

Spin-spin Coupling Constants ^{13}C – ^{13}C in Structural Studies: XXXVIII. Nonempirical Calculations: Oximes

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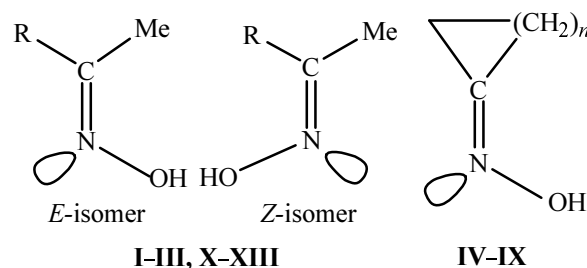
Abstract—*Ab initio* calculation of spin-spin coupling constants ^{13}C – ^{13}C for a series of ketone oximes was carried out in a framework of the second order polarization propagator approximation (SOPPA). Taking into account the electron correlation effects and the use of special correlation-consistent basic sets including functions allowing for internal correlation and dense functions provided a good agreement between the calculated and experimental values. These results open new possibilities for the configurational assignment of imine nitrogen compounds.

Oximes are important semiproducts in the preparative organic synthesis [1]. In recent years considerable study has been given to ketone oxime reactions with acetylene in superbasic media resulting in O-vinyloximes, pyrroles, and N-vinylpyrroles (Trofimov reaction) [2]. Trofimov reaction ensures an elegant way to previously unavailable or unknown compounds of pyrrole series, and the corresponding yields depend on the structure and configuration of initial oximes. Therefore the estimation of oxime configuration is among the most important problems of pyrrole synthesis [3]. The problems of oximes configuration is also extremely interesting because their isomers differ not only in physical constants but at the same time in chemical properties [4].

The configurational structure of imine nitrogen compounds can be unambiguously assigned basing on the measurement the ^{13}C – ^{13}C coupling constants in the NMR spectra for these values are very sensitive to the orientation of the lone electron pairs (the so-called LEP effect [5]). It was shown theoretically [6] that the LEP effect on the ^{13}C – ^{13}C coupling constants consisted in a through-space interaction of the lone electron pair of a heteroatom with a bonding and antibonding orbitals of the neighboring carbon-carbon bonds resulting respectively in an increase and decrease in the *s*-character of these bonds, i.e., in a positive and a negative contribution into the corresponding J_{CC} constants. The observed stereospecificity of the carbon-carbon coupling constants in oximes and their derivatives makes it possible to use the LEP effect as a reliable and universal criterion for assignment of their configurational isomers [5].

A reliable and economical procedure for nonempirical calculation of coupling constants of medium size organic molecules was reported in [7]. The method provides wide prospects for the use *ab initio* calculations in the theoretical study of the mechanism of the spin-spin coupling. The main goal of the present study is elucidation of the possibility to use procedure [7] for calculation of ^{13}C – ^{13}C coupling constants in molecules containing multiple bonds and heteroatoms with lone electron pairs. In particular, we were interested whether the LEP effect would be reproduced by nonempirical calculations of ^{13}C – ^{13}C coupling constants, and also whether this method would be promising for establishing the configuration of imine nitrogen compounds of unknown structure.

Here we report the results of *ab initio* calculations of ^{13}C – ^{13}C coupling constants for thirteen oximes the most frequently used in pyrrole syntheses. The calculation was carried out by the method of the second order polarization



R = Me (I), Et (II), *cyclo*-Pr (III), pyrrol-2-yl (X), fur-2-yl (XI), thien-2-yl (XII), Ph (XIII); *n* = 1 (IV), 2 (V), 3 (VI), 4 (VII), 5 (VIII), 6 (IX).

propagator approximation (SOPPA) [8] accounting for electron correlation within the second order perturbation theory using special correlation consistent basis sets.

In conformity to the fundamental Ramsey [9] theory, the total value of the spin-spin coupling consists of Fermi-contact (FC) and noncontact contributions: spin-dipole (SD), diamagnetic spin-orbital (DSO), and paramagnetic spin-orbital (PSO). In most coupling types the dominant contribution corresponds to the Fermi-contact interaction. In this study we calculated the total ^{13}C – ^{13}C coupling constants values taking into consideration all four contributions.

The accuracy of the *ab initio* calculations of the coupling constants depends on several factors: on the level of the chosen theory, on the quality of basis sets, on accounting for oscillation corrections, relativistic effects, and effects of medium, and on the method of geometry optimization.

Recently for calculations of coupling constants in organic molecules the density functional theory (DFT) became fashionable [10]. The application of this procedure permits a fast calculation of coupling constants for sufficiently large molecular systems with a plausible accuracy. However the DFT method is a hybrid one, for it combines the nonempirical and semiempirical approach. Analysis of a large number of studies [11, 12] demonstrated that one of the most precise approaches used for coupling constant calculation is the second order perturbation theory SOPPA [8]. The accounting for the electron correlation at the level of the second order perturbation theory used in the SOPPA procedure within the framework of the polarization propagator approximation afforded values close to experimental data for all compounds studied up till now corresponding to various types of coupling constants [7, 13].

