote on p. 964.

§ Calculations show that the energy and the distribution of electron density depend only on the absolute value of m (see for example Yoshimuzi[4]).

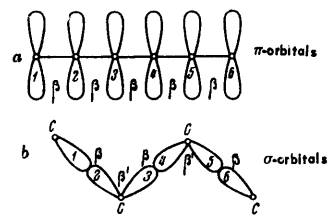


Fig. 1. Atomic orbitals: *a*) in chains of π-conjugated bonds ($m = 1$; $n = N$); *b*) in chains of σ-bonds ($m = 0.34$; $n = 2N - 2$).

2. ENERGY CHARACTERISTICS

Let us consider the simplest case, an unbranched chain of N linked atoms. For a chain molecule with conjugated π-bonds, we shall take account of only the π-electrons. Each atom will then have one p atomic orbital; the number of atomic orbitals n will therefore equal the number of atoms N. By setting up the molecular orbitals in form (1), substituting this expression in the Schrödinger equation, and solving the appropriate variational problem, we obtain n energy eigenvalues (see for example Streitwieser[5]):

$$\varepsilon_i' = \alpha + \lambda_i\beta, \; i = 1, 2, \ldots, n. \qquad (2)$$

Here α and β are the Coulombic and resonance integrals respectively, and λ_i the roots of the corresponding determinantal equation, which are different for different values of n. The solid lines in Fig. 2 show the arrangement of eigenvalues for different values of n; $\epsilon_i = \epsilon_i' - \alpha$. The upper and lower systems of levels (below and above the line $\epsilon = 0$) are fairly far apart for small values of n. The distance $\Delta\epsilon$ between the lower positive and upper negative levels (the so-called gap width), however, decreases with increase in n, and tends to zero as $n \rightarrow \infty$.

In a chain of σ-bonds, as noted above, we must take account of two types of integral, β and β'. Calculation[4,6,7] analogous to that carried out for π-systems gives for the energy the same formula (2), but now λ depends implicitly on m; as before, the number of molecular orbitals obtained is equal to the original number n of atomic orbitals, but now $n = 2N - 2$. If we assume the value $m = \beta'/\beta = 0.34$ indicated above, the energy levels obtained for different values of n will occupy the positions indicated by the broken lines in Fig. 2. The distances between energy levels with the same sign (+ or –) (Fig. 2) are much smaller than for conjugated systems ($m = 1$). Moreover, the gap width $\Delta\epsilon$ decreases with increase in n much more slowly than for π-conjugated systems, and as $n \rightarrow \infty$ it tends not to zero but to a finite value equal to 1.32β.

Fig. 2 shows the difference between the dependence on chain length of the total energy for π-conjugated bonds and for σ-bonds. In the approximation being considered, the total electronic energy is obtained if in each level, starting from the lowest, we place two electrons and take the sum of the energies of all the electrons. We then have $E = 2\sum_i \epsilon_i$. It is found that all the negative levels (number $n/2$) will be doubly occupied, and all the positive levels will be empty. If we now consider the energy corresponding to one bond (a pair of electrons), it can be seen from Fig. 2 that the absolute value of this quantity for $m = 1$ (solid lines) on going, for example, from $n = 2$ (ethylene) to $n = 4$ (butadiene) increases considerably, since the lowering of

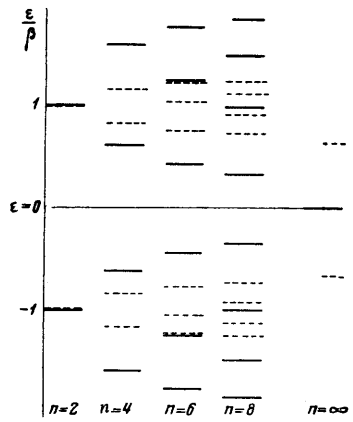


Fig.2. Energy levels for π-conjugated chains (solid lines) and for chains of σ-bonds (broken lines).

the lower level is much greater than the raising of the upper level. On the other hand, for $m = 0.34$ (broken lines) the lower and upper levels are displaced relative to the original level ($\epsilon = -1$) by approximately the same absolute amount, as a result of which the energy corresponding to each bond remains almost unchanged. For larger values of n the difference in these displacements is even smaller. This leads directly to the non-additivity of the energy for π-conjugated chains and, on the other hand, to the approximate additivity of the energy of formation of alkanes[8]; small deviations from this additivity are observed only for the first members of the homologous series.

