Translated from *Uspekhi Khimii* **59** 39–65 (1990) U.D.C. 543.422.25+547.312

The parameters of the ^{13}C NMR spectra of substituted acetylenes: relation with electronic structure and reactivity

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ABSTRACT. **Questions concerning the electronic structure of the ethynyl fragment and the effectiveness of its interaction with various heteroatomic and unsaturated substituents are examined on the basis of the analysis of an extensive set of parameters of the ^{13}C NMR spectra of mono- and di-substituted acetylenes. The additive influence of the two substituents in disubstituted acetylenes on the shielding of the *sp*-carbon atoms, due to the counterpolarisation of the orthogonal π-systems of the triple bond, is demonstrated. The question of the possible use of the ^{13}C NMR spectral parameters for the estimation of the reactivity of the triple bond is discussed.**

The bibliography includes 140 references.

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I. Introduction

The unique reactivity of acetylenic compounds is responsible for their extensive use in thermographic synthesis—both in laboratory practice and in industry. However, the development of theoretical aspects of the behaviour of acetylenic compounds in reactions lags significantly behind practical advances. The extensive employment (in careful analysis and survey of results of studies on acetylenes themselves and on the reactions with their participation) of instrumental physical methods combined with theoretical quantum-chemical methods should help to overcome this discrepancy.

The ^{13}C NMR spectroscopy with its modern apparatus (Fourier transformation, the application of multipulse sequences, ultra-high magnetic fields) is one of the most universal methods for the study of the electronic and geometrical structures of organic and organo-element molecules and it has the highest information content. Its possibilities as regards acetylenic compounds are simple unique. Indeed, of the six parameters of NMR spectra with the aid of which it is possible to characterise the terminal ethynyl fragment of monosubstituted acetylenes [the chemical shift δ and the spin–spin coupling constants (SSCC or *J*): one ^{1}H chemical shift, two ^{13}C chemical shifts, two $^{13}C-^{1}H$ SSCC, and one $^{13}C-^{13}C$ SSCC], five can be obtained from the ^{13}C NMR spectrum and in the case of disubstituted acetylenes the entire spectroscopic information about the triple bond and about the carbon atoms involved in it is contained in the ^{13}C NMR spectrum. Since the chemical shifts of the acetylenic proton in monosubstituted acetylenes are exceptionally sensitive not only to intramolecular effects but also to solvation effects, they will not be considered in this review. The constants for the spin–spin coupling of this proton with the ^{13}C nuclei are more characteristic and permit an unambiguous assignment of the ethynyl carbon atoms in the ^{13}C NMR spectrum and they are therefore discussed in this review together with the $^{13}C-^{13}C$ SSCC. Here and henceforth the relaxation times of the nuclei and isotope substitution effects will not be considered.

II. Chemical shifts of the ethynyl ^{13}C atoms

1. General features and formulation of the problems

Whereas the number of known values of δC for the carbon atoms in certain unsaturated hydrocarbon fragments, for example in the benzene ring or in the double bond, reaches several thousands, the number of δC for acetylenic compounds is smaller by an order of magnitude. Most of the data refer to alkynes, alkynols, and compounds having the general formula $R_3EC{\equiv}CH$, where E = Si, Ge, or Sn.

The signals of the ethynyl carbon atoms in the ^{13}C NMR spectra are manifested in the range 65–95 p.p.m. [relative to the signal of the carbon atom in tetramethylsilane (TMS)], which is intermediate between the regions characteristic of the ^{13}C nuclei of the sp^3- and sp^2-carbon atoms. The alkyl groups attached to the triple bond shield the C_β atoms and deshield the C_α atoms, inducing changes in the shift of approximately 4–6 and 10–20 p.p.m. relative to δC for acetylene (72.0 p.p.m.).[1] Calculation of the distribution of charges in 1-alkynes by the CNDO/2 method has shown[2] that mainly the polarisation of the triple bond takes place under the influence of the alkyl substituent. In disubstituted acetylenes, the influence of two alkyl groups on δC is additive and quantitative estimates of the contributions of the groups having normal[3,4] and branched[5] structures are available. A topological scheme has been developed for highly accurate calculations (±0.6 p.p.m.) of δC_{sp} for alkynes and alkynols from data for 86 compounds.[5,6] A characteristic feature of the influence of the Alk_3E (E = Si, Ge, Sn) groups on the chemical shifts of the C_{sp} atoms is the deshielding of both carbon atoms (an average shift of 20 p.p.m.), which is explained by the appreciable π-acceptor effect of the Alk_3E groups ($p_\pi-d_\pi$ or $p_\pi-\sigma^*$ conjugation).[7–12] The acceptor properties of the silicon atom in relation to the triple bond have been confirmed by calculations of

the charge distribution.[12,13] The influences of the X and Me_3E groups on δC_{sp} are independent within series of compounds with identical E and can be described to a first approximation by the Hammett–Taft equation.[7] This conflicts with the results of studies of substituted hexynes $Bu^nC\equiv CX$, for which the absence of a relation between δC and the induction and resonance characteristics of the groups X has been noted.[14] In a number of cases a relation has been observed between the kinetic parameters of the reactions involving addition to acetylenic compounds and the σ-constants of the substituents (see, for example, Refs. 15–19). It is noteworthy that, whereas the AlkO groups of ethynyl ethers shield anomalously strongly the β-carbon atom, the AlkE groups, where E = S, Se, or Te, actually deshield it, which is explained by the reduced capacity of these chalcogens for p_π-interaction and the dominant influence of the d_π-acceptor properties.[7,20–22] The above features require refinement, because all chalcogens exhibit π-donor properties in relation to vinyl and phenyl fragments.[23]

Limited information is available about the chemical shifts of the ^{13}C atoms in acetylenic compounds containing boron,[24,25] phosphorus,[7,20,21,26] and the halogens.[7,14] The R_2P and R_2PO groups deshield the C_β atom to virtually equal extents (a 20 to 25 p.p.m. shift), whereas their effects on C_α are different: shifts of 10–15 and 2–8 p.p.m. respectively are observed. This has been explained by the π-acceptor effect of the phosphorus-containing substituents on the triple bond.[20,21,26] The R_2P group acts similarly on the triple bond. In the series of halogen-substituted acetylenes, the changes in δC are very great: on passing from Cl- to I-substituted compounds, the shielding of C_α increases by 60 p.p.m., while that of C_β diminishes by 30 p.p.m.; the values of δC_β for iodoacetylene derivatives exceed 100 p.p.m., while the values of δC_α are close to 0 p.p.m.[7,14] The explanation of changes in δC of this kind by the effect of anisotropy[27] or intermolecular dispersion interactions[28] is hardly acceptable.

The available information about δC for acetylenic compounds containing other substituents, including unsaturated ones, is even more scanty and is less susceptible to unambiguous interpretation. Analysis of the ^{13}C NMR spectra of several substituents in the ring of phenylacetylenes permitted the hypothesis that the π-electron systems of the triple bond and the aromatic ring do not interact at all,[29] although in another study[30] the field, resonance, and π-induction effects of the substituents were accepted as determining the charge distribution on the triple bond carbon atoms. The hypothesis that the lower sensitivity of the shielding of C_{sp} compared with C_{sp^2} to changes in charge density may be the counter-polarisation of the triple bond has been put forward.[30] This was first suggested when the changes in δC_{sp} and δC_{sp^2} for arylpropynes and arylpropenes were compared.[31] The possibility of the counterpolarisation of the π-electron systems of the triple bond follows from the results of the non-empirical calculation for the hypothetical aminoacetylene molecule.[32] All these features agree with the results of the analysis of the integral intensities of the triple bond bands in the IR spectra as a measure of their resonance interaction in monosubstituted[33,34] and disubstituted[35] acetylenes, indicating a lower sensitivity of the triple bond, compared with the double bond, to the resonance effect, although the resonance interactions in acetylenic compounds involve both π-systems of the triple bond.

The question of the transmission of the π-electronic perturbations through the triple bond remains obscure. Comparison of the reactivities of the group Y in the $p\text{-}XC_6H_4-M-C_6H_4Y\text{-}p$ bridged systems has shown[36] that similar coefficients for the transmission of the π-electronic perturbations are characteristic of molecules with M = $-CH=CH-$ and $-C\equiv C-$ bridges (0.89 and 0.82 respectively). On the other hand, there is evidence that the effects of the Alk_3E (E = Si, Ge, and Sn) groups are transmitted to an extremely slight extent across the triple bond to the neighbouring $C=C$[10] and $C=O$[11] double bonds.

Among general features, we may note the hypothesis of Rosenberg and co-workers,[20,21] according to which the sum of the values of δC_{sp} characterises the overall charge on the triple bond and their difference characterises its polarisation. Doubts were subsequently cast on the legitimacy of this conclusion.[22]

Thus analysis of the literature data permits the formulation of the following key questions concerning δC_{sp} for acetylenic compounds:

(1) how independent of one another are the effects of two substituents on the shielding of ethynyl carbon atoms;

(2) what is the relation between the charge distribution and the chemical shifts of the carbon atoms in the triple bond;

(3) what are the mechanisms of the interaction of various heteroatomic and functional groups with the triple bond;

(4) to what extent is the model of the counterpolarisation of the triple bond justified;

(5) to what extent are the electronic effects of the substituents transmitted through the triple bond;

(6) is there a relation between the parameters of the ^{13}C NMR spectra and the reactivity of the triple bond.

In the analysis of experimental results, we used three main approaches: (a) comparison of NMR data with the results of quantum-chemical calculations for the molecules; (b) correlation analysis based on the principles of the linearity of free energies (LFE) and polylinearity (PPL) as a quantitative theory of organic chemistry; (c) comparison of the values of δC for the corresponding derivatives of ethane, ethylene, and acetylene.

2. Analysis of the joint effect of substituents on the chemical shifts of ^{13}C atoms in disubstituted acetylenes

The independent effects of the substituents on δC for the triple bond is a characteristic feature of certain series of disubstituted acetylenes—alkynes,[5,6,37] phosphorus derivatives,[26] and silicon, germanium, and tin derivatives.[7] This made it possible to determine the additive contributions of the individual substituents in the calculation of δC_{sp}.[38,39] A survey of all the available δC data (1184 values) showed[40,41] that the nature of the groups R^1 and R^2 in the compounds $R^1C\equiv CR^2$ influences δC and induces changes in it in the range of approximately 100 p.p.m. General relations taking into account the simultaneous changes in the structures of R^1 and R^2 within the framework of the polylinearity principle have been found.

According to the polylinearity principle, δC† can be formulated as follows:[40]

$$\delta C(R^1C\equiv CR^2) = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2, \quad (1)$$

where X_1 and X_2 are quantitative characteristics of the structures of R^1 and R^2 respectively, a_0, a_1, a_2, and a_{12} are coefficients, and $a_{12} \neq 0$ only when the effects of R^1 and R^2 are non-additive. It has been shown,[40] that the applicability of Eqn. (1) is determined by the applicability of the LFE principle to δC_{sp}. The absence of a cross term in Eqn. (1) requires that the following simple relation should

† Here and henceforth we have in mind δC_{sp} for the detector atom—the carbon atom at the substituent R^1.

hold between the values of δC for disubstituted acetylenes and the corresponding monosubstituted acetylenes:

$$\delta C(R^1C{\equiv}CR^2) = a_0 + a_1[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)], \quad (2)$$

where a_0 = δC(HC−CH) and a_1 = 1.00.

