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Nature of Carbon-Halogen Bonds

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This paper is a critical review of the literature on the problem of the nature of carbon-halogen bonds. It examines the various physical properties of halogen-containing organic compounds which are useful in discussing the problem of the chemical bond (infrared spectra, dipole moments, interatomic distances, nuclear quadrupole interaction constants, nuclear magnetic resonance). Special attention is paid to results from nuclear magnetic resonance, which show the uselessness of treating the properties of organohalogen compounds from the position of mesomerism-resonance theory. The correlation between the chemical shifts of nuclear magnetic resonance and the σ-constants of the substituents in various organohalogen compounds is considered. Attention is paid to the hybridisation of the orbitals of the carbon and halogen atoms and to the associated electronic displacements in unsaturated and aromatic systems. 85 references.

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I. INTRODUCTION

In the interpretation of the properties of molecules contemporary theories of organic chemistry employ ideas about the displacement of valence electrons by induction and conjugation mechanisms. Initially it was thought that the conjugative displacement of electrons, that is, their displacement from one bond to another, can occur in a molecule under the influence of a reagent (Robinson, Lowry, 1922–1923). It was proposed to represent graphically the effect of polarisation according to this mechanism by using curved arrows, symbolising the transfer of electrons from the octet of one atom to the octet of another. It was subsequently postulated that a state of constant polarisation by the conjugative mechanism also occurs in a non-reacting molecule (Arndt, 1924; Ingold, 1926). This conception, now known under the name of the theory of mesomerism, was subsequently used, mostly by Ingold, to explain a large number of problems in the reactivity of organic compounds. The use of quantum-mechanical calculations on unsaturated and aromatic systems using the π-electron approximation (Hückel, Pauling, 1932) was a further development of ideas on the delocalisation of valence electrons in organic molecules. To describe the electronic displacements in complex molecules which contain, in particular, hetero-atoms, the theory of resonance employs a set of structures corresponding to the limiting states of electron displacement

according to the conjugative mechanism. In this approach to the description of the electronic structure of a molecule the resonance theory becomes an adequate theory of mesomerism, differing only from the latter in the manner of representation of the electronic displacements that can be postulated.

The theory of mesomerism–resonance, or, as it is still called, the theory of conjugation (translated into Russian as teoriya sopryazheniya) has now received almost universal acknowledgement and is widely employed in dealing with the physical and chemical properties of organic compounds. Nevertheless, detailed examination shows the mesomerism–resonance theory to be in conflict with many experimental results. The most striking and convincing deficiency of this theory is in its application to organohalogen compounds, the properties of which have been thoroughly studied by physical and chemical methods and which also are the subject of detailed consideration from the standpoint of the theory of mesomerism.

We will consider below some physical properties of halogen derivatives of hydrocarbons—infrared spectra, dipole moments, interatomic distances, nuclear quadrupole resonance (NQR) constants—which are usually produced in support of the carbon–halogen bond's having partial double bond character. As will become evident from what is stated below, to explain some of the physical properties of the halogen derivatives of unsaturated and aromatic hydrocarbons it is unnecessary to have resort to mesomerism–resonance theory, since these properties can be substantially explained by the theory of the hybridisation of the orbitals of the carbon and halogen atoms and other physical criteria of the chemical bond, namely the NQR constants, are direct proof that the halogen atoms exhibit hardly any mesomeric effect. From the experimental results on the NQR constants it can be shown that the bonding orbitals of the halogen atoms in various types of halogen derivatives of hydrocarbons differ in their degree of hybridisation.

The increased strength of the carbon–halogen bond and the lower chemical lability of the halogen in a halogenobenzene as compared with an alkyl halide is explained by the greater overlap of the single-electron orbitals of the carbon and halogen exhibited in the aromatic compound with a higher *s*-character, and not by a greater number of electrons localised on the C–Hal bond in the aromatic compound (as is assumed in the mesomerism–resonance theory). The concept of the mesomerism theory of the participation of a conjugation mechanism in the transmission of the influence of the halogen atoms on the distribution of electronic charges in unsaturated and aromatic systems and the treatment (based upon this mechanism) of the reactivity of halogen-containing organic compounds are worthless.

2. ENERGETICS OF THE MESOMERIC STATE

Ingold originally assumed[1] that "in the halogen series, iodine, being the most capable of deformation, should exhibit the greatest tendency towards an increase in its covalency" and arranged the halogens in the following series according to decreasing mesomeric effect:

$$I > Br > Cl > F. \qquad (1)$$

Such a sequence of intensities in the displacement of electrons under the influence of the +M effect agrees with the order of the halogens according to their decreasing ability to withdraw electrons under the influence of the inductive (*I*) effect and hence leads solely to an increase in the difference between the electronegativities of the halogen atoms. Naturally, the attraction of ideas about the mesomeric effect for halogens, in the stated succession of its appearance, could not prove to be helpful for the interpretation of the physical and chemical properties of halogen-containing organic compounds. Progress in this respect would necessitate a system of effects opposite in their action, a system which would allow the difference between the atoms to be obliterated to the extent to which this is necessary for the interpretation of the experimental facts. Consequently, Ingold subsequently arranged the halogens according to their ability to increase the covalency in the reverse order:

$$F > Cl > Br > I, \qquad (2)$$

in which the mesomeric effect appears most strongly with fluorine and least with iodine. However, there is no physical basis for this series of decreasing mesomeric effects for the halogens, since it does not agree with the ionisation potentials, which increase from iodine to fluorine and not in the opposite direction.

To explain this contradiction it was assumed that the tendency towards an increase in covalency is determined not by the ionisation potentials of lone pairs but by the degree of overlap of the atomic orbitals which is the greater the less the atoms which form the double bond differ in size[2,3]. The worthlessness of this explanation becomes clear on examining actual data. The difference between the energies of double bonds formed by different atoms is ~ 10–50 kcal mole^{-1}.[4] Furthermore, the ionisation potentials of the electrons in the $tr^2tr^2tr\pi^2$ valence state of the halogens (as follows from the results on the energies of the ground states and the energies for promoting to the valence states[5,6]) for F, Cl, Br, and I are 18.24, 13.73, 12.37, and 10.88 eV respectively, that is, the difference in the ionisation potentials of the π-electrons of fluorine and chlorine is 104 kcal mole^{-1} and of fluorine and iodine is 170 kcal mole^{-1}. From energetic considerations, clearly if halogen atoms are capable of showing a mesomeric effect it should decrease in the order I > Br > Cl > F, but then its role as a working instrument in the treatment of the physical parameters of carbon–halogen bonds and of the chemical properties of halogen-containing organic compounds is lost.

3. INFRARED SPECTRA

Results on the vibrational frequencies of the C=C bond in halogenoethylenes will be examined for proof that a mesomeric effect is produced by halogen atoms. The position of the vibrations for this bond in chloroethylene (1608 cm^{-1}), bromoethylene (1598 cm^{-1}), and iodoethylene (1581 cm^{-1}) compared with that of the frequency of the vibration in ethylene (1621 cm^{-1}) is explained by the influence of resonance structure $\bar{C}H_2-CH=\overset{+}{X}$ with an ordinary C–C bond[7].

If the reduction in the vibrational frequencies were connected with the influence of the mesomeric effect of the halogens, then a reduction in the frequency of the vibrations of the C=C bond in fluoroethylene would also be expected, but for this compound the wavenumber is 1650 cm^{-1},[8] that is, higher than for ethylene. Undoubtedly the reduction in the vibrational frequencies for chloro-, bromo-, and iodo-ethylene is due to mechanical reasons—the replacement of hydrogen atoms by the heavy halogen atoms. When the alkene molecule is sufficiently large, the introduction of a chlorine atom has no effect on the vibrational

frequency of the C=C bond. Thus the wavenumbers for tetraethylmethylene [2,3-dimethylbut-2-ene] and trimethylchloroethylene [2-chloro-3-methylbut-2-ene] are the same (1672 cm^{-1}).

4. DIPOLE MOMENTS

There is a body of opinion that results on dipole moments provide experimental proof of the mesomeric effect of halogens [2,3,9]. That the dipole moments of the halogenobenzenes are lower than those of the methyl halides is explained by the effect of the mesomeric structures:

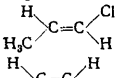
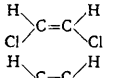
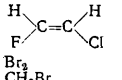


in that the difference in the dipole moments of the aliphatic and aromatic series $\mu CH_3X - \mu C_6H_5X$, is regarded as a measure of the mesomeric effect. This is illustrated by Table 1 (columns 2, 3, and 4), data taken from Coulson's book [9].

Table 1.

x	F	Cl	Br	F	Cl	Br
1	2	3	4	5	6	7
μ (CH_3X)	1.81	1.87	1.80	1.79	1.87	1.80
μ (C_6H_5X)	1.58	1.72	1.77	1.61	1.69	1.64
μ (CH_3X) — μ (C_6H_5X)	0.23	0.15	0.03	0.18	0.18	0.16

Table 2.