From the foregoing it follows that additivity in energy of formation does not indicate localisation of electrons on bonds. As noted above, complete localisation would correspond to $m = 0$. Additivity in energy simply results from the mutual compensation of small effects of opposite sign.

The quantitative calculation of the deviations from additivity is much more complex, however. The molecular model chosen is too approximate to provide a basis for a calculation with the required accuracy, although many attempts have been made (e.g. for aromatic compounds[9] and alkanes[3,7,10]). Attention must first of all be drawn to the fact that the simplest version of the LCAO-MO method chosen (Hückel's method) does not give one of the fundamental properties of chemical bonds, their degree of saturation (see e.g. Ref. 11, pp. 146, 163, *et seq.*). This simplified scheme of calculation would indicate, for example, that the approach of two H_2 molecules should lead to the formation of a stable complex H_4, since the calculated energy decreases. In actual fact, on the approach of two H_2 molecules (or in general two covalent bonds A–B), the energy increases, and this indicates the saturated character of the bonds. This result is a consequence of the fact that in the simplest version of the molecular-orbital method the calculation is carried out with non-antisymmetrised functions, and no allowance is made for the interaction of the electrons with one another. Moreover, in a systematic calculation, all the bonds and all the electrons of the molecules must naturally be taken into account[12,13].

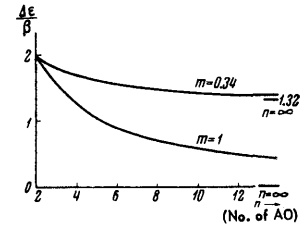


Fig.3. Dependence of the relative gap width ($\Delta\epsilon/\beta$) on the number of atomic orbitals (AO).

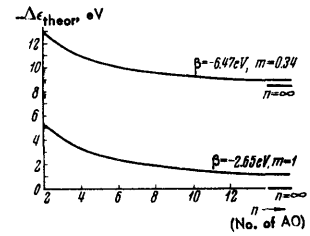


Fig.4. Dependence of the gap width ($\Delta\epsilon$) on the number of AO for $\beta_\pi = -2.65$ eV and $m = 1$ (lower curve) and for $\beta_\sigma = -6.47$ eV and $m = 0.34$ (upper curve).

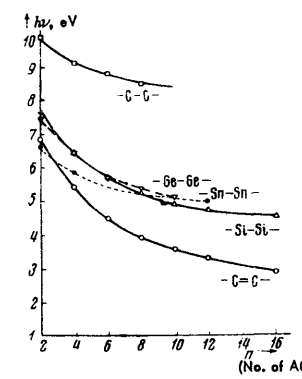


Fig.5. Experimental dependence of the absorption frequency on the length of the molecular chain[15].

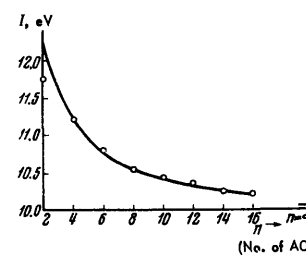


Fig.6. Dependence of the ionisation potential on the number of AO in the alkane chain.

The problem of calculating the non-additivity of energy is most clearly formulated when we compare the energies of two isoelectronic and isomeric molecules, one of which has conjugated π-bonds while the other has not. Thus, for example, for the two isomeric molecules

(A) $H_2C=CH—CH_2—CH=CH_2$ (penta-1,4-diene)
(B) $H_3C—CH=CH—CH=CH_2$ (penta-1,3-diene)

the latter has 6 kcal less energy than the former; this is usually attributed to the conjugation of the two π-bonds. In actual fact, however, this difference in energies results from the algebraic summation and partial compensation of a number of effects (by itself, the approach of the two π-bonds on going from A to B leads not to a decrease but to an increase in energy!). Thus, for example, the number of C–H bonds formed by carbon atoms having sp^2 hybridisation is six for molecule A and five for molecule B; the energies of these bonds may differ by 10–20 kcal. Analogous differences are observed in the energies of rupture of C–C bonds, in the energies of the interaction of different σ-bonds with one another and with π-bonds, etc. It is only when allowance is made for all these differences that we can hope to obtain a correct explanation[13] for the above decrease in energy on going from A to B.