Fig. 1 presents the theoretical relation (continuous line) corresponding to Eqn. (2) on which the experimental data for 369 acetylenic compounds have been plotted (of these, 366 refer to disubstituted acetylenes). A satisfactory agreement is observed between the theoretical straight line and the experimental data, which is indicated by the high statistical parameters of the equations:

$$\delta C(R^1C{\equiv}CR^2) = -75.60\,(1.13) + 1.02\,(0.007)\,[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)],$$
$$r = 0.992,\ s = 1.98,\ n = 369. \quad (2a)$$

For points whose deviations from the theoretical straight line are ⩽ ⩽43.0 p.p.m., we have

$$\delta C(R^1C{\equiv}CR^2) = -74.60\,(0.91) + 1.01\,(0.006)\,[\delta C(R^1C{\equiv}CH) + \delta C(HC{\equiv}CR^2)],$$
$$r = 0.995,\ s = 1.43,\ n = 334, \quad (2b)$$

where r is the correlation coefficient, s the standard deviation, and n the number of points included in the correlation. The coefficients a_0 and a_1 in these equations have values close to theoretical ones. A further improvement of the quality of the description is pointless, since the accuracy with which the LFE principle is maintained for $\delta C(R_1C{\equiv}CR^2)$ does not exceed ±1.3 p.p.m.[40] For 24 of the most common substituents R^1 and R^2, a resultant matrix has been set up and their additive contributions Δ to the shielding of the C_α and C_β atoms attached to the triple bond have been calculated. The regression equation obtained

$$\delta C(R^1C{\equiv}CR^2) = 72.0 + \Delta\delta C_\alpha(R^1) + \Delta\delta C_\beta(R^2) \quad (3)$$

permits the calculation of δC_{sp} for 576 of the corresponding acetylenic compounds with an accuracy not less than to within 2.0 p.p.m.[42] The additive contributions are listed in Table 1. The application of the additive scheme permits a significant simplification of the assignments of the ^{13}C signals in disubstituted acetylenes and is extremely useful for the theoretical calculation of the δC for the ethynyl carbon atoms.

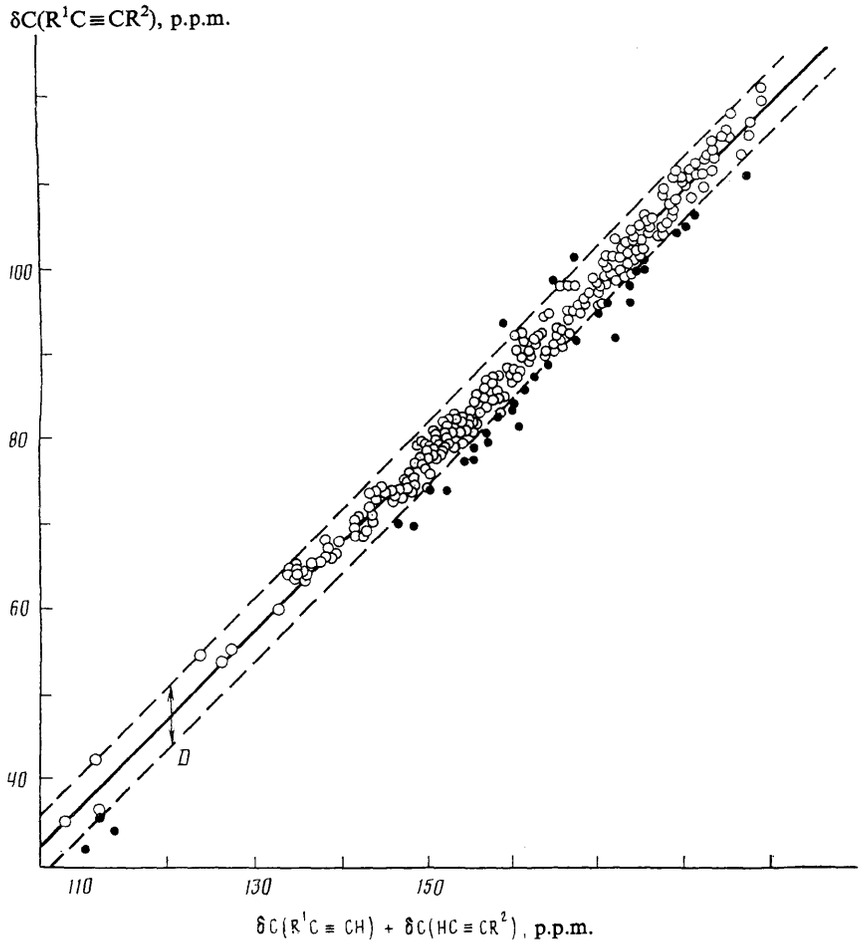


Figure 1. Dependence of the experimental shifts $\delta C(R^1C{\equiv}CR^2)$ on the theoretically calculated sums $\delta C(R^1C{\equiv}CH)$ + $\delta C(HC{\equiv}Cr^2)$ (according to the results of Kalabin and co-workers[40,41]): *D* is a ±3 p.p.m. "corridor" around a theoretical straight line; ●—points whose deviations exceed 3.0 p.p.m.; ○—points corresponding to experimental data whose deviations from the theoretical straight line do not exceed 3.0 p.p.m.

The reliable establishment of the fact that the substituents have additive effects on the δC for acetylenic compounds is extremely useful for utilitarian purposes, but it is somewhat unexpected, since it presupposes the absence of interactions between the substituents R^1 and R^2. Together with disubstituted acetylenes, model *trans*-1,2-disubstituted ethylenes and 1,4-disubstituted benzenes were also examined. These are the simplest unsaturated compounds where there is no steric interaction between the substituents but there is an effective interaction via the mechanism involving direct polar conjugation.[29,42–47]

In order to discover how the interaction of the substituents is manifested in such substituted benzenes and acetylenes, the values of δC for these series of compounds were subjected to a statistical treatment within the framework of the corresponding mathematical model.[41,48] In *trans*-1,2-disubstituted ethylenes and 1,4-disubstituted benzenes, the influence of the substituents R^1 and R^2 is significantly non-additive. In the compounds $R^1C{\equiv}CR^2$, the substituents R^1 and R^2 influence the chemical shift δC_{sp} independently of one another, and their effects are described satisfactorily within the framework of the polylinearity principle. The additivity of the effects of the substituents on the δC for ethynyl carbon atoms in disubstituted acetylenes presupposes the absence of direct interaction between the substituents through the triple bond. The possibility of the constancy of the contribution of such interaction appears unlikely.

Table 1. The additive contributions of the substituents to the shielding of the $^{13}C_{sp}$ nuclei in disubstituted acetylenes.[42]

R^1	$\Delta\delta C_\alpha$	$\Delta\delta C_\beta$	R^1	$\Delta\delta C_\alpha$	$\Delta\delta C_\beta$
H	0.0	0.0	Me_3Si	17.6	23.1
Me	7.8	—4.4	Et_3Si	15.6	23.8
Et	13.4	—4.1	Me_3Ge	17.5	21.4
Bu	13.0	—3.3	Et_3Ge	14.9	23.2
Bu^t	20.6	—5.6	Me_3Sn	15.7	26.8
Ph	12.0	6.0	Et_3Sn	14.2	26.8
p-$MeOC_6H_4$	11.9	4.9	$P(O)(OEt)_2$	1.6	17.0
p-MeC_6H_4	11.9	5.5	C≡N	—15.9	3.2
p-ClC_6H_4	10.6	7.0	COMe	10.8	6.7
$CH_2{=}CH$	9.9	6.7	COPh	9.0	9.3
$Me_2C(OH)$	17.5	0.2	OEt	16.2	—52.3
CH≡C	—3.3	—7.2	SEt	0.5	11.2

Note. The error of the determination of the contributions does not exceed ±2.0 p.p.m.

The non-additivity of the effects of substituents on δC_{sp^2} for *trans*-1,2-disubstituted ethylene derivatives is very considerable. The maximum deviations of δC from values calculated on the assumption of additivity reach 30 p.p.m. Although the deviations from additivity are much smaller for disubstituted acetylenes, (the number of compounds for which experimental δC deviate by more than 3.0 p.p.m. from the theoretical values is 27 and 3% of the total number for *trans*-disubstituted ethylenes and disubstituted acetylenes respectively[41]), analysis of these deviations can throw light on the nature of this phenomenon. Table 2 presents compounds for which the values of δC_{sp} for R^1 differ by more than 3.0 p.p.m. from the values calculated theoretically by Eqn. (2). If one excludes from consideration compounds 5 and 6 (data obtained in H_2O[49]), it is found that out of 31 compounds, 28 compounds (>90%) have substituents $ER^1R^2R^3$, where E = Si, Ge, Sn, or P, which is undoubtedly not fortuitous. We shall consider in greater detail the cause of the observed phenomenon.

3. The counterpolarisation of the π-systems of triple bonds

The π-electron systems of the triple bond in acetylene are energetically degenerate, i.e. the π-charge is distributed along the axial position relative to the molecular axis. Depending on the symmetry, the substituents remove this degeneracy to a greater or lesser extent. The degeneracy is apparently removed to the least extent by alkyl substituents and halogen atoms, in the presence of which the molecular symmetry is close to C_{3v} and the barrier to rotation is low. The non-equivalence of the π-orbitals of the triple bond increases with increase in this barrier, reaching a maximum for substituents having a symmetry plane (the COR, Ph, $CH{=}CH_2$, etc. groups). Such substituents are capable of interacting only with one of the π-systems of the triple bond, polarising it or becoming conjugated with it (an appreciable π-charge transfer takes place). The polarisation of the second, orthogonal π-system can partly compensate for the redistribution of the π-charge in the first system, i.e. the counterpolarisation of the orthogonal π-systems of the triple bond takes place. The possibility of this phenomenon has been stated in a number of studies[29–31] (see above).

Table 2. The deviations (*D*, p.p.m.) of the experimental shifts δC for the compounds $R^1{-}C{\equiv}C{-}R^2$ from the calculated values.[41]

Compound	R^1	R^2	*D*	Compound	R^1	R^2	*D*
1	Et_3Ge	n-C_6H_{11}	—4.2	17	*p*-FC_6H_4	$P(O)(OEt)_2$	—4.9
2	Et_3Sn	n-C_6H_{11}	—5.2	18	Ph	$P(O)(OEt)_2$	—4.2
3	Et_3Sn	n-Bu	—3.7	19	*p*-MeC_6H_4	$P(O)(OEt)_2$	—4.4
4	Me_3Si	CH_2CH_2OH	—3.8	20	*p*-ClC_6H_4	$P(O)(OEt)_2$	—5.2
5	$HOCH_2$	$CH_2[\overset{\oplus}{N}Me(Et)_2]\overset{\ominus}{I}$	—8.1	21	*p*-$MeOC_6H_4$	$P(O)(OEt)_2$	—4.0
				22	Ph	C≡N	—3.2
6	$\overset{\ominus}{I}[(Et)_2\overset{\oplus}{N}MeCH_2]$	CH_2OH	—5.8	23	$HOCH_2$	C≡CPh	—3.8
7	Me_3Si	CH_2OH	—3.2	24	Me_3Sn	OEt	—6.7
8	Et_3Ge	$CH_2N(CH_2)_4O$	—7.1	25	Me_3Ge	C_6F_5	3.6
9	Et_3Ge	$CH_2N(CH_2)_5$	—3.7	26	Me_3Si	C≡N	4.9
10	Et_3Si	$CH_2N(CH_2)_4O$	—3.2	27	Me_3Sn	C≡N	6.5
11	PhC(O)	C(O)Ph	—4.6	28	N≡C	$SnMe_3$	—3.1
12	Me_3Si	OEt	—4.0	29	Et_3Ge	Bu^t	—3.1
13	Et_3Ge	COH	3.9	30	Me_3Sn	Bu^t	—4.7
14	Et_3Ge	COMe	4.3	31	Et_3Sn	Bu^t	—3.8
15	Me_3Ge	OEt	—4.6	32	Me_3Sn	Et	—3.3
16	Et_3Sn	OEt	—6.5	33	Me_3Si	$SnMe_3$	3.2

If each substituent in disubstituted acetylenes interacts with only one π-electron system of the triple bond, then the effectiveness of the interaction between the substituents themselves can be minimal and their effects on the triple bond can be entirely independent. The observed additivity of the effects of substituents confirms these ideas. The substituents in disubstituted ethylenes and benzenes interact with one π-system and their effects cannot be independent. The non-additivity of the effects of substituents on δC_{sp^2} in these systems can therefore be also understood.