Compound	U_p	s-nature of carbon	x_C, eV	s-nature of halogen	x_{Hal}, eV	i	References on molecular structure and U_p	Notes
Cl_2	0.99	—	—	0.01	9.48	—	20.21	
CH_3Cl	0.68	0.220	7.81	0.20	11.35	0.15	22.21	
CF_3Cl	0.71	0.274	8.31	0.19	11.25	0.12	23.21	
CH_2Cl_2	0.70	0.228	7.89	0.19	11.25	0.14	24.25	$\angle HCH=112°$
C_6H_5Cl	0.65	0.333	8.79	0.26	11.94	0.13	26	$\angle C_2C_1C_6=120°$
$CH{\equiv}CCl$	0.726	0.500	10.38	0.24	11.75	0.05	27.21	
CH_2CHCl	0.64	0.280	8.36	0.25	11.84	0.14	28	
	0.65	0.325	8.77	0.25	11.84	0.13	29	
	0.66	0.285	8.41	0.24	11.75	0.14	30	
	0.67	0.285	8.41	0.23	11.65	0.13	31	
Br_2	0.99	—	—	0.01	8.50	—	20.21	
CH_3Br	0.75	0.202	7.65	0.17	10.08	0.11	22.21	
CF_3Br	0.80	0.274	8.31	0.14	9.79	0.07	32	$\angle FCF=108.6$
C_6H_5Br	0.74	0.333	8.79	0.21	10.47	0.06	33	
$CH_3C{\equiv}CBr$	0.84	0.500	10.38	0.17	10.08	0.01	34	
$CH_2{=}CHBr$	0.72	0.333	8.79	0.22	10.57	0.08	35	
I_2	0.94	—	—	0.06	8.55	0	20.21	
CH_3I	0.84	0.196	7.59	0.10	8.86	0.06	22.21	
$CH_3C{\equiv}CI$	0.97	0.500	10.38	0.10	8.86	0.07	34	
$CH_2{=}CHI$	0.82	0.332	8.84	0.16	9.31	0.02	20.36	

However, the dipole moments cannot serve as confirmation of the existence of a mesomeric effect for the halogens. The lower dipole moments of the halogenobenzenes is explained by the carbon atoms in the trigonal valence state (sp^2) exhibiting a higher electronegativity owing to which the polarisation of the C_{sp^2}–Hal bond is less than that of the C_{sp^3}–Hal bond. The effect of the hybridisation of the carbon orbitals on the moments of the C–Hal bond was examined by Petro [10]. Thus, the moment of the C_{sp^3}–F bond is 1.50 D, that of the C_{sp^2}–F bond is 0.95 D, that of the C_{sp^3}–Cl, C_{sp^2}–Cl, and C_{sp}–Cl bonds are 1.56, 1.07, and 0.61 D respectively, and those of the C_{sp^3}–Br and C_{sp^2}–Br bonds 1.49 and 1.01 D. The dipole moments of the halogenohydrocarbons also show the effect of the orbital hybridisation of the halogen atoms which is reflected by the electronegativities of their bonding orbitals (see Table 2). As regards the values of $\mu(CH_3X) - \mu(C_6H_5X)$, on selecting the most reliable values of the dipole moments [11] this difference disappears (Table 1, columns 5, 6, and 7).

In the CH_3X and $CH_2{=}CHX$ series the differences in the dipole moments for the fluoro-, chloro-, and bromo-derivatives are 0.36, 0.42, and 0.41 D respectively; for CH_3X and $CH{\equiv}CX$ this difference increases from fluorine to bromine (1.04, 1.43, and 1.80 D respectively) [11].

5. HYBRIDISATION OF THE ORBITALS OF HALOGEN ATOMS AND LENGTHS OF THE CARBON–HALOGEN BONDS

One of the main arguments in support of the halogen atoms exerting a mesomeric effect was the lengths of the carbon–halogen bonds in halogenohydrocarbons. Thus the shortening of the C–Cl bond in chlorobenzene and the chloroethylenes by 0.06–0.08 Å in comparison with the length of this bond in the halogenomethanes was explained by the presence of 15–18% double-bond character [12]; in the halogenoacetylenes, where the shortening of the carbon–halogen bond reaches ~ 0.15 Å, the degree of double-bond character is estimated at 30–36%. [13]

In the light of the theory of hybridisation, variations in the lengths of the carbon–halogen bonds are explained by orbital effects—the sizes of the covalent radii of carbon and the halogens in various valence states, realisable in one molecule or another [14]. The hybridisation of the orbitals of carbon atoms is determined simply from results on the geometry of the molecules [15]. Information about the hybridisation of the bonding orbitals of halogen atoms is underlined by the nuclear quadrupole interaction constants. The use of the latter for determining the degree of hybridisation of the orbitals of halogen atoms was hindered by the fact that they are functions of both the degree of hybridisation (s) and the ionicity of the bond (i). Both these parameters have a definite relation with a single experimental quantity, the number of non-bonded p-electrons [sic]:

$$U_p = -\frac{eQq_{mol}}{eQq_p},$$

in accordance with Eqn. (5):

$$U_p = (1-s)(1-i). \qquad (5)$$

Various attempts [16,17] were made earlier to find a relation between the ionic nature of a bond and the difference in electronegativities of the bound atoms, in order to substitute the ionicity of the bond in Eqn. (5) to determine the degree of hybridisation of the halogen orbitals. In this, however, no account was taken of the extremely important fact that a change in the hybridisation of the orbitals of the halogen atom is accompanied by a change in its electronegativity. After Hinze and Jaffe [5,6] had found a relation between these two parameters it was possible to determine the s-nature of the halogen orbitals and to show its effect on the length of the carbon–halogen bonds [14].

The ionic nature of a bond i is determined on the basis of the concept of bond electronegativity with the aid of Eqn. (6):[18]

$$i = |nAj - 1| = \left| \frac{\Delta\chi}{2(C_A + C_B)} \right|, \quad (6)$$

where nAj is the number of electrons in the jth orbital of atom A, $\Delta\chi$ the difference between the electronegativities of atoms A and B, eV; C_A and C_B the half-differences between the ionisation potential and the electron affinity for the orbitals of atoms A and B respectively, $C = \frac{1}{2}(I_V - E_V)$. The electronegativity of the carbon and halogen atoms depends linearly on the s-character of the bonding orbital[5], as does the ionisation potential I_V and the electron affinity E_V for the halogens. The ionisation potentials and electron affinities of the carbon atoms in a state of non-integral hybridisation are found from curves constructed from available information for sp^3, sp^2, and sp states. The valence states of the carbon atoms (s-nature) are found from results on molecular structure with the aid of the relation derived by Coulson[19]. Subsequently by selecting the values of i which satisfy the experimental results about the number of non-bonded p-electrons (5) the s-nature of the halogen bonding orbitals was calculated. To determine the degree of hybridisation of the halogen orbitals in bromo(methyl)acetylene and iodo(methyl)acetylene [1-bromo- and 1-iodo-propyne], in which the electronegativity of the halogen is less than for carbon in the sp state, Eqn. (7) is used[16]:

$$U_p = (1 - s)[1 + i(1 + 2C)] \quad (7)$$

where C is a screening constant, 0.13 for bromine and 0.12 for iodine.

The calculated values of the s-nature of the halogen orbitals in various types of halogenohydrocarbons are given in Table 2, which shows that the bonding orbitals of chlorine are 19–26% hybridised, those of bromine 14–21%, and those of iodine 10–16%.

In the analysis of results on the interatomic distances it is noteworthy that in different types of halogenohydrocarbons the carbon atoms in different valence states have different covalent radii[14,15]. A significant part is also played by the change in the covalent nature of the halogen with change in the covalent radii of the carbon and halogen in one or another valence state depending on the ionicity of the bond. Conclusions about the degree of double-bond character can only be drawn from the lengths of the carbon–halogen bonds if all these factors are taken into account.

The covalent radii of carbon, as a function of the s-nature of its orbital (r_C^{cov}), and their change with the ionicity of the bond (Δr_C) are determined by the relations (8) and (9) derived earlier[15]:

$$r_C^{cov} = (0.854 - 0.328)\,\text{Å}, \quad (8)$$

$$\Delta r_C = 0.88\,|n_C - 1|\,\text{Å}, \quad (9)$$

where n_C is the number of localised electrons in the carbon orbital.

