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The cyanide, cyanate, thiocyanate ambident anions: Structure, topological analysis of electron density and homolytic oxidative coupling regioselectivity

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Abstract: At the B3LYP/6-311++G(3df,3pd) level of theory, the spatial and electronic structure of the cyanide, cyanate and thiocyanate ambident anions has been studied. By means of the natural bond orbital (NBO) analysis and the R. F. W. Bader's quantum theory "Atoms in Molecules" (QTAIM), the electron density delocalization and topological properties in the above anions have been investigated. The distribution of electron density (NBO, QTAIM) in the XCN^- (X = O, S) anions is reflected by the scheme $[\mathrm{X}\overset{\bullet\bullet\bullet}{-\!-}\mathrm{C}\overset{\bullet\bullet\bullet}{=\!=}\mathrm{N}]^-$. The relative contribution of the hypothetical structure $X{=}C{=}N^-$ to the resonance hybrid $^-X{-}C{\equiv}N \leftrightarrow X{=}C{=}N^-$ is higher in the case of X = O. The degree of the $C{\equiv}N$ or $\mathrm{C}\overset{\bullet\bullet\bullet}{=\!=}\mathrm{N}$ bond triple character and bond strength changes in the following series of anions: $CN^- > SCN^- > OCN^-$. The occupancy of the lone electron pair (LP) orbital of the nitrogen atom in the above anions is close to 2, and the LP orbital is sp-hybridized. Condensed K. Fukui functions for the electrophilic attack have been evaluated. Local hardness of the donor reaction centres: N > C (CN^-), O > N (OCN^-), N > S (SCN^-). The regioselectivity of the homolytic oxidative coupling reactions of CN^-, OCN^-, SCN^- has been substantiated.

Keywords: density functional theory (DFT); B3LYP; natural bond orbital (NBO) analysis; R.F.W. Bader's quantum theory "Atoms in Molecules" (QTAIM); electron density delocalization; hybridization; K. Fukui functions; radical dimerization.

INTRODUCTION

The dual reactivity of the ambident anions, such as cyanide $CN^–$, cyanate $OCN^–$, thiocyanate (rhodanide) $SCN^–$,[1–8] *etc.*, as ligands in coordination compounds[1–5,8] and nucleophiles, mainly in organic chemistry,[6–8] is an important theoretical problem.

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The ambident reactivity is often treated by means of the Hard and Soft Acids and Bases (HSAB) principle.[1–8] However, the HSAB theory displayed itself as not always appropriate.

Free cyanide, CN^-, *e.g.*, is generally alkylated at carbon. N-attack is only observable in diffusion-controlled reactions with carbenium cations. Since isonitrile $RN^+\equiv C^- \leftrightarrow RN=C$ formation in reactions with $[Ag(CN)_2]^-$ is due to the change of the nucleophile, the explanation of these regioselectivities by the HSAB principle has to be abandoned.[9]

It has been shown that the cyanate anion, OCN^-, being an ambident nucleophile, may react with electrophiles either at the oxygen terminus, to yield alkyl cyanates $ROC\equiv N$, or at the nitrogen centre, to yield alkyl isocyanates $RN=C=O$. Equal amounts of alkyl cyanates and alkyl isocyanates were obtained, when secondary iodoalkanes were treated with silver(I) cyanate. The formation of *tert*-butyl isocyanate $(CH_3)_3CN=C=O$, along with 2-methylpropene $(CH_3)_2C=CH_2$ and cyanic acid, was also considered as an indication for concomitant O- and N-attack. The study also investigated the possibility of S_N1 reactions of cyanates proceeding with charge control to give alkyl cyanates.[10]

A kinetic study of SCN^- reaction with carbenium cations using laser flash photolysis and stopped-flow methods lead to the conclusion that the selectivities of the above reactions cannot be explained by the HSAB theory.[11]

For CN^-, both C- and N-coordination, and for OCN^-, both N- and O-bonding with metal cations is known.[12–15]

In accordance with the HSAB theory,[1–8] in the ambident SCN^-, donor sulphur atom is the reaction centre of a soft base, and the nitrogen atom is the centre of a hard/soft boundary base. Cations of ammonium (azanium), NH_4^+, alkaline (except in any case caesium) and alkaline earth metals, magnesium, aluminium are hard acids (Cs^+ is a soft acid), so they "gravitate" to the nitrogen atom of the thiocyanate. At the same time, thiocyanates of at least alkaline and alkaline earth elements have ionic crystal structures, and the ionic bond is non-directional, and therefore we can talk not about coordination in the literal sense, but about the mutual spatial orientation of metal or NH_4^+ and SCN^-, favourable potential or actual association of the metal or ammonium cation with the nitrogen atom of the thiocyanate anion.

The preferential orientation of the thiocyanate nitrogen atom in the direction of the lithium cation in solution finds a quantum chemical confirmation. The impact of the association of lithium cation with SCN^- n acetonitrile $CH_3C\equiv N$ on the vibrational spectrum has been studied in the B3LYP/6-31+G(d,p) approximation. The best agreement between experimental and calculated ionic association data was achieved taking into account the nonspecific solvation, oversolvation and solvability of ionic complexes within the framework of the polarizable continuum model (PCM) in a variant (IEF-PCM) based on the integral equation formalism (IEF). The microstructures of the thiocyanate in a contact ion pair with lithium cation and ion-pair dimer and trimer in acetonitrile were established.[16]

The main continuum models of solvent accounting in quantum chemical computations are listed in the work.[17]

The formulae of the above mentioned thiocyanates are preferably written as NH_4NCS, LiNCS, NaNCS, KNCS, RbNCS, CsNCS, $Mg(NCS)_2$, $Ca(NCS)_2$, $Sr(NCS)_2$, $Ba(NCS)_2$, $Al(NCS)_3$.[12,15]

On the contrary, thiocyanates of copper(I), silver(I), mercury(II), lead(II) are characterized by the coordination of the metal ion to the sulphur atom: CuSCN, AgSCN, $Hg(SCN)_2$, $Pb(SCN)_2$ (Cu^+, Ag^+, Hg^{2+} – soft acids, Pb^{2+} – boundary acid).[12,15]

Soft acid Cd^{2+} behaves ambiguously. There is a $Cd(SCN)_2$ compound. However, in an aqueous solution of sodium tetrathiocyanocadmate, SCN^- is coordinated *via* sulphur ($Na_2[Cd(SCN)_4]$), and in methanol through nitrogen ($Na_2[Cd(NCS)_4]$). Coordination *via* nitrogen in the case of cadmium thiocyanates is also observed in the melt of KNCS.[12,15]

The lead(II) ion, which is borderline in hardness/softness, is coordinated by the sulphur atom: $Pb(SCN)_2$.[12,15] However, for the boundary acids, manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc ions, there is coordination at the nitrogen atom: $Mn(NCS)_2$, $Fe(NCS)_2$, $[Fe(NCS)_4]^{2-}$, $Co(NCS)_2$, $[Co(NCS)_4]^{2-}$, $Ni(NCS)_2$, $[Ni(NCS)_4]^{2-}$, $Cu(NCS)_2$, $[Cu(NCS)_4]^{2-}$ and $Zn(NCS)_2$.[12,15]

The soft acid Cs^+, like other alkali metal cations (hard acids), orients towards SCN^- with a preference for the nitrogen atom.[12,15]

Thus, the structure of metal thiocyanates cannot always be substantiated from the standpoint of a qualitative version of the HSAB concept. This is largely due to the boundary nature of the donor nitrogen atom as the reaction centre.