The second in importance factor is the quality of the basis set used in the coupling constants calculation. The standard basis sets commonly used in energy calculations and in geometrical parameters optimization are unacceptable for coupling constants calculation. A valid coupling constants calculation requires accounting for the electron correlation of the internal electrons (internal electron correlation). In particular, the calculation of the Fermi-contact contribution strongly depends on the electron density distribution directly at the nucleus. Therefore a significant point in the nonempirical coupling constants calculation is extending the standard basis sets with dense functions [14] and functions allowing for internal correlation [15].

The dependence of the accuracy of the J_{CC} calculation in the oxime series **I–XIII** by SOPPA method on the quality of the basis set was evaluated in this study by an example of the molecule of acetone oxime (**I**). The values of ^{13}C – ^{13}C coupling constants calculated using different basis sets are given in Table 1 alongside with the existing experimental data. In these calculations were chosen correlation consistent Dunning basic sets cc-VXZ and cc-pVXZ ($X = \text{D, T}$). It is known [7] that accounting for the electron correlation is especially important for the coupled carbon atoms. Therefore the use of standard basis sets cc-VDZ, cc-pVDZ, and cc-pVTZ results in obviously wrong values of J_{CC} . Actually, coupling constants calculation without taking into consideration the internal correlation functions affords strongly underestimated energy values of the excited states which are included in summation. As a result, the Fermi-contact contribution sharply increases and therewith also the total value of the constant. However the incorporation of a single function allowing for internal correlation sharply decreases the calculated constant virtually reducing its value to the experimental figure.

The given data show that the nonpolarized basis set cc-VDZ even extended with the function accounting for internal correlation is still not sufficiently flexible to ensure the necessary accuracy in calculation of the coupling constant for the coupled carbon atoms.

The improvement of the quality of the basis set is obtained by increasing the number of the basis atomic orbitals (AO) for each atom. Thus the extension of basis sets on carbon atoms leads to gradual approach of the calculated constants to the experimental ones within the 1.5 Hz range. In a series nonempirical calculations of coupling constants the optimum version for the coupled carbon atoms is the basis set cc-pVDZ-Cs using only 15 basis AO for each atom.

In ^{13}C – ^{13}C coupling constants calculations is also important to choose correctly the basis sets for atoms not involved into coupling. In this respect the practical reasons are to be applied: the reduction of calculation time and the closeness between the calculated and experimental values should be the ruling principles. As seen from Table 1, a sequential increase of the doubly-split basis set for nitrogen and oxygen atoms from cc-VDZ to cc-pVDZ decreased the calculated constant by ~ 0.6 Hz; on the other hand, the replacement of the triplet-split basis cc-VTZ for cc-pVTZ decreased the calculated constant only by ~ 0.2 Hz. Therefore in calculation of J_{CC} in oxime series it is possible to use for uncoupled

Table 1. Effect of the basis set quality on precision of ^{13}C - ^{13}C coupling constants calculations for acetone oxime (**I**) by method SOPPA^a

C	Basis set		Number of basis AO	$J(\text{C}^1, \text{C}^2)$, Hz	$J(\text{C}^2, \text{C}^3)$, Hz
	N, O	H			
cc-VDZ	cc-VDZ	cc-VDZ	59	64.43	55.73
cc-VDZ-Cs	cc-VDZ	cc-VDZ	62	58.64	46.82
cc-pVDZ	cc-VDZ	cc-VDZ	74	66.52	55.44
cc-pVDZ-Cs	cc-VDZ	cc-VDZ	77	52.35	41.27
	cc-pVDZ	cc-VDZ	87	52.03	42.02
	cc-pVDZ	cc-pVDZ	108	52.21	42.03
cc-VTZ-Cs	cc-VDZ	cc-VDZ	107	53.15	41.19
	cc-pVDZ	cc-VDZ	117	52.57	41.80
	cc-pVDZ	cc-pVDZ	138	52.38	41.47
	cc-VTZ	cc-VDZ	135	52.22	42.06
	cc-VTZ	cc-pVDZ	156	51.95	41.83
	cc-VTZ	cc-VTZ	184	51.92	41.71
cc-pVTZ	cc-VDZ	cc-VDZ	122	62.56	50.57
cc-pVTZ-Cs	cc-VDZ	cc-VDZ	128	52.55	40.85
	cc-pVDZ	cc-VDZ	138	52.02	41.30
	cc-pVDZ	cc-pVDZ	159	52.97	41.05
	cc-VTZ	cc-VDZ	156	51.74	41.60
	cc-VTZ	cc-pVDZ	177	51.61	41.44
	cc-VTZ	cc-VTZ	205	51.49	41.13
	cc-pVTZ	cc-VDZ	170	51.66	41.59
	cc-pVTZ	cc-pVDZ	191	51.55	41.42
	cc-pVTZ	cc-VTZ	219	51.42	41.10
	cc-pVTZ	cc-pVTZ	254	51.40	40.95
Experimental data from [16]				49.8	41.2

^a Here and hereinafter C^1 , C^2 , and C^3 are carbon atoms of substituent R, oxime, and methyl groups respectively.

atoms of the second period the economical basis set cc-pVDZ.