The variation of the covalent radius of chlorine with the s-nature of its bonding orbitals and its change with the ionicity of the bond are determined by starting from results for chlorotrifluoromethane and dichloromethane, in which the s-nature of the chlorine orbitals is the same (0.19) (see Table 2). By using the results on the s-nature of the carbon orbitals and the bond ionicity i in these halogenomethanes (Table 2), by use of Eqns. (8) and (9) the covalent radii $r_C^{*\delta}$ can be found, and subtraction of these from the interatomic distances gives the covalent radii of chlorine $r_{Cl}^{-\delta}$ for CF_3Cl and CH_2Cl_2 (Table 3). From the values of $r_{Cl}^{-\delta}$ and i for these molecules can be found the covalent radius of chlorine for its hybridisation (0.934 Å) and ΔrCl, Eqn. (10), and then by bearing in mind that for the chlorine molecule the s-character is 0.01 and r_{Cl}^{cov} = 0.994 Å, the relation between the covalent radius of chlorine and the degree of hybridisation of its orbital, (11), can be found:

$$\Delta r_{Cl} = 1.30\,|n_{Cl} - 1|\,\text{Å}, \quad (10)$$

$$r_{Cl}^{cov} = (0.997 - 0.33\,s)\,\text{Å}. \quad (11)$$

[There is no Eqn. (12) in this paper (Ed. of Translation)].

Table 3.

Compound	r_C^{δ}	r_{Hal}^{δ}	d (C–Hal) calc.	d (C–Hal) published results
CH_3Cl	0.650	1.126	1.776	1.7810[22]
CF_3Cl	0.658	1.090	1.748	1.748[23]
CH_2Cl_2	0.656	1.116	1.772	1.7724[24]
C_6H_5Cl	0.631	1.080	1.711	1.712[25]
$CH{\equiv}CCl$	0.646	0.983	1.629	1.632[27]
$CH_2{=}CHCl$	0.639	1.096	1.735	1.726[28] 1.736±0.01[29]
	0.633	1.083	1.716	1.728[30]
	0.638	1.100	1.738	1.724[30]
	0.647	1.090	1.737	1.726[31]
CH_3Br	0.691	1.248	1.939	1.939[32]
CF_3Br	0.702	1.202	1.904	1.919[33]
C_6H_5Br	0.683	1.186	1.869	1.867[34]
$CH_2C{\equiv}CBr$	0.699	1.094	1.793	1.793[14]
$CH_2{=}CHBr$	0.675	1.195	1.870	1.853[35] 1.891[20]
CH_3I	0.737	1.402	2.139	2.139[36]
$CH_3C{\equiv}CI$	0.752	1.239	1.991	1.991[24]
$CH_2{=}CHI$	0.727	1.343	2.070	2.089[20]

The calculated lengths in CH_3Cl, chlorobenzene, and chloroacetylene, obtained with Eqns. (8)–(11) and the data of Table 2, agree well with experimental values (Table 3). The calculated length of the C–Cl bond in vinyl chloride differs from some of the experimental results[28] but agrees with others[20]; the differences between the calculated and experimental lengths of the C–Cl bond for 1-chloropropene, *cis*-1,2-dichloroethylene, and *cis*-2-chloro-1-fluoroethylene vary between +0.01 and −0.01 Å, attributable to the uncertainty in the structural parameters of these molecules.

The dependence of the covalent radius of bromine on the s-character of its orbitals, Eqn. (13), and the change in the orbital radius with the number of electrons localised on it, Eqn. (14) were calculated from results on CH_3Br, bromo(methyl)acetylene [1-bromopropyne] (with equal s-character of the halogen orbitals), and Br_2.

$$r_{Br}^{cov} = (1.144 - 0.23\,s)\,\text{Å}, \quad (13)$$

$$\Delta r_{Br} = 1.28 \cdot |n_{Br} - 1|\,\text{Å}. \quad (14)$$

The length of the C–Br bond in bromobenzene was calculated with the aid of Eqns. (8), (9), (13), and (14) and the data of Table 2, and differed from the experimental value by 0.002 Å. For CF_3Br the difference was 0.015 Å, which shows that the C–F bonds in this compound are of the "banana" type. The calculated value of the length of the C–Br bond in bromoethylene differs from the

experimental values (which show considerable variation) obtained from microwave spectra (1.853 and 1.891 Å).

The following relations for r_I^{cov}, Eqn. (15), and Δr_I Eqn. (16), were found from the results for CH_3I, iodomethyl)acetylene, and I_2.

$$r_I^{cov} = (1.342 - 0.15\,s)\,\text{Å}, \quad (15)$$

$$\Delta r_I = 1.25\,|n_l - 1|\,\text{Å}. \quad (16)$$

Starting from the parameters of the molecular structure adopted in work on iodoethylene [36] ($\angle C_2C_1I = 122.4°$, $\angle C_2C_1H = 120°$), the calculated length of the C–I bond is 0.019 Å shorter than that found. It is noteworthy that to calculate the length of the C–Hal bond in halogenoethylenes it is necessary to know $\angle C_2C_1H$, which was taken as 120° in work on bromoethylene and iodoethylene, The agreement of the calculated lengths of the C–I bond in iodoethylene with published data is obtained if $\angle C_2C_1H = 124°$.

Correlation equations (10) and (11) were derived from results for molecules (CF_3Cl and CH_2Cl_2) in which the mesomeric effect for chlorine should not appear. In chlorobenzene and chloroacetylene, where a mesomeric effect is theoretically possible the C–Cl interatomic distances would not obey Eqns. (10) and (11), should this effect appear, and the departure of the calculated values of the C–Cl bond lengths from the experimental ones would serve as a measure of the mesomeric effect of chlorine in aromatic and acetylene compounds.

At 5% double-bond character the length of the C–Cl bond in chlorobenzene would be shorter than that calculated by 0.021 Å, as follows from Eqn. (17):[12]

$$R = R_1 - (R_1 - R_2)\frac{3x}{2x+1}, \quad (17)$$

where R is the interatomic distance in a bond of intermediate type, R_1 the length of an ordinary bond, R_2 the length of a double bond, and x the degree of double-bond nature.

Actually the difference between the calculated and experimental lengths of the C–Cl bond in chlorobenzene is 0.001 Å.

Correlations establishing a relation between interatomic distances in carbon–halogen bonds and the hybridisation of the orbitals of the carbon and halogen atoms serves as proof of either the absence of a mesomeric effect for the halogen atoms or of its appearance to such a slight extent that it does not have any appreciable effect on the lengths of the carbon–halogen bonds.

6. NUCLEAR QUADRUPOLE RESONANCE

A most important and independent criterion of the ability of halogen atoms to show a mesomeric effect is provided by results on the nuclear quadrupole interaction, obtainable with the aid of microwave spectroscopy.

According to Goldstein and Bragg [37,38], a measure of the influence of the mesomeric effect in vinyl halides is provided by the asymmetry parameter, given by the expression:

$$\eta = \frac{\chi_{xx} - \chi_{yy}}{\chi_{zz}} \quad (18)$$

where χ_{xx}, χ_{yy}, and χ_{zz} are the quadrupole interaction constants along the corresponding coordinate axes x, y, and z, with χ_{zz} (eQq_{mol}) being the quadrupole coupling constant along the carbon–halogen bond. The degree of double-bond character of the carbon–halogen bond is determined by the quantity:

$$\delta = \frac{\eta \cdot eQq_{mol}}{^3/_2 eQq_{atom.}}, \quad (19)$$

and the percentage double-bond character = $100\,x\,\delta$.

The degree of double bond character has been calculated for various vinyl halides: 4–6% in vinyl chloride [28,38,39], 4% in *cis*-1,2-dichloroethylene [31], 4% in vinyl bromide [35], and 3% in vinyl iodide [36,39,40]. In evaluating the asymmetry parameter in the vinyl halides which are molecules of the asymmetric tap type, in which the principal axis of inertia does not lie along the direction of the carbon–halogen bond, a series of assumptions are made concerned with the impossibility of transforming the quadrupole interaction constants relative to the principal axes of the molecule a, b, and c into the new axes x, y, and z. In addition the values of the bond constants are very sensitive in relation to assumed parameters. Thus the experimental results are not inconsistent with the presence in vinyl chloride of only 2% double-bond character [28]. The difficulties in the calculation of χ_{xx} and χ_{zz} are due in particular to the insufficiently precise data about the molecular structure of the vinyl halides obtainable by electron diffraction.

The available information about the NQR in the halogen derivatives of benzene relates (except for bromobenzene) to the solid state. The quadrupole effects observed in these compounds, although distorted by the influence of the crystal field, show a very low degree of double-bond character in the carbon–halogen bond. Thus, in *p*-dichlorobenzene the double-bond character is 2.7 ± 0.7%, in *p*-chlorobenzyl chloride 2.4 ± 0.7%, in *p*-chloroaniline 2.0 ± 1%, [41] and in iodo-substituted benzenes the degree of double-bond character amounts to 1.6–2.8% (*m*-iodonitrobenzene 1.6%, *p*-iodoaniline 1.6%, *p*-di-iodobenzene 2.1%, 4-iodobenzoic acid 2.1%, 3-iodobenzoic acid 2.7%, *p*-iodonitrobenzene 2.8%) [42]. To obtain more reliable information about the degree of double-bond character of C_{sp^2}–halogen, Rosenthal and Dailey [33] made a fundamental investigation of the quadrupole effects in *gaseous* bromobenzene, in which (unlike the halogenoethylenes) the principal axis of inertia coincides with the direction of the carbon–halogen bond. It appeared that the quadrupole constants in the isotopic modification $C_6H_5{}^{79}Br$ agree with 1–2% double-bond character in the C–Br bond, and in the isotopic modification $C_6H_5{}^{81}Br$ there is no double-bond character, within the limits of accuracy of the measurements. The authors concluded that the explanation for the peculiarities of the C–Br bond in aromatic compounds in terms of the conjugation theory is implausible.