The general features of the influence of substituents on the shielding of ethynyl carbon atoms can be formulated on the basis of the counterpolarisation idea in the following manner.

1. If the substituent interacts with one only π-system of the triple bond, then, as a result of the counterpolarisation, its effect on δC_{sp} is equal to or smaller than its effect on a double bond.

2. If the substituent interacts simultaneously with both π-systems of the triple bond, then counterpolarisaiton is difficult and its effect on δC_{sp} is equal to or greater than its effect on a double bond.

3. The greatest deviations from additivity are characteristic of disubstituted acetylenes in which one of the substituents is capable of interacting with both π-systems, while the other, regardless of symmetry, exerts a complementary or competitive π-electronic effect.

The latter is confirmed by the data in Table 2: the electron-accepting properties of Si, Ge, Sn, and P in relation to the π-system depend little on the angles of rotation of the corresponding substituent relative to the multiple bond.[50] For this reason, one should expect appreciable deviations for ethynyl ethers, in which the oxygen atom has a π-donor capacity in relation to both orthogonal π-systems.[33] Finally, the orthogonal orbitals of neighbouring triple bonds also interact with one another in the same way.

Table 3. The influence of various substituents (ΔδC) on the shielding of the α- and β-carbon atoms of the double and triple bonds in monosubstituted derivatives of ethylene and acetylene.

R	R—CH=CH₂		R—C≡CH		Presence of counter-polarisation (+, −)	σ_R^0	$(\sigma_R^0)_{tw}$
	Δδ C_α	Δδ C_β	Δδ C_α	Δδ C_β			
Me	3.2	−16.6	−2.9	−14.7	+	−0.10	−0.10
Bu^t	−0.3	−16.3	−10.7	−7.8	+	−0.13	−0.13
EtO	−3.1	−47.0	−42.8	−58.5	−	−0.44	−0.23
EtS	−10.9	−23.2	−20.0	−0.5	+	−0.25	−0.05
Et_3Si	16.1	8.0	18.5	23.1	−	0.03	0.03
N≡C	−10.4	13.6	−10.1	4.4	+	0.10	0.10
CH_3=CH	−16.1	−22.9	−20.0	−10.3	+	—	—
Ph	−7.6	−20.7	−10.1	−6.0	+	−0.10	−0.06
HOC	−15.8	14.6	−21.9	11.7	+	0.24	0.0
HOOC	−16.4	7.1	−19.2	2.2	+	0.29	0.0
Cl *	−29.8	−18.5	−45.3	−27.9	−	−0.22	−0.22
$(OEt)_2(O)P$ *	0.7	11.6	2.1	16.0	−	—	—
Me_2N *	−25.2	−44.0	−25.1	−28.8	+	−0.53	−0.13

Note. Effects relative to saturated compounds are indicated, i.e. $\Delta\delta C_{sp^2(sp)} = (\delta C_{sp^2(sp)} - \delta C^0_{sp^2(sp)}) - (\delta C_{sp^3} - \delta C^0_{sp^3})$. The values $\delta C^0_{sp}(HC\equiv CH) = 72.0$, $\delta C^0_{sp^2}(CH_2=CH_2) = 122.8$, and $\delta C^0_{sp^3}(CH_3CH_3) = 5.7$ were used.

* The estimate was made for 1,2-trans-disubstituted ethylenes and disubstituted acetylenes.

The first two postulates have been confirmed by the analysis of the relative effects of different substituents on the shielding of α- and β-carbon atoms of the multiple bond in vinyl and ethynyl compounds (Table 3). The Table also indicates the resonance constants of the substituents α_R^0 and $(\sigma_R^0)_{tw}$,[33] which correspond to the interaction of the substituents with the two orthogonal π-systems of the triple bond. The signs of these constants are always the same but the constants $(\sigma_R^0)_{tw}$ are equal to or smaller than σ_R^0. The numerical values of the constants indicate a non-equivalence, in certain cases, of the π-systems of triple bonds and the possibility of their counterpolarisation. Table 3 does not include data for compounds with R = $GeEt_3$ and $SnEt_3$, since they are identical with data for R = $SiEt_3$. All the results, with the exception of those which correspond to compounds with the EtS and N≡C groups, are fully consistent with the model of the counterpolarisation of the triple bond π-orbitals developed here.

The fact that the concept of the counterpolarisation of the triple bond is well founded has been confirmed by the calculation of the distribution of π-electron densities in a series of model acetylenic compounds, which have been performed by non-empirical methods using the OST-4GF basis set (Table 3). The countertransfer of the π-charge via the orthogonal π-systems of the acetylenic fragments has been noted for aminoacetylene, formylacetylene, and phosphinoacetylene molecules‡, i.e. in the presence of substituents (π-donor and π-acceptor) capable of direct interaction with only one π-system of the triple bond.

The fluorine atom interacts effectively with both triple bond π-systems. This gives rise to the maximum transfer in the given instance of the negative π-charge to the terminal carbon atom of the triple bond and also agrees with experiment.

The presence of two hybrid orbitals with different symmetries, which include the unshared electron pairs of the oxygen atom in hydroxyacetylene, is responsible for the effective interaction of one of the unshared electron pairs in the case of a planar molecular conformation, whereas the contribution of a second electron pair to the corresponding π-MO is much smaller and compensates for the possible countertransfer of the charge (Table 4).

Table 4. The distribution of charge density ($10^3 q_\pi$) in the acetylenic fragment of the compounds $H-C_\beta\equiv C_\alpha-X$.[41]

X	q_{C_α}			q_{C_β}		
	π_y	π_z	Σπ	π_y	π_z	Σπ
H	0	0	0	0	0	0
$CH=CH_2$	1	16	17	−6	−20	−26
CHO	−16	16	0	36	−15	21
COOH	−19	1	−18	36	4	40
NH_2 (planar molecule)	−48	58	10	44	−134	−90
NH_2 (non-planar molecule)	−31	38	7	21	−93	−72
PH_2	31	−51	−20	−25	26	1
OH	19	−30	−11	−79	1	−78
F	−28	−28	−56	−48	−48	−96

The results presented in Tables 3 and 4 make it possible to estimate the sensitivity of the chemical shifts of the *sp*-carbon atoms to π-electronic effects (it amounts to 600 p.p.m. per charge unit, which is approximately three times greater than the analogous characteristic of the sp^2-carbon atoms of substituted ethylenes).

Overall, the results of quantum-chemical calculations for monosubstituted acetylenes, the analysis of the chemical shift δC_{sp} for mono- and di-substituted acetylenes, and their comparison with the analogous results for disubstituted ethylenes indicates the occurrence of the counterpolarisation of the orthogonal π-systems of the triple bond.

‡ The calculation for the phosphinoacetylene molecule was performed in terms of the *sp*-basis set (without taking into account the *d* orbitals) and the phosphorus atom therefore behaves as a π-donor as a result of the presence of its unshared electron pair.

4. The ability of the triple bond to transmit the effects of substituents

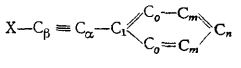
We shall consider the character and degree of the transition of the electronic effects of the groups X through the triple bond in relation to the compound X−C≡C−R, where R = Ph, $CH=CH_2$, or C≡CH. In vinylacetylenes $X-C_\alpha\equiv C_\beta-C^1H=C^2H_2$,[51–53] there is no explicit relation between the changes in δC_β and δC^2. One may note that the effect of X on the triple bond is specific, since the substituent X induces a displacement of δC_β by more than 40 p.p.m., whereas δC^2 is displaced by only 4 p.p.m. and δC^1 by only 2 p.p.m. The effect of X on the terminal vinyl group is mainly manifested by the polarisation of π-electrons by the dipole of the X−C bond (the changes in δC^1 and ΔC^2 take place in the opposite directions and agree with the direction of the dipole). This can be seen from a comparison of the δC for the two compounds $Et_2NCH_2C_\alpha\equiv C_\beta-C^1H=C^2H-SEt$ (A) and $[Et_2MeNCH_2-C_\alpha\equiv C_\beta-C^1H=C_2H-SEt]I$ (B):[54]

	C_α	C_β	C^1	C^2
δC(A), p.p.m.	92.4	81.6	104.9	139.6
δC(B), p.p.m.	87.2	84.1	101.9	144.8
Δδ C	−5.2	2.5	−3.0	5.2

The results presented as well as the available data for diacetylenic compounds[53,55–57] agree fully with the model involving a significant polarisation of the triple bond.

The ability of the triple bond to transmit electronic effects to the benzene ring can be characterised and the degree of interaction of the ethynyl and phenyl groups can be elucidated most correctly by analysing the data for β-substituted phenylacetylenes X−C≡CPh. This series of compounds is attractive because the values of δC for the compounds X−Ph are known for virtually any groups X and the $Ph-C_\alpha\equiv C_\beta-X$ fragment has a rigid conformation, while the presence of four indicator centres in the benzene ring facilitates the classification of the effects of the group X.

The values of δC for 39 β-substituted phenylacetylenes



have been published.[41] As for other series of compounds, not even a qualitative relation is observed in this instance between the δC_{sp} and any of the sets of the σ constants of the group X. We shall consider the characteristics of the variation of the degree of shielding of the aromatic carbon atom. The changes in the latter amount to 9.2, 10.0, 4.0, and 18.0 p.p.m. for C_1, C_o, C_m, and C_p respectively. The effect of the substituent X on the shielding of the C_{sp^2} atoms in the compounds X−C≡C−Ph is formally of the same type,[41] which follows from the equation

$$\delta C_m = 0.183(0.006)\delta C_p + 104.9(0.8),$$
$$r = 0.985,\ s = 0.14;$$
$$\delta C_o = 0.545(0.018)\delta C_p + 61.5(2.3),$$
$$r = 0.981,\ s = 0.41;$$
$$\delta C_1 = -1.27(0.07)\delta C_p + 286.5(8.4),$$
$$r = 0.97,\ s = 0.46. \quad (4)$$

The principal causes of the influence of X on the benzene ring are the field and resonance effects,[41] which have been described most fully for various substituted benzenes in terms of resonance (R) and field (F) constants.[58] The difference between the values of δC for the *para*- and *meta*-positions in the ring of X−Ph is usually determined by the pure resonance effect of the group X.[59] In our case, the corresponding equation is

$$\delta C_p - \delta C_m = 0.22(0.09) + 4.7(0.3)F + 4.9(0.5)R,$$
$$r = 0.987,\ s = 0.2,\ n = 14. \quad (5)$$

Consequently the field effect is the principal factor governing the influence of the groups X on the aromatic fragment through the triple bond. Examination of the shielding of the proton at the β-carbon atom of the triple bond in the *para*-substituted phenylactylenes $X-C_6H_4-C_\alpha\equiv C_\beta-H$, carried out by Klasine et al.,[29] leads to a similar conclusion.