Iron(III), cobalt(III) and nickel(III) ions are hard acids and add SCN^- with the participation of its nitrogen atom, for example $Fe(NCS)_3$, $[Fe(NCS)_6]^{3-}$.[12,15]

Such a nature of the binding of SCN^- with highly charged cations such as Al^{3+}, Fe^{3+} and in general with metal ions – hard acids, can be due to a higher negative charge on the nitrogen atom of the thiocyanate anion, since the hard–hard (and hard-boundary to a large extent) interaction in the framework of a simple version of the perturbation theory[18] is treated as charge-controlled.[8]

The HSAB principle is usually expressed *via* the charge, electronegativity, size, polarizability, oxidation ability, energies of the frontier orbitals of an atom, ion, closed or open electronic shell molecule.[1–8] All the above characteristics directly or indirectly depend upon the electron density distribution in molecule, including the electronic delocalization and topological properties. The electronic distribution is significant regardless of whether it is considered within the framework of the HSAB theory or beyond.

CN^-, OCN^- and SCN^- are capable of undergoing chemical and electrochemical homolytic oxidative coupling (dimerization) with the intermediate appearance of the $^{\bullet}CN$, $OCN^{\bullet}$ and $^{\bullet}SCN$.

In particular, CN^- dimerizes upon interaction with acidified $S_2O_8^{2-}$, with copper(II) and gold(III).

CN^- reduces Cu^{2+} to Cu^+, oxidizing to cyanogen $N{\equiv}C{-}C{\equiv}N$, and binds copper(I) into complex anions, tricyanocuprate(I) $[Cu(CN)_3]^{2-}$ and tetracyanocuprate(I) $[Cu(CN)_4]^{3-}$, for example:

$$2Cu^{2+} + 4CN^- \rightarrow 2CuCN\downarrow + N{\equiv}C{-}C{\equiv}N,$$
$$CuCN\downarrow + 2CN^- \rightleftarrows [Cu(CN)_3]^{2-},$$

or in total:

$$2Cu^{2+} + 8CN^- \rightarrow 2[Cu(CN)_3]^{2-} + N{\equiv}C{-}C{\equiv}N$$

The above chemical reactions are used to mask the copper(II) ion in the analytical determination of other ions, to change the redox potential of the $Cu(II)/Cu\downarrow$ conjugate redox pair in the separate electrolytic and polarographic determination of copper and other metals, *etc.*

Similarly, the interaction of gold(III) with CN^- includes the preliminary reduction of Au(III) to Au(I) followed by the formation of the dicyanoaurate(I) anion $[Au(CN)_2]^-$:

$$Au^{3+} + 3CN^- \rightarrow AuCN\downarrow + N{\equiv}C{-}C{\equiv}N,$$
$$AuCN\downarrow + CN^- \rightleftarrows [Au(CN)_2]^-,$$

or in total:

$$Au^{3+} + 4CN^- \rightarrow [Au(CN)_2]^- + N{\equiv}C{-}C{\equiv}N$$

Hydrocyanic acid or gaseous hydrogen cyanide $HC{\equiv}N$ is oxidized to cyanogen $N{\equiv}C{-}C{\equiv}N$ under the action of O_2 or air in the presence of a silver catalyst, NO_2 in the presence of calcium glasses, Cl_2 on activated carbon or quartz, when passing dry hydrogen cyanide over MnO_2 heated to 250 °C, as well as when interacting with H_2O_2 in the presence of copper(II) and iron(III) salts, with $Na_2S_2O_8$, MnO_2, PbO_2 in the 0.05 M H_2SO_4 medium, *etc.*[1,2,12,19]

The fact of the existence of oxocyanogen $(OCN)_2$ remains controversial. The formation of a colorless compound $(OCN)_2$, which is stable only at low temperature (down to −12 °C), has been reported by the exchange reaction of silver(I) cyanate with I_2.[12] There is an assumption that oxocyanogen can be obtained by the reaction of silver(I) cyanate with Br_2, but no conclusive evidence is provided. It has been shown that $O{=}C{=}N{-}N{=}C{=}O$ is obtained in this and other similar reactions.[12,19] However, data on the anodic oxidation of cyanates in $CH_3C{\equiv}N$ cast doubt on the existence of $(OCN)_2$.[12]

Thiocyanogen N≡C–S–S–C≡N is obtained by mild oxidation of metal thiocyanates with an aqueous solution of Cl_2, with Br_2, I_2, MnO_2, copper(II) salts at a temperature of about 0 °C, $Pb(CH_3COO)_4$, as well as by electrochemical oxidation of $SCN^–$.[1,2,12]

Previously,[20–22] it has been shown that the regioselectivity of reactions of homolytic (radical) oxidative and reductive coupling (dimerization) of organic compounds of various classes is controlled by the spin density on atoms in the reaction intermediates (electroneutral radicals, radical cations, radical anions), calculated by *ab initio*, DFT, HMDFT and semi-empirical methods of quantum chemistry. In this case, such intermediates are $^\bullet CN$, $OCN^\bullet$ and $^\bullet SCN$.

The aim of the present work consists in quantum chemical investigation of spatial, electronic structure of the cyanide, cyanate, thiocyanate ambident anions, including study of the electron density delocalization and topological properties, comparative local hardness of the donor reaction centres, as well as substantiation of regioselectivity of the homolytic oxidative coupling reactions of $CN^–$, $OCN^–$ and $SCN^–$.

