^{35}Cl NQR spectra of alkylsulfanylchloracetylenes. The nature of the Cl–C$_{sp}$ bond

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Dedicated to Academician Mikhail Voronkov on the occassion of his 80th birthday

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Abstract

^{35}Cl NQR Spectra of chloro-substituted acetylenes of the Cl–C≡C–R series and the results of *ab initio* calculations are discussed. The electronic structure of the Cl–Csp bond in the chloro-acetylenes under consideration is controlled by the inductive effect of the C≡CR group and interaction of the chlorine lone electron pairs with antibonding π*-bonds of the C≡C group. These factors act independently of each other in different directions that are responsible for the narrow range of ^{35}Cl NQR frequency variation and the expected non-zero parameters of the EFG asymmetry tensor in the series studied.

Keywords: ^{35}Cl NQR, chloroacetylenes, *ab initio,* NBO analysis, asymmetry parameter

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Introduction

Haloalkynes are known to be poorly stable and reactive compounds.[1–3] Their high reactivity is caused, in particular, by repulsion of lone pairs of the halogen atom with π-electrons of the C≡C triple bond.[1] The Cl–C$_{sp}$ bonds (1.62–1.65 Å, Table 1) are the shortest Cl-C bonds (the range of Cl–C$_{sp}{}^{3}$ bond length variation is 1.71–1.83 Å, that of Cl–C$_{sp}{}^{2}$ is 1.70–1.80 Å);[4] this can be explained in terms of the high electronegativity of the sp-hydridized carbon atom.

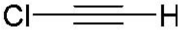
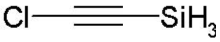
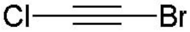
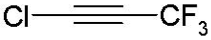
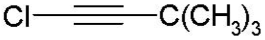
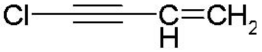
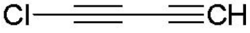
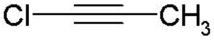
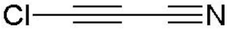
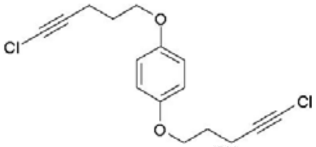
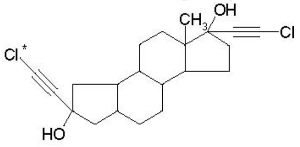
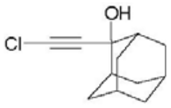
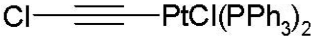
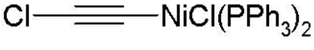
The Cl–C$_{sp}$ bonds (1.66–1.69 Å) in σ-chloroacetylene complexes with nickel and platinum are markedly longer than those in compounds without coordination bonds (Table 1). Lengthening of this kind seems to be due to a strong effect of the metal on the electron density distribution in the Cl–C≡C group. This is also reflected by the length of the C≡C bond, the shortest one in the complexes (Table 1).

Noteworthy, in many compounds the Cl–C≡C fragment has a non-linear structure, and the

Cl–C≡C angle can vary from 180.0° to 173.4°.

The explanations for the Cl–C_{sp} shortening compared to Cl–C_{sp}^2 and Cl–C_{sp}^3 bonds and for some other properties of haloacetylenes are not sufficiently convincing.[14] Nevertheless, an axial symmetry of the halogen atom electronic surrounding is implied. In this regard, nuclear quadrupole resonance (NQR) spectroscopy provides a convenient tool to reveal some properties of the electronic structure of chlorine-containing compounds, e.g. polarity (ionic character) and bond order of the C-Cl bond. This method deals with transitions between energy levels due to dissimilar quadrupole nuclear interactions with external non-uniform electric field in the case of their different orientation.

Table 1. Bond lengths Cl–C_{sp} ($r_{C–Cl}$) and C≡C ($r_{C≡C}$) and bond angles φ (Cl–C≡C) of chloroacetylene derivatives

Compound	$r_{C–Cl}$ [Å]	$r_{C≡C}$ [Å]	φ [°]	Method[a]	Ref.
	1.637	1.204		MW	4
	1.620	1.234		ED	5
	1.628	1.209		MW	6
	1.627			MW	4
	1.637			ED	4
	1.637			ED	4
	1.625	1.207		MW	6
	1.6428	1.201		X–Ray	7
	1.630	1.173	179.70	X–Ray	8
	1.630	1.171	176.48	X–Ray	9
	1.646*	1.180*	178.43*	X–Ray	10
1.634		1.179		177.26	
	1.634[b]	1.180b	177.76b	X–Ray	11
	1.688	1.157	176.94	X–Ray	12
	1.663	1.155	173.426	X–Ray	13

[a] MW = Microwave Spectroscopy, ED = electron diffraction. [b] Averaged data.