The ability of the −C≡C− bridging group to transmit the influence of substituents can be estimated by comparing the values of δC_p for the compounds Ph−X, Ph−CH=CHX (*trans*-isomer), and Ph−C≡CX. The regression equations are presented below (the values of δC_p are quoted relative to the corresponding unsubstituted compounds with X = H). For monosubstituted benzenes, the values of δC_p were taken from Ewing[60] and those for *trans*-styrenes were taken from Glukhikh et al.[61]

$$\delta C_p(PhC\equiv CX) = 0.55(0.02)\delta C_p(PhX) + 0.75(0.18),$$
$$r = 0.98,\ s = 0.8,\ n = 29; \quad (6a)$$
$$\delta C_p(PhCH=CHX) = 0.88(0.04)\delta C_p(PhC\equiv CX) - 0.19(0.09),$$
$$r = 0.99,\ s = 0.2,\ n = 11. \quad (6b)$$

The transmission coefficient in Eqn. (6a) is identical with the value determined as a result of the investigation of the reactivities of dinuclear bridged systems (see, for example, Litvinenko, et al.[62]). It follows from Eqn. (6b) that the coefficient of the transmission of substituent effects to the benzene ring through the triple bond is close to the corresponding value for the double bond. The high confidence level of Eqn. (6b) can serve as evidence for the similarity of the formal mechanisms of the transmission of the substituent effect through the double and triple carbon−carbon bonds.

5. Characteristic features of the influence of substituents on the shielding of C_{sp}

Group IVA elements. The nature of the influence of substituents on the shielding of *sp*-carbon atoms in acetylenic compounds can be usefully examined by comparing the experimental values of δC_{sp} for acetylene itself and for its monosubstituted derivatives or by analysing the additive contributions found (Table 1). The characteristic features of the effects of alkyl groups on δC_{sp} can be seen from the comparison of the corresponding data for substituted acetylenes, ethanes,[63] ethylenes,[64,65] and benzenes[60,66] (the values of δC for the carbon atoms in these compounds are presented in Table 5).

A good relation is observed between the values of δC in the series of alkylacetylenes and alkylethylenes, the shielding of C_α in the series of alkyl-acetylenes being less sensitive (approximately by 30%) to the nature of the alkyl substituent than in the series of alkylethylenes.[67] The values of δC_{sp} for the β-carbon atoms in alkyl acetylenes remain virtually constant within the series. This is also characteristic of the C_p atoms of the benzene ring and reflects the independence of the π-polarisation of the unsaturated fragment of the size of the alkyl group. The increase in the shielding of the C_β atoms in ethynyl and vinyl derivatives and of the C_o atoms in phenyl derivatives is a consequence of the enhancement of the steric interaction of these atoms with the alkyl group as the bulk of the latter increases.

Substituents containing other Group IVA atoms influence the ethynyl fragment of the substituent quite differently. Since the effects of the $EAlk_3$ groups depend little on the character of E (Si, Ge, Sn) and of the alkyl (Alk), we shall examine them in relation to only the $SiEt_3$ group. The values of δC for hydrocarbon fragments

containing the $SiEt_3$ substituent (data taken from Proidakov[74]) are presented in Table 5. The deshielding effect of the $EAlk_3$ group on the C_β atom of the triple bond is stronger than for a single bond (by a factor of 20) and a double bond (by a factor of 2.5), while the shielding of the C_α atom in all the unsaturated fragments is the same.[52] The enhanced π-acceptor properties of the Si, Ge, and Sn atoms in relation to the triple bond have been explained by their ability to participate in the interaction with both its π-systems.[68] The fact that $EAlk_3$ groups deshield the C_β (C_o) atoms of the unsaturated fragments and hardly affect C_p in the benzene ring makes it possible to exclude from consideration the mechanism in which the effect is exerted through π-polarisation and through $p_\pi - d_\pi$ conjugation. Since the $EAlk_3$ groups act predominantly on the two nearest unsaturated carbon atoms, one can assume that the atomic orbitals of the two nearest sp^2- and sp-carbon atoms participate in the formation of the molecular orbitals (MO) responsible for the charge transfer from the π-system of the substituent to the atom E, which agrees with the model postulating the participation of the unoccupied σ* orbitals of the E–C bonds in the donor–acceptor interaction.[68]

Table 5. The ^{13}C chemical shifts (p.p.m. relative to TMS) of substituted ethanes, ethylenes, acetylenes, and benzenes.

R	$R-C_\alpha H_2-C_\beta H_3$		$R-C_\alpha H=C_\beta H_2$		$R-C_\alpha \equiv C_\beta H$	
	C_α	C_β	C_α	C_β	C_α	C_β
H	5.7	5.7	122.8	122.8	72.0	72.0
Me	15.9	15.4	136.2	115.9	79.3	67.0
Et	24.8	13.0	140.2	113.3	85.0	67.3
Pr^i	31.6	11.3	146.0	111.3	89.3	67.7
Bu^t	36.5	8.5	149.3	109.3	92.1	67.0
Et_3Si	2.8	6.9	137.8	132.6	86.2	95.4

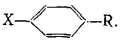
R	$R-C_6H_5$			
	C_1	C_o	C_m	C_p
H	128.5	128.5	128.5	128.5
Me	137.8	129.3	128.5	125.6
Et	144.1	128.1	128.5	125.9
Pr^i	148.7	126.6	128.6	126.1
Bu^t	149.1	125.4	128.4	125.9
Et_3Si	140.4	133.6	128.6	128.7

Group VIA and VIIA elements. Alkoxy- and aryloxy-groups significantly shield the C_β atom at the triple bond, displacing its signal by 20–30 p.p.m. relative to that of the TMS carbon atom,[20,21,69] which is explained by the effective conjugation of the lone electron pairs (LEP) of the oxygen atom with the π-electron system of the triple bond, i.e. with the appreciable contribution of the canonical structure of the type $R-\overset{\oplus}{O}=C=\overset{\ominus}{C}H$. The extent of such interaction has been examined in relation to ethynyl ethers.[69] The shielding of the C_β atom in the ether $PhOC_\alpha \equiv C_\beta H$ is less pronounced than in the ether $EtOC_\alpha \equiv C_\beta H$ (the difference between the displacements is 10 p.p.m.) in view of the competing interaction of two π-electron substituents with the ether oxygen as the electron donor. This is confirmed by the comparison of the values of δC of the phenyl group (p.p.m. relative to δC_{TMS}) for isoelectronic ethers R–O–Ph:

R	C_1	C_o	C_m	C_p
CH_3-CH_2	159.26	114.53	129.38	120.57
$CH_2=CH$	156.25	117.03	129.24	122.67
$CH \equiv C$	155.54	114.81	129.36	124.23

Comparison of the degrees of shielding of C_p in these compounds shows that the delocalisation of the charge of the oxygen LEP over the benzene ring diminishes by a factor of 1.4 on passing from the vinyl to the ethynyl ether and by a factor of 2 on passing from the ethyl to the ethynyl ether§, i.e. the degree of charge transfer from the oxygen atom to the triple bond is appreciably greater than the charge transfer to the double bond. This follows from a comparison of the excess shielding of the C_β atom in the ethynyl group (the displacement of the shift is by 38.4 p.p.m. relative to acetylene) and in the vinyl group (the displacement is by 28.2 p.p.m. relative to ethylene).[69] Bearing in mind the different sensitivities of the shielding of the C_{sp} and C_{sp^2} atoms to changes in their charge density,[29] one may conclude that the excess charge on the C_β atom in the ethynyl ether is greater by a factor of 1.6 than in the vinyl ether. The similarity of the excess charge follows from the results in the literature[33,50] subject to the condition that in acetylenic ethers both orthogonal π orbitals of the triple bond participate in the p_π interaction with oxygen. These results agree with the results of the calculation of the charge distribution in the hypothetical $HC \equiv COH$ and $H_2C \equiv CHOH$ molecules by the OST-3G method.[70]

The sensitivities of the chemical shifts of the C_p atom of the benzene ring and of the C_β atom of the multiple bond of the group R to the effects of the substituent X in the compounds



have been compared for *para*-substituted ethynyl phenyl,[69] phenyl vinyl,[23] and phenyl propargyl[71] ethers, substituted styrenes,[72] and phenylacetylenes.[29] It is seen from the data in Table 6 that the ΔC_p for these series of compounds are fairly close, in contrast to ΔC_β. The ratio $\Delta C_\beta / \Delta C_p$ is appreciably lower for ethynyl and especially propargyl ethers. The numbers presented in the last two columns of Table 6 indicate a decrease of the resonance effect in the case of substituted acetylenes, while the field effect, i.e. the π-induction effect, remains unchanged. As was to be expected, it becomes dominant in propargyl ethers. This is also confirmed by the relation between δC for *para*-substituted propargyl ethers $CH \equiv CCH_2O-C_6H_4X$ and the dipole moments[73] of the corresponding monosubstituted benzene derivatives Ph–X:

$$\delta C_\beta = 0.34\,(0.04)\,\mu_{PhX}, \quad r = 0.975,\ s = 0.14,\ n = 7. \qquad (7)$$

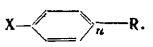
§ The charge transfer from the ether oxygen atom to the benzene ring can be most correctly estimated from the change in δC_p (this value is proportional to the change in the charge on the atom):

	δC_p, p.p.m.	$\Delta\delta C_p$, p.p.m. (relative to benzene)
C_6H_6	128.5	0
$C_2H_5OC_6H_5$	120.4	−8.1
$CH_2=CHOC_6H_5$	122.7	−5.8
$CH \equiv COC_6H_5$	124.2	−4.3

i.e. the charge transfer to the benzene ring on passing from the ethyl to the vinyl ether diminishes by a factor of (−8.1/−5.8) ≃ 1.4 whilst on passing from the ethyl to the ethynyl ether the decrease is by a factor of (−8.1/−4.3) ≃ 2.

Thus the influence of substituents capable of conjugation on the shielding of the carbon atoms of the triple bond through the saturated fragment is exerted via its π-polarisation.

Table 6. The displacements of the chemical shifts of the C_p atom of the benzene ring and the C_β atom of the multiple bond (in p.p.m.) and their sensitivity to the effects of the substituent X in the compounds



R	ΔC_n	ΔC_β	$\Delta C_\beta/\Delta C_n$	$\lambda(C_n)$	$\lambda(C_\beta)$	$\rho_R(C_\beta)/\rho_R(C_n)$	$\rho_F(C_\beta)/\rho_F(C_n)$
CH_2=CH	13.1	7.0	0.54	6.8	2.6	0.45	1.03
CH≡C	13.8	6.1	0.44	6.4	1.8	0.28	0.98
CH_2=CHO	10.6	5.5	0.52	6.9	1.9	0.32	1.17
CH≡CO	10.0	2.9	0.29	8.8	1.7	0.20	1.00
CH≡CCH_2O	11.2	1.6	0.14	6.1	1.0	0.08	0.45

Note. ΔC is the range of variation of δC when X is varied in the series from the NO_2 acceptor to the OMe donor; $\lambda = \rho_R/\rho_F$ is the ratio of the sensitivities of δC to the resonance and field effects obtained from statistically reliable correlations ($r \geqslant 0.99$).

