

^{13}C – ^{13}C Spin-Spin Coupling Constants in Structural Studies: XXXIV. Nonempirical Calculations: Small Heterocycles

L. B. Krivdin and T. A. Kuznetsova

Angarsk State Technical Academy, Angarsk, 665835 Russia

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Abstract—An *ab initio* calculation was carried out for ^{13}C – ^{13}C spin-spin coupling constants in a series of saturated three- and four-membered heterocycles within a framework of second order perturbation theory using an approximation of second order polarization propagator. The accounting for electron correlation effects and the use of correlation-consistent basis sets with addition of functions allowing for internal correlation and of dense functions on nuclei permitted to obtain good quantitative agreement with experimental data.

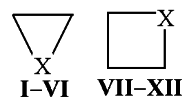
Spin-spin coupling constants of carbon nuclei are extensively used in the studies of the nature of chemical bonds and electron effects of substituents [1], and also in stereochemical investigations of organic and biological substances [2]. The theoretical consideration of the coupling mechanism between the carbon nuclei can provide a deeper understanding of the nature of structural and stereochemical relations of these parameters and extend the range of their practical use in the chemistry and biology. However the general progress in *ab initio* calculations of organic molecules has not yet extended to the estimation of spin-spin couplings. The latter studies are essentially still in infancy, they are rare and require enormous time-consuming calculations.

The most studies concerning nonempirical calculation of coupling constants by methods taking into account the electron correlation (SOPPA, SOPPA CCSD, EOM CCSD, RAS and CAS MCSCF, FCI) treat diatomic and triatomic molecules, as HD [3, 4, 5], HF [3, 5, 6], H_2O [5, 7, 8], N_2 [5, 9], HCN [8], CO [9], LiF, NaF, KF, ClF, and some others [10], and also the simplest organic molecules [11], inorganic hydrides [12], and inorganic associates containing hydrogen bond [13].

As significant achievement in the field of organic chemistry may be regarded two studies [14, 15] where by SOPPA procedure using specially contracted basis sets an *ab initio* calculation of coupling constants has been performed for various types of haloethenes $\text{C}_2\text{H}_5\text{X}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) [14] and ethylene heteroanalogs $\text{CH}_2=\text{X}$ ($\text{X} = \text{CH}_2, \text{NH}, \text{O}, \text{S}$) [15]. The studies should also be mentioned with a somewhat different approach using electron density

functional method DFT where were carried out coupling constants calculations (mostly only the Fermi-contact contribution) in some larger organic molecules [16], up to carbohydrates [17] and even triplex DNA rests [18]. Nonetheless the wide application of the nonempirical coupling constants calculations is yet a long way off, although some progress in this field is obvious [19].

In this study we for the first time accomplished the *ab initio* calculation of ^{13}C – ^{13}C spin-spin coupling constants for a series of saturated three- and four-membered heterocycles **I–XII** within a framework of second order perturbation theory using an approximation of coupled Hartree–Fock theory (CHF) that did not take into account the electron correlation, and also using a second order polarization propagator approximation (SOPPA) accounting for electron correlation and applying special correlation-consistent basis sets optimized for coupling constants evaluation.



$\text{X} = \text{CH}_2$ (**I**, **VII**), NH (**II**, **VIII**), O (**III**, **IX**), SiH_2 (**IV**, **X**), PH (**V**, **XI**), S (**VI**, **XII**).

As will be shown further the accounting for electron correlation alongside the use of special basis sets supplemented with functions allowing for internal correlation and with dense functions on nuclei is crucial for the proper calculation of ^{13}C – ^{13}C coupling constants in organic molecules.

To our knowledge this publication is the first in Russia treating the nonempirical ¹³C-¹³C coupling constants calculations, therefore we believe it necessary to give concise description of the main theoretical methods underlying these calculations.

In the framework of the non-relativistic theory of indirect spin-spin coupling [20] the interaction between the nuclear spins is transmitted through the surrounding electrons (it is just why this coupling is termed as indirect) by two different mechanisms: by interaction between nuclear and electronic spins, and on the other hand, by interaction between the nuclear spins and orbital angular momenta of the electrons.

The first mechanism compiles two contributions to the coupling constants: Fermi-contact (FC) and spin-dipole (SD) ones. The Fermi-contact contribution originates from interaction between the nuclear and electronic spins at their direct contact on the

nuclear surface (the probability for each electron to contact the nucleus is a finite value), and the spin-dipole contribution is due to dipole through-space interaction between the nuclear and electronic spins. To the second (spin-orbital) mechanism also correspond two contributions: orbital paramagnetic (OP) and orbital diamagnetic (OD) ones.