METHODOLOGY OF THEORETICAL RESEARCH

Quantum chemical computations (within the restricted (RHF) D. R. Hartree – V. A. Fock (HF) approach[23] for the closed-shell anions CN^-, OCN^-, SCN^- and unrestricted (UHF) D. R. Hartree – V. A. Fock (HF) approach[23] for $^\bullet CN$, $^\bullet OCN$, $^\bullet SCN$ derived from the above anions by homolytic oxidative coupling) were carried out by means of the hybrid density functional theory (DFT) method[23-26] using the Gaussian 09W package[27] without any geometrical restrictions. Within the SCF, the hybrid B3LYP functional, which combines the three-parameter exchange functional by A. D. Becke[28,29] with the Chengteh Lee – Weitao Yang – R. G. Parr (LYP) correlation functional,[30] was applied. The computations were performed using "tight" convergence criteria.[30,31] The rather wide 6-311++G(3df,3pd)[32,33] basis set was used. Diffuse functions were included in order to treat the nonbonding (unshared, lone) electron pairs (LP) and blurred character of electron cloud in the anions properly. Harmonic vibrational frequencies were computed. All equilibrium structures without the imaginary frequencies correspond to the minima points on the potential energy surfaces. Requested convergence on *RMS* density matrix amounted 1×10^{-8} within 200 cycles, on *MAX* density matrix – 1×10^{-6}, and on energy – 1×10^{-6} Hartree (a.u). The initial geometries were generated by means of HyperChem Professional 8.0.10 software[34] and optimized by the PM3 method.[35,36]

The natural bond orbital (NBO) analysis[37-40] was performed by the NBO Version 3.1 program.[41]

To describe the electronic structure of molecules, the topological analysis of electron density by means of R. F. W. Bader's quantum theory "Atoms in Molecules" (QTAIM)[42-54] at the B3LYP/6-311++G(3df,3pd) level of theory was performed by the AIMAll Version 19.10.12 software[55] to calculate the charge density (ρ_b), Laplacian of the charge density ($\nabla^2\rho_b$), local electronic energy (h_e) in the saddle (which are indicators of binding) bond critical points (3, −1) and ellipticity (ε).

RESULTS AND DISCUSSION

By means of the DFT method at the B3LYP/6-311++G(3df,3pd) level of theory with the use of the NBO and QTAIM analysis, we have computed the spatial and electronic structure of the ambident CN^-, OCN^- and SCN^-.

In CN^-, the $C\equiv N$ bond length is 1.171 Å. The calculation is in agreement with the experiment: a neutron diffraction study of KCN at room temperature gives a length of 1.16 Å for the $C\equiv N$ bond.[15] The natural (one of the most objective, most consistent with chemical intuition) charge on carbon and nitrogen atoms is –0.236 and –0.764, respectively. The natural order (natural K. B. Wiberg index) of the $C\equiv N$ bond is 2.854.

The values of the second-order perturbation energy $E(2)$, obtained as a result of the NBO analysis for CN^-, indicate that the main directions of electron density transfer are from the LP orbital of the nitrogen atom to the antibonding (loosening) J. R. Rydberg orbital of the carbon atom ($E(2)$ = 75.7 kJ mol^{-1}), from the core level of the nitrogen atom to the same J. R. Rydberg orbital ($E(2)$ = 26.1 kJ mol^{-1}) and from the LP orbital of the carbon atom to the antibonding J. R. Rydberg orbital of the nitrogen atom ($E(2)$ = 20.6 kJ mol^{-1}).

OCN^- and SCN^- have a linear structure.

In OCN^-, bonds have the following lengths: 1.224 ($C\overset{\cdots}{-}O$) and 1.187 Å ($C\overset{\cdots}{=}N$); the bond angle OCN is 180.000°. X-ray diffraction analysis of NaNCO gives a length of 1.21 Å for the $C\overset{\cdots}{-}O$ bond and 1.13 Å for the $C\overset{\cdots}{=}N$ bond. In this case, the linear structure of the anion is confirmed, but the low accuracy of the values of the bond lengths,[15] which nonetheless agree with our computation, is stipulated.

The natural charge on atoms in OCN^- is: –0.776 (O), 0.600 (C), –0.823 (N). The negative charge on the O- and N-atoms is almost the same, slightly higher on the nitrogen atom. The natural orders of bonds in OCN^- are: 1.493 ($C\overset{\cdots}{-}O$) and 2.444 ($C\overset{\cdots}{=}N$).

According to the results of our quantum chemical computation, the bond lengths in SCN^- are: 1.661 ($C\overset{\cdots}{-}S$) and 1.172 Å ($C\overset{\cdots}{=}N$), the SCN bond angle is 180.000°. In accordance with the data of X-ray diffraction analysis of NaNCS, KNCS,[15] the corresponding values are 1.65, 1.17 Å and 180°. The calculation agrees well with experiment.

The natural charge on the atoms is: –0.463 (S), 0.055 (C), –0.592 (N). The nitrogen atom is somewhat more negatively charged compared to the sulphur atom, which is consistent with the regioselectivity of the interaction of metal ions – hard G. N. Lewis acids with SCN^-. The natural orders of bonds in SCN^- are: 1.403 ($C\overset{\cdots}{-}S$) and 2.608 ($C\overset{\cdots}{=}N$).

Based on the charge distribution in the ambident CN^- and XCN^- (X = O, S), the negative charge of which is delocalized between the X and N atoms, it is expedient to write the minus sign at the nitrogen atom when depicting these anions.

For the entire set of C≡N, $C\overset{\bullet\bullet\bullet}{=}N$, $C\overset{\bullet\bullet\bullet}{-}O$ and $C\overset{\bullet\bullet\bullet}{-}S$ bonds in CN^-, OCN^- and SCN^-, the following trend is observed: the longer the bond, the smaller its natural order.

OCN^- and SCN^- have a number of energetically significant donor–acceptor interactions. However, the dominant contributions are:

– in OCN^-: electron transfer from two different LP orbitals of the oxygen atom to the antibonding π-orbital of the $C\overset{\bullet\bullet\bullet}{=}N$ bond (each such transition has an energy effect $E(2) = 341.8$ kJ mol^{-1}), from the LP orbital of the nitrogen atom to the antibonding J. R. Rydberg orbital of the carbon atom ($E(2) = 75.3$ kJ mol^{-1}), from the LP orbital of the nitrogen atom to the antibonding σ-orbital of the $C\overset{\bullet\bullet\bullet}{-}O$ bond ($E(2) = 71.5$ kJ mol^{-1}), from the orbital of the third LP of the oxygen atom to the antibonding σ-orbital of the $C\overset{\bullet\bullet\bullet}{=}N$ bond ($E(2) = 69.0$ kJ mol^{-1}) and from the orbital of the same (third) LP orbital of the oxygen atom to the same J. R. Rydberg orbital ($E(2) = 63.2$ kJ mol^{-1});

– in SCN^-: transfer of electron density from two LP orbitals of the sulphur atom to the antibonding π-orbital of the $C\overset{\bullet\bullet\bullet}{=}N$ bond with the same second-order perturbation energy contribution $E(2) = 169.5$ kJ mol^{-1}, from the LP orbital of the nitrogen atom to the antibonding J. R. Rydberg orbital of the carbon atom ($E(2) = 84.1$ kJ mol^{-1}), from the orbital of the third LP of the sulphur atom to the antibonding σ-orbital of the $C\overset{\bullet\bullet\bullet}{=}N$ bond ($E(2) = 81.6$ kJ mol^{-1}) and from the LP orbital of the nitrogen atom to the loosening σ-orbital of the $C\overset{\bullet\bullet\bullet}{-}S$ bond ($E(2) = 59.4$ kJ mol^{-1}).