Hence modern results on the NQR spectra show either the complete absence of mesomeric effect for halogen atoms, or its appearance to such a slight extent that its influence should hardly be reflected in the physical parameters of the carbon–halogen bond and in the chemical properties of halogen-containing organic compounds.

7. NUCLEAR MAGNETIC RESONANCE AND CORRELATION OF THE CHEMICAL SHIFTS WITH THE σ-CONSTANTS OF THE SUBSTITUENTS

A discussion of the electronic structure of molecules often is based on a joint examination of NQR spectroscopic and chemical results and is greatly subject to the establishment and analysis of correlations between the ^{13}C, ^{1}H, and ^{19}F chemical shifts and the σ-constants of the substituents. This is quite regular, since the system of

inductive and mesomeric effects of the substituents, including halogen atoms, was developed on the basis of an examination of chemical properties. The dissociation constants of halogen-substituted phenylboric and benzoic acids, phenol, and aniline were the experimental material which stimulated Ingold to examine the problem of the relative intensity of the mesomeric effect at the halogens. As follows from the positive values of the substituent constants [43,44], the replacement of hydrogen in any position of the benzene ring hy a halogen atom leads to an increase in the strength of the substituted acid, but not in the same order as would be expected on the basis of the relative electronegativities of the halogen atoms. To explain the experimental facts required not only that the halogens have the ability to show a mesomeric effect but also their arrangement according to decreasing mesomeric effect in the same order (F > Cl > Br > I) as would give a fluorine atom attached to an aromatic system the least electronegativity and an iodine atom the greatest.

If the concepts of the quantitative theory of the reactivity of organic compounds are followed and the σ-constant of a substituent is regarded as the sum of inductive and mesomeric constituents ($\sigma = \sigma_I + \sigma_R$), the mesomeric influence of halogen atoms on the strength of, for example, *p*-halogenobenzoic acids is very pronounced. Thus in *p*-fluorobenzoic acid the aliphatic constant of the substituent (σ_I), which is 0.52, is reduced to 0.48, and in *p*-chloro-, *p*-bromo-, and *p*-iodo-benzoic acids the aliphatic constants of the substituents (0.47, 0.45, and 0.38) are reduced to 0.24, 0.22, and 0.10 respectively. Hence the mesomeric effect, if it appears in the aromatic system, reduces the aliphatic constant of the substituent by 30–90%.

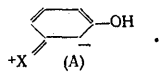
Table 4. Chemical shifts of ^{13}C in monosubstituted benzenes (in magnetic units in relation to benzene).

Substituent	C–X	*ortho-*	*meta-*	*para-*
F	—35.1	14.3	—0.9	4.4
Cl	—6.4	—0.16	—1.0	2.0
Br	5.4	—3.3	—2.2	1.0
I	32.3	—9.9	—2.6	0.4
CH_3	—9.1	—0.3	—0.3	2.8
OCH_3	—30.2	14.7	—0.9	8.1
NH_2	—19.2	12.4	—1.3	9.5
$N(CH_3)_2$	—22.4	15.7	—0.8	11.5
CHO	—9.0	—1.2	—1.2	—6.0
NO_2	—19.6	5.3	—0.8	—6.0
$COCH_3$	—9.3	—0.2	—0.2	—4.2

Let us examine to what extent the information about the distribution of electronic density in substituted benzenes based on the chemical properties reflects the electronic structure of the molecules in their ground state, by comparing the chemical results with those on the magnetic resonance of ^{13}C, ^{1}H, and ^{19}F nuclei, and also let us attempt to discover certain features of the effect of the substituent (halogens and alkyl groups) on their introduction into unsaturated and aromatic systems.

As Table 4 shows, the ^{13}C chemical shifts in the meta-position in all the monosubstituted benzenes investigated are found at weaker fields relative to benzene, and with the halogens the screening decreases steadily from fluorine to iodine [45].

The chemical shifts of ^{13}C in the para-position for all the substituents without multiple bonds, including halogens and CH_3, are located at higher fields. Among the halogens the strongest screening effect is exerted by fluorine, the least by iodine. The methyl group has less influence than fluorine on the chemical shift, but more than chlorine, bromine, and iodine. In the theory of electronic displacements it is assumed that the inductive effect of the substituents is transmitted along the aromatic system of bonds to the same extent in both the meta- and the para-positions but the mesomeric effect of the substituent appears only in the ortho- and para-positions. If the relative electron densities at the carbon atoms in the meta-position were determined solely by the inductive effect then their screening under the influence of the halogens should be reduced from iodine to fluorine and not in the opposite direction, as is actually observed; under the influence of the methyl group (which is regarded theoretically as electron-repulsive) the electron density at the meta-carbon atom should be increased: in reality it is decreased in comparison with benzene. The same contradiction arose in the theory of the reactivity of organic compounds when explaining the relative strength of the *m*-halogeno-substituted benzoic acids with the aid of the inductive effect. Since, according to the theory of mesomerism the mesomeric effect can be transmitted to the reaction centre solely from the para- and ortho-position, the strength of the *m*-halogenobenzoic acids should be determined by *I*, the inductive effect of the substituent and their acidity should increase steadily from *m*-iodobenzoic to *m*-fluorobenzoic acid as occurs in the series of halogenoacetic acids. However, *m*-fluorobenzoic acid ($\sigma_m = 0.34$) is weaker than *m*-chlorobenzoic acid ($\sigma_m = 0.37$) and the latter is weaker than *m*-bromobenzoic acid ($\sigma_m = 0.39$) (see Table 5). The same sequence in the degree of dissociation is observed in the series of *m*-halogenophenols. To explain this phenomenon it was suggested [46] that the halogens (and also other similar substituents) in the meta-position bring about a mesomeric shift of π-electrons into the other-position, from which they are transmitted to the reaction centre by an *induction mechanism* as is shown by the following resonance structure (A):



(A)

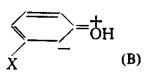
Table 5. Values of the constants δ_m, δ_m^0, δ_R^m, δ_p, δ_p^0, δ_R^0, and δ_I for the substituents.

Substituents	δ_m after Brown and Danielo	δ_p after Taft	δ_R^m	δ_p after Brown and Danielo	δ_p^0	δ_R^0	δ_I
F	0.34	0.35	—0.17	0.06	0.17	—0.35	0.52
Cl	0.37	0.37	—0.10	0.23	0.27	—0.20	0.47
Br	0.39	0.38	—0.07	0.23	0.26	—0.19	0.45
I	0.35	0.35	—0.03	0.28	0.27	—0.11	0.38
CH_3	—0.07	—0.07	—0.02	—0.17	—0.15	—0.10	—0.05
OCH_3	0.12	0.13	—0.12	—0.27	—0.12	—0.37	0.25
NH_2	—0.16	—0.14	—0.24	—0.66	—0.38	—0.48	0.10
$N(CH_3)_2$	—0.21	—0.15	—0.25	—0.83	—0.44	—0.54	0.10
CHO	0.36	—	—	0.22	—	—	—
NO_2	0.71	0.70	0.07	0.78	0.82	0.19	0.63
$COCH_3$	0.38	0.34	0.06	0.50	0.46	0.18	0.28

The displacement of π-electrons towards the reaction centre by this mechanism should proceed to such an extent that the usual series of relative electronegativity of the

halogens (F > Cl > Br > I) is reversed (F < Cl < Br < I). From the energetic point of view the assumption about the displacement of negative charge from the ortho-carbon in structure (A) to the electronegative (oxygen) and not to the electropositive centre ($X^+=$) is quite unfounded.

In connection with the problem, already discussed, of the delocalisation of π-electrons within the framework of the localised pairs method, mention must be made of the effect of resonance structure (B):



(B)

with an additional stabilising localisation of charge at the ortho-carbon.

On the basis of a procedure of partitioning the substituent constants into inductive and mesomeric constituents, Taft and Lewis quantitatively estimated the capability of meta-substituents to show a mesomeric effect (σ_R^m), by assuming that it is one-third [47] or one-half [48] the mesomeric effect of the substituents in the para-position (σ_R^0). Actually, however, the ratio σ_R^m/σ_R^0 is not constant and varies (Table 5) from 0.2 (for CH_3) to 0.5 (F, Cl, and other substituents). It is still not clear why even in a series of monotypical substituents (halogens) the transmission of the *m*-effect from the meta-position takes place with different intensity (for example, for Cl $\sigma_R^m/\sigma_R^0 = 0.5$ and for iodine $\sigma_R^m/\sigma_R^0 = 0.3$).