Any indirect coupling constant between K and L nuclei can thus be expressed as a sum of four contributions to the spin-spin coupling:

$$J_{KL} = J_{KL}^{FC} + J_{KL}^{SD} + J_{KL}^{OP} + J_{KL}^{OD} \quad (1)$$

The former three contributions (FC, SD, and OP) are determined by the wave function of the first order and consequently may be expressed by the same formula (2) in the framework of the second order perturbation theory by summation over the states:

$$J_{KL}^A = \frac{2\gamma_K\gamma_L}{3h} \sum_{\alpha=x,y,z} \sum_{n \neq 0} \frac{\langle \Psi_0 | (\hat{J}_{KL}^A)_{\alpha} | \Psi_n \rangle \times \langle \Psi_n | (\hat{J}_K^A)_{\alpha} | \Psi_0 \rangle}{E_n - E_0} \quad (2)$$

where for the K nucleus they are distinguished only by the respective operators \hat{J}_A^K (the upper index A designates one of the three mechanisms, FC, SD, or OP):

$$(\hat{J}_{KL}^{FC})_{\alpha} = \frac{\mu_0}{4\pi} \frac{4\pi g_e e \hbar}{3m_e} \sum_i (\vec{s}_i)_{\alpha} \delta(\vec{r}_{iK}) \quad (3)$$

$$(\hat{J}_{KL}^{SD})_{\alpha} = \frac{\mu_0}{4\pi} \frac{g_e e \hbar}{2m_e} \sum_i \frac{3(\vec{s}_i \cdot \vec{r}_{iK})(\vec{r}_{iK})_{\alpha} - r_{iK}^2 (\vec{s}_i)_{\alpha}}{|\vec{r}_{iK}|^5} \quad (4)$$

$$(\hat{J}_{KL}^{OP})_{\alpha} = \frac{\mu_0}{4\pi} \frac{e \hbar}{m_e} \sum_i \frac{(\vec{l}_{iK})_{\alpha}}{|\vec{r}_{iK}|^3} \quad (5)$$

The Fermi-contact and spin-dipole contributions include the operators of electron spins, therefore they are summed over excited triplet states (the operator of electronic spin provides in the wave function a change from the singlet symmetry of the ground state to the triplet symmetry of the excited state), whereas the orbital paramagnetic contribution contains an operator of the orbital angular momentum and therefore is summed over excited singlet states.

In contrast to the mentioned three contributions to the coupling constant (FC, SD, and OP) which are second order molecular characteristics, i.e. second derivatives with respect to energy, the orbital diamagnetic contribution (OD) is calculated as average

(expected) value of nonexcited state by summing only over the ground (singlet) state:

$$J_{KL}^{OD} = \frac{1\gamma_K\gamma_L}{3h} \sum_{\alpha=x,y,z} \langle \Psi_0 | (\hat{J}_{KL}^{OD})_{\alpha\alpha} | \Psi_0 \rangle \quad (6)$$

$$(\hat{J}_{KL}^{OD})_{\alpha} = \left(\frac{\mu_0}{4\pi} \right) \frac{e^2 \hbar^2}{m_e} \sum_i \frac{\vec{r}_{iL} \cdot \vec{r}_{iK} - (\vec{r}_{iL})_{\alpha} (\vec{r}_{iK})_{\alpha}}{|\vec{r}_{iK}|^3 |\vec{r}_{iL}|^5} \quad (7)$$

The above description of contributions into coupling constants reveals that a proper nonempirical calculation of FC and SD contributions involving estimation of the energy of triplet excited states requires accounting for electron correlation. This factor is also important but not so crucially for the orbital paramagnetic contribution OP involving summation over singlet excited states. Only the orbital diamagnetic contribution OD averaged over the singlet ground state should by its nature be insensitive to the electron correlation effects.

Simple calculations according to coupled Hartree-Fock method (CHF) or by equivalent thereto the random phase approximation with the use of the formalism of the first order polarization propagator (RPA) do not take into consideration the electron correlation and give *a fortiori* incorrect results: the calculated coupling constants can differ from the cor-

responding experimental data several times. Actually the neglecting of the electron correlation in calculations results in significant underestimation of the energies of the excited triplet states leading to drastic overestimation of the Fermi-contact contribution to a value several times larger than the experimental coupling constant proper. Besides in the calculation without accounting for electron correlations frequently arises the so-called triplet instability problem when the energy of one among triplet excited states is close to or even lower than the energy of the ground state; such calculations result in absurd values of coupling constants.

Thus any *ab initio* calculation of coupling constants should be carried out with taking into account high level electron correlation. In the present study the ^{13}C - ^{13}C coupling constants are calculated allowing for electron correlation within the framework of the method of the second order polarization propagator (SOPPA). We chose this calculation procedure for the SOPPA approach was shown to be very successful in several studies treating the evaluation of versatile coupling constants (those of ^{13}C - ^{13}C included) for small organic molecules [5, 12, 14, 15].

SOPPA method is based on the general approximation of polarization propagator considering the coupling constants as a function of a linear response of the principal matrix of the polarization propagator (instead of approach of summing over the excited states in the CHF method). The SOPPA method as compared to the RPA theory of the first order is distinguished by introducing a correction for two-particle perturbation of the second order. Therewith the wave function of Hartree-Fock used in the RPA approximation is replaced by the Møller-Plesset wave function, and all the matrix elements are calculated in the approximation of the second order perturbation theory. Thus SOPPA method is considerably more effective as compared to, e.g., the original MP2 procedure. The formalism of the SOPPA method applied to coupling constants calculation is treated in detail in [21].

