

^{13}C – ^{13}C Spin–Spin Coupling Constants in Structural Studies: XXXIX. Nonempirical Calculations of Heteroaromatic Oximes

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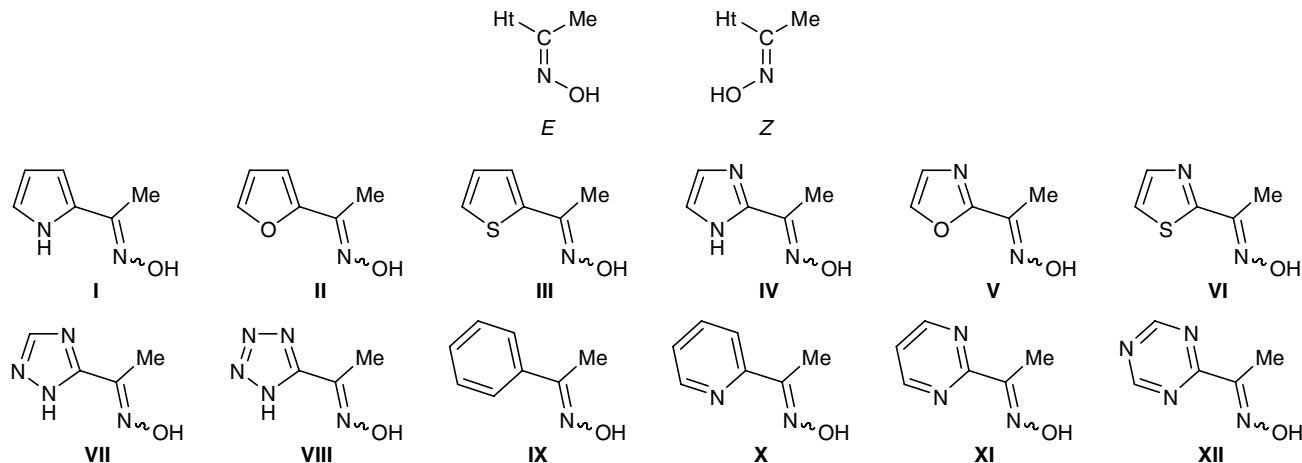
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Abstract—The results of high-level nonempirical quantum-chemical calculations of ^{13}C – ^{13}C coupling constants in twelve heteroaromatic ketone oximes are well consistent with the available experimental data. In all the examined compounds, the effect of the unshared electron pair on the oxime nitrogen atom on J_{CC} strongly predominates over conformational and electronic effects, which makes it possible to unambiguously assign J_{CC} values to different configurations.

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More than 20 years ago we were the first to report on prospects in using ^{13}C – ^{13}C coupling constants for the determination of configuration of compounds having an oxime moiety [1]. Since that time, the proposed approach was widely used to assign configuration at C=N bond in various compounds on the basis of both experimental coupling constants J_{CC} [2] and combination of experimental and theoretical data [3]. The present work continues our studies involving nonempirical calculations of ^{13}C – ^{13}C coupling constants in compounds having a C=N bond [3, 4] and considers problems in determining the configuration of heteroaromatic oximes **I–XII**.

Oximes constitute a vast class of organic compounds that are widely used in analytical and organic chemistry. Oximes are intermediate products in fine organic synthesis, e.g., in the preparation of amines, hydroxylamines, nitriles, amides, ketones, amino ketones, and various heterocyclic systems. Depending on the substituent and reagent nature and reaction conditions, oximes are capable of acting as N-, O-, and C-nucleophiles, 1,3-dipoles (as NH-nitrones), selective ligands toward transition metal cations, and components of highly effective palladium catalysts; they can also undergo nucleophilic attack at the C=N bond, dehydration, Beckmann and Neber rearrangement,



Hoch-Campbell and Trofimov reactions, transformations into parent aldehydes and ketones, reduction, and addition of organometallic compounds. The remarkable chemical versatility of oximes in the presence of bases makes them universal building blocks, whose significance for purposeful organic synthesis is difficult to overestimate.