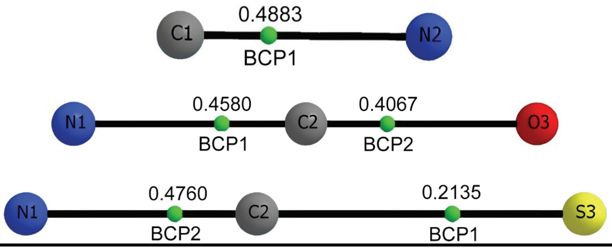
It can be seen that in the donor–acceptor redistribution of the electron density in OCN^- and SCN^-, the orbitals of nonbonding electron pairs of the oxygen and sulphur atoms take an active part as donors, *i.e.*, the possibilities absent in CN^-, are realized.

To describe the electronic structure of the anions in more detail, we have carried out a topological analysis of the electron density using the QTAIM[42–54] at the B3LYP/6-311++G(3df,3pd) level of theory.

The electron density (ρ_b) in the bond critical points (BCP), the Laplacian of the electron density ($\nabla^2\rho_b$) in the BCP, the local electronic energy (h_e), which is estimated as the density (taken with the opposite sign) of the local kinetic energy in the form of Hamiltonian (Hamiltonian form of kinetic energy density) in the critical points (3, –1) and the ellipticity (ε) have been computed (Table I).

Comment. ρ_b – the value of the electron density in the bond critical point (3, –1); $\nabla^2\rho_b$ – second derivative of electron density (density Laplacian); h_e – local electronic energy in the bond critical point (3, –1). Units: e – atomic unit of charge (elementary charge) $e = 1.60219\times10^{-19}$ C); Bohr – atomic unit of length (the radius of the first Bohr orbit): 1 Bohr = 0.529177 Å = 5.29177×10^{-11} m); Hartree – atomic unit of energy: 1 Hartree = e^2 Bohr^{-1} = 627.5095 kcal mol^{-1} = 2.6255×10^3 kJ mol^{-1} = 27.212 eV = 2.1947×10^5 cm^{-1}.

TABLE I. Some properties of the bond critical points (3, –1)



Bond	ρ_b / e Bohr^{-3}	$\nabla^2\rho_b$ /e Bohr^{-5}	h_e / Hartree Bohr^{-3}
		CN^-	
C≡N	0.488	–0.849	–0.951
		OCN^-	
C$\overset{\cdots}{-}$O	0.407	–0.510	–0.715
C$\overset{\cdots}{=}$N	0.458	–0.896	–0.827
		SCN^-	
C$\overset{\cdots}{-}$S	0.213	–0.132	–0.243
C$\overset{\cdots}{=}$N	0.476	–0.680	–0.905

According to the general pattern, the positive value of the electron density (ρ_b) in the bond critical point (BCP) and the negative value of the Laplacian of the electron density ($\nabla^2\rho_b$) in the BCP indicate the concentration of the electron charge in the internuclear region and its exhaustion in the direction of the nuclei, *i.e.*, the presence of strong covalent bond (shared interaction, in which the compression of the electron density along the bond line, directed to the critical point (3, –1), dominates).[42–54] A negative value of the local electronic energy (h_e) is a necessary criterion for a covalent bond (shared interaction).[43,54]

Fulfillment of the conditions $\rho_b > 0$, $\nabla^2\rho_b < 0$, $h_e < 0$ and sufficiently large absolute ρ_b, $\nabla^2\rho_b$, h_e values in the saddle (which are indicators of binding) critical points (3, –1) (Table I) show a high strength of all covalent bonds in CN^-, OCN^- and SCN^-, in accordance with the bonds lengths and natural orders (see above).

The position of BCP of an A–B bond shifts towards A and thus leaves more electron density for B if B is more electronegative than A.[42–54] As it can be seen from Table I, the aforesaid is confirmed for CN^-, OCN^- and SCN^-.

The ellipticity of all bonds in all three anions is essentially zero (according to our calculations, it is 10^{-15}–10^{-14}), which allows us to state the presence of a cylindrical symmetry of the electronic distribution in bonds.

According to our NBO and QTAIM analysis, in accordance with the criteria of natural charge on atoms, natural order and electron density (ρ_b) in the bond critical point (3, –1) it has been shown that in XCN^- (X = O, S) the C$\overset{\cdots}{-}$X bond is "one and a half", the C$\overset{\cdots}{=}$N bond carries a significant proportion of triple bonding. The distribution of electron density (NBO, QTAIM) in XCN$^-$ is reflected by the scheme $[\mathrm{X}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{=}\mathrm{N}]^-$.

There is an electronic delocalization due to which there is a certain alignment of the negative charge on the X- and N-atoms, and not its significant predominance on the oxygen atom in the case of X = O and unconditional dominance on the nitrogen atom at X = S.

Herewith in OCN$^-$, the electronic distribution is more even compared to SCN$^-$: the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ bond is more "one and a half" than $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ and the $\mathrm{C}\overset{\cdots}{=}\mathrm{N}$ bond is more close to triple in the sulphur-containing anion.

One of the factors of more effective delocalization of electron density in OCN$^-$ as compared to SCN$^-$ is, apparently, the fact that the key donor–acceptor interaction for delocalization, namely the electron transfer from the LP orbital of the heteroatom X to the antibonding π-orbital of the $\mathrm{C}\overset{\cdots}{=}\mathrm{N}$ bond, is energetically much more favorable for X = O compared to X = S. The remaining second-order perturbation energy $E(2)$ contributions noted above are basically comparable in magnitude and are less significant for the delocalization of the π-electron density.

If, on the basis of our quantum chemical computations by the molecular orbital method, we pass to a visual qualitative interpretation using the method of valence bonds, then OCN$^-$ and SCN$^-$ can be represented as resonance hybrids of two imaginary limiting canonical structures (X = O, S):

$$^{-}\mathrm{X{-}C{\equiv}N} \leftrightarrow \mathrm{X{=}C{=}N}^{-}$$

Wherein the relative contribution of the hypothetical structure X=C=N$^-$ to the hybrid is higher in the case of X = O.