The electric field non-uniformity is described by electric field gradient (EFG) tensor fully characterized by its main axis orientation relative to molecules, EFG component with maximal absolute value, eq_{zz}, and asymmetry parameter (η) which characterizes the EFG tensor deviation from axial symmetry.

$$\eta = (eq_{xx} - eq_{yy}) / eq_{zz} \qquad \textbf{Eq. 1}$$

For the ^{35}C1 nucleus with nuclear spin I = 3/2, there is observed an NQR absorption line with a frequency

$$\nu = e^2Qq_{zz} / 2h^*(1 + \eta^2/3)^{1/2} \qquad \textbf{Eq. 2}$$

where e^2Q represents the ^{35}C1 quadrupole moment. As seen from this formula, at low η values the experimental frequency ν is directly proportional to q_{zz}. This means that the experimental NQR frequencies carry some information concerning electric field non-homogeneity in the chlorine atom nucleus site during the chemical bond formation. Since the electric field gradient formed by resonance nuclear charge decreases fast enough (inverse proportionally to the cube of the distance), the major contribution to EFG is made from the electron shells whose density distribution differs from spherical symmetry, *i.e.*, valent p-electrons. The account taken of only their contribution to the EFG tensor underlies the widely accepted Towns-Daily approximation[15] relating eq_{zz} and η with valent electron occupations (N_{xx}, N_{yy}, N_{zz}):

$$eq_{zz} = eq_{at}^*(N_{zz} - (N_{xx} + N_{yy}) / 2) \qquad \textbf{Eq. 3}$$

$$\eta = 1.5^*(N_{xx} - N_{yy})/(N_{zz} - (N_{xx} + N_{yy}) /2) \qquad \textbf{Eq. 4.}$$

eq_{at} is the field gradient formed by valent p-electron. The value eq_{at} is a semiempiric parameter at this approximation. The directions of major EFG tensor axes and p-electrons are coincident: the direction of σ-electrons coincides with that of z-axis, whereas the direction of lone electron pairs is coincident with the direction of x- and y-axes.

Results and Discussion

In the present work the ^{35}Cl NQR spectra of chloro-substituted acetylenes of the Cl–C≡C–R series and the results of quantum chemical calculations are discussed. For compounds of the above type (Table 2) quantum chemical calculations were performed using *ab-initio* RHF 6-31G* with total geometry optimization.

In Table 2 are collected literature data of some experimental ^{35}Cl NQR spectral and our data for compounds Cl–C≡C–R with R = SC_3H_7, S-*i*C_4H_9, and S-*n*$C_{12}H_{25}$ presented.

Because the range of ^{35}Cl NQR frequencies of the above chloroacetylenes is rather narrow

(38.15–39.66 MHz) and the interval of Taft inductive constants of the substituents R (σ^*) is rather large (from –0.72 to +3.6),[21] the NQR frequencies are in rather poor linear correlation with the Taft inductive constants. That such correlations do take place has been widely shown and discussed in other publications.[16,17,22]

In substituted chloroacetylenes the charge on the chlorine atoms is positive (0.12–0.19) and is in agreement with the experimental ^{35}Cl NQR frequencies: The greater the positive charge at the chlorine atom is, the higher is the frequency. The calculated bond lengths are practically invariable (1.64–1.65 Å) and close to the experimental values (Table 1). The calculations suggest angular distortion of Cl–C≡C–R fragment to be expected for some compounds.

Table 2. Experimental frequencies (ν^{77})[16–20] calculated by Eq. 2 and Eq. 1; ^{35}Cl NQR spectral parameters (ν_{calc} and η_{calc}), charges at Cl atoms (q_{Cl}) and C–Cl bond lengths ($r_{C–Cl}$) of substituted chloroacetylenes Cl–C≡C–R

R	ν^{77} [MHz]	$\nu_{calc.}$ [MHz]	$\eta_{calc.}$ [%]	q_{Cl} [e]	$r_{C–Cl}$ [Å]
$SiMe_3$	38.150	40.225	0.0	0.121	1.650
CN	39.660	42.324	0.0	0.191	1.639
C≡C–Cl	39.373	41.890	0.0	0.168	1.644
Ph	39.050	41.062	0.02	0.130	1.651
H	39.220[a]	40.927	0.0	0.125	1.649
SC_3H_7	39.026	40.925	3.51	0.122	1.650
S-iC_4H_9	38.984	40.906	3.55	0.121	1.650
S-$nC_{12}H_{25}$	39.007	–	–	–	–

[a] Average value.