To compare the calculation results obtained for ^{13}C - ^{13}C coupling constants in small cyclic molecules with and without accounting for the electron correlation we also worked out the corresponding data within the CHF framework. All calculations of coupling constants along CHF and SOPPA methods were performed with the use of license version of DALTON routine [22] that ensured essentially the important advance into the field of nonempirical calculations of the coupling constants.

Apart the level of the method used the second problem arising in any *ab initio* calculation of the coupling constants is the selection of a basis set. The trouble lies in the fact that the standard basis sets optimized for calculation of energy and geometry of molecular systems poorly fit requirements of determination of the second order molecular characteristics (among them also coupling constants) which depend on the electron density at the nucleus. In the coupling constants calculations special basis sets should be used optimized for the calculations of the second order characteristics.

First of all these bases should be optimized for calculations allowing for the electron correlation. Therefore correlation-consistent valence-split basis sets originating from bases of the types cc-pVXZ or aug-cc-pVXZ ($X = \text{D, T, Q}$) are often used [23]. These are well accounting for the electron correlation of the external (valence) electrons but are not optimized for calculations involving the correlation effects of the internal electrons. To take into consideration the electron correlation including that of internal electrons special functions were suggested in the bases cc-pCVXZ and aug-cc-pCVXZ ($X = \text{D, T, Q}$) which were fairly successfully used in coupling constants calculations [24].

Secondly, the bases optimized for coupling constants calculations should correctly describe the internal electron density distribution directly at the nucleus surface; this point is crucial for the evaluation of the Fermi-contact contribution into the coupling constants. Even the most cumbersome multi-split basic sets extended by a great number of polarization and diffuse functions are not sufficiently flexible in their internal part and do not fit to the above requirement. Therefore the basic sets used in coupling constants calculations are extended with special dense *s*-functions on the nucleus with large values of the exponential coefficients growing according to geometric progression. These dense *s*-functions were used for the first time in calculation of a coupling constant $^1J(\text{H, D})$ in the HD molecule [25].

Finally, these basis sets should be multi-split in the valence part and should contain the necessary number of polarization and diffuse functions (notably more than in simple calculations of the energy or geometry of molecules) to provide proper description of the valence zone; the latter is crucial for the calculation of the orbital diamagnetic contribution (OD). Besides these basis sets should be maximally decontracted, at least in their *s*- and *p*-parts, for it is necessary for proper division of electron correlation effects of the

external and internal electrons in the calculation of triplet excited states originating from the Fermi-contact coupling of the nuclear and electronic spins.

In the present study we selected correlation-consistent basis sets with the functions taking into consideration internal electron correlation cc-pCVXZ and aug-cc-pCVXZ ($X = \text{D, T}$) [24], and also cc-pVXZ and aug-cc-pVXZ ($X = \text{D, T}$) [23] supplemented with noncontracted dense s -functions on the nucleus [25] with exponential coefficients growing according to geometric progression, similarly to basis sets sad-J and aug-cc-pVTZ-J [15].

In order to compare the dependence of accuracy of coupling constants calculations by SOPPA procedure on the quality of the basis set we also tried the library basises non-optimized for calculation of the second order characteristics (the complete basis list is available from the authors). These are standard basises (6-31G, 6-31G*, 6-31G**, 6-311G, 6-311G*, 6-311G**) [26] and correlation-consistent basises (cc-pVXZ and aug-cc-pVXZ, $X = \text{D, T}$) [23]. In coupling constants calculations these basises were used to present the atoms not taking part in coupling.

In the present study to present the atoms participating in coupling we used special basis sets. The distinguishing feature of these basises was the presence of special non-contracted functions optimized for coupling constants calculation: Dunning functions accounting for internal correlation [24], dense s -functions [25], and standard diffuse functions. In this study were also used the completely contracted basis sets sad-J and aug-cc-pVTZ-J [15] extended with the dense s -functions. The latter basis sets were specially optimized for coupling constants calculation with accounting for electron correlation within the framework of the SOPPA method. These sets are also available from the authors.

The approach of separate presentation of basises for different atoms in coupling constants calculations get a title of "local dense basises" [14]; it is extensively used in nonempirical calculations of coupling constants.

In the coupling constants calculations for all small cycles under study (**I-XII**) we used geometrical parameters optimized in the framework of the theory of electron density functional DFT applying the most popular nowadays three-parametric hybrid Becke functional [27] combined with the Lee-Yang-Parr functional [28] (B3LYP) in a triplet-split basis cc-pVTZ [23].