Table 7. The influence of the heteroatomic groups Alk_nE on the shielding of α- and β-carbon atoms of substituted acetylene, benzene, and ethane derivatives (displacements of the chemical shifts, p.p.m.).[78]

n	E	Electro-negativity E*	$Alk_nE-C\equiv CH$		Alk_nE-Ph		Alk_nE-Et	
			δC_α	δC_β	δC_α	δC_β	δC_α	δC_β
3	C	2.50	19.9	—5.0	22.5	—3.2	—	—
	Si	1.74	17.3	21.7	11.7	4.9	—1.1	1.7
	Ge	2.02	17.2	20.3	13.7	4.5	0.1	3.2
	Sn	1.72	17.3	24.3	13.4	7.4	—3.4	5.1
	Δ **	—0.02	0.0	2.6	1.7	2.5	—2.3	3.4
1	O	3.50	22.1	—50.9	31.3	—14.0	57.3	9.2
	S	2.44	2.4	8.9	8.4	0.1	21.5	8.7
	Se	2.48	—8.2	14.9	1.9	3.8	15.2	9.7
	Te	2.01	—34.3	27.0	—16.5	9.6	—6.1	10.5
	Δ **	—0.43	—36.7	18.1	—24.9	9.7	—27.6	1.8
0	F	4.10	—	—	35.3	—13.9	63.6	8.9
	Cl	2.83	—11.1	—14.7	6.6	—1.6	34.2	13.0
	Br	2.74	—29.4	—3.7	—5.2	3.5	20.6	14.6
	I	2.21	—71.1	13.3	—13.8	10.4	—5.5	15.9
	Δ **	—0.62	—60.0	28.0	—38.4	12.0	—39.7	2.9

Note. The displacements of the chemical shifts are quoted relative to the corresponding unsubstituted compounds.

* The electronegativities of the heteroatoms taken from Batsanov[77] are quoted.

** The differences between the corresponding values obtained on passing from elements of the 3rd Period to those of the 5th Period are quoted.

The results presented characterise the ability of bridging groups to transmit the electronic effects and show that the employment of "transmission factors" for individual bridging groups as stable characteristics is erroneous.[62] Comparison of the values of $\Delta C_\beta/\Delta C_p$ for the first four compounds demonstrates that the ability of the ether oxygen to transmit perturbations is significantly different even in fairly close structural series and depends on the conformational structure of the molecules, the character of the detector group, and, finally, on the property or parameter of the group chosen for the comparison. The ether oxygen atom has an enhanced π-donor capacity in relation to the triple bond because it can interact simultaneously with two orthogonal π orbitals. This is reflected in the non-universality of the existing scales of the resonance constants σ_R (with the possible exception of Katritzky's scale[33,50] mentioned above), which is due to the unequal effectiveness of the interaction of the group R with different (as regards the character of the symmetry of the π-system) unsaturated fragments. In the compounds $AlkEC_\alpha\equiv C_\beta R$, where E = S, Se, or Te, an increased shielding is characteristic of the C_α atoms (regardless of the character of R); the chemical shift is displaced by 9—11 p.p.m. on passing from the sulphides to the selenides and by 33—36 p.p.m. on passing from the sulphides to the tellurides. On the other hand, the C atom is deshielded and the corresponding displacements are 5—6 and 17—18 p.p.m.[53] Evidently chalcogens exhibit π-acceptor properties in relation to the triple bond, because the EtS and $EtCH_2$ groups, having similar induction constants, exhibit significantly different effects on the vinyl and ethynyl fragments, while the effects on the ethyl groups are similar (the values of δC are listed below in p.p.m.):[74]

	$R-C_\alpha H_2-C_\beta H_3$		$R-C_\alpha H=C_\beta H_2$		$R-C_\alpha\equiv C_\beta H$	
	C_α	C_β	C_α	C_β	C_α	C_β
δC(R=EtS)	26.5	15.8	132.7	109.7	74.0	82.2
δC(R=$EtCH_2$)	22.6	13.7	137.6	113.5	83.6	68.2
Δδ C	3.9	2.1	—4.9	—3.8	—9.6	14.0

Whereas the π-electronic effect of the ethylthio-group on the C_β atom of the double bond is shielding, in the case of the triple bond it has the opposite sign and is three times greater. It may be that in the latter case this effect has the character of $d_\pi-p_\pi$ conjugation. Such conjugation is promoted by the increase in the electronegativity of the substituent at the sulphide sulphur atom.[68,75] This is confirmed by the X-ray fluorescence spectra of the compounds $AlkEt\equiv CH$, which indicate an appreciable contribution of the charge on the *3d* orbitals of the sulphur atom.[76] A non-empirical calculation for the $HSC\equiv CH$ molecule in terms of the contracted STO-3G basis set[70] indicates nevertheless the existence of an appreciable negative charge (−0.19) on the ethynyl fragment. On the basis of the concept of the π-acceptor nature of the deshielding of the C_β atom, one may conclude that, since it increases significantly from sulphur to tellurium, the $5d-2p$ π-interaction is energetically most favourable. In view of the unexpected nature of this conclusion, we shall consider the characteristic features of the influence of Group VIA elements on the δC of the closest carbon atoms of the group R in the series of isologous compounds of Group IVA, VIA, and VIIA elements (Table 7). With increase in the number of the Period, the shielding of the C_{sp^2} atom, in the α-position relative to the Group VIA element, leads to an increase in the chemical shift by 50—70 p.p.m., while δC_β hardly changes. In the series of halogenoalkanes, the character of the changes in δC is analogous, although their range is wider by 20—30%.[79,80] In the isologous series of compounds of Group IVA elements (Alk_3ER), the changes in δC for the alkyl group are not regular and their range is much narrower.[81]

The shielding effect of the chalcogens on C_α in the case of sp^2-carbon atoms increases with increase in the number of the Period, as for sp^3-carbon atoms, although the range of variation of

δC in the latter case is somewhat wider. The values of δC_β for the C_{sp^2} atoms increase with increase in the atomic number of E and for the vinyl fragment this increase is more appreciable than for the phenyl fragment (Table 7). This is apparently induced by the redistribution of the π-charge of the heteroatom in the case of the phenyl substituent between two positions (*ortho*- and *para*-positions).[78]

The shift δC_{sp} changes under the influence of the heteroatom E (E = O, S, Se, Te) approximately in the same way as in halogenoacetylenes, but the change is different from that observed in Group IVA elements (Table 7).

In the isologous series of compounds of Group IVA, VIA, and VIIA elements (Table 7), the "heavy atom effect" apparently makes a considerable contribution to the change in the shielding of the C_α and C_β atoms of the triple bond in the chalcogenides and halides. The occurrence of this effect for the halogens has been noted in a number of studies.[80,82,83] Although the electronegativity of Group IVA elements also changes appreciably, this effect is not manifested in this instance. The following qualitative model of the observed phenomenon can be proposed. The effect of the elements of different Groups in the Periodic System on neighbouring hydrocarbon fragments is determined by the presence in these elements of different numbers of LEP (O for C, Si, Ge, Sn, and Pb, 2 for O, S, Se, and Te, and 3 for F, Cl, Br, and I), which are capable of interacting with substituents at a distance more strongly the greater the increase of the diffuseness of the corresponding *p* orbitals within the Group. The size of the substituent, the presence in the latter of a π-system, and the polarisability of the system determine the extent of the influence of the heteroatom on the substituent, i.e. the extent of the changes in δC. The absence of the "heavy atom effect" in Group IVA elements is a consequence of the absence of the LEP from them.

Since a rigorous test of this concept by a reliable quantum-chemical calculation of the shielding of the ^{13}C nuclei for the set of compounds examined has not been carried out, the results are mainly of applied interest—they assist in the correct assignment of the ^{13}C signals.

III. The constants for the spin–spin coupling in the acetylenic fragment

For all acetylenes without exception, it is possible to measure only one spin–spin coupling constant $^1J_{CC}$. In addition, for monosubstituted acetylenes it is possible to measure the SSCC between the terminal proton and the acetylenic carbon atoms across one and two bonds: $^1J_{CH}$ and $^2J_{CH}$ respectively.

1. The spin–spin coupling constants $^1J_{CH}$ and $^2J_{CH}$

The values of the SSCC $^1J_{CH}$ and $^2J_{CH}$ for acetylene (these constants have been measured most accurately by Mohantry[84]) are +248.97 and +49.62 Hz respectively. The SSCC for more than 60 monosubstituted acetylenes are presented in Table 8. The range of variation of $^1J_{CH}$ is about 50 Hz and that of $^2J_{CH}$ is about 25 Hz. For the series of compounds HC≡CX, a relation has been obtained from which it follows that the electronegativity X exerts a decisive influence on $^1J_{CH}$:[88]

$$^1J_{CH} = 208.4\,(4,7) + 17.4\,(1.8)\,E_X,\ r = 0,95,\ n = 13. \quad (8)$$

The following relation has also been put forward:[89]

$$^1J_{CH} = 5,7\,(\%s) - 18,4, \quad (9)$$

It has been used to estimate the amount of *s* character of the carbon atom in discussing the mechanisms of the interaction of various heteroatomic substituents with the triple bond.[20,21] The appreciable decrease of these SSCC for compounds containing Si, Ge, or Sn atoms as substituents at the triple bond has been explained in a number of publications[3,7,8,90] by the decrease in the amount of *s* character of the hybrid orbital of the terminal carbon atom, participating in the formation of the C–H bond, as a result of the π=acceptor effect of E: $R_3\overset{\ominus}{E}=C=\overset{\oplus}{C}-H$. This model is relatively unconvincing because $d_\pi - p_\pi$ interaction is also characteristic of the substituents R_2SO_2 (this follows from the appreciable population of the *d* orbitals of the sulphur atom according to X-ray fluorescence data), although for these compounds $^1J_{CH}$ is greater by 13 Hz than for alkynes (Table 8). Furthermore, the decrease in the amount of *s* character of the terminal carbon orbital in ethynyl ethers can be induced by the π-donor properties of oxygen:

$$RO-C\equiv C-H \longleftrightarrow R\overset{\oplus}{O}=C=\overset{\ominus}{C}-H.$$

However, in this case too there is an appreciable increase in $^1J_{CH}$ and the influence of the nature of R on $^1J_{CH}$ is insignificant (Table 8).

Table 8. The spin–spin coupling constants $^1J_{CH}$ and $^2J_{CH}$ (in Hz) for monosubstituted acetylene derivatives R–C≡CH.