The sequentially increased basis set on the hydrogen atoms provides a J_{CC} decrease only by ~ 0.2 Hz. Therefore the incorporation of the polarization p -functions for the hydrogen virtually does not affect the precision of the calculation as has been already stated in [7]. Thus for the hydrogen atoms the supereconomical basis cc-VDZ can be used where only two basis AO are present for each atom whereas the application of the basis cc-pVDZ requires five AO for each hydrogen atom.

Although the sum of the noncontact contributions J_{PSO} , J_{DSO} , and J_{SD} is usually less than 10% of the total constant value the disregarding of the noncontact contributions can result in significant errors. It is worth mentioning that the

variations in the spin-dipole contribution are small although the time required for its calculation exceeds that necessary for the Fermi-contact contribution by an order of magnitude. Therefore it is feasible to carry out the estimation of the J_{SD} separately with the use of the most economical basis sets, and that would not impair the accuracy of results.

In conclusion of the consideration of the data given in Table 1 it should be noted that the optimal procedure for the ^{13}C - ^{13}C coupling constants calculations in the series of oximes studied **I–XIII** is SOPPA using special correlation consistent basis sets. For the coupled carbon atoms correlation consistent polarization basis sets should be used incorporating functions taking into account internal correlation cc-pVDZ-Cs or cc-pVTZ-Cs (depending on

Table 2. Effect of the basis set quality on precision of ^{13}C – ^{13}C coupling constants calculations for thienyl methyl ketone oxime (**XII**) by method SOPPA^a

Basis set		Number of basis AO	<i>E</i> -isomer		<i>Z</i> -isomer	
C^1, C^2, C^3	S		$J(C^1, C^2)$, Hz	$J(C^2, C^3)$, Hz	$J(C^1, C^2)$, Hz	$J(C^2, C^3)$, Hz
cc-pVDZ-Cs	cc-pVDZ	147	74.08	42.36	61.87	52.36
	aug-cc-pVDZ	156	73.98	42.42	61.80	52.37
cc-pVTZ-Cs	cc-pVTZ	163	74.35	42.34	62.27	52.31
	aug-cc-pVTZ	179	74.05	42.37	62.20	52.33
	cc-pVDZ	198	74.69	41.54	61.63	52.17
	aug-cc-pVDZ	207	74.77	41.55	61.81	52.17
	cc-pVTZ	214	74.81	41.51	61.81	52.14
	aug-cc-pVTZ	230	74.62	41.53	61.84	52.12
Experimental data from [5]			70.2	41.9	60.4	46.4

the size of the molecule); at the same time for the atoms of the second period polarization basis sets cc-pVDZ should be applied, and for hydrogen atoms nonpolarization basis sets cc-VdZ.

The effect of the basis set quality on the calculated constants values was additionally investigated for the thienyl methyl ketone oxime (**XII**) containing a sulfur atom. As seen from Table 2, the use for sulfur atoms of correlation consistent basis sets extended with diffuse functions (aug-cc-pVDZ and aug-cc-pVTZ) virtually does not affect the calculation quality. The sequential extension of the basis set for the coupled carbon atoms provides a more significant contribution and results in better agreement with the experimental data. These results show that in the nonempirical coupling constants calculations for the atoms belonging to the third period may be applied sufficiently economical basis cc-pVDZ.

Strictly speaking, the correct comparison of the calculated values of the coupling constants with the experimental data should be performed with accounting for oscillation corrections, relativistic effects, and effect of the medium [17]. However the mentioned factors only slightly affect the calculation of the carbon-carbon coupling constants. Actually, it was shown in [5, 16] that the dielectric permeability of the medium virtually did not affect the calculated constants values, and the relativistic corrections were significant only in calculations of molecules containing heavy atoms [17]. On the other hand, the oscillation corrections are less than 1 Hz [18] and also cannot notably affect the calculation of J_{CC} .

Let us consider the effect on the precision of ^{13}C – ^{13}C coupling constants calculation of the procedures used in the optimization of geometrical parameters. To this end

we carried out the geometry optimization of the acetone oxime (**I**) along four procedures: restricted Hartree–Fock theory (RHF), Møller–Plesset second order perturbation theory (MP2), electron density functional theory (DFT) applying Becke’s three-parameter hybrid functional with the use of Lee–Yang–Parr correlation functional (B3LYP), and coupled clusters theory with singlet and doublet amplitudes (CCSD). We used triply valence-split Pople basis sets 6-311G*, containing polarization *d*-function for atoms of the second and third periods, 6-311G** incorporating polarization *p*-functions for hydrogen atoms, and 6-311++G** including diffuse *s*-functions for hydrogen and *s,p*-functions for the atoms of the second period. The calculated geometrical parameters were compared with the experimental data obtained by electron diffraction measurements in the gas phase [19].