There is a satisfactory correlation between the theoretical and experimental values in spite of the fact that the experimental frequencies were measured in the solid phase that contributes some deal to their values, whereas the calculated frequencies are closer to the gas phase:

$$\nu_{theor} = -13.620\ (9.73695) + 1.405\ (0.24939)\nu^{77}\quad R = 0.942;\ SD = 0.28334 \qquad \textbf{Eq. 6}$$

Chloroacetylene drops out from this correlation. Therefore, the existence of intermolecular interaction in the crystal can be suggested. A slight splitting of NQR signals[16] indirectly supports this suggestion. It should be noted that for some compounds a non–zero parameter of EFG tensor asymmetry is expected.

In order to elucidate the effect of the nature of substituent R on NQR frequencies and asymmetry parameters, apart from the compounds presented in Table 2, model substituted chloroacetylenes and acetylenes of the H–C≡C–R series were calculated and NBO[23,24] analyzed for electron density. For all the compounds the Cl-C bond is formed by the hybrid atomic orbital of the chlorine and by sp hybrid orbital of the carbon atom, whereas the triple carbon-carbon bond is formed by one σ-bond and two π-bonds.[25] The electron effect of substituent R on the chlorine atom in substituted chloroacetylenes is transmitted through the carbon-carbon triple bond, that changes the population of the chlorine p_σ (N_z) atomic orbitals and the populations p_π (N_x and N_y), related to those of lone pairs, the values of which are presented in Table 3.

Table 3. Population of atomic p orbitals (N_z, N_x and N_y), number of unbalanced electrons (U_p) and the asymmetry parameter (η) of chlorine in the series Cl–C≡C–R, and the populations AO of the acetylene hydrogen atom (Ns_H) of compounds of the H–C≡C–R series

R	N_z	N_x	N_y	U_p	η [%]	Ns_H
$SiMe_3$	1.19780	1.93304	1.93304	0.73524	0.000	0.76103
CN	1.17401	1.92227	1.92227	0.74826	0.000	0.74600
C≡C–Cl	1.18746	1.93070	1.93070	0.74594	0.000	0.75389
Ph	1.19428	1.93790	1.93652	0.74293	0.280	0.75978
H	1.19198	1.93610	1.93610	0.74412	0.000	0.75798
SC_3H_7	1.19125	1.94206	1.92978	0.74467	2.473	0.75729
SF	1.18236	1.94097	1.91552	0.74588	5.118	0.75117
SCl	1.18203	1.93936	1.91799	0.74664	4.293	0.75506
OCH_3	1.19238	1.94931	1.94198	0.75326	1.459	0.75757
NH_2	1.19470	1.95109	1.93668	0.74930	2.836	0.76111

As can be seen from Table 3, under the effect of substituent, the population of chlorine p_σ and p_π electrons is changed approximately to the same degree, that in turn causes a change in the NQR frequency proportional to the number of unbalanced U_p electrons. The applicability of Towns-Daily approximation and the correct description of electron distribution in terms of NBO analysis of the chlorine p-electrons are confirmed by the existence of reasonable correlation between the experimental NQR frequencies ν^{77} (Table 2) and the number of unbalanced p-electrons (U_p):

$$\nu^{77} = -45.100\ (7.73055) + 113.214\ (10.39698)\ U_p \quad R = 0.984,\ SD = 0.1034 \quad \textbf{Eq. 7}$$

Judging by generally accepted concepts, the AO population of the hydrogen atom (N_{sH} from Table 3) in the H–C≡C–R series undergoes changes only under the inductive effect of substituent R[22]. The existence of linear correlation between N_z of the chlorine atom and N_{sH} of the hydrogen atom indicates that the chlorine atom electron density p_σ charges correspondingly to the inductive effect of substituent R.

$$N_z = 0.0967\ (0.059) + 1.445\ (0.078)\ N_{sH} \quad R=0.991,\ SD = 0.001 \qquad \textbf{Eq. 8.}$$