In conclusion of the theoretical part of the paper we should point out that the listed factors of the

calculations of the second order molecular characteristics put severe requirements both on the level of the nonempirical theory applied and on the quality of the basis set. Thus the *ab initio* calculation of coupling constants becomes a subject of real art and enormous consumption of calculation resources. This study is in a way pioneering and opens a series of our publications on the nonempirical calculations of ^{13}C - ^{13}C coupling constants in organic molecules.

As was mentioned the accounting for electron correlation is indispensable in *ab initio* calculations of coupling constants, and the most appropriate method (from the viewpoint of accuracy and calculation time saving) is the approach of the second order polarization propagator SOPPA. On the other hand, the selection of an optimal basis set is hardly unambiguous. Therefore previously to starting the calculation of ^{13}C - ^{13}C coupling constants in the series of small rings **I-XII** we carried out a thorough study of the effect of the basis set quality on the accuracy of calculation of J_{CC} by SOPPA method by an example of oxirane (**III**).

For the special basis sets used in presentation of atoms taking part in coupling we studied the effect of adding functions of various type accounting for internal correlation (Table 1) and also the effect produced by successive adding dense s -function with exponential coefficients growing in geometric progression (Table 2). The data on the influence on the accuracy of SOPPA calculations of the quality (first of all of the size) of the standard basis sets for hydrogens and oxygens (which were not the atoms whose coupling was subjected to consideration) are compiled in Table 3, and in Table 4 are given the calculation results for J_{CC} in oxirane using the most effective special basis sets in the framework of CHF on the one hand and of SOPPA on the other hand; therewith it is possible directly evaluate the contribution of electron correlation to each basis set.

As seen from Table 1, the application of the standard basis sets cc-pVDZ and cc-pVTZ led to obviously incorrect J_{CC} values. However addition to each of these sets of a single function of s -type accounting for internal correlation results in sharp decrease of the calculated coupling constants and its agreement with the experimental value virtually within the experimental accuracy (!) Further addition to these basis sets functions accounting for electron correlation of s -, p -, and even d -type is accompanied with drastically growing number of basis AO and accordingly requires several days of computer opera-

Table 1. Effect on ^{13}C - ^{13}C coupling constants in oxirane of functions accounting for internal correlation at calculations by SOPPA method^a; experimental, J 28.0 Hz [1]

Basis set C ^b	Functions accounting for internal correlation	Number of basis AO	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J
cc-pVDZ	None	62	0.18	-0.47	-0.38	41.65	40.97
cc-pVDZ-Cs	1s	64	0.18	-0.47	-0.38	28.45	27.78
cc-pCVDZ	1s, 1p	70	0.18	-0.50	-0.42	28.49	27.74
aug-cc-pCVDZ	1s, 1p	88	0.18	-0.49	-0.45	28.30	27.54
cc-pVTZ	None	94	0.17	-0.53	-0.52	41.78	40.91
cc-pVTZ-Cs	2s	98	0.17	-0.54	-0.51	28.74	27.85
cc-pVTZ-Csp	2s, 2p	110	0.17	-0.47	-0.54	28.90	28.06
cc-pCVTZ	2s, 2p, 1d	120	0.17	-0.47	-0.57	29.06	28.18
aug-cc-pVTZ	None	126	0.17	-0.56	-0.51	24.62	23.73
aug-cc-pVTZ-Cs	2s	130	0.17	-0.56	-0.51	28.57	27.67
aug-cc-pVTZ-Csp	2s, 2p	142	0.17	-0.47	-0.54	28.83	27.99
aug-cc-pCVTZ	2s, 2p, 1d	152	0.17	-0.47	-0.57	28.98	28.11

^a The values of ^{13}C - ^{13}C coupling constants and contributions thereto are expressed in Hz.

^b For O and H atoms the basis set cc-pVDZ was used.

tion, but no additional improvement of the calculated value is attained.

At the use of a cumbersome standard basis set aug-cc-pVTZ extended with diffuse functions of s -, p -, d -, and f -types the J_{CC} value obtained is lower than experimental result by 4 Hz, and the extension of the basis set with the functions accounting for the internal electron correlation gives J_{CC} value that agrees with the experimental one within 0.1 Hz!

In conclusion to the discussion of results compiled in Table 1 we should point out that the use of the functions accounting for internal correlation [24] in the framework of SOPPA method magically affects the quality of calculation results and makes plausible even so small basis sets as cc-pVDZ-Cs and cc-pCVDZ. Therewith the use of the functions accounting for internal correlation of p - and even d -type does not provide considerable further improvement, and so for conventional nonempirical calculations of J_{CC} in organic molecules the optimal presentation of the coupled carbon atoms would be with the basis set cc-pVDZ-Cs employing only 15 basis AO for each carbon atom. Note that the use of this set for the atoms participating in the coupling gives an enormous economy of computation time since the special triplet-split bases extended with internal, dense, and diffuse functions employ from 32 to 59 basis AO for each carbon atom.