The degree of the C≡N or $\mathrm{C}\overset{\cdots}{=}\mathrm{N}$ bond triple character and bond strength changes in the following series: CN$^-$ > SCN$^-$ > OCN$^-$. The weakest $\mathrm{C}\overset{\cdots}{=}\mathrm{N}$ bond (in OCN$^-$) is the longest.

As the results of the NBO analysis show (Table II), the occupancy of the LP orbital of the nitrogen atom in CN$^-$, OCN$^-$ and SCN$^-$ is close to 2, that is, the named orbital is practically not involved in the electron density delocalization.

TABLE II. Occupancy and hybrid state of the LP orbital of the nitrogen atom according to the NBO analysis

Anion	Occupancy	Hybridization character, %			
		s	p	d	f
CN$^-$	1.978	49.04	50.75	0.21	0.00
OCN$^-$	1.962	57.92	41.94	0.14	0.00
SCN$^-$	1.958	51.38	48.44	0.17	0.01

This orbital is sp-hybridized. The complementary (symbiotic) hard–hard interaction is largely electrostatic in nature, while the soft–soft interaction includes a significant covalent component.[8] The highest negative charge on the nitrogen atom compared to other atoms of all the studied anions, on the one hand, and the wide possibility of nonbonding electrons showing donor properties, on the other hand, along with the parity contribution of 2s- and 2p-atomic orbitals to the LP orbital, providing favourable steric conditions of reactions with various (from the HSAB theory viewpoint) G. N. Lewis acids, in many respects predetermine the nitrogen atom character as an electron-donating centre, which is borderline in hardness/softness.

The interrelated concepts of hardness (softness) and electronegativity are becoming increasingly important in chemistry to implement a unified approach to two most important chemical problems – the construction of reaction barriers and molecular design, to explain regioselectivity and ambivalence (nucleophilic–electrophilic dichotomy),[56–58] to describe and model chemical bond, properties of molecules and crystals, intermolecular interactions,[59] solvation, extraction.[60,61]

The concept of electronegativity (including in connection with the HSAB), especially in the version of variable orbital electronegativity, turns out to be essentially the language of chemistry, thanks to which it is easily integrated into the general theory of systems. Indeed, the distinct periodicity of electronegativity and the contrast of properties emphasized by it (electropositive and electronegative elements, hard and soft acids and bases) underlie the nature of the chemical interaction and the emergence of new qualities as a result of the alignment of electronegativity (or electronic chemical potential), the repayment of opposites in the course of acid–base reactions, *etc.*[59]

Without focusing on theoretical premises, we note that global (absolute) hardness (η) is interpreted as the energy gap between the boundary molecular orbitals – the highest occupied (HOMO) and the lowest unoccupied (LUMO) ones:[8,62,63]

$$\eta = 0.5(E(\mathrm{LUMO}) - E(\mathrm{HOMO})) \tag{1}$$

where E(HOMO) and E(LUMO) are the energy values of HOMO and LUMO, respectively.

We have shown that in $\mathrm{CN^-}$, the HOMO is a σ-orbital; in $\mathrm{OCN^-}$ and $\mathrm{SCN^-}$, the HOMO level corresponds to two degenerate π-orbitals. In all three anions, the LUMO is a σ-type orbital.

To evaluate the local hardness of the electrophilic attack (h) of individual reaction centres of a molecular system, including N electrons, the condensed K. Fukui function (f_k^-) is used:[8,62–64]

$$f_\mathrm{k}^- = q_\mathrm{k}^N - q_\mathrm{k}^{N-1} \tag{2}$$

where q_k^N and q_k^{N-1} is the charge on the atoms (natural one in our work) of the initial systems (in our case, $\mathrm{CN^-}$, $\mathrm{OCN^-}$ and $\mathrm{SCN^-}$) and radicals ($^\bullet$CN, OCN$^\bullet$ and $^\bullet$SCN) having the same arrangement of nuclei (*i.e.*, geometry), but a different number of electrons (N for anions and N–1 for radicals).

Local hardness (h) is calculated by the formula:[8,62,63,65]

$$h = f_k^- \eta \tag{3}$$

For anions, the B3LYP method unsatisfactorily conveys all parameters, the evaluation of which uses the HOMO and LUMO energy values, and the smaller the molecular system, the more pronounced the errors.[66] To ensure the correctness of the calculations, it is necessary either to take into account countercations (contradicting the purpose of this study, which requires consideration of isolated anions), or go[66] to the second-order Ch. Møller – M.S. Plesset perturbation theory (MP2)[67–70] level with a basis set of at least 6-311++G(d,p).[32,33]

However, K. Fukui's local indices (and, consequently, the charge characteristics of atoms) are calculated correctly.[66]

Thus, using the B3LYP method, we cannot reliably estimate the global (absolute) hardness (η) of the anions under study, but we are able to determine the relationship between the values of the local hardness of individual donor reaction centres.

Below are the f_k^- (Table III) values computed by us at the B3LYP/6-311++G(3df,3pd) and UB3LYP/6-311++G(3df,3pd) level of theory.

TABLE III. Condensed electrophilic K. Fukui functions (f_k^-)

Anion	Condensed electrophilic K. Fukui function			
	C	N	O	S
	Geometry of radicals is fixed like anions			
CN^-	–0.655	–0.345	–	–
OCN^-	–0.021	–0.557	–0.422	–
SCN^-	0.077	–0.350	–	–0.727
	Geometry of radicals is optimized			
CN^-	–0.657	–0.343	–	–
OCN^-	–0.058	–0.536	–0.406	–
SCN^-	0.094	–0.357	–	–0.737

Values close to each other were obtained both with the spatial structure of the radicals, the same as that of the anions, and with the optimized geometry of the radicals.

In $CN^–$, the local hardness of the nitrogen donor atom is higher compared to the carbon atom. In $OCN^–$, the oxygen atom is a slightly more hard donor centre than the nitrogen atom. In $SCN^–$, the sulphur atom is a softer centre than the N atom. Such results are consistent with known patterns[1–8] and explain many of the above examples of coordination in the formation of metal thiocyanates.[12,15]

As noted above, the homolytic oxidative coupling of $CN^–$, $OCN^–$ and $SCN^–$ is accompanied by $^\bullet CN$, $OCN^\bullet$ and $^\bullet SCN$ intermediates formation.