Our initial simple model is adequate, however, for a semi-quantitative explanation of a number of the properties of molecules, e.g. the energy of electronic absorption. Within the framework of this model, the long-wave absorption band should correspond to a transition from the upper occupied level to the lower empty level, the distance between which is equal to the gap width $\Delta\epsilon$.

This quantity should be directly equated to $h\nu$, where ν is the frequency of the transition. Fig. 3 shows the calculated dependence of the quantity $\Delta\epsilon/\beta$ on n for a chain of π-conjugated bonds ($m = 1$) and for a chain of σ-bonds ($m = 0.34$). The quantity $\Delta\epsilon/\beta$ decreases much more slowly in the second instance than in the first. It should however be remembered that the resonance integrals for π-bonds (β_π) are smaller than those for σ-bonds (β_σ). Thus for the values $\beta_\pi = -2.65$ eV and $\beta_\sigma = -6.47$ eV adopted by Pople and Santry[14], for example, we obtain for $\Delta\epsilon$ the curves shown in Fig. 4. The similarity between these curves is greater than for identical values of β.

Fig. 5 gives experimental curves showing the dependence of $h\nu$ on n for polyenes (–C=C–), alkanes (–C–C–), and various other chain molecules containing σ-bonds (–Ge–Ge–, –Sn–Sn–, and –Si–Si–) according to published data[15]. The nature of the dependence of $h\nu$ on n is analogous to that expected on the basis of the model being considered. In each instance values of m and β can be selected which make it possible to reproduce these curves approximately by calculating $\Delta\epsilon$. The steep descent of the curve for the chain of silicon atoms apparently indicates that the corresponding integral β' has a comparatively large absolute value.

According to these calculations, the significant difference between the electronic spectra of polyenes and linear molecules having σ-bonds lies in the nature of the $\nu(n)$ relationships at large values of n. As noted above, as $n \to \infty$ within the framework of our model, the gap width in polyenes ($\Delta\epsilon_\pi$) tends to zero, whereas for chains of σ-bonds ($\Delta\epsilon_\sigma$) it tends to a finite limit of the same order of magnitude as β. This last feature is a direct consequence of the fact that $\beta' \neq \beta$. If we had $\beta' = \beta$, then $\Delta\epsilon_\sigma$ would also tend to zero as $n \to \infty$.

Our model, however, greatly simplifies the situation for polyenes with large values of n. Here effects which go beyond the scope of the model begin to play a part. Thus it is possible that alternation of bond lengths begins at large values of n in polyenes, yielding two different resonance integrals for adjacent bonds[16]; it can be seen from the foregoing that in such a situation the gap width does not tend to zero. Moreover, when $\Delta\epsilon$ is sufficiently small, the spacing between the electronic levels reaches the same order of magnitude as the vibrational quanta, so that the electronic and vibrational motion, strictly speaking, can no longer be considered independently. Moreover, with long chains there may be very significant interaction between the electrons[17,18]. This factor is apparently the most significant.

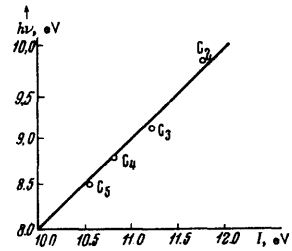


Fig. 7. Relationship between ionisation potential and absorption frequency.

The ionisation potential of a molecule in this model is simply equal to the energy (with opposite sign) of the upper filled orbital, for which $i = n/2$ in formula (2):

$$-I = \varepsilon_{n/2} = \alpha + \lambda_{n/2}\beta. \qquad (3)$$

Fukui and his coworkers[10] showed that, with $\alpha = -5.85$ eV, $\beta = -6.36$, and $m = 0.34$, good agreement is observed between the calculated and experimental values of I (with the exception of ethane, Fig. 6).