The addition to the basis sets of dense s -functions [25] as show data of Table 2 are not so crucial as

extension of the correlation-consistent bases with the functions accounting for internal correlation. In the case of obviously insufficiently determined basis cc-pVDZ the decontraction of the s -functions present in the basis is important. The successive addition of dense s -functions results in gradual convergence of the calculated constant value to 31.13, 28.54, and 28.50 Hz for basis sets cc-pVDZ-suN, cc-pVTZ-suN, and aug-cc-pVTZ-suN respectively (where N is the number of the added dense functions). The results obtained for both triplet-split basis sets are close to the experimental value (28 Hz). In the latter two cases the completely convergence of the calculated J_{CC} with the experimental data was attained by adding five dense s -functions ($N = 4$). On the other hand, in the incompletely determined double-split basis cc-pVDZ the convergence is not accomplished even on addition of nine dense s -functions (Table 2).

Thus the extension of the basis sets with dense s -functions gave good results only with triplet-split basis sets and did not compensate the insufficient determinacy of small double-split sets. However in the latter case the situation is remedied with addition of a single function accounting for internal correlation, thus permitting the use of these supereconomic basis sets (cc-pVDZ-Cs and cc-pCVDZ) in calculation of J_{CC} coupling constant.

In coupling constants calculations an important point is also a selection of basis set for the atoms whose coupling is not considered. Here the special

Table 2. Effect on ^{13}C - ^{13}C coupling constants in oxirane of dense s -functions at calculations by SOPPA method^a

Basis set C ^b	Dense functions	Number of basis AO	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J
cc-pVDZ	None	62	0.18	-0.47	-0.38	41.65	40.97
cc-pVDZ-su0	None	74	0.18	-0.47	-0.38	29.27	28.59
cc-pVDZ-su1	1s	76	0.18	-0.47	-0.38	30.94	30.27
cc-pVDZ-su2	2s	78	0.18	-0.47	-0.38	31.43	30.76
cc-pVDZ-su3	3s	80	0.18	-0.47	-0.38	31.68	31.00
cc-pVDZ-su4	4s	82	0.18	-0.47	-0.38	31.75	31.07
cc-pVDZ-su5	5s	84	0.18	-0.47	-0.38	31.78	31.11
cc-pVDZ-su6	6s	86	0.18	-0.47	-0.38	31.79	31.12
cc-pVDZ-su7	7s	88	0.18	-0.47	-0.38	31.80	31.12
cc-pVDZ-su8	8s	90	0.18	-0.47	-0.38	31.80	31.13
cc-pVDZ-su9	9s	92	0.18	-0.47	-0.38	31.80	31.13
cc-pVTZ	None	146	0.17	-0.58	-0.52	27.31	26.39
cc-pVTZ-su0	None	158	0.17	-0.58	-0.51	27.33	26.41
cc-pVTZ-su1	1s	160	0.17	-0.58	-0.51	28.62	27.69
cc-pVTZ-su2	2s	162	0.17	-0.58	-0.51	29.15	28.22
cc-pVTZ-su3	3s	164	0.17	-0.58	-0.51	29.34	28.42
cc-pVTZ-su4	4s	166	0.17	-0.58	-0.51	29.42	28.50
cc-pVTZ-su5	5s	168	0.17	-0.58	-0.51	29.45	28.52
cc-pVTZ-su6	6s	170	0.17	-0.58	-0.51	29.46	28.53
cc-pVTZ-su7	7s	172	0.17	-0.58	-0.51	29.46	28.54
cc-pVTZ-su8	8s	174	0.17	-0.58	-0.51	29.47	28.54
cc-pVTZ-su9	9s	176	0.17	-0.58	-0.51	29.47	28.54
aug-cc-pVTZ	None	178	0.17	-0.61	-0.51	24.84	23.89
aug-cc-pVTZ-su0	None	190	0.17	-0.62	-0.51	27.32	26.37
aug-cc-pVTZ-su1	1s	192	0.17	-0.62	-0.51	28.61	27.66
aug-cc-pVTZ-su2	2s	194	0.17	-0.62	-0.51	29.14	28.19
aug-cc-pVTZ-su3	3s	196	0.17	-0.62	-0.51	29.33	28.38
aug-cc-pVTZ-su4	4s	198	0.17	-0.62	-0.51	29.41	28.46
aug-cc-pVTZ-su5	5s	200	0.17	-0.62	-0.51	29.44	28.49
aug-cc-pVTZ-su6	6s	202	0.17	-0.62	-0.51	29.45	28.50
aug-cc-pVTZ-su7	7s	204	0.17	-0.62	-0.51	29.46	28.50
aug-cc-pVTZ-su8	8s	206	0.17	-0.62	-0.51	29.46	28.50
aug-cc-pVTZ-su9	9s	208	0.17	-0.62	-0.51	29.46	28.50

^a The values of ^{13}C - ^{13}C coupling constants and contributions thereto are expressed in Hz.