A decrease in the lone pair population is due to the interaction with an appropriate vacant orbital. In the compounds under consideration the lone pair of chlorine interacts with the antibonding π*-orbital of the acetylene triple bond by a mechanism of n–π* conjugation. The orbital interaction of this kind may be represented by the following Figure 1:

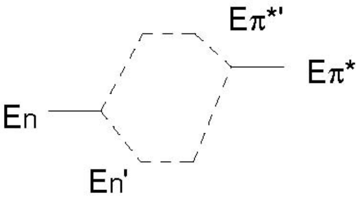


Figure 1

E_n and E_π* indicate the energy levels of lone pair and antibonding π-bond prior to conjugation, E_n', E_π'* stand for the same after conjugation the value of which is equal to $F_{n\pi*}$, $F_{n\pi*}$ denotes a Fokian element in the natural orbital basis, which is the measure of n and π* MO interaction. If the conjugation effect is regarded as $|F_{n\pi*}| << (E_n - E_\pi*)$ perturbation, then

$$E_\pi'* = E_\pi* + (F_{n\pi*})^2 / (E_\pi* - E_n) \quad \textbf{Eq. 9}$$

$$E_n' = E_n + (F_{n\pi*})^2 / (E_n - E_\pi*) \quad \textbf{Eq. 10}$$

In the first order of perturbation theory the molecular orbitals are also changed:

$$\psi_\pi'* = \psi_\pi* + \psi_n F_{n\pi*} / (E_\pi* - E_n) \quad \textbf{Eq 11}$$

$$\psi_n' = \psi_n + \psi* F_{n\pi*} / (E_n - E_\pi*) \quad \textbf{Eq 12}$$

Due to the participation of ψ_n in ψ_π'*, the LP population is decreased by a value proportional to square coefficient ψ_n in ψ_π'* :

$$\Delta N=2 \{F_{n\pi*} / (E_\pi* - E_n)\}^2 \quad \textbf{Eq. 13}$$

The same influence on the composition of antibonding orbital and its level energy will be exerted by the substituent R orbital, Ψ_R, prone to donor–acceptor interaction with the acetylene fragment π-electrons:

$$E_\pi'* = E_\pi* + (F_{nR})^2 / (E_\pi* - E_R) \quad \textbf{Eq. 14}$$

In the first approximation, the substituent influence on the change in the chlorine lone pair population can be presented as follows: the orbital Ψ_R conjugation results in an increase in E_π'*, that leads, in turn, to a change in ΔN, according to (Eq 13):

$$\Delta N = 2\,(F_{n\pi^*} / (E_{\pi}^* + \{(F_{nR})^2 / (E_{\pi}^* - E_R)\} - E_n)^2 \qquad \textbf{Eq. 15}$$

The values of variables in the left hand part of equation (Eq 15), the ψ_R orbital type and the calculated ΔN values are presented in Table 4.

The conjugation with π* MO of the acetylene fragment can involve different MOs of the substituent R (those of σ and π bonds and lone electron pairs). It should be noted that for some substituents different MO types could simultaneously participate in conjugation.

In spite of rough approximation (application of second order theory of perturbation to energy, ignorance of minor interactions), there is a satisfactory linear correlation between the populations of lone electron pairs, $N_{\pi,}$ equal to $N_{x\ \mathrm{and}}\,N_x$ from Table 3, and their changes ΔN (Table 4) caused by n–π* conjugation.

$$N_{\pi} = 2.000\ (0.006) - 1.1607\ (0.112)\ \Delta N \qquad R = 0.941,\ SD = 0.004 \qquad \textbf{Eq 16}$$

This suggests the prevailing effect of conjugation of this kind on the chlorine lone electron pairs.

The changes in ^{35}Cl NQR frequencies are induced by electronic effects of the substituent R, the inductive effect of which influences the change in the population of chlorine p_{σ} electrons. The populations of chlorine lone electron pairs are decreased under the influence of n–π* conjugation with π*-orbital of the triple bond, which, in turn, is able to interact with one or some occupied molecular orbitals of the substituent R.

The type of these MOs may differ depending on the substituent nature (n, σ, or π) (Table 4). The simultaneous interaction between the chlorine lone electron pairs and the occupied orbital of the substituent R leads to an increase in the triple bond π*-level energy, thus enlarging the energy gap between the chlorine lone pair and the antibonding π*-orbital, that results in a decrease in the chlorine atom n–π* conjugation.