As seen from Table 3, the methods MP2, B3LYP, and CCSD ensure the best agreement between the calculated and experimental values of the geometrical parameters and ^{13}C – ^{13}C coupling constants estimated by SOPPA procedure using the corresponding geometrical parameters. It should be indicated that application of the methods MP2 and CCSD requires large time expenditures. On the other hand the RHF procedure gave inadequate description of the experiment due to lack of accounting for the electron correlation. The quality of the basis set within the same method does not affect the geometrical parameters and consequently the coupling constants. The deviations in the bond lengths do not exceed 0.005 Å, in the bond angles 0.8°, and in the values of constants 0.5 Hz (Table 3). Therefore the incorporation of polarization *p*-functions for hydrogen atoms and also of diffuse functions (*s*-functions for hydrogen and *s,p*-functions for

Table 3. Comparison of methods for optimization of geometrical parameters by the example of acetone oxime (**I**)

Procedure	Geometrical parameters ^a						^{13}C – ^{13}C coupling constants, Hz	
	$r(\text{C}^1\text{C}^2)$	$r(\text{C}^2\text{C}^3)$	$r(\text{C}^2\text{N})$	$\alpha(\text{C}^1\text{C}^2\text{N})$	$\alpha(\text{C}^3\text{C}^2\text{N})$	$\alpha(\text{C}^2\text{NO})$	$J(\text{C}^1, \text{C}^2)$	$J(\text{C}^2, \text{C}^3)$
RHF/6-311G*	1.502	1.507	1.253	117.1	123.8	112.6	52.10	39.69
RHF/6-311G**	1.502	1.507	1.253	117.1	123.8	112.6	51.67	39.40
RHF/6-311++G**	1.502	1.507	1.254	117.1	123.8	112.6	51.72	39.40
MP2/6-311G*	1.500	1.502	1.288	116.3	123.3	110.8	51.54	41.53
MP2/6-311G**	1.501	1.504	1.288	116.3	123.4	110.8	51.05	41.22
MP2/6-311++G**	1.501	1.504	1.289	116.3	123.4	110.8	51.10	41.28
B3LYP/6-311G*	1.503	1.506	1.276	116.1	124.1	111.6	51.97	41.23
B3LYP/6-311G**	1.503	1.506	1.275	116.3	124.1	111.6	51.48	40.87
B3LYP/6-311++G**	1.504	1.506	1.278	116.1	124.2	111.6	51.47	40.90
CCSD/6-311G*	1.505	1.508	1.282	116.6	123.5	110.9	51.43	40.96
CCSD/6-311G**	1.506	1.510	1.282	116.7	123.6	110.9	50.86	40.54
CCSD/6-311++G**	1.506	1.510	1.283	116.7	123.6	110.9	50.91	40.57
Experimental data ^b	1.521(5)	1.490(3)	1.289(1)	116.4(2)	123.4(3)	111.2(2)	49.8	41.2

^a Bond lengths are given in Å, bond angles in degrees.

^b Experimental values of geometrical parameters were obtained by electron diffraction [19], ^{13}C – ^{13}C coupling constants are taken from [16].

atoms of the second period) is not of fundamental importance for the calculation.

Thus from the viewpoint of the accuracy of the calculated values and economizing the calculation time the optimum method of *ab initio* calculation for the oximes **I–XIII** series is B3LYP using the triply valence-split Pople basis set 6-311G*.

Apart from the fundamentals of the procedure for the nonempirical coupling constants calculation we were interested also in the stereochemical aspect related to the effect of methyl groups rotation and conformational structure of the rings in compounds **I–XIII** on the values of the ^{13}C – ^{13}C coupling constants.

Let us consider in more detail the rotation of methyl groups and its effect on the constants values by the

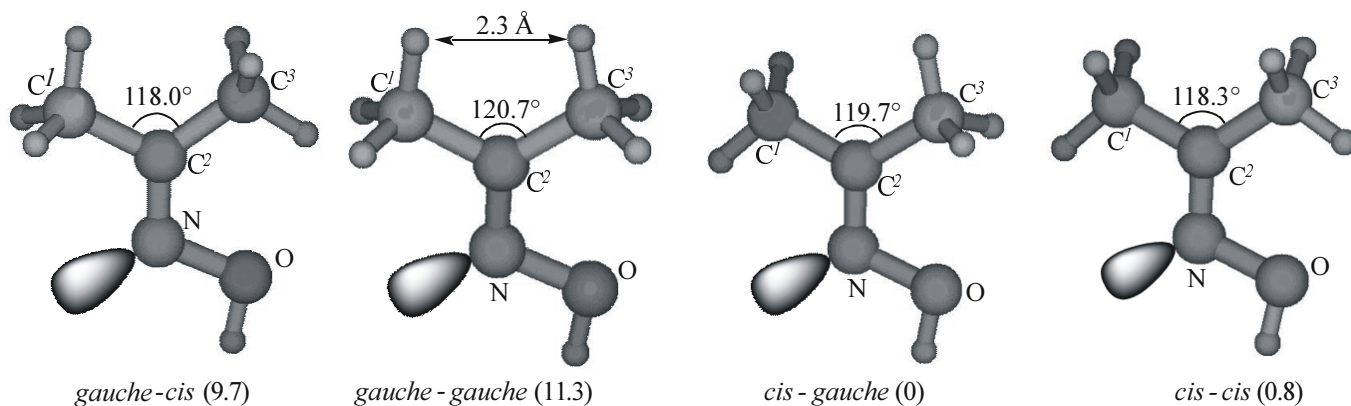


Fig. 1. Rotational conformation of acetone oxime (**I**) optimized by B3LYP/6-311G* procedure (the relative energy of conformations, kJ mol^{-1} , are given in parentheses)