In the recent years, reactions of oximes with acetylene in superbasic media have been extensively studied. These reactions are known as Trofimov's reaction [5]; they lead in one step to pyrroles and *N*-vinylpyrroles. Derivatives of the latter are widely spread in the nature and are interesting from the viewpoints of various fields of human activity, from pharmacology to electronics. The oxime fragment per se is a pharmacophore; therefore, oximes exhibit versatile biological activity. For example, oximes of the furan and thiophene series possess vasodilating, antispasmodic, sedative, antidepressant, tranquilizing, anticonvulsant, analgetic, antiinflammatory, cytotoxic, antitumor, antiviral, and bactericide properties [6]. Oximes derived from azines, azoles [7], isatin [8], pyrroles [9], and quinolines [10] are also characterized by comparable spectrum of biological activity. Therefore, development of criteria for reliable assignment of configuration of oximes and determination of their electronic and conformational specificities are important problems.

We previously [4] performed a theoretical study on the effect of the lone electron pair on the oxime nitrogen atom on ^{13}C - ^{13}C coupling constants for a representative series of aliphatic and alicyclic oximes using the second-order polarization propagator approximation (SOPPA) [11]. This procedure gave well consistent results and was therefore applied in the present work. The ^{13}C - ^{13}C coupling constants were calculated with account taken of all four contributions to spin-spin coupling: Fermi contact (J_{FC}), spin-dipole (J_{SD}), diamagnetic spin-orbital (J_{DSO}), and paramagnetic spin-orbital (J_{PSO}) using special correlation-consistent Dunning basis sets [12] which were supplemented by adding internal correlation functions [13] as described in [4, 14].

The results are given in Tables 1 and 2; they show a good agreement with the known experimental values. The differences between the calculated and experimental ^{13}C - ^{13}C coupling constants generally do not exceed ~1 Hz. The overall contribution of noncontact interactions ($J_{\text{PSO}} + J_{\text{DSO}} + J_{\text{SD}}$) is negative for most of the examined compounds and is less than 0.5% of the overall coupling constant for the C^2 - C^3 and about 1%

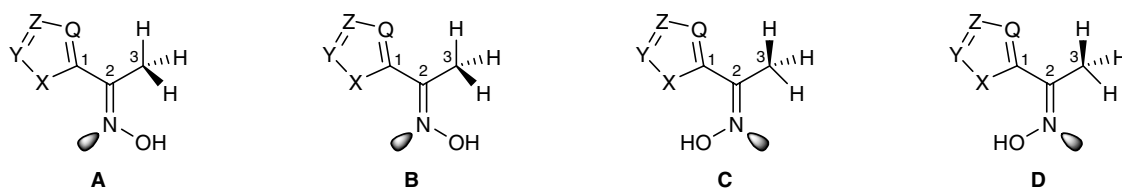
for the C^1 - C^2 bond. The diamagnetic spin-orbital contributions J_{DSO} are positive, and they change within a narrow range (0.3–0.4 Hz), indicating its low sensitivity to substituent nature. The paramagnetic spin-orbital contributions J_{PSO} are negative for all compounds **I–XII**; they range from –0.8 to –2.5 Hz. The spin-dipole contributions J_{SD} are positive (0.7–1.2 Hz). Thus the noncontact contributions are insignificant as compared to the Fermi-contact contribution; the latter ranges from 56.3 to 95.0 Hz for the C^1 - C^2 bond with the heteroaromatic substituent and from 42.5 to 55.8 Hz for the C^2 - C^3 bond in oximes **I–XII**.

The main factor determining the overall ^{13}C - ^{13}C value for the $\text{C}=\text{N}$ carbon nucleus is so-called UEP effect [1, 2]. It originates from the positive through-space contribution of the oxime nitrogen UEP to the ^{13}C - ^{13}C coupling constant for the neighboring carbon-carbon bond oriented *cis* with respect to the UEP (J_{cis}). On the other hand, electron density transfer from the nitrogen UEP on the antibonding molecular orbital of the neighboring *trans*-carbon-carbon bond (n_{σ} - σ^* interaction [15]) makes that bond longer, and the corresponding coupling constant J_{trans} decreases, i.e., the contribution of UEP to the overall J_{trans} value is negative. This effect was studied theoretically in a number of publications [16]. Thus the UEP effect on ^{13}C - ^{13}C coupling constants leads to increase in the difference between J_{cis} and J_{trans} , so that these parameters may be regarded as a reliable and universal criterion for the assignment of configuration about the $\text{C}=\text{N}$ bond [1–4]. The overall UEP effect ($\Delta J = J_{\text{cis}} - J_{\text{trans}}$) for oximes **I–XII** amounts to 20% of the total J value.