Since both the frequency of absorption and the ionisation potential are linearly dependent on $\lambda_{n/2}$, we should expect a linear relationship between these quantities, and this is confirmed for the alkanes (Fig. 7). For other classes of compound there are insufficient published experimental data to enable us to make a similar comparison of ν and I.

3. ELECTRON DENSITY DISTRIBUTION AND DELOCALISATION

The distribution of electronic charge in conjugated systems exhibits characteristic features, resulting from the delocalisation of the π-electrons. The most remarkable feature is that, under the influence of a substituent or a heteroatom, the electron density distribution changes throughout the conjugated chain, and alternation of charge is observed. This involves the alternation of the charges of the atoms with respect to sign or magnitude.

The charges q on the atoms in a polyene chain XC_5 (where X represents e.g. a halogen atom) are given in Fig. 8 (broken line)[6]. The "amplitude" of the alternation falls off very slowly with increasing distance from X. This alternation of the charges of the atoms does not take place in alkane chains XC_5 (solid line in Fig. 8). The positive charge produced on the C atoms by the substituent X decreases fairly rapidly to zero: it is almost equal to zero on the third atom from X [6¶].

¶ In Sandorfy's paper[6] the calculations for the σ-chains were carried out with $m = 0.25$.

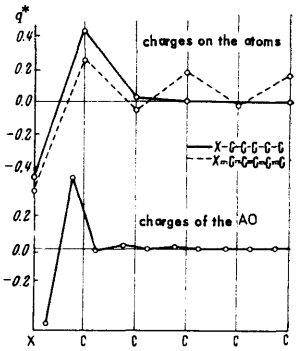


Fig. 8. Upper—charges on the atoms in an XC_5 σ-chain (solid line) and an XC_5 π-conjugated chain (broken line); lower—"charges" of the atomic orbitals in an XC_5 σ-chain.

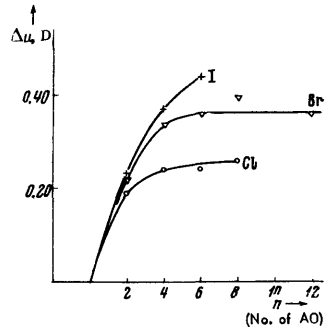


Fig. 9. Dependence of the difference in dipole moments $\Delta\mu = \mu(XC_NH_{2N+1}) - \mu(XCH_3)$ on the number of atomic orbitals [4].

It may be noted that, if we were speaking of the charges not on the atoms but corresponding to individual atomic orbitals (for polyenes these concepts are the same), we would find rapidly damped alternation for the latter in a chain of σ-bonds [6] (Fig. 8). The alternation disappears on passing to the charges on the atoms, since in order to obtain the latter it is necessary to sum the charges of the two atomic orbitals of each atom. Even if $m = 1$, alternation of the charges on the atoms would not take place in a chain of σ-bonds in which each atom had two atomic orbitals.

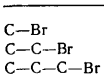
Calculation [19] has shown that the negative charge on the halogen atom X in halogenoalkanes XR increases with increasing length of the hydrocarbon radical R, as a direct consequence of the delocalisation of electrons along the chain of bonds. Thus an effect familiar in chemistry is obtained even with a simplified model which does not take account of the hydrogen atoms. It is found [19] that this increase in charge is accompanied by a simultaneous increase in the rate of nucleophilic substitution. Table 1 gives as example values of the charge q^* on the Br atom and of the relative rates of the reaction

$$RX + OH^- \rightarrow OH + X^-$$

for a number of normal alkanes and isoalkanes.

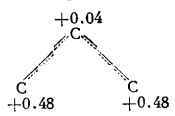
Knowing the charges of the atomic orbitals of a chain of σ-bonds and assuming that they are situated at the "centres of gravity" of these atomic orbitals, we can calculate the dipole moments of substituted alkanes [4]. Since the positive charge produced on the alkane radical under the influence of an electronegative substituent X is not localised on the single carbon atom nearest to X, the dipole moments are non-additive. The dependence of the difference $\Delta\mu = \mu(XC_NH_{2N+1}) - \mu(XCH_3)$ on the number of atomic orbitals is shown in Fig. 9. [4] The theoretical curves were calculated for $m = 0.34$. The dipole moment becomes constant at $n \geq 6$ (Fig. 9), i.e. beginning approximately at substituted propanes. Thus the delocalised character of the electrons in monosubstituted halogenoalkanes apparently has a significant influence on the charge distribution over not more than three atoms of the σ-chain.