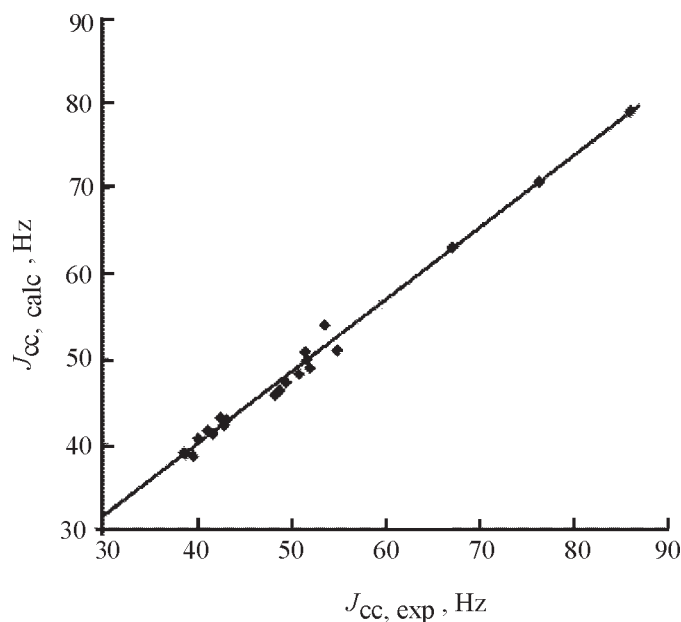
example of acetone oxime (**I**). The analysis of the rotational potential energy surface of compound (**I**) revealed the presence of four stationary points corresponding to four rotational conformations of the acetone oxime: *cis-cis*, *cis-gauche*, *gauche-cis*, and *gauche-gauche* (Fig. 1). The calculation of vibration spectra of each among these forms revealed the presence of imaginary frequencies for high-energy conformations, therefore the conformations *gauche-cis* and *gauche-gauche* are the transition states of the molecule. On the other hand, the vibration spectra of low-energy conformations *cis-gauche* and *cis-cis* lack imaginary frequencies, and thus they can be regarded as the ground states of the molecule (conformers).

In both low-energy conformers of acetone oxime one of the methyl group (the first) occupies a *cis*-position

Table 4. ^{13}C – ^{13}C coupling constants in different rotational conformers of acetone oxime (I)

Rotational conformation	Relative energy, kJ mol^{-1}	$J(\text{C}^1, \text{C}^2)$, Hz	$J(\text{C}^2, \text{C}^3)$, Hz
<i>cis-gauche</i>	0	51.7	41.9
<i>cis-cis</i>	0.8	51.7	41.9
<i>gauche-cis</i>	9.7	51.9	42.0
<i>gauche-gauche</i>	11.3	52.1	42.0
Experimental data of [5]		49.8	41.2

with respect to the LEP of the nitrogen atom. In this orientation a proton of one of the C–H bonds of the first methyl group is in the immediate vicinity to the LEP of the nitrogen. This is facilitated by the electrostatic attraction of the atoms C, H, N and the donor-acceptor interactions between atoms N and H. It is highly probable that alongside the extension of the C–H bond it also suffers a considerable polarization (electron density shift from H to C) which favors an appearance of the so-called nonclassical pseudointramolecular hydrogen bond $\text{H}\cdots\text{N}$ described by Afonin *et al.* for related systems [20]. This intramolecular interaction results in an important effect of additional stabilization of the said conformation. Thus the rotation of methyl group in the conformers *cis-cis* and *cis-gauche* with respect to the C–C bond through 60° induces the increase in the relative energy of the

**Fig. 2.** Comparison of calculated and experimental J_{CC} for oxime series I–XIII, r 0.998, s 1.02 Hz, n 21.

system to 10–11 kJ mol^{-1} leading to *gauche-cis* and *gauche-gauche* conformations respectively.

The relative stability of the two low-energy conformers *cis-cis* and *cis-gauche* depends on the rotational orientation of the second methyl group. It is significant that in the *cis-cis* conformer a torsional strain arises in the fragment $\text{HC}^3\text{C}^2=\text{NO}$ leading to the opening of the bond angles HC^3C^2 , $\text{C}^3\text{C}^2\text{N}$, and C^2NO by over 2° . On the other hand the torsional strain in the *cis-gauche* conformer is weakened. The low-energy conformations can easily transform into each other for the energy barrier between them is insignificant (around 1 kJ mol^{-1}).