If ^{13}C - ^{13}C coupling constants can be measured for both configurational isomers (J_{cis} and J_{trans}), their assignment is evident; however, if J_{CC} for only one isomer can be determined experimentally (J_{cis} or J_{trans}), additional quantum-chemical calculation of ^{13}C - ^{13}C coupling constants and comparison of the theoretical and experimental values are necessary.

The results of our calculations well reproduce general trends in the variation of ^{13}C - ^{13}C coupling constants, depending on orientation of the nitrogen UEP with respect to the heteroaromatic fragment. We can distinguish characteristic ranges of variation of ΔJ_{CC}

Table 1. ^{13}C - ^{13}C coupling constants (J , Hz) and relative energies of ketone oximes **I-VIII**, calculated by the SOPPA method^a

Comp. no.	X	Y	Z	Q	Isomer	Conformer	E_{rel} , kcal/mol	Coupled nuclei	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J
I	NH	CH	CH	CH	<i>E</i>	<i>s-cis</i> (A)	1.4	1, 2	0.4	-2.2	0.9	77.1	76.0; 70.7 [1, 2]
								2, 3	0.3	-1.1	0.7	43.2	43.1; 42.8 [1, 2]
	CH	CH	CH	NH	<i>E</i>	<i>s-trans</i> (B)	6.4	1, 2	0.4	-2.1	1.0	81.3	80.6
								2, 3	0.3	-1.0	0.7	42.4	42.4
	NH	CH	CH	CH	<i>Z</i>	<i>s-cis</i> (C)	0.0	1, 2	0.4	-2.4	0.7	66.9	65.6
								2, 3	0.3	-0.9	0.8	51.5	51.7
	CH	CH	CH	NH	<i>Z</i>	<i>s-trans</i> (D)	4.8	1, 2	0.4	-2.4	0.8	69.3	68.1
								2, 3	0.3	-0.9	0.8	52.2	52.4; 50.7 [1, 2]
II	O	CH	CH	CH	<i>E</i>	<i>s-cis</i> (A)	2.5	1, 2	0.4	-2.1	1.1	83.8	83.2; 79.1 [1, 2]
								2, 3	0.3	-1.0	0.7	43.2	43.2; 43.0 [1, 2]
	CH	CH	CH	O	<i>E</i>	<i>s-trans</i> (B)	0.9	1, 2	0.4	-2.1	1.2	86.7	86.2
								2, 3	0.3	-1.1	0.7	42.5	42.4
	O	CH	CH	CH	<i>Z</i>	<i>s-cis</i> (C)	4.6	1, 2	0.4	-2.2	1.0	71.0	70.2 (69.8) ^b
								2, 3	0.3	-0.8	0.8	53.4	53.7 (53.3) ^b
	CH	CH	CH	O	<i>Z</i>	<i>s-trans</i> (D)	0.0	1, 2	0.4	-2.4	1.0	73.5	72.5
								2, 3	0.3	-1.0	0.7	52.6	52.6
III	S	CH	CH	CH	<i>E</i>	<i>s-cis</i> (A)	0.0	1, 2	0.4	-2.0	1.1	75.4	74.9; 70.22 [1, 2]
								2, 3	0.3	-1.1	0.7	43.8	43.7; 41.9
	CH	CH	CH	S	<i>E</i>	<i>s-trans</i> (B)	1.5	1, 2	0.4	-1.9	1.2	77.2	76.9
								2, 3	0.3	-1.0	0.7	43.9	43.9
	S	CH	CH	CH	<i>Z</i>	<i>s-cis</i> (C)	0.0	1, 2	0.4	-2.2	0.9	62.8	61.9; 60.44 [1, 2]
								2, 3	0.3	-0.9	0.8	52.8	53.0; 46.4 [1, 2]
	CH	CH	CH	S	<i>Z</i>	<i>s-trans</i> (D)	1.4	1, 2	0.4	-2.2	1.0	65.1	64.3
								2, 3	0.3	-0.8	0.8	53.0	53.3
IV	NH	CH	CH	N	<i>E</i>	<i>s-cis</i> (A)	0.6	1, 2	0.4	-1.9	0.9	84.6	84.0
								2, 3	0.3	-1.2	0.7	43.1	42.9
	N	CH	CH	NH	<i>E</i>	<i>s-trans</i> (B)	9.7	1, 2	0.4	-1.8	1.0	89.9	89.5
								2, 3	0.3	-1.0	0.7	43.4	43.4
	NH	CH	CH	N	<i>Z</i>	<i>s-cis</i> (C)	0.0	1, 2	0.4	-2.2	0.8	73.1	72.1
								2, 3	0.3	-1.0	0.7	52.2	52.2
	N	CH	CH	NH	<i>Z</i>	<i>s-trans</i> (D)	10.9	1, 2	0.4	-2.0	0.9	75.9	75.2
								2, 3	0.3	-0.8	0.8	53.7	54.0