TABLE 1. Charges on the Br atom and relative reaction rates.

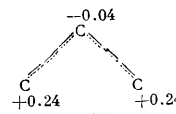
RBr	q^*	Relative rate of reaction $RX + OH^- \rightarrow ROX + X^-$	RBr	q^*	Relative rate of reaction $RX+OH^- \rightarrow ROX+X^-$
C–Br	0.423	1		0.467	10^8
C–C–Br	0.436	1.7			
C–C–C–Br	0.440	—			
	0 444	45		0.487	—

The example of the halogenoalkanes shows that the dipole moments of the σ-framework μ_σ may lead to non-additivity of the dipole moments for molecules having conjugated π-bonds. Allowance must be made for the fact that the value of β' is about 30% greater for sp^2 hybridisation than for sp^3 hybridisation. In general, μ_σ and μ_π are of the same order of magnitude; in some instances μ_σ may even exceed μ_π (for example, according to Berthod and Pullman [20], for pyridine $\mu_\sigma = 1.44$ D, $\mu_\pi = 0.86$ D, and $\mu_{exp} = 2.23$ D).

The change in the calculated charge distribution in a molecule containing π-bonds, occurring when allowance is made for the σ-electrons, can be assessed from the example of the allyl cation [2]. The electron density distribution represented in scheme (I) was calculated in the π-electron approximation without allowance for the C–H bonds. Scheme (II) gives the charges on the carbon atoms of the same cation, determined with allowance for both the π-electrons and the σ-electrons. It is found that the sign of the charge on the central carbon atom has changed, and that the magnitude of the charges on the terminal carbon atoms has decreased considerably, owing to the appearance of positive charges on the hydrogen atoms†.



(I)



(II)

† E. Clementi (U.S.A.) reported at the International Symposium on Quantum Chemistry in Kutna Hora, Czechoslovakia (1967), that, according to his calculations for polyatomic molecules, carried out in the self-consistent field approximation with allowance for all the electrons and integrals, the calculated electron density distribution of conjugated systems changes considerably when allowance is made for σ-electrons. Some of this work by Clementi has been published in the Journal of Chemical Physics [21].

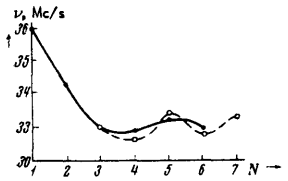


Fig. 10. Dependence of the n.q.r. frequency of the Cl atoms in compounds $Cl-[CH_2]_N-Cl$ on N (solid line—experimental, broken line—calculated).

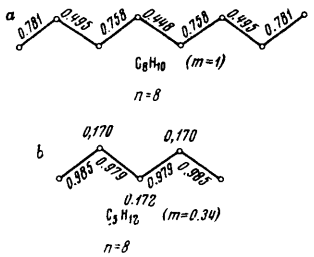


Fig. 11. Bond orders:
a) in a π-conjugated chain for $n = 8$ ($m = 1$);
b) in the chain of σ-bonds for $n = 8$ ($m = 0.34$).

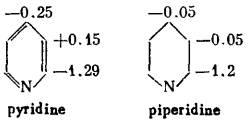
With symmetrical αω-dihalogenoalkanes the situation is apparently slightly different from that with monosubstituted alkanes. Calculations carried out by the molecular-orbital method for $m = 0.34$ show that the effective (negative) charge on the chlorine atoms in molecules of the type $Cl-[CH_2]_N-Cl$ show a characteristic dependence on the number N of CH_2 groups. When $N > 3$, the charges on the chlorine atoms vary periodically with increase in N: they are slightly greater for even values of N than for odd values, the difference amounting to 0.005–0.01 of a unit charge for the calculated examples with $N = 3$–7. This effect is apparently manifested in the nuclear quadrupole resonance (n.q.r.) spectra [22]. According to the calculations, the n.q.r. frequency of the chlorine atoms in these molecules is smaller for $N = 4$ than for $N = 3$ or 5 (Fig. 10). For $N > 5$ the dependence of the n.q.r. frequency on N is apparently more complex.