Since in a correlation analysis it is assumed that the σ-constants of the substituents are proportional to the charges induced by the substituents in the meta- or para-positions of the benzene ring, correlation between the σ-constants and ^{13}C chemical shifts should be expected. A comparison of the $m^{13}C$ chemical shifts with the σ_m^0-constants (Fig. 1) shows, however, the absence of a linear relation between these two parameters; for CH_3, NH_2, and $N(CH_3)_2$ there is not a correspondence, even in sign.

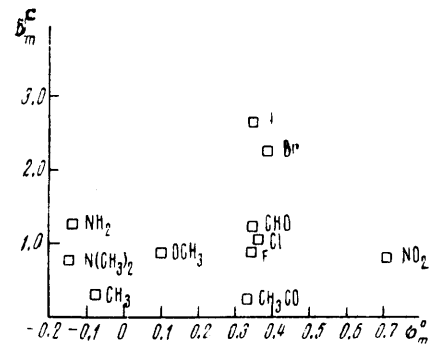


Figure 1. Comparison of the chemical shifts of m-^{13}C and the constant σ_m^0.

Judging from the values of the σ-constants of the substituents the electronic charge on the meta-carbon atoms in fluorobenzene and iodobenzene should be the same, whereas according to the NMR spectra the meta-carbon atom in iodobenzene is much less screened than that in fluorobenzene; *m*-chlorobenzoic acid is stronger than *m*-iodobenzoic acid, furthermore according to the results on the ^{13}C chemical shift *m*-chlorobenzoic acid should be weaker than *m*-iodobenzoic.

Bystrov [43] (see Chapter 1, section 7) attempted to find a correlation between the m-^{13}C chemical shifts and the inductive (σ_I) and mesomeric constants of the substituents (σ_R^m), and proposed the following equation:

$$\delta_m^C = -1.7\sigma_I + 0.82\sigma_R^m - 0.4. \quad (20)$$

Eqn. (20) is not used for halogen atoms. Actually, the experimental results show a monotonic decrease in the screening of m-^{13}C on going from fluorobenzene to iodobenzene, and according to Eqn. (20) the screening decreases in the reverse direction, from iodobenzene to fluorobenzene (the values calculated for F, Cl, Br, and I were respectively 1.57, 1.36, 1.32, and 1.14).

Table 6. ^{19}F chemical shifts in monosubstituted benzenes (in magnetic units in relation to fluorobenzene).

Substituent	*meta*-	*para*-	Substituent	*meta*-	*para*-
F	—3.03	6.80	NH_2	0.50	14.40
Cl	—2.00	3.20	$N(CH_3)_2$	—0.08	15.90
Br	—2.30	2.60	CHO	—1.30	—9.15
I	—2.40	1.70	NO_2	—3.43	—9.20
CH_3	1.23	5.40	$COCH_3$	—0.60	—6.10
OCH_3	—0.98	11.70			

We will compare the chemical shifts of m-^{13}C in halogenobenzenes with the chemical shifts of ^{19}F in *m*-halogenofluorobenzenes and consider the correlation between the ^{19}F chemical shifts in the latter compounds with the σ-constants of the halogens. As Table 6 shows, the ^{19}F chemical shifts in *meta*-fluoro-substituted halogenobenzenes are located in a weak field in relation to fluorobenzene and the least screening to the ^{19}F nucleus is in *meta*-difluorobenzene and then in order of screening follow I, Br, and Cl. Since the m-^{13}C chemical shifts in the halogenobenzenes alter monotonically from F to Cl the correlation between the screening of the ^{13}C nucleus and the ^{19}F chemical shifts is not expected.

Gutowsky and coworkers [49] attempted to find the relation between the ^{19}F chemical shifts in *meta*-substituted fluorobenzenes and the Hammett σm-constants. The correlation they proposed is:

$$\delta_m^F = -5.92\sigma_m \quad (21)$$

which, in general, is badly observed—for example, for ethyl *m*-fluorobenzoate the experimental value of σ_m^F is 2.19 m.u. (magnetic units), and the calculated value is 0.15 m.u.—particularly for the halogeno-substituted compounds. Thus the ^{19}F chemical shifts in *m*-difluorobenzene and *m*-fluoroiodobenzene are at lower fields than those in the chloro- and bromo-substituted compounds, yet according to Eqn. (21) they should be found at strong fields.

Taft [47] examined the linear relation between the ^{19}F chemical shifts in meta-substituted fluorobenzenes and the inductive constants (σ_I), expressing it by the equation:

$$\delta_m^F = -7.1\sigma_I + 0.6. \quad (22)$$

However, correlation (22) cannot be regarded as satisfactory. For various substituents there are considerable departures of the calculated values of the ^{19}F chemical shift from the experimental ones, for example, for the $CO_2C_2H_5$ group the calculated δ_m^F is −1.53 m.u. and the experimental is −0.15 m.u., for NH_2 and C_6H_5 the calculated values of δ_m^F (−0.10 and −0.10) differ from the experimental ones (respectively 0.50 m.u. and 0.15 m.u.) even in sign. The absence of a linear relation between δ_m^F and σ_I for halogens is shown in Fig. 2.

However, the problems of the accuracy with which Eqns. (21) and (22) are obeyed does not exist in considering the problem of the effect of the substituent on the electronic density at the meta-carbon atom in the compounds used for measuring the constants of the substituents, since, as Fig. 3 shows, there is no correlation between the ^{13}C and ^{19}F chemical shifts. The absence of a correlation between the m-^{13}C chemical shifts in the monosubstituted benzenes and the ^{19}F chemical shifts in the meta-substituted fluorobenzenes is not unexpected. When such a strongly electronegative atom as fluorine is introduced into the meta-position a considerable non-additive redistribution of the electron densities can take place.

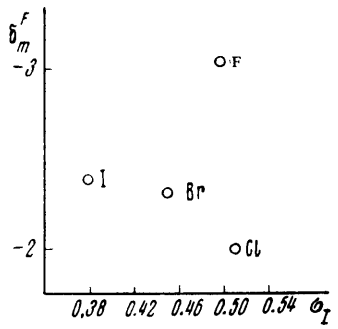


Figure 2. Comparison of the ^{19}F chemical shifts in m-halogeno-substituted fluorobenzenes with the σ_I constants.

In examining the effect of substituents on the screening of a para-carbon atom in monosubstituted benzene we must return to Table 4, from which clearly all the halogens—and also the CH_3, OCH_3, NH_2, and $N(CH_3)_2$ groups—increases the electron density at the para-carbon, and the effect decreases in the order F > Cl > Br > I.

A comparison of the p-^{13}C chemical shifts in the monosubstituted benzenes with ^{19}F chemical shifts in the para-substituted fluorobenzenes enables a correlation to be found between these two parameters, expressed by Eqn. (23):

$$\delta_p^C = 1.52\delta_p^C, \quad \delta_p^C = 0.66\delta_p^F. \tag{23}$$

Although Eqn. (23) is obeyed for certain substituents (Br, I, CH_3) with moderate accuracy, it allows the degree of screening of p-^{13}C to be evaluated for those monosubstituted benzenes for which there are no experimental results on p-^{13}C chemical shifts.

There is also a correlation between the proton chemical shifts [45,51] and the ^{13}C chemical shifts [45] that can be expressed by Eqn. (24), which is satisfied for most groups:

$$\delta_p^C = 17.3\,\delta_p^H + 0.5, \tag{24}$$

where δ_p^H is the chemical shift of para-protons in m.u.

The question naturally arises as to the correspondence between the p-^{13}C chemical shifts in the monosubstituted benzenes or the ^{19}F chemical shifts in para-substituted fluorobenzenes (since there is a correlation between these two parameters) and the σ-constants of the substituents.

Gutowsky and coworkers [49] proposed the correlation equation:

$$\delta_p^F = -17.9\sigma_p + 4.84, \tag{25}$$

which expresses the relation between the ^{19}F chemical shifts and the σ_p Hammett constants, which for most substituents is not obeyed. Taft and coworkers, having proposed various versions [51-53] of equations relating the ^{19}F with the constants of the substituents, finally settled on Eqn. (26):[54]

$$\delta_p^F = -29.5\sigma_R^0 - 7.1\sigma_I + 0.6 \tag{26}$$

in which σ_I is an inductive constant, σ_R^0 a mesomeric constituent of the σ^0 constant of the substituent.

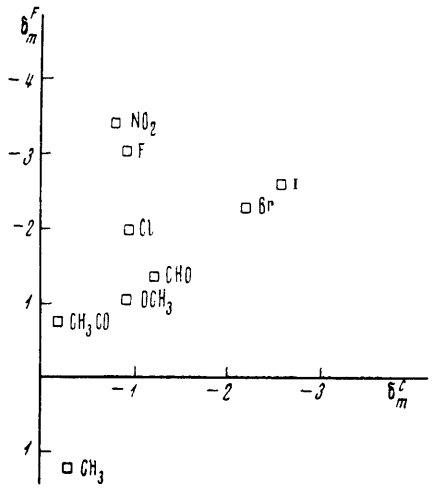
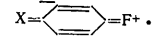


Figure 3. Comparison of the chemical shifts ^{13}C and ^{19}F of *meta*-substituted fluorobenzenes.