Table 1. (Contd.)

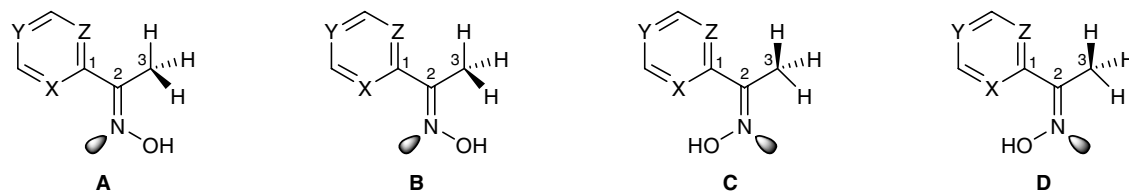
Comp. no.	X	Y	Z	Q	Isomer	Conformer	E_{rel} , kcal/mol	Coupled nuclei	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J
V	S	CH	CH	N	<i>E</i>	<i>s-cis</i> (A)	0.0	1, 2	0.4	-2.0	1.0	91.0	90.4
								2, 3	0.3	-1.1	0.7	43.5	43.4
	N	CH	CH	S		<i>s-trans</i> (B)	3.0	1, 2	0.4	-1.9	1.1	95.0	94.6
								2, 3	0.3	-1.1	0.7	43.5	43.4
	S	CH	CH	N	<i>Z</i>	<i>s-cis</i> (C)	3.1	1, 2	0.4	-2.0	0.9	76.3	75.6
								2, 3	0.3	-1.0	0.7	54.4	54.4
	N	CH	CH	S		<i>s-trans</i> (D)	5.0	1, 2	0.4	-2.0	1.0	79.3	78.7
								2, 3	0.3	-0.9	0.7	54.3	54.4
VI	O	CH	CH	N	<i>E</i>	<i>s-cis</i> (A)	0.0	1, 2	0.4	-1.9	1.0	83.2	82.7
								2, 3	0.3	-1.2	0.7	43.8	43.6
	N	CH	CH	O		<i>s-trans</i> (B)	6.2	1, 2	0.4	-1.9	1.1	86.5	86.1
								2, 3	0.3	-1.0	0.7	45.1	45.1
	O	CH	CH	N	<i>Z</i>	<i>s-cis</i> (C)	1.1	1, 2	0.4	-2.1	0.9	69.4	68.6
								2, 3	0.3	-1.0	0.7	53.2	53.2
	N	CH	CH	O		<i>s-trans</i> (D)	8.4	1, 2	0.4	-1.9	1.0	71.9	71.4
								2, 3	0.3	-0.8	0.7	54.8	55.0
VII	NH	N	CH	N	<i>E</i>	<i>s-cis</i> (A)	0.6	1, 2	0.4	-1.8	0.9	82.8	82.4
								2, 3	0.3	-1.2	0.7	43.5	43.3
	N	CH	N	NH		<i>s-trans</i> (B)	8.1	1, 2	0.4	-1.8	1.0	87.1	86.7
								2, 3	0.3	-1.0	0.7	43.7	43.7
	NH	N	CH	N	<i>Z</i>	<i>s-cis</i> (C)	0.0	1, 2	0.4	-1.9	0.8	70.0	69.3
								2, 3	0.3	-1.2	0.7	52.7	52.5
	N	CH	N	NH		<i>s-trans</i> (D)	9.9	1, 2	0.4	-1.9	0.9	72.5	71.9
								2, 3	0.3	-0.8	0.8	54.2	54.5
VIII	NH	N	N	N	<i>E</i>	<i>s-cis</i> (A)	0.5	1, 2	0.4	-1.7	0.9	83.9	83.5
								2, 3	0.3	-1.2	0.7	43.6	43.4
	N	N	N	NH		<i>s-trans</i> (B)	8.3	1, 2	0.4	-1.7	0.9	88.3	87.9
								2, 3	0.3	-1.0	0.7	44.3	44.3
	NH	N	N	N	<i>Z</i>	<i>s-cis</i> (C)	0.0	1, 2	0.4	-1.8	0.8	70.1	69.5
								2, 3	0.3	-1.0	0.7	52.9	52.9
	N	N	N	NH		<i>s-trans</i> (D)	9.9	1, 2	0.4	-1.8	0.9	72.2	71.7
								2, 3	0.3	-0.8	0.7	55.0	55.2