It is presumable that a similar relation exists also for the high-energy conformations *gauche-cis* and *gauche-gauche*. The *gauche-gauche* conformation is the least stable due to the strong repulsion of the protons from the two methyl groups located at a distance of only $\sim 2.3 \text{ \AA}$. This sterical strain results in the maximum opening of the bond angle $\text{C}^1\text{C}^2\text{C}^3$ to 121° (Fig. 1). The value of the sterical interaction of methyl groups taking into account the overlapping with the torsional strain in the fragment $\text{C}=\text{NO}$ may be estimated at $\sim 2.5 \text{ kJ mol}^{-1}$.

Thus both the theoretical conformational analysis and electronographic measurements [19] demonstrated that the most stable was *cis-gauche* conformation.

The data in Table 4 show that the methyl groups rotation virtually does not affect the coupling constants values. In keeping with this observation we carried out the ^{13}C – ^{13}C coupling constants calculation for the dominant conformations in the oximes series I–XIII under study (detailed information on the conformational composition of all oximes studies is available by E-mail from the authors).

The calculated J_{CC} of oximes I–XIII well consistent with the known experimental data are presented in Table 5 (Fig. 2).

The sum of noncontact interactions J_{PSO} , J_{DSO} , and J_{SD} is negative practically for all oximes and amounts to less than 0.5% for compounds I, II, and VI–IX and 1% for aromatic and heteroaromatic oximes X–XIII. Two compounds IV and V form an exception where this sum amounts from 2.5 to 6%. The values of the diamagnetic spin-orbital contribution J_{DSO} are positive and do not exceed 0.4 Hz evidencing that this contribution is insensitive to the character of substituent and the size of the ring. The orbital paramagnetic contribution J_{PSO} is negative for all the compounds from the series under investigation. It varies in the range from -2.5 to -0.01 Hz and attains in the absolute value around 1 Hz. The values of the

Table 5. ^{13}C - ^{13}C coupling constants of oximes **I–XIII** calculated by SOPPA method^a

Compd. no.	Isomer	Coupled nuclei	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experimental data	Reference
I		C^1, C^2	0.23	-1.08	0.74	51.77	51.66	49.8	[16]
		C^2, C^3	0.24	-1.10	0.74	41.71	41.59	41.2	[16]
II	<i>E</i>	C^1, C^2	0.27	-1.06	0.75	50.76	50.72	48.2	[21]
		C^2, C^3	0.25	-1.07	0.74	41.18	41.10	41.5	[21]
III	<i>Z</i>	C^1, C^2	0.27	-1.12	0.69	40.27	40.11	40.6	[21]
		C^2, C^3	0.24	-1.00	0.78	51.84	51.86	48.8	[21]
IV	<i>E</i>	C^1, C^2	0.32	-1.54	0.64	67.58	67.00	63.1	[22]
		C^2, C^3	0.27	-1.15	0.71	42.86	42.69	42.1	[22]
V	<i>Z</i>	C^1, C^2	0.32	-1.68	0.61	55.65	54.90	51.0	[22]
		C^2, C^3	0.25	-1.05	0.74	53.44	53.38	54.0	[22]
VI		C^1, C^2	0.23	-1.29	-0.26	34.93	33.61	–	–
		C^2, C^3	0.23	-1.43	-0.25	23.20	21.75	–	–
VII		C^1, C^2	0.27	-0.01	0.82	41.22	42.30	–	–
		C^2, C^3	0.27	-0.30	0.85	31.58	32.40	–	–
VIII		C^1, C^2	0.29	-0.94	0.77	48.12	48.24	45.7	[21]
		C^2, C^3	0.30	-1.27	0.74	38.81	38.58	38.9	[21]
IX		C^1, C^2	0.30	-1.11	0.76	48.71	48.66	46.2	[21]
		C^2, C^3	0.31	-1.24	0.74	38.94	38.75	38.7	[21]
X	<i>E</i>	C^1, C^2	0.30	-1.08	0.75	49.34	49.31	47.09	[21]
		C^2, C^3	0.31	-1.15	0.73	39.56	39.45	38.45	[21]
XI	<i>Z</i>	C^1, C^2	0.30	-1.04	0.74	50.76	50.76	–	–
		C^2, C^3	0.31	-1.16	0.72	40.86	40.73	–	–
XII	<i>E</i>	C^1, C^2	0.36	-2.15	0.88	77.15	76.24	70.7	[22]
		C^2, C^3	0.27	-1.07	0.64	43.17	43.01	42.8	[22]
XIII	<i>Z</i>	C^1, C^2	0.37	-2.43	0.72	66.72	65.38	–	–
		C^2, C^3	0.26	-0.90	0.72	51.33	51.41	50.7	[22]
XIV	<i>E</i>	C^1, C^2	0.37	-2.06	1.22	86.47	86.00	79.1	[5]
		C^2, C^3	0.27	-1.10	0.75	42.51	42.43	43.0	[5]
XV	<i>Z</i>	C^1, C^2	0.38	-2.38	1.00	73.45	72.45	(69.8) ^b	[5]
		C^2, C^3	0.27	-0.96	0.73	52.82	52.86	(53.3)	[5]
XVI	<i>E</i>	C^1, C^2	0.37	-0.24	1.03	75.33	76.49	70.2	[5]
		C^2, C^3	0.27	-1.07	0.65	41.69	41.54	41.9	[5]
XVII	<i>Z</i>	C^1, C^2	0.37	-2.31	0.89	62.68	61.63	60.4	[5]
		C^2, C^3	0.26	-0.91	0.69	52.13	52.17	46.4	[5]
XVIII	<i>E</i>	C^1, C^2	0.34	-1.67	1.01	65.83	65.51	61.7	[23]
		C^2, C^3	0.27	-1.14	0.71	42.66	42.50	42.8	[5]
XIX	<i>Z</i>	C^1, C^2	0.34	-1.88	0.90	55.61	54.97	(51.7)	[5]
		C^2, C^3	0.25	-0.97	0.76	53.31	53.35	52.5	[23]