As with π-conjugated systems, it is possible to calculate the bond orders $p_{\mu\nu}$ for alkane molecules. A corresponding value of $p_{\mu\nu}$ is obtained for each pair of neighbouring atomic orbitals. For conjugated systems the values of $p_{\mu\nu}$ alternate along the chain of carbon atoms. The values of $p_{\mu\nu}$ for octatriene are given in Fig. 11*a*. Many conjugated systems show parallel changes in the bond orders, bond lengths, and force constants (see for example Streitwieser [5]). According to Konarski's calculations [23] the alternation of $p_{\mu\nu}$ is even more marked for a chain of σ-bonds (Fig. 11*b*); the low values of $p_{\mu\nu}$, however, are due to the intra-atomic interaction, characterised by the integral β'. Thus there is almost no alternation in the orders of real bonds in saturated hydrocarbons. On this basis it may be expected that these compounds should show alternation neither of bond lengths nor of force constants.

4. MAGNETIC RESONANCE SPECTRA AND DELOCALISATION

The experimental data on chemical shifts in n.m.r. spectra occurring when a substituent or a heteroatom is introduced into a molecule indicate that their influence is transmitted for a fairly large distance along a chain of either π-bonds or σ-bonds.

This influence, associated with delocalisation of electrons, resembles slightly the influence of substituents and heteroatoms on electron density distribution, but it does not reduce to this. The magnetic screening of nuclei is due to the precession of electrons in the external magnetic field, and in general it depends in a complex fashion on the properties of the molecule. Measurements of the proton chemical shifts σ_H and calculations of the π-electron charges for a number of nitrogen-containing aromatic compounds [24] showed that the discrepancy between the experimentally observed values of σ_H and the values calculated from data on the π-charge distribution is large: it may amount to 100–250% and have either sign. This comparison, it is true, made no allowance for the fact that not only the π-electrons, but also the σ-electrons, are in fact responsible for the chemical shift. The contribution made by the σ-electrons of the molecular framework is apparently fairly large. This follows, for example, from a comparison of σ_H for pyridine and piperidine [24]. The proton chemical shifts given below were measured relative to benzene and cyclohexane respectively.



As in the production of charges by induction, the influence of the perturbation on the atoms joined by σ-bonds is rapidly damped, and, in contrast to π-conjugated systems, the values of σ_H do not show alternation.

One consequence of electron delocalisation in aromatic compounds is the displacement of the n.m.r. signal from the protons towards weaker fields under the influence of the magnetic field of the "ring current". A similar effect, of small magnitude, is apparently observed with cyclic saturated hydrocarbons. For example, the equatorial hydrogen atoms in cyclohexane give an n.m.r. signal which is displaced slightly towards weaker fields relative to the signal from the axial protons [25]. The possibility of the production of ring currents in rings with alternation in the magnitude of the resonance integral was examined by London [26] in connection with the theory of the anisotropy of diamagnetic susceptibility in aromatic compounds. He concluded that the magnitude of the ring current is proportional to $(\beta'/\beta)_{n/2}$, i.e. that it is comparatively small.

The indirect spin–spin coupling of nuclei, taking place through the electron clouds separating them, is one of the most striking manifestations of the delocalisation of electrons through a system of σ-bonds. This coupling is due to "magnetic polarisation" of the electron cloud by the magnetic field of the nuclei. This polarisation can readily be imagined if we start from the picture of two-electron bonds interacting with one another. The magnetic field of the nucleus leads to partial (very small) "unpairing" of the spins of the pair of electrons in direct contact with this nucleus. The electronic magnetic moment produced in this way in turn produces a magnetic moment in the electron

pair of the neighbouring bond (as a result of the interaction of the bonds), etc.; the induced magnetic moment of one of the electron pairs interacts with the second nucleus and thus leads to magnetic interaction of the nuclei with one another. If the interaction (β') between the bonds, examined above, did not take place, indirect spin–spin coupling would not exist.