^a All calculations of ^{13}C - ^{13}C coupling constants were performed assuming C_1 point symmetry group and using cc-pVTZ-Cs basis set for carbon nuclei and cc-pVDZ basis set for all other nuclei without polarization p -functions on hydrogen atoms. The geometric parameters were optimized by the B3LYP/6-311G* method with no symmetry taken into account.

^b In parentheses are given J_{CC} values estimated by the correlation equations presented in [2].

for oximes **I–XII** with *cis* and *trans* orientation of the nitrogen UEP: azole derivatives: $\Delta J_{\text{cis}} = 76\text{--}89$ Hz, $\Delta J_{\text{trans}} = 66\text{--}75$ Hz; furan and oxazole derivatives: $\Delta J_{\text{cis}} = 83\text{--}95$ Hz, $\Delta J_{\text{trans}} = 70\text{--}79$ Hz; thiophene and thiazole derivatives: $\Delta J_{\text{cis}} = 75\text{--}86$ Hz, $\Delta J_{\text{trans}} = 62\text{--}$

71 Hz; azine derivatives: $\Delta J_{\text{cis}} = 73\text{--}83$ Hz, $\Delta J_{\text{trans}} = 63\text{--}71$ Hz. The coupling constant between the oxime and methyl carbon atoms in all compounds **I–XII** are on the average as follows: $J_{\text{cis}} = 52$, $J_{\text{trans}} = 42$ Hz. It is seen that the above intervals for different oxime iso-

Table 2. ^{13}C - ^{13}C coupling constants (J , Hz) and relative energies of ketone oximes **IX–XII**, calculated by the SOPPA method^a

Comp. no.	X	Y	Z	Isomer	Conformer	E_{rel} , kcal/mol	Coupled nuclei	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J
IX	CH	CH	CH	<i>E</i>		0.0	1, 2	0.3	-1.6	1.0	65.8	65.5; 61.7 [1, 2]
							2, 3	0.3	-1.1	0.7	43.3	
				<i>Z</i>		3.2	1, 2	0.4	-1.8	0.9	56.3	55.8 (51.7) ^b
							2, 3	0.3	-0.9	0.8	53.3	
X	N	CH	CH	<i>E</i>	<i>s-cis</i> (A)	6.2	1, 2	0.4	-1.6	1.0	74.3	74.1
							2, 3	0.3	-1.0	0.7	43.7	
	CH	CH	N		<i>s-trans</i> (B)	0.0	1, 2	0.4	-1.6	1.0	73.4	73.2
							2, 3	0.3	-1.3	0.7	44.9	
	N	CH	CH	<i>Z</i>	<i>s-cis</i> (C)	10.6	1, 2	0.4	-1.7	1.0	63.9	63.6
							2, 3	0.3	-0.9	0.8	53.9	
	CH	CH	N		<i>s-trans</i> (D)	3.2	1, 2	0.4	-1.7	0.9	62.6	62.2
							2, 3	0.3	-1.0	0.7	54.7	
XI	N	CH	N	<i>E</i>		0	1, 2	0.4	-1.7	0.9	83.9	83.5
							2, 3	0.3	-1.2	0.7	45.5	
				<i>Z</i>		4.7	1, 2	0.4	-1.7	0.9	71.6	71.2
							2, 3	0.3	-1.0	0.7	55.6	
XII	N	N	N	<i>E</i>		0	1, 2	0.4	-1.8	0.9	82.4	81.9
							2, 3	0.3	-1.2	0.7	45.7	
				<i>Z</i>		5.1	1, 2	0.4	-1.8	0.9	69.9	69.5
							2, 3	0.3	-1.0	0.7	55.8	