^b For O and H atoms the basis sets used were cc-pVDZ in case of doubly valence-split basis for C and cc-pVTZ in case of triply valence-split basis for C; the following values of the exponential coefficients of dense s -functions on carbon were applied: ζ_1 60000, ζ_2 400000, ζ_3 2800000, ζ_4 20000000, ζ_5 140000000, ζ_6 1000000000, ζ_7 7000000000, ζ_8 50000000000, and ζ_9 350000000000.

basis sets with dense s -functions and functions accounting for internal correlation are not required, but the purely practical position connected with the reduction of computation time necessitates reasonable selection of these basis sizes (provided that they should possibly be optimized for correlation calculations).

As seen from Table 3, successive increase in the size of hydrogen basis almost does not affect the J_{CC}

of oxirane which increases only by 0.5–0.8 Hz only at the use of the triplet-split sets cc-pVTZ and aug-cc-pVTZ. Especially gratifying is the fact that the difference in J_{CC} values for basis sets cc-pVDZ and cc-pVTZ is less than 0.1 Hz (that is below the experimental error in measuring the coupling constant). In other words, the adding of polarization p -functions for hydrogen virtually does not affect the accuracy of J_{CC} calculation. It should permit in the common calcula-

Table 3. Effect on ^{13}C - ^{13}C coupling constants in oxirane of the quality of the basis set for noncoupled atoms at calculations by SOPPA method^a

Basis set C ^b		Number of basis AO	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J
O	H						
cc-pVDZ	6-31G	58	0.18	-0.51	-0.41	28.52	27.78
cc-pVDZ	cc-VDZ	58	0.18	-0.51	-0.42	28.58	27.83
cc-pVDZ	6-311G	62	0.18	-0.50	-0.41	28.56	27.82
cc-pVDZ	6-31G	70	0.18	-0.50	-0.41	28.26	27.53
cc-pVDZ	cc-pVDZ	70	0.18	-0.50	-0.42	28.48	27.74
cc-pVDZ	6-311G	74	0.18	-0.51	-0.42	28.59	27.84
cc-pVDZ	cc-pVTZ	106	0.18	-0.49	-0.43	29.41	28.66
cc-pVDZ	aug-cc-pVTZ	142	0.18	-0.49	-0.44	29.08	28.33
6-31G	cc-pVDZ	65	0.17	-0.46	-0.39	28.82	28.14
cc-VDZ	cc-pVDZ	65	0.17	-0.46	-0.39	28.86	28.19
6-311G	cc-pVDZ	69	0.17	-0.48	-0.39	28.85	28.15
6-31G	cc-pVDZ	70	0.18	-0.48	-0.44	28.37	27.63
cc-pVDZ	cc-pVDZ	70	0.18	-0.50	-0.42	28.48	27.74
cc-pCVDZ	cc-pVDZ	74	0.18	-0.52	-0.42	28.48	27.72
6-311G	cc-pVDZ	74	0.18	-0.52	-0.42	28.51	27.75
cc-pVTZ	cc-pVDZ	86	0.18	-0.52	-0.46	28.48	27.67
cc-pCVTZ	cc-pVDZ	99	0.18	-0.53	-0.46	28.47	27.65
aug-cc-pVTZ	cc-pVDZ	102	0.17	-0.59	-0.49	28.26	27.35

^a The values of ^{13}C - ^{13}C coupling constants and contributions thereto are expressed in Hz.

^b For carbon atom was used basis set cc-pCVDZ.

Table 4. Effect on ^{13}C - ^{13}C coupling constants in oxirane of accounting for electron correlation at calculations with the use of the most efficient basis sets^a

Calculation method	Basis set		Number of basis AO	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J
	C	O, H						
CHF	cc-pVDZ-Cs	cc-pVDZ	64	0.18	-0.84	-0.66	47.56	46.23
	cc-pCVDZ	cc-pVDZ	70	0.17	-0.86	-0.70	47.53	46.14
	cc-pCVTZ	cc-pVTZ	172	0.17	-0.85	-0.90	51.35	49.77
	sad-J	sad-J	204	0.17	-0.87	-0.82	53.88	52.36
	aug-cc-pCVTZ	cc-pVTZ	204	0.17	-0.86	-0.90	52.04	50.45
	aug-cc-pVTZ-J	aug-cc-pVTZ-J	218	0.17	-0.88	-0.84	54.02	52.47
SOPPA	cc-pVDZ-Cs	cc-pVDZ	64	0.18	-0.47	-0.38	28.45	27.78
	cc-pCVDZ	cc-pVDZ	70	0.18	-0.50	-0.42	28.48	27.74
	cc-pCVTZ	cc-pVTZ	172	0.17	-0.50	-0.58	28.98	28.08
	sad-J	sad-J	204	0.17	-0.52	-0.53	30.15	29.27
	aug-cc-pCVTZ	cc-pVTZ	204	0.17	-0.50	-0.57	29.55	28.64
	aug-cc-pVTZ-J	aug-cc-pVTZ-J	218	0.17	-0.51	-0.54	29.31	28.44

^a The values of ^{13}C - ^{13}C coupling constants and contributions thereto are expressed in Hz.

tions of ^{13}C - ^{13}C coupling constants to present the hydrogen atoms in the supereconomic basis cc-VDZ where only two basis AO are used for each hydrogen atom as compared to five AO in cc-pVDZ.