R	$^1J_{CH}$	$^2J_{CH}$	Refs.	R	$^1J_{CH}$	$^2J_{CH}$	Refs.
H	249.0	49.6	[85]	$HOCH_2C\equiv C$	259.0	52.5	[41]
Me	247.6	50.8	[37]	N≡C	266.8	53.4	[41]
Bu	247.7	50.0	[86]	EtO	263	—	[21]
Hex	247.3	49.9	[86]	PhO	265.5	60.3	[41]
Bu^t	246.5	48.9	[86]	*p*-$MeOC_6H_4O$	265.5	59.5	[41]
$(CH_2)_5C(OH)$	248.7	49.0	[86]	*p*-MeC_6H_4O	265.3	59.3	[41]
$HOCH_2$	251.3	50.0	[86]	*p*-ClC_6H_4O	266.0	59.7	[41]
$PhOCH_2$	251.5	50.7	[86]	*p*-$NO_2C_6H_4O$	269.1	60.9	[41]
o-$NO_2C_6H_4OCH_2$	253.0	50.0	[86]	EtS	253	—	[21]
p-$NO_2C_6H_4OCH_2$	254.2	50.9	[41]	PhS	256	51.6	[87]
p-$C_6H_4OCH_2$	251.5	50,6	[41]	$BuSO_2$	266	—	[21]
p-$BrC_6H_4OCH_2$	252.0	50.0	[41]	Me(Ph)N	258	—	[21]
p-$FC_6H_4OCH_2$	251.3	49.8	[41]	Ph_2N	259	55.5	[21]
p-$MeC_6H_4OCH_2$	251.5	49.9	[41]	$Pr_3^i P$	244	45	[41]
p-$MeOC_6H_4OCH_2$	251.5	49.9	[41]	$Bu_2^t P$	246	46	[41]
$CCl_2=CHOCH_2$	252.9	50.3	[41]	Ph_2P	247	45.8	[87]
$(CCl_2=CHOCH_2)_2$	250.8	49.5	[41]	Bu_3^tPO	252	49	[21]
$BrCH_2$	252.4	49.3	[86]	$Pr^iP(S)$	250	46	[41]
$ClCH_2$	252.6	50.5	[86]	Me_3Si	236.8	42.2	[86]
$PhCH_2$	251.0	49.7	[86]	Et_3Si	236.8	42.3	[86]
$MeOCH_2$	253	49	[41]	Cl_3Si	249.1	44.0	[86]
Ph_3SiCH_2	247.1	50.0	[87]	Ph_3Si	241.2	41.2	[9]
$(CH_2)_4NCH_2$	247.9	49.5	[41]	Me_3Ge	236.0	42.0	[41]
$(CH_2)_5NCH_2$	248.2	48.9	[41]	Et_3Ge	235.7	41.9	[86]
$(CH_2)_6NCH_2$	247.3	48.5	[41]	Cl_3Ge	253.1	45.9	[86]
$O(CH_2)_4NCH_2$	248.8	49.7	[41]	Ph_3Ge	238.2	41.2	[9]
$CH_2=CH$	251.1	50.1	[41]	Et_3Sn	232.6	41.3	[86]
Ph	250.6	49.1	[41]	Ph_3Sn	238	41	[41]
HC≡C	257.3	52.6	[41]	F	277.5	65.5	[88]
MeC≡C	257.3	52.4	[41]	Cl	270	60.5	[88]
$Bu^tC\equiv C$	256.6	50.6	[41]	Br	261	56.0	[88]
PhC≡C	256.9	51.6	[41]	I	255	51.5	[88]
				COOH	259.3	50.1	[41]

A reliable relation between $^1J_{CH}$ for monosubstituted acetylenes and characteristics of the substituents (σ_I, σ_R, *F*, *R*) other than E_X could not be observed, although the correlation between the constants $^1J_{CH}$ and $^2J_{CH}$ is reliable:[41]

$$^1J_{CH} = 1,73\,(0,07)\,^2J_{CH} + 164\,(3.5),$$
$$r = 0.975,\ s = 2.0,\ n = 35. \quad (10)$$

The latter shows that both these SSCC are controlled by the same factors.

2. The spin–spin coupling constants $^1J_{CC}$

The values of $^1J_{CC}$ increase sharply with increase in the *s* bond order: in the calculation by the method involving summation with respect to states in terms of the "average excitation energy" approximation, the Fermi-contact contribution is proportional to the product of the amounts of *s* character of the hybrid orbitals of the interacting carbon atoms forming the C–C bond.[91] In acetylenic compounds, the *s* order has the maximum possible value (50%), which is the reason for the very high values of $^1J_{CC}$ and the wide range of their variation.

For acetylenic compounds, the constants $^1J_{CC}$ increase linearly, like the constant $^1J_{CH}$, with increase in the electronegativity of the substituent,[86,92,93] which is induced by the increase in the Fermi-contact contribution.[94] A specific feature of the $^1J_{CC}$ for acetylenic compounds is a significant contribution of non-contact interactions transmitted predominantly via the π-electron system.[95]

The range of the experimental values of $^1J_{CC}$ (for 100 acetylenic compounds[96]) is unusually large: from 56.8 to 230.4 Hz, i.e. more than 170 Hz. According to theoretical estimates,[97] the limiting values may be 31.8 Hz (LiC≡CLi) and 356.0 Hz (FC≡CF). If the group electronegativity parameter of the substituent σ^2, calculated from the atomic charge density of hydrogen in the H–X molecules by the *ab initio* method in terms of the 6-31GF basis set[98] disregarding π-interactions, is used as a characteristic of the substituent in monosubstituted acetylenes, it is possible to obtain the relation

$$^1J_{CC} = 317.6\,(11.9)\,\sigma_\chi^2 + 164.9\,(0,8),\quad r = 0.983,\ s = 4.0,\ n = 27. \qquad (11)$$

Equations of a similar type have also been found for disubstituted acetylenes with a single fixed substituent, although this approach does not take into account the mutual influence of the substituents, which leads to non-additivity. A general relation for all acetylenic compounds of the type XC≡CY assumes the form[96]

$$^1J_{CC} = 270.8\,(7.3)\,(\sigma_\chi^2 X + \sigma_\chi^2 Y) + 720.4\,(151.8)\,\sigma_\chi^2 X \sigma_\chi^2 Y + 162.4\,(0.7),\quad r = 0.982,\ s = 5.4,\ n = 59. \qquad (12)$$

The cross-term in Eqn. (12), which is statistically significant, reflects the non-additivity of the influence of the substituents. It is greatest when the α-atom of one of the substituents is Si, Ge, Sn, Br, I, or Hg, which influences significantly the π-system of the acetylenic compound.

There is a reliable relation between the constant $^1J_{CC}$, on the one hand, and $^1J_{CH}$ and $^2J_{CH}$ for monosubstituted acetylenes:[96]

$$^1J_{CC} = 2.87\,(0.15)\,^1J_{CH} - 545.6\,(37.1),\quad r = 0.981,\ s = 4.37,\ n = 16; \qquad (13a)$$

$$^1J_{CC} = 5.67\,(0.25)\,^2J_{CH} - 109.6\,(12.0),\quad r = 0.986,\ s = 3.70,\ n = 17. \qquad (13b)$$

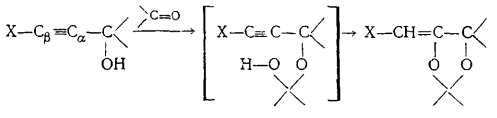
The statistically significant (r = 0.995) relation between the constants $^1J_{CC}$ for disubstituted acetylenes and the force constants of the triple bonds in these compounds must be regarded as the most reliable relation for practical purposes.[99]

IV. Relation between the reactivity of substituted acetylenes and the chemical shifts of the ethynyl carbon atoms

The reactivity of acetylenic compounds and the stereospecificity of the addition of various reactants to them depend on the nature of the substituents, which determine the energy of the transition state, the steric accessibility of the triple bond to the attack by reactants, and the distribution of electron density in the molecule.

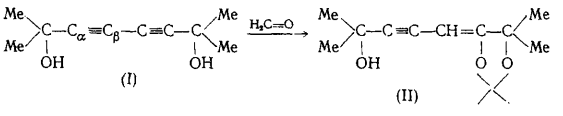
Since, according to literature data,[20,21] the values of δC_{sp} on the ^{13}C NMR spectra reflect the distribution of electron density in the acetylenic fragment, the difference between them ($\Delta\delta C$) characterises the polarisation of the triple bond. Presumably, these parameters can have a definite importance for the explanation and prediction of the regiospecificities and stereospecificities of reactions involving addition to the triple bond and in general as regards the possibility of their occurrence. The search for such relations is the aspect of the application of NMR to acetylene chemistry of greatest current interest.

The reaction involving the addition of carbonyl compounds to α-ethynyl alcohols containing a wide range of functional groups, both directly at the triple bond and separated from them by the methylene bridge, has been studied:[49,100–107]



Heterocyclisation proceeds readily in the series of α-ethynyl alcohols with X = Br, CN, COOR, COR, or C≡CR, but does not occur when X = H, CH=CH$_2$, PhO, ROCH$_2$, or R$_2$NCH$_2$. This difference in the chemical behaviour agrees well with the parameters of the ^{13}C NMR spectra of the corresponding acetylenic compounds.[49,100] Thus, whereas $\Delta\delta C_{\alpha,\beta}$ for the terminal alcohols (X = H) is 8–19 p.p.m., for the bromo-derivatives (X = Br) this quantity reaches 32–42 p.p.m., i.e. in the halogenoalcohols the degree of polarisation of the triple bond is greater, which favours nucleophilic addition. The direction of polarisation is determined mainly by the σ-acceptor effect of the bromine atom.

It is of interest to note that formaldehyde interacts with only one hydroxyethynyl group of the diacetylenic glycol (I):



Analysis of the values of δC for the dyne (I) and the enyne dioxolan (II) permits the conclusion that in the former case polarisation promotes the nucleophilic addition of the hydroxy-group with formation of the dioxolan ring, while in the latter case polarisation has the opposite direction and hinders the heterocyclisation ($\Delta\delta C_{\alpha,\beta}$ = 19.2 and –20.6 p.p.m. respectively[49]). In the isotypical compounds XCH$_2$C$_\beta$≡C$_\alpha$CH$_2$OH, in which the substituent X is separated from the triple bond by the methylene bridge, the changes in δC are determined mainly by its polar influence:[49]

$$\delta C_\alpha = 78.4\,(1.4) + 12.0\,(1.4)\,\sigma^*(XCH_2),\quad r = 0.977 \qquad (14)$$

The qualitative relation between $\Delta\delta C$ and the reactivity of substituted propargyl alcohols suggested an increase in the reactivity of substrates on passing from bases (aminoalcohols) to their quaternary

salts, for which the values of $\Delta\delta C$ are higher:[49]

$R_2NCH_2C_\beta{\equiv}C_\alpha C(OH)R^1R^2$ $\quad$ $^{\ominus}I^{\oplus}MeR_2NCH_2C_\beta{\equiv}C_\alpha C(OH)R^1R^2$

$\Delta\delta C_{\alpha,\beta}=4-7$ p.p.m. $\quad$ $\Delta\delta C_{\alpha,\beta}=17-22$ p.p.m.

The heterocyclisation of aminoalcohols on heating with paraformaldehyde in the presence of bases (potassium carbonate, potassium hydroxide, tetraethylammonium hydroxide) in boiling methanol for 8 h does not take place although the corresponding methiodides readily cyclise even at room temperature, affording high yields (75–90%) of the methiodides or 4-(2-dialkylaminoethylidene)-1,3-dioxolans. The latter were also obtained from the methiodides (IIIa–c) and the reactivity of these salts also agrees with the differences in δC_{sp}:[101]

$$^{\ominus}I^{\oplus}MeR_2NCH_2C{\equiv}CH \xrightarrow[KOH-EtOH]{H_2C=O} {}^{\ominus}I^{\oplus}MeR_2NCH_2CH{=}C(O)CH_2O$$

(IIIa–c) $\quad$ (IVa–c)

R = Me (a), Et (b), C_5H_{10} (c).