The energy of the spin–spin coupling is

$$W = K_{HH} I_1 I_2, \qquad (4)$$

where I_1 and I_2 are the spin moments of the first and second nuclei respectively, and K_{HH} is the so-called spin–spin coupling constant. Some values of K_{HH} for hydrogen and fluorine nuclei are given in Table 2.

These data show that conjugation does not always lead to an increase in K_{HH} (examples 5–7 in Table 2). The dependence of the absolute magnitude and sign of K_{HH} on the length of the chain of bonds and on the structure is apparently fairly complex. It is possible that in some instances, the curvature of a long chain allows the terminal atoms to interact directly with one another.

The simplest example is provided by the interaction of geminal hydrogen atoms (i.e. hydrogen atoms attached to the same carbon atom). It has been established experimentally that for these atoms the constant K_{HH} increases (becomes less negative or more positive) when the H–C–H valency angle increases. Moreover, the introduction of an electronegative X atom in the α-position to the CH_2 group leads to an increase in K_{HH} (e.g. for ethylene $K_{HH} = +2.5$, and for formaldehyde $K_{HH} = +4.0$). These regular features can be explained qualitatively as follows[27].

Two mechanisms apparently exist for the interaction of geminal atoms. Firstly, the magnetic moment of the nucleus may induce a magnetic moment in the electron pair of the $CH^{(1)}$ bond; as a result of the difference in the signs of the gyromagnetic ratio of the proton and electron, the direction of this moment will be the same as that of the nucleus (Fig. 12*a*). The electronic moment of the $CH^{(1)}$ bond will in turn "polarise" the electron pair of the $CH^{(2)}$ bond, whose induced magnetic moment will interact with the second H nucleus. The moment of the latter (Fig. 12*a*) is antiparallel to the spin of $H^{(1)}$. In accordance with Eqn. (4), the energy W will be negative (i.e. have a minimum) for the condition $K_{HH} > 0$. Secondly, we may have a mechanism in which the magnetic moment of the proton $H^{(1)}$, as a result of contact with the electron pair of the $CH^{(2)}$ bond, directly induces a magnetic moment in this bond (Fig. 12*b*). Analogous arguments lead to the conclusion that in this instance the spins of the nuclei will be parallel, and K_{HH} will be negative.

TABLE 2. Spin–spin coupling constants.

No.	No. of bonds	Carbon framework of molecule	K_{HH}, c/s
1	2	H–C–H (methane)	−12.4
2	2	H–C–H (cyclopropane)	− 4.0
3	2	H–C–H (ethylene)	+ 2.5
4	4	H–C–C–C–H	7–13
5	4	H–C=C=C–H	6
6	5	H–C–C=C–C–H	+2.7
7	5	H–C=C–C–C–H	0.7–1.3
8	6	H–C≡C–C–C≡C–H	1.3
9	7	H–C–C=C–C=C–C–H	1.0
10	5	F–C$_6$H$_4$–F	11
11	5	F–C–C–C–C–F	4.3
12	6	F–C–C–C–C–C–F	1.9

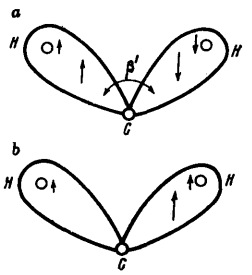


Fig. 12. Indirect magnetic interaction of geminal hydrogen atoms.

These two mechanisms compete with one another. The first is determined by the magnitude of the exchange integral β', which, as noted above, depends on the energy of the s–p splitting in the carbon atom, and the second is determined by the magnitude of the exchange integral between the atomic orbital of the $H^{(1)}$ atom and the atomic orbital of the carbon atom of the second bond. With increase in the s-character of the hydridisation of the carbon atom, the absolute magnitude of the integral β' increases[14] by 33%—$\beta'(sp^3) = -2.45$ eV, $\beta'(sp^2) = -3.27$ eV—whereas the absolute magnitude of the second integral decreases, because of the increase in the valency angle. Thus it is to be expected that K_{HH} will increase, i.e. will become more positive, and this is confirmed experimentally (see examples *1–3* in Table 2). The attachment of an electronegative atom X to the carbon atom will lead to a decrease in the population of the C–H orbitals and hence to a decrease in the negative contribution from the second mechanism: i.e. it will lead to an increase in K_{HH}.