The variation of the oxygen basis set from the simplest bases 6-31G and cc-VDZ till an extended one, aug-cc-pVTZ resulted in gradual reduction of the calculated constant by ~0.8 Hz; therewith going from

nonpolarization basis cc-VDZ to the polarization one cc-pVDZ diminished the constant by ~ 0.5 Hz, and this value is no more negligible, as it was in the hydrogen case. On the other hand the replacement of the basis cc-pVDZ by cc-pVTZ led to the constant J_{CC} increase only by ~ 0.1 Hz, and addition of functions accounting for internal correlation both to basis cc-pVDZ and cc-pVTZ absolutely did not affect the constant value. All the above should permit in the common calculations of ^{13}C - ^{13}C coupling constants in organic molecules bravely use the economic basis cc-pVDZ for the atoms of the second Period whose coupling is not the object of calculation.

The calculations in keeping with the second order perturbation theory using Hartree-Fock wave functions (CHF) gives obviously incorrect results; however their comparison with the respective values obtained by SOPPA procedure provides a possibility to estimate quantitatively the contribution of electron correlation effect in every given case (Table 4).

It is easily seen that neglecting the electron correlation effect results in 1.5–2 times overestimation of coupling constant values calculated with the use of all most efficient basises; thus the calculation of J_{CC} by CHF procedure is absolutely senseless. It is interesting to point out that the consideration for the electron correlation on the level of MP2-SOPPA does not in any way affect the value of the orbital diamagnetic contribution (that is understandable due to the nature of the diamagnetic contribution of the spin-orbital interaction averaged over the ground singlet state) and approximately to an equal degree affects three other contributions (J_{OP} , J_{SD} and J_{FC}) decreasing their absolute value 1.6–2-fold. Nonetheless, remembering that the noncontact interactions provide insignificant contributions (about 3% on the average) the main effect from accounting for the electron correlation should be attributed to the sharp decrease in the Fermi-contact contribution; as a result the total calculated ^{13}C - ^{13}C coupling constants reach agreement with the experimental values almost within the accuracy of the measurement.

Summing up the discussion of results presented in Tables 1–4 we are able to finally formulate the main requirements for the theoretical level and basis sets quality in *ab initio* calculations of coupling constants in organic molecules.

(1) Nonempirical calculations of coupling constants should be necessarily carried out with accounting for electron correlation on the level of FCI, MCSCF, CCSD, MP2-SOPPA or DFT. From the viewpoint of calculation precision and economy of the

computation time the optimal methods are SOPPA and B3LYP. The coupling constant calculation in the framework of the second order coupled Hartree-Fock theory gives *a fortiori* incorrect results.

(2) The presentation of atoms whose coupling constant is calculated should be carried out with the use of economical basis sets with functions accounting for internal correlation cc-pVDZ-Cs or cc-pCVDZ, and for small molecules when sufficient computational sources are available may be used special basis sets of Sauer sad-J and aug-cc-pTVZ-J.

(3) For presentation of the atoms of the second Period whose coupling is not the object of calculation the basis cc-pVDZ should be used, and when the computational resources are limited, its version free of polarization functions, cc-VDZ, may be used.

(4) The presentation of hydrogens whose coupling is not the object of calculation the economical basis set cc-VDZ should be used, and when sufficient computational sources are available, the polarization basis cc-pVDZ.

Thus the optimal way for calculating ^{13}C - ^{13}C coupling constants in the medium size organic molecules is the application of SOPPA procedure using the locally dense basis cc-pVDZ-Cs for coupling carbon atoms, polarization basis cc-VDZ for the atoms from the second Period, and nonpolarization correlation-consistent basis cc-VDZ for hydrogen. In this study in keeping with relatively small size of the cycles under investigation **I–XII** we carried out ^{13}C - ^{13}C coupling constants calculation in approximation SOPPA/cc-pCVDZ(C), cc-pVDZ (H, N, O, Si, P, S); the presentation of the atoms from the third Period was also done with the use of the triplet-split correlation-consistent polarization basis extended with diffuse functions aug-cc-pVTZ (Table 5).

As seen from Table 5, the calculated values of $^1J_{\text{CC}}$ coincide with available experimental data within 1–2 Hz. Since the precision of the experimental measurement of ^{13}C - ^{13}C coupling constants is not too high and taking into account the effect of temperature and medium does not exceed ~ 0.5 Hz, the calculated values obtained reliably show that the level of calculation method and the quality of basis sets for coupled carbons and uncoupled hydrogen and the atoms of the second and third Period are selected properly.