Comparison of the parameters of the ^{13}C NMR spectra of propargylamines $R_2NCH_2C_\beta{\equiv}C_\alpha H$ ($\Delta\delta C_{\alpha,\beta}$ = –5–6 p.p.m.) and their salts ($\Delta\delta C_{\alpha,\beta}$ = 8–12 p.p.m.)[101] permits the assumption that the triple bond in the molecules of the salts is polarised by the σ-acceptor effect of the ammonium group, which increases the acidity of the acetylenic proton and facilitates the interaction with paraformaldehyde under the conditions of the Favorskii reaction. This hypothesis has been confirmed by experimental data: on interaction with paraformaldehyde in alcoholic potassium hydroxide solution (60 °C, 1 h), the methiodides readily form substituted 1,3-dioxolans (IVa–c) in 90–91% yield.[101]

Terminal α-ethynyl alcohols react with phenyl isocyanate to form the corresponding *N*-phenylcarbamates, which isomerise to 4-alkylidene-2-oxazolidinones in the presence of bases:[108–110]

$$H{-}C{\equiv}C{-}CR_2(OH) \xrightarrow{PhNCO} H{-}C{\equiv}C{-}CR_2(O{-}C(=O){-}NHPh) \rightarrow CH_2{=}C(O{-}C(=O){-}NPh){-}CR_2$$

Substituted 4-dialkylaminobut-2-yn-1-ols (V) also react with phenyl isocyanate to form the corresponding *N*-phenylcarbamates (VI), but their cyclisation in the presence of bases to the corresponding 2-oxazolidines does not occur:[111]

$$R_2NCH_2C_\beta{\equiv}C_\alpha{-}CR'_2(OH) \xrightarrow{PhNCO} R_2NCH_2C{\equiv}C{-}CR'_2(O{-}C(=O){-}NHPh) \longrightarrow$$

(V) $\quad$ (VI)

$$\rightarrow {}^{\ominus}I^{\oplus}MeR_2NCH_2C{\equiv}CCR'_2(O{-}C(=O){-}NHPh) \rightarrow {}^{\ominus}I^{\oplus}MeR_2NCH_2CH{=}C(O{-}C(=O){-}NPh){-}CR'_2$$

(VII) $\quad$ (VIII)

R, R′ = Alk

This difference between the reactivities of the carbamates of terminal ethynyl alcohols[108–110] and their aminomethyl analogues can be explained on the basis of ^{13}C NMR spectroscopic data. The polarisation of the triple bond is essential for the nucleophilic attack by the nitrogen atom on the ethynyl carbon atom. The electron-donating substituents R_2NCH_2 give rise to an unfavourable polarisation: $\Delta\delta C_{\alpha,\beta}$ = 0–7 p.p.m. For the methiodides (VII), $\Delta\delta C_{\alpha,\beta}$ = 10–15 p.p.m., i.e. a deficiency of electron density arises on the C_α atom, creating favourable conditions for nucleophilic attack. Indeed, in the presence of sodium methoxide at room temperature, the methiodides (VII) cyclise to the oxazolidines (VIII) in high yields.[111]

The set of data obtained for aminoalkyl- and bromo-ethynyl alcohols in the heterocyclisation reaction justifies the hypothesis that the polar and not the steric influence of the substituents at the ethynyl carbon atom is the decisive factor for its occurrence.

Thus, according to the available data, for the reaction involving addition to the ethynyl alcohols there is a qualitative correspondence between the reactivity and the ^{13}C chemical shifts of the initial acetylenic compounds, although the values of δC_{sp} themselves cannot serve as an adequate criterion of the charge distribution on the triple bond.

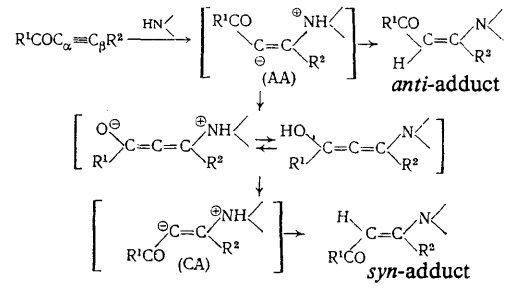
The results of a kinetic study of the hydroboration reaction of 1-halogenoalk-1-ynes, which is important for synthesis, have shown[112] that the rate of reaction and its regioselectivity agree with the parameters of the ^{13}C NMR spectra.

The addition of nucleophiles to α-ethynyl ketones is an important and widely occurring reaction. The conjugation of the triple bond with the carbonyl group ($-C^4{=}C^3{-}C^2{=}O^1$) permits 1,2-, 3,4-, and 1,4-addition. Thus alcohols and amines add to the 3,4-positions, while hydrazines and semicarbazides add to the 1,2-positions. Hydroxylamines, which occupy an intermediate position as regards nucleophilicity between strong (hydrazines) and weak (amines, alcohols) nucleophiles, react with both electrophilic centres simultaneously.[113] However, there is no rigorous correlation between the basicity of the amines and the reactivity of acetylenic ketones.[114,115] The relation between the reactivity of acetylenic ketones and other parameters—the Hammett constants[114] and entropy characteristics,[116] including parameters of the ^{13}C NMR spectra[117,118]—have been investigated. NMR parameters serve as an extremely useful source of information, provided that δC_{sp} does indeed characterise the electron density on these compounds and the difference between them characterises the polarisation of the triple bond,[20,21] which determines the reactivity of acetylenes in nucleophilic addition reactions.

One of the first attempts on these lines involved the study of the reactivity α-ethynyl ketones in reactions with amines and the search for a relation between the reactivity of substrates and the characteristics of the ^{13}C NMR spectra.[117] If the variable substituents R^1 and R^2 are located directly at the ynone fragment ($R^1COC_\alpha{\equiv}C_\beta R_2$), when their anisotropic and steric effects on δC_{sp} are considerable, the changes in δC_{sp} do not reflect the true changes in electron density on the C_α and C_β atoms, and the values of $\Delta\delta C_{\alpha,\beta}$ are not related to the corresponding kinetic parameters.[117,118] If the R^1 and R^2 substituents are remote from the triple bond in space (for example, in $R^1C_6H_4COC_\alpha{\equiv}C_\beta C_6H_4R^2$), then a relation between δC_{sp} and the electronic properties of the substituents is manifested. However, in this case too there is no linear relation between the rate constants for the addition of morpholine to these substances and $\Delta\delta C$.[41,74,118] The electron-donating substituents R^1 in the *para*-position in the benzene ring reduce both the reaction rate and $\Delta\delta C$, while electron-donating substituents R^2 reduce the reaction rate but increase $\Delta\delta C$ (Fig. 2). On the other hand, a satisfactory relation is observed between the reaction rate and the ratio of the products formed (Fig. 3).

Both the reaction rate and the yield of the *syn*-adduct increase with the enhancement of the electron-accepting character of the substituents. This is apparently associated with the fact that, in

conformity with the reaction mechanism established,[74] the probability of the isomerisation of the *anti*-anion, formed initially, to the *syn*-anion (SA) and hence also the fraction of the *syn*-adduct should increase as a result of the stabilisation of the intermediate by the electron-accepting substituents:



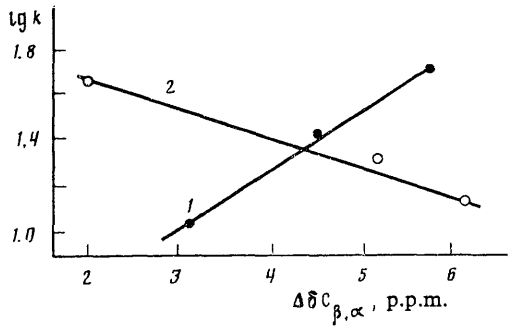


Figure 2. Dependence of the rate constants for the reactions between $R^1C_6H_4COC{\equiv}CC_6H_4R^2$ and



on $\Delta\delta C_{\beta,\alpha}$:[74] (1) variation of the substituents R^1; (2) variation of the substituents R^2.

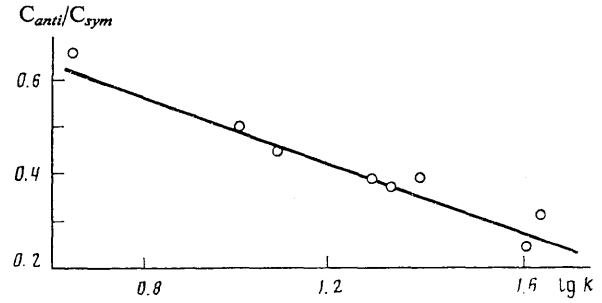


Figure 3. Dependence of the isomer ratio (determined from ^1H NMR spectra) on the reaction rate constant (lg *k*).[74]

It is also possible that the reaction rate and the ratio of the isomers are determined by the rate of protonation of the oxygen of the carbonyl group in the intermediate, which depends on the charge on the oxygen atom.[118]

A qualitative relation between the reactivity of acetylenes and the parameters of their ^{13}C NMR spectra has been noted in a number of studies. Thus the reactivity of thiacycloalkynes increases with increase in δC_{sp} (the polarisation of the triple bond).[119]

The site where nucleophiles are inserted into the acetylenic fragment of halogenoacetylenes cannot be predicted unambiguously, because it is known[120] that they contain three centres susceptible to nucleophilic attack: the halogen atom and the C_α and C_β carbon atoms of the triple bond. Under the conditions of the Arbuzov rearrangement, halogenoacetylenes react with trialkyl phosphites to form the products resulting from the substitution of the halogen (attack on C_α):[121,122]

$$RC_\beta{\equiv}C_\alpha X + P(OAlk)_3 \rightarrow [RC{\equiv}CP(OAlk)_3]^{\oplus}X^{\ominus} \rightarrow RC{\equiv}CP(O)(OAlk)_2 + AlkX.$$

Both the values of δC_{sp} (Table 9) and the distribution of the effective charges in model compounds calculated in terms of the CNDO/2 approximation agree with the experimental composition of the products.[122,126] The value of δC_α is lowest for the ynamine probably because of the strong π-donor effect of the dimethylamino-group in the "push-pull" system (a system with concerted effects of two substituents).

Table 9. The ^{13}C chemical shifts of the *sp* carbon atoms (in p.p.m. relative to TMS) and the differences between them ($\Delta\delta C$, p.p.m.) for certain heteroatomic substituted acetylenes $R^1C_\alpha{\equiv}C_\beta R^2$.

R^1	R^2	δC_α	δC_β	$\Delta\delta C_{\alpha,\beta}$	Refs.
$(MeO)_2P(O)$	Cl	54.04	75.88	−18.84	[121]
$(EtO)_2P(O)$	Cl	57.49	74.56	−17.07	[121]
$(MeO)_2P(O)$	Br	66.71	62.15	4.56	[121]
$(EtO)_2P(O)$	SEt	82.10	90.00	−7.90	[122]
$(EtO)_2P(O)$	SEt	86.15	93.71	−7.56	[123]
$(EtO)_2P(O)$	SPr	86.74	93.30	−6.56	[123]
$(EtO)_2P(O)$	SBu	85.87	92.68	−7.71	[123]
$Cl(PPh_3)$	SPh	76.97	112.30	−35.33	[123]
$(PrO)_2P(O)$	NMe_2	48 01	63.89	−14.88	[123]
Cl	SEt	69.57	59.71	9.81	[123]
Cl	SPr	68.65	59.71	8.94	[123]
$CH_2{=}CH$	SMe	91.38	82.20	9.18	[22]
$CH_2{=}CH$	SeMe	97.53	72.57	24.96	[22]
$CH_2{=}CH$	TeMe	109.66	49.48	60.18	[22]
$CH_2{=}CH$	H	78.4	82.5	−4.1	[124]
***cis*-MeCH=CH**	NEt_2	62.65	99.45	−36.80	[125]
***trans*-MeCH=CH**	NEt_2	63.50	98.75	−35.25	[125]
***cis*-MeCH=CH**	NPr_2	62.08	99.02	−36.94	[125]
$Me_2C{=}CH$	NPr_2	63.10	99.45	−36.35	[125]
$Me_2C{=}CH$	NEt_2	62.30	97.20	−34.90	[125]
H	OEt	23.4	89.6	−66.2	[21]
Me	OMe	28.2	88.6	−60.4	[21]
Et	OEt	35.7	87.8	−52.1	[21]

The preferential attack by the nucleophile on the carbon atom joined to the halogen atom occurs in the reaction of alkyl(aryl) chloroethynyl sulphides with triphenylphosphine and trialkyl phosphites. In the latter case, the only reaction products are the normal products of the Arbuzov rearrangement:[123]

$$\underset{(A)}{(RSC{\equiv}\overset{\oplus}{C}PPh_3)Cl^{\ominus}} \xleftarrow{PPh_3} RSC{\equiv}CCl \xrightarrow{P(OEt)_3} \underset{(B)}{RSC{\equiv}CP(O)(OEt)_2}.$$

The signals of the C_α and C_β atoms in the ^{13}C NMR spectra of the reaction products (A) and (B) are deshielded relative to chloroacetylenes (Table 8) and the greatest degree of polarisation is observed in the ionic compound.