^a Total values of calculated coupling constants and contributions thereto are given in Hz.^b The values given in parentheses are estimated J_{CC} values calculated from correlation expressions in [5].

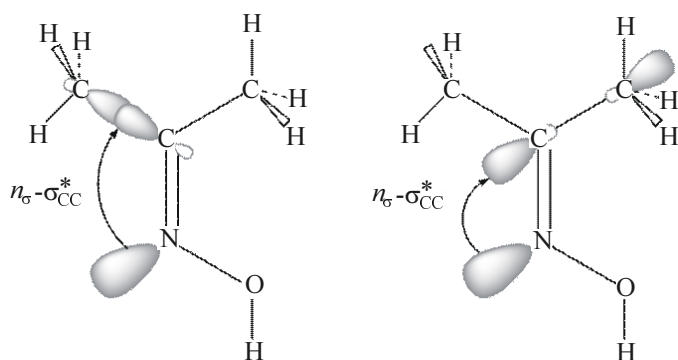


Fig. 3. Intramolecular interactions in acetone oxime (**I**).

spin-dipole contribution J_{SD} are positive and change from 0.6 to 1.2 Hz. The exception here is the spin-dipole contribution for cyclopropanone oxime (**IV**) equal to -0.3 Hz in agreement with the data of [11, 24], where the J_{SD} in the three-membered ring has been shown to be negative.

Thus in calculation of ^{13}C – ^{13}C coupling constants for the oximes series **I–XIII** under study prevails the Fermi-contact contribution varying from 21.8 to 86.5 Hz. The

following relation was observed: for the cyclic oximes the Fermi-contact contribution sharply increased (on the average by 6 Hz) with growing size of the ring in compounds **IV–VI**, and at further ring expansion in compounds **VII–IX** this contribution steadily but insignificantly grew. This fact is due to the considerable strain in the small rings that is lacking in compounds with more than five carbon atoms in the cycle.

It is well known that the ^{13}C – ^{13}C coupling constants exhibit pronounced stereospecificity originating from the reciprocal orientation of the lone pairs on the heteroatom and the corresponding carbon-carbon bonds [5]. This effect for all compounds in question amounts on the average to 10–20% of the total coupling constant value. Therefore the problem of reproducibility of the LEP effect in the calculated values of ^{13}C – ^{13}C coupling constants of oximes **I–XIII** is extremely important.

The effect of lone electron pairs is among the fundamental properties of the ^{13}C – ^{13}C coupling constants, and it is extensively used in stereochemical investigation

Table 6. Basis sets used in calculation of ^{13}C – ^{13}C coupling constants by SOPPA procedure