Hence, according to Taft, the relation between the contributions of the mesomeric and inductive effects for the reactivity of para-substituted compounds is determined by the ratio σ_R^0/σ_I, since—according to Eqn. (26)—the contributions of the mesomeric and inductive effects in the electron density of the para-carbon atom in monosubstituted benzenes is determined by the ratio $4\sigma_R^0/\sigma_I$. It is quite unknown why the influence of the mesomeric effect of the substituent in para-substituted fluorobenzene is four times its influence in para-substituted phenylacetic acids (from the dissociation constants of which the values of σ^0 are derived). On the contrary, it would appear that the introduction of a fluorine atom instead of the $-CH_2COOH$ group should (since according to the mesomerism–resonance theory the fluorine atom exhibits a large +M effect) suppress the mesomeric effect of halogen atoms in the para-position:



It must be pointed out that Eqn. (26) is satisfied by only certain substituents, and for many others there are considerable discrepancies between the calculated and experimental ^{19}F chemical shifts, for example, for Br, I, CH_3, OCF_3, CF_3, SCH_3, CN, and CH=O.

As the above shows, in the mesomeric–resonance interpretation of results on the NMR-spectroscopy of halogen-containing compounds the mesomeric effect of the halogen atoms plays an even greater part than in the treatment of acid–base equilibria.

The discrepancy between the results from ^{13}C NMR spectroscopy, which shows increased electron density at the *p*-carbon atom of halogenobenzenes, with the σ_p constants of the halogens, which indicate a decreased electron density at the carbon, linked with the reaction centre, can be attributed to various causes.

One of these could be the change in the electron density distribution of the halogenobenzene as a result of the introduction of reactive groups (OH, COOH, CH_2COOH) into its para-position, so that the halogen will show less screening of the *p*-carbon atom.

Another reason for the non-correspondence between the ^{13}C (or ^{19}F) chemical shifts and the σ_p-constants of the substituents, derivable from acid–base equilibria, could be the influence of diverse solvation processes. The role of the solvent in acid–base equilibria appears clearly in the change in the σ-constants of various substituents, especially tendency towards the formation of hydrogen bonds with water or alcohols, such as OH or NH_2. The variations in the values of the σ-constants of, for example, the OH group in *m*- and *p*-hydroxybenzoic acids with the nature of the solvent is very great and there is even a reversal of sign for the σ_m constant [55]. A considerable solvent effect on the value of the σ′-constant of bromine is observed in 4-bromocyclo[2,2,2]octane-1-carboxylic acid and the σ′-constant in this series changes particularly sharply for the $N(CH_3)_3^+$ group [56].

The σ-constants of the halogens in halogenophenols and halogenbenzoic acids change considerably on going from aqueous [57] to alcoholic solutions [58]. Thus in aqueous solution *m*-chlorophenol is less dissociated than *m*-bromo- and *m*-iodo-phenols, whereas in 50% aqueous ethanol *m*-chlorophenol is the strongest acid of these three substituted phenols. *m*-Fluorobenzoic acid is weaker than the other halogenobenzoic acids in aqueous solution but in 50% aqueous ethanol it is equal in strength to *m*-iodobenzoic acid, dissociates somewhat better than *m*-chlorobenzoic acid, and much more than *m*-bromobenzoic acid.

In aqueous solution *p*-fluorobenzoic acid ($\sigma = 0.06$) is considerably weaker than the other *p*-halogenobenzoic acids ($\sigma = 0.23–0.27$), whereas in 50% ethanol it does not differ so markedly from them ($\sigma_F = 0.20$, $\sigma_{Cl,Br,I} = 0.24–0.26$).

There are many similar examples of the pronounced differentiating effect of the solvent on relative changes in the values of the σ-constants of the substituents (for example, see Bykova and Petrova [59]).

PMR spectra are very convenient for the quantitative estimation of the influence of the solvent on the change in the electronic structure of a molecule. Diehl [60], who investigated the chemical shifts of ring protons in meta- and para-disubstituted benzenes in various solvents (hexane, acetone, benzene) found the additive nature of the effect of the substituents to be expressed as follows:

$$L_{\alpha,total} = \sum L'_{\alpha} + L_{H,\alpha}, \qquad (27)$$

where $L_{\alpha,\text{total}}$ is the total effect of the solvent α, L'_{α} the effect of the solvent α on the chemical shifts of the ortho-, meta-, and para-protons, and $L_{H,\alpha}$ the effect of the solvent on the chemical shifts of the protons of unsubstituted benzene.

By using the values found experimentally for L_H for acetone (-13×10^{-2} m.u. for a 5% molar solution in acetone) $L'_{o,x}$, $L'_{m,x}$, and $L'_{p,x}$ (listed in Table 7) the chemical shifts of the protons in monosubstituted benzenes can be found and then the changes in the electronic structure of the molecules in given solvent estimated.

The following diagrams show the chemical shifts of the protons in chlorobenzene, bromobenzene, toluene, and anisole in hexane and acetone solutions [61]:

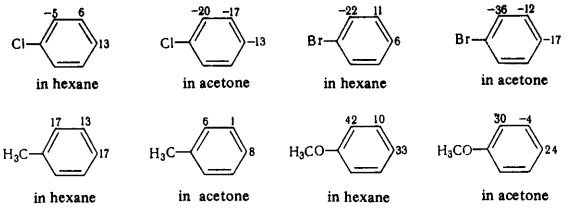


Table 7. Values of the increments L' in acetone solution (in 10^{-2} magnetic units in relation to benzene).

Substituent	L'_o	L'_m	L'_p
NH_2	−5	10	
OH	2	3	
OCH_3	1	−1	4
F	−5	−7	
CH_3	2	1	4
Cl	−2	−10	−13
Br	−1	−10	−10
I	0	−9	
CN	−9	−10	
NO_2	11	−13	

Clearly, with a polar solvent (acetone), the screening of the para-protons, and consequently also p-^{13}C, varies considerably. Nevertheless, as in hexane solution, the para-protons in the halogenobenzenes are screened to a greater extent than in the benzene molecule but in acetone solution they are less screened.

In acetone solution the screening of the para-protons of toluene and anisole is also reduced but nevertheless it remains greater than in benzene.

Since the polarity of water is greater than that of acetone, a change in the same order in the electron distribution in substituted benzenes also takes place in aqueous solutions. At the para-carbon atoms of the halogen-substituted compounds the charge decreases to the same extent as the electron-accepting properties of the XC_6H_4 radicals—it surpasses the electronegativity of phenyl and the *p*-halogenobenzoic acids are stronger than benzoic; the electron-accepting property of the para-tolyl and para-anisyl radicals remains less than that of the phenyl in water, as a result of which *p*-tolyl and *p*-methoxybenzoic acid are weaker than benzoic acid. Since the degree of solvation of a molecule depends both on the nature of the substituent and the type of reaction centre, the constants of the substituents do not remain constant even in a single solvent, which also explains the existence of different scales of substituents.

Let us return to a consideration of the quantum-chemical approaches to the solution of the problem of the screening of the nuclei of atoms. Karplus and Das [62] derived, on the basis of Hartree–Fock molecular wave functions, the complex relation between the ^{19}F screening in aromatic molecules and the ionic character, the order of the fluorine–carbon bond, and the hybridisation of the fluorine atom being considered. To simplify further

calculations the change in the hybridisation of the bonding orbitals of fluorine was not considered. As a result of a series of assumptions the following expression was derived for the ^{19}F chemical shifts in difluorobenzene:

$$\Delta\delta^F(\text{m.u.}) = (\delta^F - \delta^F_{\text{fluorobenzene}}) \times 10^6 = 777\,\Delta\rho - 765\,\Delta I \qquad (28)$$

where $\Delta\rho$ is the difference between the orders of the C–F π-bonds in difluorobenzene and fluorobenzene, and ΔI the difference between the polarities of the C–F sigma bond.

It was not possible to calculate the ^{19}F chemical shift in difluorobenzene from Eqn. (28) owing to the uncertainty in the values of ΔI. From the experimental results on the screening of ^{19}F in the difluorobenzenes and the calculated values of $\Delta\rho$, values of ΔI can be calculated by Eqn. (28). It appears that the contribution to the screening of ^{19}F from the mesomeric effect of fluorine is ~ 80% of the total influence of the fluorine atom found in the para-position to another fluorine atom. ΔI for *o*-difluorobenzene is negative ($\Delta I = -0.0246$), which shows that the polarity of the C–F bond is not increased when fluorine is introduced into the ortho-position of fluorobenzene; it decreases, and 75% of the total contribution to the ^{19}F screening comes from the fraction of this incomprehensively reversed inductive effect.