The least lone electron pair → chlorine transfer is observed for compounds in which lone pairs of the substituent R characterized by an enhanced donating ability (Table 4, **6**–**10**) are conjugated with the triple bond π*-orbitals. At the same time, the participation in conjugation of MOs having lower donating ability facilitates the conjugation of lone electron pair of chlorine p-electrons with the C≡C bond. Thus, contribution of the molecular orbital of S-C, S-Cl, S-F σ-bonds (Table 4, **6**–**8**) to the conjugation increases with a decrease in their energy (E_R) and ability to conjugation (F_R–π*). Different types of conjugation of the chlorine p_x and p_y electrons with π_x and π_y electrons of the triple bond may result in deviation of the Cl-C bond charge distribution from the axial symmetry. A structural consequence of different degrees of conjugation of p_x and p_y electrons of the chlorine atom may be deviation of the Cl–C≡C angle from 180°.

Table 4. Energies of chlorine lone electron pairs (E_n), antibonding (E_{π}*) and localized (E_R) orbitals of chloroacetylenes, degree of conjugation between antibonding π-orbitals of the triple bond with chlorine lone electron pair ($F_{n\pi^*}$) and substituent R ($F_{R\pi^*}$), degree of transfer from the chlorine lone electron pair as a result of n–π* conjugation (ΔN)

	R	E_n	E_{π}*	E_R	$F_{n\pi^*}$	$F_{R\pi^*}$	Type ψ_R	ΔN
1	$SiMe_3$	–0.47753	0.30479	–0.65968	0.135	0.072	σ Si–C	0.05874
2	C≡N	–0.51188	0.27326	–0.49934	0.141	0.094	π C≡N	0.06266
3	C≡CC1	–0.49122	0.30313	–0.44413	0.137	0.107	π C≡CC1	0.05726
4	Ph	–0.47654	0.32913	–0.30985	0.133	0.109	π –C=C–	0.05207
		–0.47605	0.32184	–0.29396	0.133	0.082	σ C–C	0.05408
5	H	–0.48186	0.29810	–	0.133	–	–	0.05815
		-0.48094	0.28600	–0.35436	0.129	0.139	n(2) S	0.05380
6	SC_3H_7	–0.47874	0.29647	–0.78567	0.137	0.051	n(1) S	–
		–	–	–0.77607	0.137	0.070	σ S–C	0.06135
		–0.48781	0.25795	–0.39749	0.130	0.151	n(2) S	0.05408
7	SF	–0.49381	0.26574	–0.84621	0.145	0.038	n(2)S	–
		–	–	–1.07984	0.145	0.053	σ S–F	0.07224
		–0.49730	0.26063	–.400901	0.131	0.143	N(2)S	0.05520
8	SCl	–0.49397	0.27013	–0.86974	0.143	0.039	N(1)S	–
		–	–	–0.80059	0.143	0.067	σ S–C1	0.06904
		–0.47047	0.31894	–0.51999	0.126	0.184	n (2)O	0.04611
9	OCH_3	–0.46946	0.38963	–0.80332	0.128	0.084	n(1)O	–
		–	–	–1.07815	0.128	0.107	σ O–C	0.04301
10	NH_2	–0.46925	0.35969	–0.46884	0.122	0.081	n N	0.04280
		–0.46728	0.32840	–0.86788	0.135	0.156	σ N–H	0.05473

Thus, the electron structure of the Cl-C_{sp} bond in the chloroacetylenes under consideration is controlled by the following factors:

- inductive effect of the C≡C–R group, and
- conjugation of lone electron pairs of chlorine (p_x and p_y) with antibonding π-bonds of the C≡C group.

These factors act independently of each other in different directions that is responsible for the narrow range of ^{35}Cl NQR frequency variation and the expected non–zero parameters of the EFG asymmetry tensor in the series studied.

Experimental Section

General Procedures. Compounds Cl–C≡C–R (R = SC_3H_7, S-iC_4H_9, S-$nC_{12}H_{25}$) were prepared according to the literature.[26]

^{35}Cl NQR Spectra were recorded using a IS-3 instrument at 77 K. Quantum chemical calculations were carried out using the Gaussian 98 program.[27] The theoretical values of ν_{calc} frequencies and asymmetry parameters η_{calc} were calculated using formulae (Eq. 2 and Eq. 1) (the ^{35}Cl nucleus quadrupole moment Q[28] was taken to be equal to $-8.1\cdot10^{-26}$ cm^{-2}).