In case of heterocycles containing atoms of the third Period with diffuse unshared electron pairs and/or vacant *d*-orbitals (Si, P, S) the quality of calculation is considerably improved at the use for this

Table 5. Results of *ab initio* calculation of ^{13}C - ^{13}C coupling constants in three- and four-membered heterocycles performed by SOPPA method^a

Compd. no.	X ^b	Basis set	Number of basis AO	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	$J_{\text{exp}}[1]$
I	CH ₂	cc-pVDZ	80	0.15	-0.57	-0.14	14.75	14.19	12.14
II	NH	cc-pVDZ	75	0.16	-0.51	-0.29	22.55	21.91	21.0
III	O	cc-pVDZ	70	0.18	-0.52	-0.42	28.48	27.72	28.0
IV	SiH ₂	cc-pVDZ	84	0.18	-0.16	0.35	10.63	11.00	
		aug-cc-pVTZ	116	0.18	-0.01	0.34	11.02	11.53	
V	PH	cc-pVDZ	79	0.19	-1.63	-0.01	26.89	25.45	
		aug-cc-pVTZ	111	0.19	-1.56	-0.02	25.42	24.04	
VI	S ^c	cc-pVDZ	74	0.20	-1.90	0.00	29.75	28.05	
		aug-cc-pVTZ	106	0.20	-1.85	-0.06	28.62	26.91	
VII	CH ₂	cc-pCVDZ	112	0.19	1.20	1.26	27.88	30.54	28.4
VIII	NH	cc-pCVDZ	107	0.20	0.83	1.14	28.66	30.83	
IX	O	cc-pCVDZ	102	0.21	0.97	1.21	28.22	30.60	29.54
X	SiH ₂	cc-pVDZ	112	0.20	0.96	1.23	26.80	29.19	
		aug-cc-pVTZ	144	0.20	0.95	1.21	26.47	28.83	24.6
XI	PH	cc-pVDZ	107	0.21	0.67	1.15	30.40	31.43	
		aug-cc-pVTZ	139	0.21	0.64	1.13	30.22	32.20	
XII	S	cc-pVDZ	102	0.22	1.08	1.34	31.48	34.12	
		aug-cc-pVTZ	134	0.22	1.06	1.33	31.37	33.98	
		aug-cc-pVQZ	168	0.22	1.05	1.30	30.80	33.37	31.52

^a The values of ^{13}C - ^{13}C coupling constants and contributions thereto are expressed in Hz; geometric parameters optimized by the method B3LYP/cc-pVTZ have been used in all calculations.

^b Basis sets cc-pCVDZ and cc-pVDZ were used for C and H atoms respectively.

atoms of the triplet-split correlation-consistent polarization basis set aug-cc-pVTZ extended with diffuse functions of *s*-, *p*-, *d*-, and *f*-types. With a relatively high accuracy (1–2 Hz) we for the first time have predicted the ^{13}C - ^{13}C coupling constants in silirane, phosphirane, thiirane, and phosphetane that wait for the experimental confirmation.

The insignificant overall contribution of the non-contact interactions also should be mentioned: in all cases it was no more than 10% from the total constant value. The orbital diamagnetic contribution was almost insensitive to the heterocycle size and heteroatom character, and it amounted on the average to 0.2 Hz. The orbital paramagnetic contribution was negative in three-membered heterocycles varying from -0.5 to -2 and positive in four-membered heterocycles amounting on the average to ~1 Hz. The spin-dipole contribution in the three-membered heterocycles is negligible, and in four-membered heterocycles it equals to 1.0–1.3 Hz.

Thus the main variations in the ^{13}C - ^{13}C coupling constants in the heterocycle series under study were governed by the Fermi-contact contribution which was highly sensitive to the heteroatom character and ring size. It is especially obvious in the series of the

three-membered heterocycles. The least $^1J_{\text{CC}}$ value (~12 Hz) is observed in the silirane containing an electropositive silicon atom whereas the highest values were obtained for thiirane (~27 Hz) and oxirane (~28 Hz).

In the four-membered heterocycles the dependence of $^1J_{\text{CC}}$ on the heteroatom character is not so clear. In this series the ^{13}C - ^{13}C coupling constants amount on the average to 31–34 Hz reflecting firstly the large contribution from the vicinal way of spin-spin coupling transmission which according to our estimations [29, 30] attains no less than 12–15 Hz within the framework of an additive transmission model.

In conclusion of results obtained it should be noted that in this study was suggested for the first time an adequate and economical nonempirical calculation method for ^{13}C - ^{13}C coupling constants for medium size organic molecules. The procedures advanced open wide prospects for application of *ab initio* procedures to calculation and theoretical study of transmission mechanism of the spin-spin coupling. In further publications we plan to demonstrate the prospects of the ^{13}C - ^{13}C coupling constants calculation by nonempirical methods for investigation of

electronic and steric effects in a wide range of organic and biological substances.

The quantum-chemical calculations were performed with the use of software MOPAC [31], GAMESS [32], and DALTON [22] in the operation system Linux Red Hat 7.2 (Kernel 2.4.7-10).

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