In the work mentioned the order of the fluorine–carbon bonds was calculated in parametric form by the molecular orbital method using the Hückel approximation (LCAO MO). It must be borne in mind that it does not follow from the approximate quantum-chemical calculations that delocalisation of the unshared pairs of electrons of the heteroatom of the substituent actually occurs; this is postulated from general considerations. The exchange interaction of an unshared pair with the π-electronic system of the aromatic ring can occur theoretically to a certain extent but it cannot exist at all if this is energetically unfavourable. In the MO method the calculation of the orders of the carbon–element bonds (the degree of double-bond character) is based on the use of parameters (estimated relative values of the coulombic and resonance integrals), arbitrarily chosen in such a way that the results of the calculations show the maximal agreement with the predictions of the resonance–mesomerism theory. The parameters for the halogen atoms are chosen in such a way that the degree of double-bond character of the carbon–halogen bond increases from iodine to fluorine, that is, so that the mesomeric effect of the halogens decreases in the order F > Cl > Br > I.

It is quite significant that in the same paper Karplus and Das compare the ^{19}F chemical shifts with the constants of the quadrupole interaction in substituted chloro- and bromo-benzenes. On the basis of the available experimental results on the asymmetry parameters for chlorobenzene ("which correspond to ~ 3% double bond nature in the C–Cl bond"), they arrived at "the important conclusion that the contribution of double-bond character to the value of $\Delta\delta$ in fluorobenzenes is significant, whereas the agreement in the values of Δq (the difference in the quadrupole interaction constants) can be reached without allowing for double-bond character in chloro- and bromo-benzenes".

In analysing the Ramsey equation for the ^{19}F screening constants with the aid of Hartree–Fock wave functions, making various assumptions about the bond parameters, Prosser and Goodman [63] derived a relation which took into account quantitatively the effect on the screening constant of the charge density of the π-electrons at the fluorine atom, the C–F bond, and the carbon atom connected with the atom being considered. The effect of the polarisation of the C–F sigma bond, that is, the influence of the inductive effect was not considered in this approximation, and the changes in the screening of the ^{19}F nuclei are explained solely by the polarisation of the π-electron cloud due to the mesomeric effect of the substituent.

According to Wu and Dailey [64] the ^{19}F chemical shift in fluorobenzene derivatives is determined by the equation:

$$\Delta\delta^F(\text{m.u.}) = \delta^F - \delta^F_{\text{fluorobenzene}} \cdot 10^6 \simeq 627\,\Delta\rho - 155.1\,\Delta P_{CF} + 574.9\,\Delta\lambda_F \qquad (29)$$

where $\Delta\rho$, ΔP_{CF}, and $\Delta\lambda_F$ denote respectively the changes in the π-electron density at the fluorine atom, the order of the C–F π-bond, and the polarity of the C–F σ-bond in the substituted fluorobenzene compared with fluorobenzene itself. The values of $\Delta\rho$ and ΔP_{CF} were calculated in that investigation by the molecular orbitals method again. The ^{19}F chemical shifts cannot be calculated by Eqn. (29), since values of $\Delta\lambda_F$ are unknown. The latter parameter was found from Eqn. (29) by use of experimental results on ^{19}F chemical shifts. As the positive values of $\Delta\lambda_F$ show, when an electron-withdrawing substituent is introduced into fluorobenzene a decrease in the polarity of the C–F σ-bond does not occur, as should happen under the inductive influence of the substituent. There is an increase in the polarity, that is, the effect of the substituent on the polarisation of the C–F bond is a mesomeric mechanism. In other words, according to Eqn. (29) the screening of ^{19}F is due solely to the mesomeric effect of the substituent (halogens, NH_2, OCH_3, CH_3).

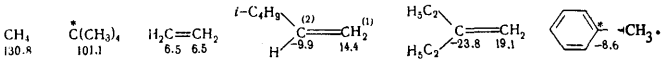
A theoretical discussion of the ^{13}C chemical shifts in substituted benzenes leads to an examination of the influence of the π-electron density and free valency at the given carbon atom, that is, with allowance solely for the mesomeric effect of the substituent [64,65].

Clearly, in the theoretical studies it is assumed that the only or the main factor which determines the screening of ^{19}F and ^{13}C in substituted benzenes is the mesomeric effect of the substituent. On the basis of what has been stated in the section on nuclear quadrupole interaction it follows that at least as regards the halogen-substituted benzenes the approach to the problem of screening in the π-electron approximation is invalid. There are evidently other factors which affect the distribution of electron density in the substituted unsaturated and aromatic systems.

We think that in examining this problem the transmission of the inductive effect of the substituent in them merits special attention. In discussing this problem the homologues of ethylene and toluene must be considered first. These are convenient models in two respects. Firstly, owing to the low polarisation of the alkyl–C bond the effect of the field in these molecules is insignificant and secondly here the influence of the mesomeric effect is excluded, since alkyl groups do not possess it [66–68].

Alkyl groups must be regarded as electron-donating substituents in comparison with hydrogen. This opinion is based on results on the relative strength of aliphatic acids, the dissociation constants of which are affected by the solvation processes. In the ground state of a molecule methyl and other alkyl groups exert an electron-withdrawing action, as should logically follow from the high electronegativity of the carbon atom compared with hydrogen and as appears from the results on magnetic resonance at ^{13}C nuclei. Thus the replacement of the hydrogen atoms in methane by methyl groups leads to a successive decrease in the screening of the central carbon [69], the introduction of alkyl radicals into the ethylene molecule causes a displacement of the signals of the ^{13}C at $C_{(2)}$ to weaker fields [70] than for ethylene, in toluene the chemical shift at $C_{(1)}$ is −8.6 m.u. in comparison with benzene. The ^{13}C

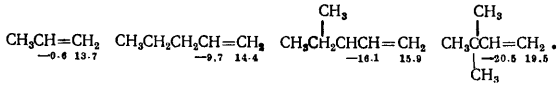
chemical shifts in relation to benzene for various compounds are as follows:



If the alkyl groups exhibited at $+I$ effect, the electronic density at $C_{(1)}$ should also be increased but to a lesser extent than at $C_{(2)}$; if the alkyl groups had a $-I$ effect (as actually happens) then the electron density at $C_{(1)}$ in the ethylene homologues would also be depressed but to a lesser extent than in $C_{(2)}$. Actually the screening of the terminal carbon $C_{(1)}$ in alkenes-1 is higher than in ethylene. Supporters of the hyperconjugation theory explain this by the mesomeric effect of the groups:

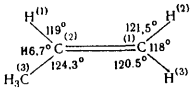
$$RCH_2CH{=}CH_2 \leftrightarrow \overset{H^+}{RCH}{=}CH{-}\overset{-}{C}H_2 .$$

Since the radicals can be arranged according to hyperconjugation effect in the order: $CH_3 > RCH_2 > R_2CH$, but the t-butyl group does not exhibit a mesomeric effect according to hyperconjugation theory, a successive decrease in the electronic charge on the terminal carbon atom of alkenes-1 would be expected on going from propene to t-butylethylene. However, in reality, as is evident from the diagrams below (the numbers denote the ^{13}C chemical shifts in relation to benzene [70]; those for propene were calculated from Savitsky and Namikava's results [71]), the order of change in the screening of the terminal carbon is the reverse of that predicted by hyperconjugation theory:



Hence the $C_{(1)}$ electron density is not determined by either the mesomeric effect of the alkyl groups (since they do not exhibit one), or the inductive effect transmitted along the carbon chain with gradual damping.

How then is the influence of the primary polarisation of the $C_{sp^3}{-}C_{sp^2}$ transmitted to the terminal carbon in alkenes-1? We think that the most important factor which determines the effect of a radical on the electron density in unsaturated and aromatic molecules is the change in its molecular structure on the introduction of a substituent, which will ensure that the potential energy of the system is a minimum. As structural investigations of propene [72] and isobutene [73] show, the replacement of hydrogen atoms in ethylene by methyl radicals involves significant changes in the geometry of the molecules. In propene $\angle H_{(1)}C_{(2)}C_{(3)} = 116.7°$, $\angle H_{(1)}C_{(2)}C_{(1)} = 119°$, and $\angle C_{(3)}C_{(2)}C_{(1)} = 124.3°$, from which it follows that the s-nature of the $C_{(2)}$ orbitals in the direction towards $C_{(1)}$ is 0.400, that is, greater than the s-nature of the orbitals of carbon in ethylene ($s = 0.368$).



From the angles of the bonds at $C_{(1)}$ it follows that the s-character of the $C_{(1)}$ orbitals in the direction towards $C_{(2)}$ ($s = 0.364$) is somewhat less than in ethylene (where $\angle HCH = 117.2°$ [74]) but the total s-character of the $C_{(1)}$ and $C_{(2)}$ orbitals ($s_{C_{(1)}} + s_{C_{(2)}} = 0.764$) exceeds the total s-character of those in ethylene ($2s_C = 0.736$), which naturally leads to an increase in the overlap of the orbitals in propene (in comparison with ethylene) and to the appearance of screening of both carbon atoms. However, the $C_{(2)}$ screening is markedly affected by the negative inductive effect of the methyl group, so that in the end $C_{(2)}$ is less screened than the carbon atoms in ethylene. The decrease in the electron density for $C_{(2)}$ is due to the displacement of the signal from $H_{(1)}$ to weaker field and correspondingly an increase in the electron density of $C_{(1)}$ brings about an increase in the screening of the $H_{(2)}$ and $H_{(3)}$ protons (in comparison with ethylene).