Table IV gives the R. S. Mulliken spin density, calculated at the UB3LYP/6-311++G(3df,3pd) level of theory, on atoms of •CN, OCN• and •SCN with optimized geometry.

TABLE IV. R. S. Mulliken spin density on atoms in •CN, OCN• and •SCN

Radical	Spin density on atom			
	C	N	O	S
•CN	0.889	0.111	–	–
OCN•	–0.122	0.764	0.358	–
•SCN	–0.144	0.384	–	0.760

The wave function in the unrestricted D. R. Hartree – V. A. Fock approach[19] used for computing the spin density, is not the $\hat{S}^2$ operator eigenfunction, and contains the admixed components of higher multiplicities. For avoiding the wave function spin contamination at the quantum chemical computations, we used the spin annihilating procedure.[19] As a result, the full spin S^2 after annihilation for •CN, OCN• and •SCN was 0.7501, that coincides with the value of 0.75 for the pure doublet state, characteristic for the radical particles with one uncoupled electron in the ground state.[19]

The latter fact testifies to the correct implementation of spin density as a reactivity index, alike the previous studies.[20–22] Then again, the above index has proved its predictive power even in the cases, in which the uncontaminated spin state is not provided.[71,72]

The significant predominance of the spin density on the carbon atom in •CN and on the sulphur atom in •SCN naturally explains the appearance of cyanogen N≡C–C≡N and thiocyanogen N≡C–S–S–C≡N during the oxidation of CN⁻ and SCN⁻, respectively:[12,19]

$$CN^- \rightleftarrows {}^\bullet CN + \bar{e},$$
$$2{}^\bullet CN \rightleftarrows N{\equiv}C{-}C{\equiv}N;$$

$$SCN^- \rightleftarrows {}^\bullet SCN + \bar{e},$$
$$2{}^\bullet SCN \rightleftarrows N{\equiv}C{-}S{-}S{-}C{\equiv}N$$

For CN⁻, the specified process of oxidative dimerization is also promoted by the higher stability of cyanogen N≡C–C≡N compared to the hypothetical products of C,N- and N,N-coupling, including quite labile bonds between the monomer units.

In OCN•, the excess of spin density on the nitrogen atom is much higher than on the oxygen centre. This testifies in favour of the possible emergence of an unstable product O=C=N–N=C=O:[12,19]

$$\mathrm{OCN^-} \rightleftarrows \mathrm{OCN^{\bullet}} + \bar{e},$$

$$\mathrm{2OCN^{\bullet}} \rightleftarrows \mathrm{O{=}C{=}N{-}N{=}C{=}O}.$$

CONCLUSION

The key features of the structure, some aspects of the ambident reactivity of CN^-, OCN^- and SCN^- have been substantiated, along with the above anions homolytic oxidative coupling behaviour.

We have used the B3LYP method since it is the most widely used, tested and well-proven DFT option. The results obtained are consistent with the known patterns and experimental data:

1. The calculated lengths of the C≡N, C$\overset{\bullet\bullet\bullet}{=}N, C\overset{\bullet\bullet\bullet}{-}$O and C$\overset{\bullet\bullet\bullet}{-}$S bonds correspond to the experimental values. Calculations represent the linear structure of OCN^- and SCN^-.

2. In the series of CN^-, OCN^- and SCN^-, the values changes for the lengths and natural orders of the C≡N, C$\overset{\bullet\bullet\bullet}{=}N, C\overset{\bullet\bullet\bullet}{-}$O and C$\overset{\bullet\bullet\bullet}{-}$S bonds are of an antibate character.

3. The bond critical points (3, −1) in CN^-, OCN^- and SCN^- are located closer to less electronegative atoms.

4. Local hardness of the donor reaction centres has been reproduced: N > C (in CN^-), O > N (in OCN^-), N > S (in SCN^-).

5. The regioselectivities of the homolytic oxidative coupling reactions have been explained and predicted. The oxidative dimerization of CN^- occurs as C,C-coupling, SCN^- undergoes S,S-coupling, and OCN^- would provide the product of N,N-dimerization.

Probably, results similar to those obtained in this work would be also provided by other functionals, as well as by methods of the hybrid meta density functional theory (HMDFT) and by advanced, sophisticated *ab initio* approaches (MP2, MP3, MP4 (including MP4SDTQ), MP5 (for $^{\bullet}CN$, $OCN^{\bullet}$ and $^{\bullet}SCN$), CISD, QCISD, QCISD(T), CCSD, CCSD(T), G1, G2, G2M, CASSCF, GVB-PP, *etc.*).

ИЗВОД

ЦИЈАНИДНИ, ЦИЈАНАТНИ, ТИОЦИЈАНАТНИ АМБИДЕНТНИ АНЈОНИ: СТРУКТУРА, ТОПОЛОШКА АНАЛИЗА ЕЛЕКТРОНСКЕ ГУСТИНЕ И РЕГОСЕЛЕКТИВНОСТ ХОМОЛИТИЧКОГ ОКСИДАТИВНОГ КУПЛОВАЊА

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На B3LYP/6-311++G(3df,3pd) нивоу теорије, проучавана је просторна и електронска структура цијанидног, цијанатног и тиоцијанатног јона. Помоћу анализе природних орбитала веза (NBO) и Р.Ф.В. Бејдерове квантне теорије “атома у молекулима” (QTAIM), испитиване су делокализација електронске густине и тополошке особине горепоменутих анјона. Расподела електронске густине (NBO, QTAIM) у XCN^- ($X = O, S$) одражава се у шеми $[X\overset{\cdots}{-}C\overset{\cdots}{=}N]^-$. Релативни допринос хипотетичке структуре $X=C=N^-$ у резонанционом хибриду $^-X-C\equiv N \leftrightarrow X=C=N^-$ је виши у случају када је $X = O$. Удео $C\equiv N$ или $C\overset{\cdots}{=}N$ карактера троструког везивања и степена јачине везе у анјонима мења се на следећи начин: $CN^- > SCN^- > OCN^-$. Насељеност орбитале слободног електронског пара (LP) на атому азота у горњим анјонима је близу 2, а LP орбитала је sp-хибридизована. Процењене су кондензоване К. Фукуијеве функције за електрофилни напад. Локална тврдоћа донорских реакционих центара је: N > C (CN^-), O > N (OCN^-), N > S (SCN^-). Поткрепљена је региоселективност реакција хомолитичког оксидативног купловања CN^-, OCN^- и SCN^-.