Basis set	Atom	Number of basis AO per one atom	Contraction scheme ^a	Internal and (or) dense <i>s</i> -functions	
				Exponential factor value	Contraction coefficient
cc-VDZ	HC	29	(4 <i>s</i>) → [2 <i>s</i>] (9 <i>s</i> , 4 <i>p</i>) → [3 <i>s</i> , 2 <i>p</i>]	4.530	1.0000000000
cc-VDZ-Cs	C	10	(10 <i>s</i> , 4 <i>p</i>) → [4 <i>s</i> , 2 <i>p</i>]		
cc-pVDZ	HC	514	(4 <i>s</i> , 1 <i>p</i>) → [2 <i>s</i> , 1 <i>p</i>] (9 <i>s</i> , 4 <i>p</i> , 1 <i>d</i>) → [3 <i>s</i> , 2 <i>p</i> , 1 <i>d</i>]	4.530	1.0000000000
cc-pVDZ-Cs	C	15	(10 <i>s</i> , 4 <i>p</i> , 1 <i>d</i>) → [4 <i>s</i> , 2 <i>p</i> , 1 <i>d</i>]		
cc-VTZ	HC	923	(5 <i>s</i> , 2 <i>p</i>) → [3 <i>s</i> , 2 <i>p</i>] (10 <i>s</i> , 5 <i>p</i> , 2 <i>d</i>) → [4 <i>s</i> , 3 <i>p</i> , 2 <i>d</i>]	4.292 11.876	1.0000000000 1.0000000000
cc-VTZ-Cs	C	25	(12 <i>s</i> , 5 <i>p</i> , 2 <i>d</i>) → [6 <i>s</i> , 3 <i>p</i> , 2 <i>d</i>]		
cc-pVTZ	HC	1430	(5 <i>s</i> , 2 <i>p</i> , 1 <i>d</i>) → [3 <i>s</i> , 2 <i>p</i> , 1 <i>d</i>] (10 <i>s</i> , 5 <i>p</i> , 2 <i>d</i> , 1 <i>f</i>) → [4 <i>s</i> , 3 <i>p</i> , 2 <i>d</i> , 1 <i>f</i>]	4.292 11.876	1.0000000000 1.0000000000
cc-pVTZ-Cs	C	32	(12 <i>s</i> , 5 <i>p</i> , 2 <i>d</i> , 1 <i>f</i>) → [6 <i>s</i> , 3 <i>p</i> , 2 <i>d</i> , 1 <i>f</i>]		
aug-cc-pVTZ-J	HC	2046	(10 <i>s</i> , 3 <i>p</i> , 1 <i>d</i>) → [6 <i>s</i> , 3 <i>p</i> , 1 <i>d</i>] (15 <i>s</i> , 6 <i>p</i> , 3 <i>d</i> , 1 <i>f</i>) → [9 <i>s</i> , 5 <i>p</i> , 3 <i>d</i> , 1 <i>f</i>]	225.000	0.00036650000
				1496.000	0.00004256000
				9950.000	0.00000309700
				66145.000	0.00000041370
				54924.000	0.00003761000
				366281.000	0.00000434900
				2442668.000	0.00000031470
16289729.000	0.00000004196				

^a In all contraction schemes we used spherical sets of Gaussian functions (1*s*, 3*p*, 5*d*, and 7*f*). The total set of contraction factors of *s*-, *p*-, *d*- and *f*-functions was published in [16, 29, 30].

of heteroatomic compounds [25]. The effect consists in electron density transfer from the orbital of the lone electron pair of nitrogen to the antibonding orbital of the C^2 - C^3 bond located in the *trans*-position to LEP (n_{σ} - σ^* -interaction, Fig. 3). Due to this effect the C^2 - C^3 bond gets longer, and the constant value decreases; thus the LEP contribution to the total constant value is negative. The n_{σ} - σ^* interaction underlying the nature of the anomeric effect is well known in chemistry and is described in a number of theoretical publications [26]. The appearance of an additional channel for spin-spin coupling transfer resulting in a positive contribution into the total constant value is apparently connected with an intramolecular interaction of LEP with the C^1 - C^2 bond located in the *cis*-position to LEP (n_{σ} - σ -interaction).

The calculated values of coupling constants for the bond in the *trans*-position with respect to LEP (J_{trans}), agree with the existing experimental data within 1 Hz. This permits a conclusion that the SOPPA procedure combined with special correlation-consistent basis sets describes well the n_{σ} - σ^* -interaction. As regards the constant for the bond in the *cis*-position with respect to LEP (J_{cis}), the agreement between the calculated and experimental values is somewhat worse (2–3 Hz). However the ranges of ΔJ_{cis} and ΔJ_{trans} for the same substituents never coincide thus providing a possibility to make an unambiguous assignment of the configurational isomers of oximes in all instances, for example, when one of the isomers is unstable, the isomer mixture cannot be separated, the signals in the spectrum are overlapping etc. The range of ^{13}C - ^{13}C coupling constants values in the series of compounds studies is for the aliphatic oximes ΔJ_{cis} 50.7–51.9 and ΔJ_{trans} 40.1–41.6 Hz; for the alicyclic oximes ΔJ_{cis} 33.6–50.8 and ΔJ_{trans} 21.8–40.8 Hz; for aromatic and heteroaromatic oximes ΔJ_{cis} 76.2–86.0 and ΔJ_{trans} 55.0–72.5 Hz. Cyclopropyl methyl ketone oxime (**III**) is an exception with coupling constants values equal to J_{cis} 67.0, J_{trans} 54.9 Hz, sharply differing from the common constants of aliphatic oximes. This difference may be due to the abnormal hybridization of the C^1 atom in oxime **III** which has an enhanced *s*-character of the exocyclic orbital. In all the oximes **I**–**XIII** under study the coupling constants between the methyl group and the oxime carbon are on the average J_{cis} 52, J_{trans} 42 Hz.

The data obtained evidence a good reproducibility of LEP effect in the ^{13}C - ^{13}C coupling constants calculated in the framework of the method of the second order polarization propagator approximation (SOPPA) with the use of special basis sets. The results of this study open new possibilities for the configurational assignment of

imine nitrogen compounds of any structure and they are a break-through of nonempirical calculation of coupling constants into the field of organic chemistry.

Quantum-chemical calculations were carried out with the use of GAMESS [27] and DALTON [28] software applying of standard basis sets or those modified by the authors of this study. The basis sets are thoroughly specified in Table 6.

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