^a All calculations of ^{13}C - ^{13}C coupling constants were performed assuming C_1 point symmetry group and using cc-pVTZ-Cs basis set for carbon nuclei and cc-pVDZ basis set for all other nuclei without polarization p -functions on hydrogen atoms. The geometric parameters were optimized by the B3LYP/6-311G* method with no symmetry taken into account.

^b In parentheses are given J_{CC} values estimated by the correlation equations presented in [2].

mers do not overlap each other, which is very important for determination of their configuration.

Apart from the predominating UEP effect, the ^{13}C - ^{13}C coupling constants appreciably depend on the number and nature of heteroatoms in the ring. It was interesting to estimate the contribution of the latter factors relative to the UEP effect. As follows from the data for azole and azine derivatives **I**, **IV**, **X**, and **XI**, the presence of one more electronegative heteroatom in the α -position considerably increases the C^1 - C^2 coupling constant. Further increase in the number of

nitrogen atoms in the ring almost does not affect the coupling constant between C^1 and C^2 . An analogous relation was found previously for aza aromatic compounds; in particular, the coupling constants $J(\text{C}^\alpha, \text{CH}_3)$ in azines were shown to include a considerable positive contribution of the sp^2 -hybridized UEP on the pyridine-type nitrogen atom. This contribution was estimated at 6–8 Hz per UEP for picolines, pyridazines, pyrazines, and pyrimidines [17].

In the present work, the ^{13}C - ^{13}C coupling constants for oximes **I–XII** were calculated with account taken