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References

1. Chambers, R. D.; James, C. P. In *Obshchaya organicheskaya khimiya*; Barton, D.; Ollis, W. D. Eds.; Khimiya: Moskva, 1981, Vol 1, pp 694–697. Transl. from *Comprehensive Organic Chemistry 1–7*; Barton, D.; Ollis, W. D. Eds.; Pergamon Press: New York, 1979.
2. Smirnov, K. M.; Tomilov, A. P.; Shchekotikhin, A. I. *Usp. Khim.* **1967**, 36,. 777. *Chem.Abstr*. **1967**, *67*, 108101
3. Hopf, H.; Witulski, B. In *Modern Acetylene Chemistry*; Stang, P. J.; Diederich, F. Eds.; Wiley-VCH: Weinheim, New York, 1995, pp 33–66.
4. Vilkov, L. V.; Mastryukov, V. S.; Sadova, N. I. *Opredelenie geometricheskogo stroeniya svobodnykh molekul*; Khimiya: Leningrad, 1978, p 224.
5. Cradock, S.; Fraser, A.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 209.
6. Bjorseth, A.; Kloster-Jensen, E.; Marstokk, K.-M.; Mollendal, H. *J. Mol. Struct*. **1970**, *6*, 181.
7. Cox, A. P.; Ellis, M. C.; Perrett, T. *J. Chem. Soc., Farad. Trans*. **1992**, *88*, 2611.
8. Bjorvatten, T. *Acta Chem. Scand*. **1968**, *22*, 410.
9. Bart, J. C. J.; Bassi, I. W.; Calcaterra, M.; Piccardi, P. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1561.
10. Baert, F.; Foulon, M.; Odou, G. *Acta Crystallogr., Sect. B*, **1982**, *B38*, 3139.
11. Keller, M. B.; Rzepa, H. S.; White, A. J. P.; Williams, D. J. *Electronic Conference on Trends in Organic Chemistry (ECTOC-1);* 1995, 50. http://www.ch.ic.ac.uk/ectoc/papers/50/; http://www.ch.ic.ac.uk/ectoc/papers/keller/
12. Suenkel, K. *J. Organomet. Chem*. **1988**, *348*, C12.
13. Sunkel, K.; Birk U. *Polyhedron* **1999**, *18*, 3187.
14. *Khimiya atsetilenovykh soedinenii*; Viehe, H. G. Red.; Khimiya: Moskva, 1973, p 416. Transl. from *Chemistry of acetylenes*; Viehe, H. G. Ed.; Marcel Dekker: New York, 1969.

15. Townes, C. H.; Dailey, P. P. *J. Chem. Phys.* **1949**, *17*, 782.
16. Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Primenenie yadernogo kvadrupol'nogo rezonansa v khimii*; Khimiya: Leningrad, 1972, p 536.
17. Lucken, E. A. C. In: *The Chemistry of Functional Groups, Suppl. D*; Patai, S.; Rappoport, Z. Eds.; Wiley: Chichester, New York, 1983, pp 107–159.
18. Zeil, W. *Angew. Chem*. **1964**, *76*, 654.
19. Zeil, W.; Haas, B. *Z. Naturforsch. A* **1967**, *22*, 2011.
20. Gerber, P.; Labhart, H.; Kloster-Jensen, E. *Helv. Chim. Acta* **1971**, *54*, 2030.
21. (a) Zhdanov, Yu. A.; Minkin, V. I. *Korrelyatsionnyi Analiz v Khimii*; Izd. Rostovskogo universiteta: Rostov-on-Don, 1966, p 470. *Chem. Abstr*. **1967**, *66*, 111330.
22. Vereshchagin A. N. *Induktivnyi Effect*; Nauka: Moskva 1987, p 325. *Chem. Abstr*. **1988**, *108*, 230511
23. Reed, A. E.; Weinhold, F. *J. Chem. Phys*. **1983**, *78*, 4066.
24. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899.
25. Plattner, D. A.; Yi Li,. Houk, K. N. In *Modern Acetylene Chemistry* Stang, P. J.; Diederich, F. Eds.; VCH: Weinheim, New York, 1995, pp 1-32.
26. Mirskova A. N., Seredkina S. G., Voronkov M. G. Pat. SU 1204616; **1986**. *Chem. Abstr.* **1986**, *105*, 208464
27. Frisch, M. J; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.;. Cheeseman, J. R; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al–Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head–Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98, Revision A.6,* Gaussian, Pittsburgh, 1998.
28. Pyykkö, P. *Z. Naturforsch. A* **1992**, *47*, 189.
29. Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31.