Organoelement compounds of the acetylenic series frequently exhibit a specific reactivity. An attempt has been made[11] to estimate the reactivity of silyl- and germyl-acetylenic carbonyl compounds from ^{13}C NMR data. Table 1 shows that the effects of the Si- and Ge-groups as well as carbonyl-containing groups are deshielding. Reactions of a silylacetylenic ketone with methyl- and dimethylamines proceed anomalously:

$$R_3SiC{\equiv}CC(O)Me + HNR^1R^2 \rightarrow R_3SiNR^1R^2 + R^2R^1N{-}CH{=}CHC(O)Me.$$

This unusual result has been explained[11] by the fact that the R_3E and C=O groups, which behave as acceptors in relation to the triple bond, diminish the electron density on both C_α and C_β atoms, which should reduce the reactivity of the triple bond in nucleophilic addition reactions. It is hardly possible to agree with this explanation. Electron-accepting groups are known to increase and not to decrease the reactivity of the triple bond in relation to nucleophiles. Thus it has been stated[113] that acetylenic compounds containing two electron-accepting substituents [the compounds PhC(O)C≡CC(O)Ph, PhC(O)C≡CC(O)Me, etc.] readily combine with amines at the triple bond. On the other hand, the result obtained by Arshavshkya et al.[11] is apparently associated with the fact that trialkylsilylacetylenes are very readily desilylated even at room temperature in the presence of a base,[127] whose role in the given reaction is probably assumed by the amine.

Alkynylamines and the related alkynyl ethers exhibit an unusual chemical reactivity, the reactivity of alkynyl ethers in ionic reactions being lower.[125,128]

The mode of addition of electrophiles and nucleophiles to alkenylamines[125] corresponds to their electronic structure, established by the CNDO/2 method, and the characteristics of their ^{13}C NMR spectra

$$\underset{}{\overset{-0.014}{}}\ \ \overset{0.034}{}\ \ \overset{-0.120}{}\ \ \overset{0.061}{}\ \ \overset{-0.176}{}$$
$$cis\text{-}CH_3{-}CH{=}CH{-}C_\alpha{\equiv}C_\beta{-}N(C_2H_5)_2$$

The excess electron density on the C_α atom agrees with the manifestation of the π-donor effects of nitrogen in the ^{13}C NMR spectra (Table 8). Although the values of δC_α for diethylamino- and dipropylamino-pent-3-en-1-ynes (62.65 and 62.08 p.p.m. respectively) as well as the values of δC_β for these compounds (99.45 and 99.02 p.p.m.) agree with the calculated charges, the upfield shift of the C_α signal and the value of $\Delta\delta C_{\alpha,\beta}$ for the alkynylamines are significantly smaller than might have been expected from data for the alkynyl ethers.[21] This indicates a more effective interaction of the ether oxygen with the π-systems of the triple bond,[41] but conflicts with experimental data according to which alkynylamines are much more reactive than alkynyl ethers in electrophilic addition reactions (attack on the C_α atom).[125] It has been suggested[125] that this is associated with the dynamic shift of the *p* electrons of the nitrogen atom towards the triple bond at the instant of reaction.

The regiospecificity of the addition of organocopper compounds to various heterosubstituted acetylenes is determined by the influence of the heteroatoms:[129]

$$\underset{\text{E=N, O, S.}}{\underset{\text{(IX)}}{RCu + R^1C{\equiv}CEAlk_n}} \xrightarrow[H_2O]{THF} \underset{\text{(X)}}{\overset{H}{\underset{R^1}{>}}C{=}C\overset{R}{<}EAlk_n} + \underset{\text{(XI)}}{\overset{R}{\underset{R^1}{>}}C{=}C\overset{H}{<}EAlk_n};$$

Under these conditions, compounds with E = S form exclusively the isomer (XI), while compounds with E = N or O give rise preferentially to the isomer (X). Thus in the given instance the mode of addition of RCu to compound (IX) agrees with the changes in δC_{sp} as a result of the effect of E on the triple bond (Tables 3 and 9).

Electrophiles add to the triple bond in the compounds $RC{\equiv}CER^1$ (E = S, Se, Te) and in the analogous ethers in the same manner, but the mode of addition differs from that in hydrocarbons.[130,131] The addition of hydrogen chloride and bromide to alkylthio- and alkylseleno-vinylacetylenes always takes place at the triple bond and the halogen atom adds to the C_α atom:

$$CH_2{=}CH - C_\beta{\equiv}C_\alpha ER^1 \xrightarrow[X_2]{HX} CH_2{=}CH - CH{=}CXER^1;$$

E=S, Se; X=Cl, Br.

Comparison of the experimental data with the distribution of electron density in the molecules of 1-methylthio- and 1-methylseleno-but-3-en-1-ynes (without taking into account the *d* orbitals of the heteroatom) shows that the maximum electronic charge is concentrated on the β-carbon atom of the triple bond, which is consistent with the order and orientation of the electrophilic addition:[131,132]

$$\overset{-0.051}{CH_2}{=}\overset{-0.008}{CH}{-}\overset{-0.104}{C_\beta}{\equiv}\overset{0.014}{C_\alpha}{-}\overset{0.160}{S}{-}\overset{0.008}{Me}$$
$$\overset{-0.036}{CH_2}{=}\overset{-0.005}{CH}{-}\overset{-0.073}{C_\beta}{\equiv}\overset{0.003}{C_\alpha}{-}\overset{0.006}{Se}{-}\overset{0.006}{Me}$$

The ^{13}C NMR spectra of these compounds contain valuable information about the degree of conjugation of the heteroatoms (S, Se, Te) and the triple and double bonds.[22] The character of the polarisation of the triple bond (Table 8), indicating an enhancement of the electron-accepting properties on passing from alkylthio- to alkyltelluro-vinylacetylenes, conflicts with the data on the reactivities of these compounds.[22]

The data presented demonstrate yet again that the experimental values of δC_{sp} and the differences between them do not permit, despite the hypotheses expressed in the literature,[20,21] the prediction of not only the reactivity but also of the mode of addition of the reactants even in an isologous series of compounds. One of the causes of this is the "heavy atom effect" mentioned above, whose influence on the shielding of the C_{sp} atom in selenium-, bromine-, and especially tellurium-substituted acetylenic compounds cannot so far be estimated quantitatively.

The high reactivity of monosubstituted acetylenes in many reactions (acetylene condensation, Favorskii, Mannich, oxidative coupling, etc. reactions) is usually explained by the CH acidity, although little information is available about the equilibrium CH acidity. This is associated both with the difficulty of measuring the p*K* (which requires special apparatus and the use of dry media) and with the fact that certain derivatives (nitro-, alkoxycarbonyl, and other compounds) undergo side reactions under the conditions of the measurement (a highly basic medium). The acidity of monosubstituted acetylenes should be higher the lower the charge on the C_β atom. There are correlations between the energies of the heterolytic dissociation of the ≡C−H bonds and the charge on the ethynyl group[133] and also between the values of δC_β and the charge density on the same atom in *para*-substituted phenylacetylenes.[29] It therefore appeared useful to compare the values of δC_β with the p*K* for the monoacetylenic compounds. A linear relation has been observed between the p*K* for ethynylpyrazoles, the heterolytic dissociation energies of the ≡C−H bonds (the thermodynamic CH acidity of these compounds was measured in dimethyl sulphoxide by the transmetallation method[134,135]), and the charges on the ethynyl groups (calculated by the CNDO/2 method[133]).[136] These results agree with the fact that the relative rate of the Mannich reaction (piperidine, 35 °C) in the series of isomeric 3-, 4-, and 5-ethynyl-1-methyl pyrazoles is four times higher for the 5-C≡CH isomer than

for the 4-C≡CH isomer and 1.6 times higher than for the 3-C≡CH isomer.[137] However, a linear relation has not been observed between the pK or the charge $q\,C_\beta$ and the values of δC_β for these compounds. Presumably in the given series the shift δC_{sp} does not reflect the charge density.

The parallel variation of the acidities of *para*-substituted phenylacetylenes with δC_β and $\Delta\delta C_{\beta,\alpha}$ (Fig. 4) justifies the assumption that in the given series the shift $\delta C_{\beta(\alpha)}$ reflects the charge density on the atoms indicated.[29]

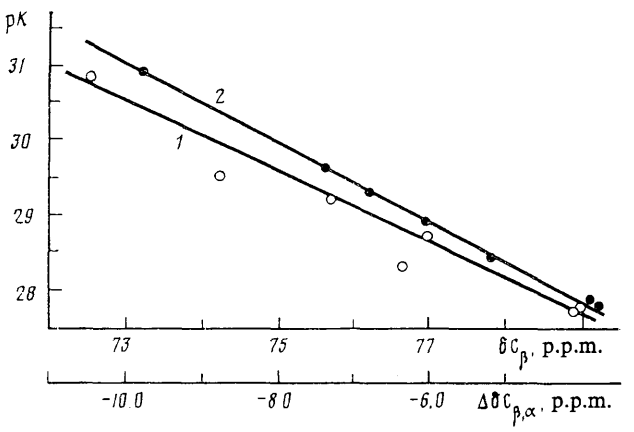


Figure 4. Dependence of pK on δC_β (line *1*) and $\Delta\delta C_{\beta,\alpha}$ (line *2*) in the series of *para*-substituted phenylacetylenes (the values of δC_{sp} were taken from Klasine et al.[29]).

A linear relation has also been observed reliably between the regiospecificity and stereospecificity of the nucleophilic addition of *p*-fluorophenol to *para*-substituted phenylacetylenes[138] and the values of δC_{sp}.[116]

On the whole, comparison of the calculated charge densities on the ethynyl carbon atoms[41,74] with the measured shifts δC_{sp} both for the simplest monosubstituted acetylenes[139] and for acetylenes containing heteroatomic substituents at the triple bond[140] does not exhibit a rigorous relation between these characteristics. This is associated primarily with the fact that substituents located close to the triple bond exert an appreciable steric and anisotropic influence on δC_{sp}.

Thus the relation between the reactivities of acetylenic compounds and the parameters of their ^{13}C NMR spectra is mainly qualitative. One of the main reasons for this is apparently the different distributions of electron density in the molecule, especially on the triple bond, in the stationary and dynamic states. Another possible explanation is the multifunctionality of the dependence of $\delta^{13}C$ on the structural parameters of the test compounds, which is not susceptible to a quantum-chemical description.

There is in general no justification for relating the degree of polarisation of the triple bond to the difference between the chemical shifts of the *sp*-carbon atoms or the overall charge on the triple bond to the sum of the shifts. This approach is valid only for chemical compounds in which the substituent is fairly reliably separated from the triple bond by a conformationally rigid fragment, for example, the benzene ring.

The state of the NMR theory at the present time is such that one can explain the available experimental facts rather than make predictions. There is no doubt about the usefulness of further studies on these lines, particularly if they are directed towards individual classes of reactions with participation of structurally similar acetylenic compounds.

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