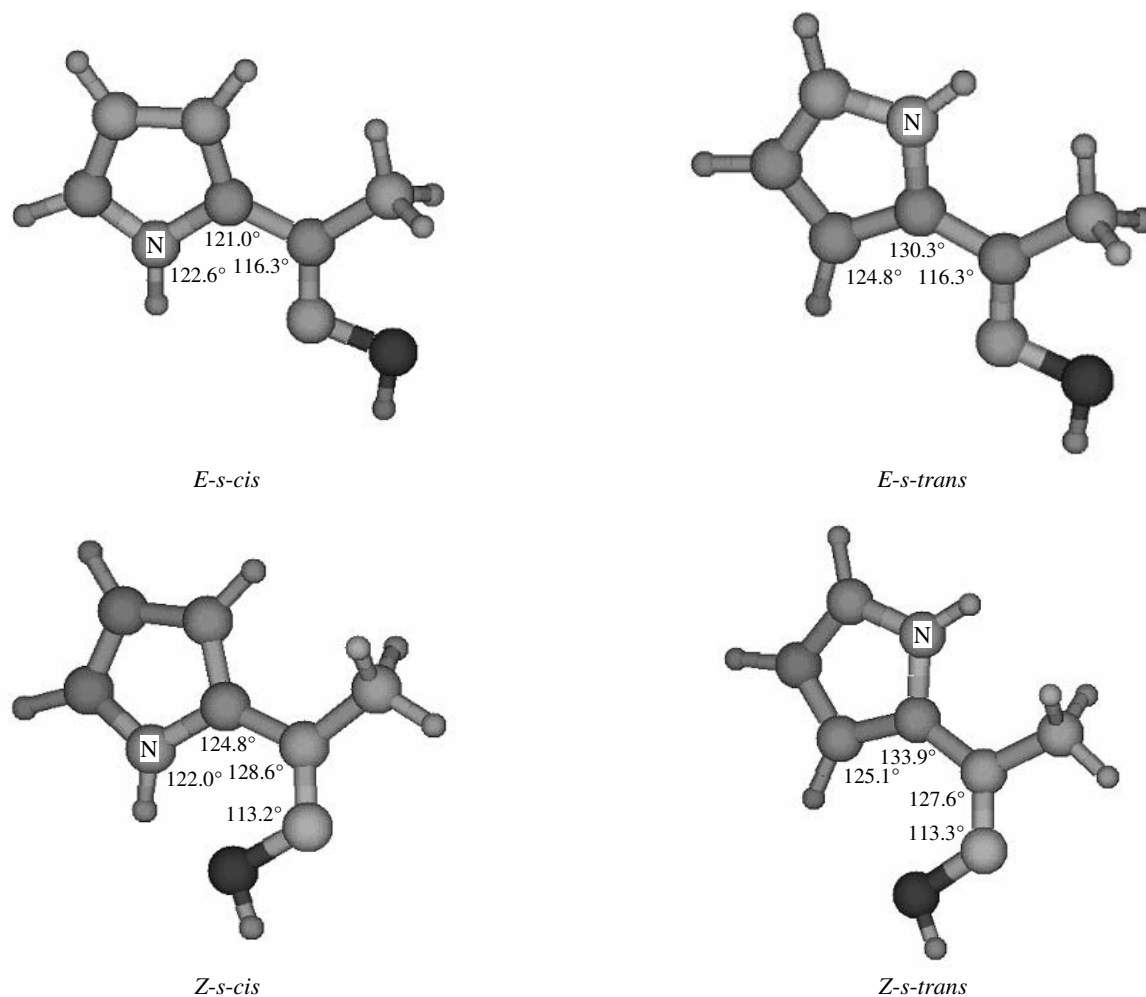


Fig. 1. Rotational conformations of the *E* and *Z* isomers of methyl 2-pyrrolyl ketone oxime (**I**), optimized by the B3LYP/6-311G* method; given are internal angles in deg.

of preferential rotational conformations of the methyl groups, which were determined previously [4]. The most favorable conformations of heteroaromatic substituents in compounds **I–XII** were optimized by the B3LYP/6-311G* calculations. Both *E* and *Z* isomers of oximes **I**, **IV**, **VII**, and **VIII** derived from azolyl ketones are more likely to exist as *s-cis* rather than *s-trans* conformers ($\Delta E = 8\text{--}11$ kcal/mol); presumably, their *s-cis* conformers are stabilized by formation of weak intramolecular hydrogen bond with participation of the oxime nitrogen atom, as in oxime **I**. This follows, e.g., from the bond angles in the *s-cis* and *s-trans* conformers of *E-I* and *Z-I* shown in Fig. 1. No such conformational homogeneity was found for oximes **X–XII** derived from azines.

Rotation of the heteroaromatic substituent from the *cis* position to *trans* in all oximes **I–XII** is accompanied by increase of J_{CC} by 3–5 Hz for the *E* isomers

and 2.5 Hz (on the average) for the *Z* isomers. Taking this fact into account, we performed conformational analysis of compounds **I** and **II** for which the above effect is most pronounced (Fig. 2). In the calculations we used geometric parameters of their molecules with fixed dihedral angle φ that characterizes internal rotation of the heteroaromatic substituent about the $\text{C}^1\text{--}\text{C}^2$ bond. The geometric parameters were optimized by the B3LYP/6-311G* method at each point in the φ range from 0 to 180° through a step of 15°. The dihedral angle $\varphi = 0^\circ$ corresponds to the planar conformation where the substituent is arranged *cis* with respect to the nitrogen UEP.

The plots of $J(\text{C}^1, \text{C}^2)$ versus φ are shown in Fig. 2. It is seen that all internal rotation curves pass through a minimum at $\varphi = 0^\circ$, i.e., when proton on the azole nitrogen atom is spatially close to either UEP on the oxime nitrogen atom in *E* isomers or oxime oxygen