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REFERENCES

1. J. E. House, *Inorganic Chemistry*, Academic Press (imprint of Elsevier Inc.), Amsterdam, 2008 (ISBN: 978-0-12-356786-4)
2. G. L. Miessler, P. J. Fischer, D. A. Tarr, *Inorganic Chemistry*, Pearson Education, Inc. (Pearson advanced chemistry series), Boston, MA, 2014 (ISBN-10: 0321811054; ISBN-13: 978-0-321-81105-9)
3. R. K. Sharma, *Text Book of Coordination Chemistry*, Discovery Publishing House, New Delhi, 2007 (ISBN-10: 81-8356-223-X; ISBN-13: 978-8183562232)
4. M. H. Najar, *A Comprehensive Guide to Coordination Chemistry, Spectra and Magnetism: Frontiers of Inorganic Chemistry*, LAP LAMBERT Academic Publishing, Saarbrücken, 2020 (ISBN-10: 6202516321; ISBN-13: 978-6202516327)
5. B. Weber, *Coordination Chemistry: Basics and Current Trends*, Springer Spektrum, Berlin, 2023 (https://doi.org/10.1007/978-3-662-66441-4)
6. *Theoretical Organic Chemistry*, C. Párkányi, Ed., Elsevier Science, Amstrdam, 2011 (ISBN: 978-0444546227)
7. P. Vogel., P. N. Houk, *Organic Chemistry: Theory, Reactivity and Mechanisms in Modern Synthesis*, Wiley-VCH Verlag GmbH, Weinheim, 2019 (ISBN: 978-3-527-81927-0)
8. R. G. Pearson, *Chemical Hardness: Applications from Molecules to Solids*, Wiley-VCH Verlag GmbH, Weinheim, 1997 (https://doi.org/10.1002/3527606173)
9. A. A. Tishkov, H. Mayr, *Angew. Chem. Int. Ed.* **44** (2005) 142 (https://doi.org/10.1002/anie.200461640)
10. H. F. Schaller, U. Schmidhammer, E. Riedle, H. Mayr, *Chem. – Eur. J.* **14** (2008) 3866 (https://doi.org/10.1002/chem.200800314)
11. R. Loos, Sh. Kobayashi, H. Mayr, *J. Amer. Chem. Soc.* **125** (2003) 14126 (https://doi.org/10.1021/ja037317u)
12. A. M. Golub, H. Kőhler, V. V. Skopenko, H. Boland, T. P. Lishko, V. M. Samoilenko, G. V. Tsintsadze, *Chemistry of Pseudohalides*, A. M. Golub, H. Kőhler, V. V. Skopenko, Eds., Elsevier Science Ltd, Amsterdam, 1986 (ISBN-10: 0444416269; ISBN-13: 9780444416261)
13. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry*, John Wiley & Sons, Inc., Hoboken, NJ, 2009 (https://doi.org/10.1002/9780470405840)

14. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry*, John Wiley & Sons, Inc., Hoboken, NJ, 2009 (https://doi.org/10.1002/9780470405888)
15. A. F. Wells, *Structural Inorganic Chemistry*, Oxford Univ. Press, Oxford, 2012 (ISBN-10: 0199657637; ISBN-13: 978-0199657636)
16. G. P. Mikhailov, *J. Appl. Spectrosc.* **83** (2016) 339 (https://doi.org/10.1007/s10812-016-0305-2)
17. A. N. Pankratov, O. M. Tsivileva, *Current Phys. Chem.* **6** (2016) 210 (https://doi.org/10.2174/1877946806666160524154445)
18. F. M. Fernández, *Introduction to Perturbation Theory in Quantum Mechanics*, CRC Press, Inc., Boca Raton, FL, 2000 (https://doi.org/10.1201/9781420039641)
19. R. V. Selezenev, *Psevdogalogeny i ikh soedineniya Pseudohalogens and Their Compounds*, https://present5.com/psevdogalogeny-i-ix-soedineniya-selezenev-r-v/ (accessed 7th December 2023)
20. A. N. Pankratov, *J. Mol. Struct.: THEOCHEM* **315** (1994) 179 (https://doi.org/10.1016/0166-1280(94)03779-K)
21. A. N. Pankratov, A. N. Stepanov, *Croat. Chem. Acta* **70** (1997) 585 (ISSN: 0011-1643; e-ISSN: 1334-417X)
22. A. N. Pankratov, *J. Anal. Chem.* **77** (2022) 1063 (https://doi.org/10.1134/S106193482209009X)
23. I. N. Levine, *Quantum Chemistry*, Pearson, Boston, MA, 2014 (ISBN-10: 0321803450; ISBN-13: 978-0321803450)
24. W. Kohn, *Rev. Mod. Phys.* **71** (1999) 1253 (https://doi.org/10.1103/RevModPhys.71.1253)
25. W. Koch, M. C. Holthausen, *Chemist's Guide to Density Functional Theory*, Willey-VCH Verlag GmbH, Toronto, 2001 (https://doi.org/10.1002/3527600043)
26. S. F. Sousa, P. A. Fernandes, M. J. Ramos, *J. Phys. Chem., A* **111** (2007) 10439 (https://doi.org/10.1021/jp0734474)
27. *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford, CT, 2013 https://gaussian.com (accessed 7th December 2023)
28. A. D. Becke, *Phys. Rev. A* **38** (1988) 3098 (https://doi.org/10.1103/physreva.38.3098)
29. A. D. Becke, *J. Chem. Phys.* **98** (1993) 5648 (https://doi.org/10.1063/1.464913)
30. Chengteh Lee, Weitao Yang, R. G. Parr, *Phys. Rev., B* **37** (1988) 785 (https://doi.org/10.1103/PhysRevB.37.785)
31. H. B. Schlegel, J. J. W. McDouall, in *Computational Advances in Organic Chemistry*, C. Ögretir, I. G. Csizmadia, Eds., Kluwer Academic, Dordrecht, 1991, pp. 167–185 (https://doi.org/10.1007/978-94-011-3262-6)
32. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **72** (1980) 650 (https://doi.org/10.1063/1.438955)
33. A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **72** (1980) 5639 (https://doi.org/10.1063/1.438980)
34. *HyperChem Professional 8.0*, Hypercube, Inc., Gainesville, FL, http://hypercubeusa.com/Products/HyperChemProfessional/tabid/360/Default.aspx; http://www.hypercubeusa.com/Products/HyperChemProfessional/tabid/360/Default.aspx (accessed 7th December 2023)
35. J. J. P. Stewart, *J. Comput. Chem.* **10** (1989) 209 (https://doi.org/10.1002/jcc.540100208)