A semi-quantitative treatment of these effects was put forward by Pople and Bothner-By[27]. There is as yet, however, no completely satisfactory theory of spin–spin coupling in molecules.

Electron delocalisation is revealed in e.s.r. spectra in the presence of a hyperfine structure from not one but several nuclei. The hyperfine structure of e.s.r. spectra is due chiefly to "contact" spin–spin coupling of the unpaired electron with protons or other nuclei having spins differing from zero. This interaction is possible as a result not only of the actual delocalisation of the unpaired electron but also of spin polarisation of the electron cloud, similar to the polarisation examined above, causing indirect spin–spin coupling of nuclei. It follows from the e.s.r. spectra of alkyl radicals[28,29] that the hyperfine structure is due not only to hydrogen atoms which are attached to α- and β-carbon atoms, but also to those on γ-carbon atoms. This means that in the e.s.r. spectra of these radicals the delocalised character of the unpaired electron influences atoms which are separated by three σ-bonds from the "mother" carbon atom‡.

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‡ The e.s.r. spectra show another extremely characteristic manifestation of delocalisation of the unpaired electron, which is observed in the spectra of organic radical-anions consisting of two aromatic rings joined by a bridging group. Here, however, the delocalisation does not take place through a chain of σ-bonds and is apparently due to π–σ conjugation, so that this effect lies beyond the scope of the present review[30–35] (the theory of the effect has been examined by a number of authors[36–38]).

This analysis of the electronic structure of molecules of saturated hydrocarbons confirms the view that in the theoretical examination of these molecules, as in π-conjugated systems, it is necessary to use delocalised molecular orbitals. The delocalised character of a molecular σ-orbital is reflected in the properties of the molecules much less strongly, however, than with a molecular π-orbital, as a consequence of the fact that, in contrast to π-conjugated systems, not all the resonance integrals in a chain of σ-bonds are equal. The intra-atomic resonance integral β', characterising the interaction of the σ-bonds, is smaller than the interatomic resonance integral β, responsible for the formation of the σ-bonds themselves.

The delocalised character of the σ-electrons is reflected to varying extents in different properties of saturated hydrocarbons. It has almost no influence on the energy of formation, which can therefore be calculated by an additive scheme. The delocalised character of the σ-electrons has a significant influence on the positions of the electronic absorption bands, the ionisation potentials, the electron density distributions, and in particular the dipole moments of the molecules. As a rule, however, the influence of electron delocalisation on these properties does not extend over more than 3–4 atoms in the chain of σ-bonds. It extends over a large number of atoms, for example, in the spin–spin coupling in n.m.r. spectra, because of the high sensitivity of nuclear magnetic radiospectroscopy.

The influence of delocalisation of σ-electrons is more marked in conjugated systems than in saturated molecules, since the intra-atomic exchange integral β' is 30% greater in these bonds than in saturated molecules. Thus, in the study of the transmission of the effect of structural changes along a chain of bonds in conjugated systems, it is necessary to make allowance not only for the part played by π-electrons but also for that played by σ-electrons.

The calculations of the properties of chains of σ-bonds given above are of course greatly simplified. They are based on the simplest version of the one-electron approximation, and a number of additional, strictly speaking unjustified, assumptions have been made. These include neglect of the integral β'' mentioned above, neglect of the C–H bonds, etc. In the treatment of comparatively simple properties such as the dependence of the ionisation potential on the length of the chain, appropriate refinements in the calculation would make it possible to obtain quantitative results, but should not alter significantly the qualitative picture obtained. For such complex properties as e.g. the spin–spin coupling of nuclei, however, comparatively extensive approximation is necessary in order to obtain even qualitative results. Thus the above interpretation of the indirect interaction of nuclear spins is based on more refined calculations than the treatment of the ionisation potentials or dipole moments.

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