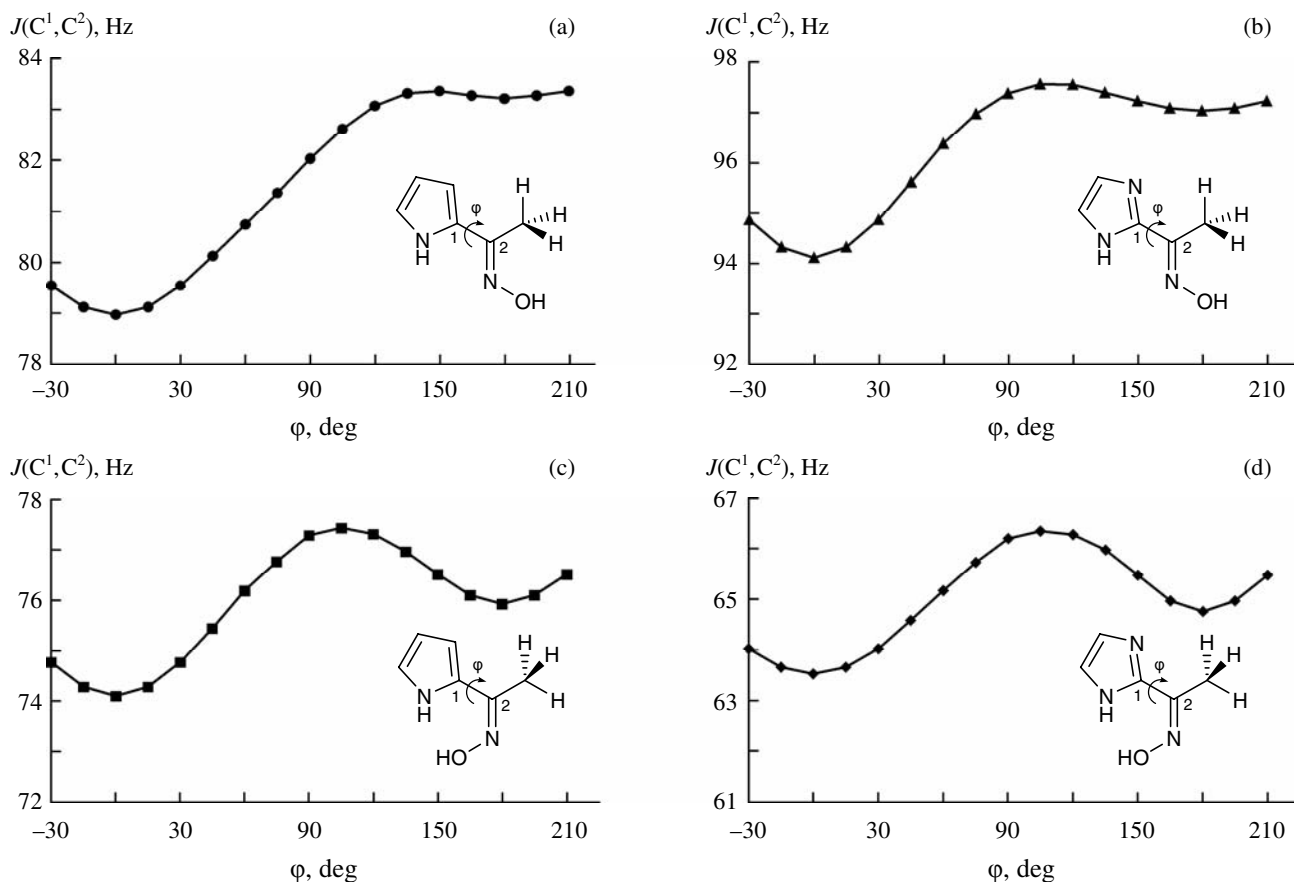


Fig. 2. Plots of $J(C^1, C^2)$ versus angle of rotation of the heteroaromatic fragment about the C^1-C^2 bond in the *E* and *Z* isomers of (a, c) oxime **I** and (b, d) oxime **IV**, calculated by the SOPPA method.

atom in *Z* isomers. Obviously, intramolecular hydrogen bonding is possible in both cases. Rotation of the azole substituent in the ϕ range from 0 to 120° is accompanied by considerable increase of $J(C^1, C^2)$ due to rupture of intramolecular hydrogen bond, and further increase of ϕ almost does not affect the C^1-C^2 coupling constant. These data suggest the existence of an appreciable stereochemical dependence of J_{CC} , which is related to internal rotation of the heteroaromatic fragment. Nevertheless, the UEP effect on J_{CC} (which is estimated at about 10–15 Hz) strongly prevails.

Quantum-chemical calculations were performed using GAMESS [18] and DALTON programs [19] with either standard built-in basis sets or those modified by the authors (for detailed specification, see [4]).

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