36. J. J. P. Stewart, *J. Comput. Chem.* **10** (1989) 221 (https://doi.org/10.1002/jcc.540100209)
37. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev*. **88** (1988) 899 (https://doi.org/10.1021/cr00088a005)
38. A. V. Nemukhin, F. Weinhold, *Ros. Khim. Zh.* (*Zh. Ros. Khim. Obshchestva im. D. I. Mendeleeva* **38** (1994) 5 (ISSN: 0373-0247)
39. F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge Univ. Press, Cambridge, 2005 (https://doi.org/10.1017/CBO9780511614569)
40. I. Mayer*, Bond Orders and Energy Components: Extracting Chemical Information from Molecular Wave Functions*, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2016 (https://doi.org/10.1201/9781315374895)
41. *NBO Version 3.1*, 1995, https://gaussian.com (accessed 7th December 2023)
42. R. F. W. Bader, in *Chemical Applications of Topology and Graph Theory: A Collection of Papers from a Symposium Held at the Univ. of Georgia. Athens, Georgia, USA, 18-22 April, 1983*, R. B. King, Ed., Elsevier Science Ltd, Amsterdam, 1983, pp. 40–56 (ISBN-10: 0444422447; ISBN-13: 978-0444422446)
43. D. Cremer, E. Kraka, *Croat. Chem. Acta* **37** (1984) 1259 (ISSN: 0011-1643; e-ISSN: 1334-417X)
44. R. F. W. Bader, *Acc. Chem. Res.* **18** (1985) 9 (https://doi.org/10.1021/ar00109a003)
45. R. F. W. Bader, *Pure Appl. Chem.* **60** (1988) 145 (https://doi.org/10.1351/pac198860020145)
46. R.F.W. Bader, *Chem. Rev.* **91** (1991) 893 (https://doi.org/10.1021/cr00005a013)
47. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford Univ. Press, Clarendon Press, New York, 1994 (ISBN-10: 0198551681; ISBN-13: 978-0198551683)
48. R. F. W. Bader, P. L. A. Popelier, T. A. Keith, *Angew. Chem.* **106** (1994) 647 (https://doi.org/10.1002/ange.19941060605)
49. P. L. A. Popelier, *Atoms in Molecules: An Introduction*, Prentice Hall, London, 2000 (ISBN-10: 0582367980; ISBN-13: 978-0582367982)
50. P. L. A. Popelier, F. M. Aicken, S. E. O'Brien, in *Chemical Modelling: Applications and Theory. Vol. 1*, Ch. A. Reynolds, J. Tennyson, J. Ladik, P. Pyykko, R. I. Maurer, Th. E. Simos, S. Wilson, S. E. O'Brien, D. Pugh, P. L. A. Popelier, A. J. Richardson, H. Stoll, M. Springborg, F. M. Aicken, Eds., Roy. Soc. Chem., Cambridge, 2000, pp. 143–198 (ISBN 978-0854042548)
51. J. R. Mohallem, *Theor. Chim. Acta* **107** (2002) 372 (https://doi.org/10.1007/s00214-002-0345-y)
52. R. F. W. Bader, *Monatsh. Chem.* **136** (2005) 819 (https://doi.org/10.1007/s00706-005-0307-x)
53. R. F. W. Bader, *J. Phys. Chem., A* **111** (2007) 7966 (https://doi.org/10.1021/jp073213k)
54. I. S. Bushmarinov, K. A. Lyssenko, M. Yu. Antipin, *Russ. Chem. Rev.* **78** (2009) 283 (https://doi.org/10.1070/RC2009v078n04ABEH004017)
55. *Computational Chemistry Using the Quantum Theory of Atoms in Molecules* (*QTAIM*), *AIMAll Version 19.10.12*, http://aim.tkgristmill.com (accessed 7th December 2023)
56. S. V. Volovik, G. G. Dyadyusha, V. I. Staninets, *Regioselektivnost' i reaktsionnaya sposobnost' svobodnykh radikalov v protsessakh prisoedineniya i aromaticheskogo zameshcheniya*, V. D. Pokhodenko, Ed., Naukova Dumka, Kiev, 1988 (ISBN: 5-12-000209-9)

57. S. V. Volovik, V. I. Staninets, N. S. Zefirov, *Theor. Exp. Chem.* **26** (1990) 390 (https://doi.org/10.1007/BF00530251)
58. S. V. Volovik, V. I. Staninets, N. S. Zefirov, *Doklady Akad. Nauk Ros.* **330** (1993) 321 (ISSN: 0869-5652)
59. V. S. Urusov, *J. Struct. Chem.* **35** (1994) 101 (https://doi.org/10.1007/BF02578507)
60. A. M. Rozen, B. V. Krupnov, *Russ. Chem. Rev.* **65** (1996) 973 (https://doi.org/10.1070/RC1996v065n11ABEH000241)
61. E. P. Buchikhin, A. M. Chekmarev, N. A. Bobyrenko, *Russ. J. Inorg. Chem.* **55** (2010) 790 (https://doi.org/10.1134/s0036023610050219)
62. Weitao Yang, W. J. Mortier, *J. Amer. Chem. Soc.* **108** (1986) 5708 (https://doi.org/10.1021/ja00279a008)
63. M. V. Lebedev, *Semiconductors* **35** (2001) 1291 (https://doi.org/10.1134/1.1418074)
64. P. W. Ayers, R. G. Parr, *J. Amer. Chem. Soc.* **122** (2000) 2010 (https://doi.org/10.1021/ja9924039)
65. F. Méndez, J. L. Gázquez, *J. Amer. Chem. Soc.* **116** (1994) 9298 (https://doi.org/10.1021/ja00099a054)
66. M. E. Kletskii, O. N. Burov, N. S. Fedik, S. V. Kurbatov, *Chem. Heterocycl. Compounds* **52** (2016) 700 (https://doi.org/10.1007/s10593-016-1952-1)
67. M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.* **153** (1988) 503 (https://doi.org/10.1016/0009-2614(88)85250-3)
68. O. Christiansen, *J. Chem. Phys.* **119** (2003) 5773 (https://doi.org/10.1063/1.1601593)
69. M. Del Ben, J. Hutter, J. VandeVondele, *J. Chem. Theory Comput.* **8** (2012) 4177 (https://doi.org/10.1021/ct300531w)
70. M. Ochi, Sh. Tsuneyuki, *Chem. Phys. Lett.* **621** (2015) 177 (https://doi.org/10.1016/j.cplett.2015.01.009)
71. I. A. Abronin, G. M. Zhidomirov, *Theor. Exp. Chem.* **12** (1976) 68 (https://doi.org/10.1007/BF00524932)
72. G. M. Zhidomirov, A. A. Bagatur'yants, I. A. Abronin, *Prikladnaya kvantovaya khimiya. Raschety reaktsionnoi sposobnosti i mekhanizmov khimicheskikh reaktsii*, Khimiya, Moscow, 1979.