From the geometry of isobutene ($C_{(3)}C_{(2)}C_{(4)} = 115.3°$) there is also an increase in the overlap of the $C_{(1)}$ and $C_{(2)}$ orbitals and a greater screening of $C_{(1)}$.

In chloroethylene [28] $\angle HCCl = 113°53'$ and therefore an increase in the screening of the carbon in the CH_2 groups is to be expected. Values of 115.4° [75], 117°55', [76] and 119° [77] have been given for $\angle HCF$ in fluoroethylene. Judging by the ^1H chemical shifts in the CH_2 group of fluoroethylene, which is at a stronger field than for ethylene [78], the first value is probably the most correct.

The replacement of hydrogen in benzene by any group leads to a distortion of the regular hexagonal form of the benzene ring. This has been shown by a few but completely reliable results. Thus, in nitrobenzene [79] and benzonitrile [80] the benzene ring has the form of an irregular hexagon and in these molecules there is a change (in comparison with benzene) in both the angles and the C–C and C–H interatomic distances. Distortion of the benzene ring can have a very significant effect on the distribution of electron density and so can the change in the s-character of the carbon orbitals in the substituted benzenes which do not possess strongly polarised bonds, for example in toluene. The methyl group, which exhibits a $-I$ effect, withdraws electrons and therefore the increase in the screening of the p-carbon atom in toluene cannot be explained by the transfer of its inductive influence along the chain of atoms. Evidently the introduction of a methyl group distorts the benzene ring so that $\angle C_{(3)}C_{(4)}C_{(5)}$ becomes $> 120°$, the s-nature of the $C_{(4)}$ orbitals in the direction towards the neighbouring carbons is increased and the overlap of the $C_{(4)}$, $C_{(3)}$, and $C_{(5)}$ orbitals and the electron density at $C_{(4)}$ is increased.

If the inductive effect of the halogens (primary polarisation of the C–Hal bond), which exhibit hardly any mesomeric effects, were transferred by an aromatic system, just as in aliphatic compounds, then a decrease in the screening of the p-carbon atoms would be expected. Since the p-^{13}C-chemical shifts in the halogenobenzenes are at higher field than for benzene those changes in the hybridisation of the orbitals of carbon atoms in halogenobenzenes which facilitate the observed effect would be expected. According to one version [81] in fluorobenzene $\angle C_{(2)}C_{(1)}C_{(6)} = 121°$, $\angle C_{(1)}C_{(2)}C_{(3)} = 119°23'$, $\angle C_{(2)}C_{(3)}C_{(4)} = 119°47'$, and $\angle C_{(3)}C_{(4)}C_{(5)} = 120°40'$. In accordance with these parameters the s-character of the $C_{(4)}$ orbitals in the direction towards $C_{(3)}$ and $C_{(5)}$ is 0.338, and that of the $C_{(3)}$ and $C_{(5)}$ orbitals is 0.332. Hence in fluorobenzene the rigidity of the $C_{(4)}{-}C_{(3)}$ and $C_{(4)}{-}C_{(5)}$ bonds is somewhat above that for benzene and there is somewhat greater screening of the $C_{(4)}$ carbon atom. Naturally, during the rehybridisation of the carbon orbitals in C_6H_5X polarisation of the π-electron cloud can also take place but this is scarcely grounds for assuming considerable redistribution of it, since during the rehybridisation the electronegativity of the π-orbitals changes insignificantly (in the $trtrtr\pi$ valence state of carbon the electronegativity of the π-orbitals is 5.58 eV but in the $didi\pi\pi$ state it is 5.64 [5]).

The influence of the internal electric field of the molecules must be taken into account to a greater extent [82].

Hence we conclude that the influence of the primary polarisation of the C–X bond is transmitted in unsaturated or aromatic systems by a mechanism different from that in aliphatic or acyclic systems. Strictly speaking, the generally accepted idea that the "inductive" effect of a substituent appears in an aromatic system just as it does in an aliphatic one does not have any basis. The so-called scale of the σ_I-constants of the substituents in an aromatic system is none other than the scale of the σ_f constants of 4-substituted bicyclo[2,2,2]octane-1-carboxylic acid [83,84].

The comparison of this scale with the scale of σ_I-constants in the benzene ring [85] solely on the basis that between the bicyclo[2,2,2]octane and benzene systems there may be a geometric similarity and therefore the distribution of the $I\sigma$- and F-effects in these systems should be analogous is arbitrary. From these assumptions came attempts to separate the influence of alkyl groups and halogen atoms into inductive and mesomeric constituents, attempts which failed.

On the basis of the experimental value $\sigma'_{Br} = 0.45$ [83] and the derived value of the polar constant of the substituent for CH_2Br (1.00), Taft [85] used the relation

$$\sigma'_R = 0.45\,\sigma^*_{CH_2R} \qquad (30)$$

to calculate the $\sigma'(\sigma_I)$ constant of the substituent, since the constants $\sigma^*_{CH_2R}$ are known for a large number of substituents. However, further experimental determinations of the dissociation constants of 4-substituted bicyclo-[2,2,2]octanes carboxylic acid [84] showed that the ratio $\sigma'/\sigma^*_{CH_2R}$ is not constant for different substituents but varies from 0.08 (for CH_3) to 0.67 (for OH). From relation (30) the $\sigma'(\sigma_I)$ constants for Cl and Br are 0.45 and 0.47 respectively, whereas new experimental results have shown [84] that the σ' constant for Cl and Br are almost equal (0.471 and 0.469). It was found further that the values, calculated from (30), of the σ' constant for CH_3, OCH_3, and OH (0.045, 0.23, and 0.25 respectively) differ considerably from the experimental results—0.008, 0.30, and 0.37 respectively. On starting from the ratio $\sigma'/\sigma^*_{CH_2R} = 0.58$, which corresponds with the experimental results for the OCH_3 group, then considerable differences are found between the experimental and calculated values of σ' for various other substituents. Starting from the experimental values of $\sigma^0_p = -0.15$ and $\sigma'(\sigma_I) = -0.008$ for CH_3, it is found that $\sigma^0_R(CH_3) = -0.14$, that is, it seems that the effect of the methyl group in an aromatic system is due almost completely to its mesomeric effect (which in reality it does not exhibit at all).

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Thus the theory of mesomerism as applied to halogen-containing organic molecules does not find experimental confirmation. From an examination of the energetics of the mesomeric state of carbon–halogen bonds the arrangement of the halogens in the following order of decreasing mesomeric effect: F > Cl > Br > I (as assumed in the theory of mesomerism) is not substantiated physically. The dipole moments of halogenomethanes and halogen-substituted benzene, ethylene, and acetylene do not confirm the existence of a mesomeric effect at the halogen atoms. Variations in the lengths of the carbon–carbon bonds are explained not by the mesomeric influence of the halogens but by the hybridisation of the orbitals of the atoms which form the bond. Correlation between the lengths of the carbon–halogen bonds and the hybridisation of the orbitals of the bound atoms shows the absence of a mesomeric effect with the halogens (within the limits of accuracy of the measurements of interatomic distances).

The NQR results show that halogen atoms either do not exhibit any mesomeric effect or show it to such a small extent that it cannot have any significant influence on the physical and chemical properties of halogen-containing organic compounds.

Information about the electronic structure of organic compounds based on their reactivities does not reflect the electronic structure of the molecules in their ground state. Equilibrium constants and constants derivable from them for the substituents characterise the total influence of the substituents in non-specific and specific solvation effects on the distribution of the electronic charges in the molecule. The principal factors which determine the electron distribution on the introduction of a substituent into a molecule is the changes in hybridisation of the atomic orbitals, which ensure that the potential energy of the system is a minimum. The hybridisation of the orbitals of the σ-framework of the molecule, experimentally observable by investigations of the molecular structure of the molecules results in changes in the electronegativity of the carbon orbitals and in the polarisation of the bonds.

The inductive effect of the substituent is transmitted directly solely to the carbon atom connected with it in an unsaturated or aromatic system and subsequently its effect differs qualitatively from that in an aliphatic system.

Results on the screening of para-carbon atoms in benzene derivatives with alkyl groups or halogen atoms as substituents show that the so-called scale of inductive constants in the benzene series σ_I is a speculative concept. This scale, which is a set of constants for the substituents in the 4-substituted bicyclo[2,2,2]octane-1-carboxylic acid series does not correspond with the actual change in the electronic structure of the aromatic molecule under the influence of a non-resonating substituent. Therefore all procedures for the quantitative separation of inductive and mesomeric effects which are based on the use of a scale of inductive constants of substituents in the aromatic series are useless.

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