

^{13}C – ^{13}C Coupling Constants in Structural Studies: XXXII. Additivity of Spin–Spin Couplings in Sterically Strained Heterocycles

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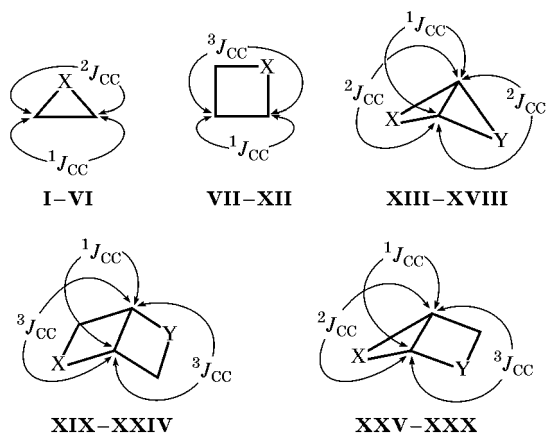
Abstract—Calculations in terms of the self-consistent finite perturbation theory (SCPT) and analysis of contributions of localized molecular orbitals in terms of the polarization propagator theory (CLOPPA) indicate additivity of ^{13}C – ^{13}C coupling constants in saturated sterically strained heterocycles. Their fused derivatives, especially those containing 3rd Period elements, show considerable deviations of the calculated coupling constants from the additive values.

Spin–spin coupling constants between carbon nuclei are widely used in studies of the nature of chemical bonds and electronic effects of substituents [1, 2]. We previously studied ^{13}C – ^{13}C coupling constants in sterically strained carbo- and heterocycles, namely derivatives of cyclopropane, cyclobutane [3, 4], bicyclo[1.1.0]butane [5], bicyclo[2.1.0]pentane, bicyclo[2.2.0]hexane [6], propellanes [7], cage-like carbocycles [8], oxirane [9], and other heterocyclic compounds [10]. In continuation of these studies, the present communication discusses the additivity of ^{13}C – ^{13}C coupling constants in saturated sterically

strained heterocycles **I–XII** and their fused derivatives **XIII–XXX** in terms of the self-consistent finite perturbation theory (SCPT) [11] in the INDO approximation [12], as well as by analysis of contributions of localized molecular orbitals (CLOPPA) [13] according to the polarization propagator theory (IPPP) [14] in the INDO approximation.

Some authors [15] interpret spin–spin coupling constants in terms of the so-called additivity model according to which spin–spin interaction is transmitted through bond electrons via several independent pathways. As applied to compounds **I–XII**, the additivity approach implies that spin–spin interactions therein are transmitted via two pathways (direct and geminal or direct and vicinal). Compounds **XIII–XXX** give rise to three independent transmission pathways (direct and two geminal; direct, geminal, and vicinal; or direct and two vicinal).

The goal of this study was to divide ^{13}C – ^{13}C coupling constants into particular components in monocyclic compounds **I–XII** and examine their additivity in heteroelement derivatives of bicyclo[1.1.0]butane (**XIII–XVIII**), bicyclo[2.2.0]hexane (**XIX–XXIV**), and bicyclo[2.1.0]pentane (**XXV–XXX**). For this purpose, we applied two radically different approaches to separation of the calculated total ^{13}C – ^{13}C coupling constants into components. The first approach is based on the known correlation between direct ^{13}C – ^{13}C coupling constants and s orders of the corresponding carbon–carbon bonds.



I, VII, XIII, XIX, XXV, X = CH₂; **II, VIII, XIV, XX, XXVI**, X = NH; **III, IX, XV, XXI, XXVII**, X = O; **IV, X, XVI, XXII, XXVIII**, X = Si; **V, XI, XVII, XXIII, XXIX**, X = PH; **VI, XII, XVIII, XXIV, XXX**, X = S.

Such correlations were established for both experimental and calculated total coupling constants and for the corresponding Fermi-contact contributions [16]. Using correlation (2) between total ^{13}C - ^{13}C coupling constants and squared s elements of the density matrix P_{SS}^2 [4], the direct path of spin-spin coupling can readily be estimated from the calculated P_{SS}^2 values; by subtracting the direct component from the total ^{13}C - ^{13}C coupling constant for monocyclic compounds **I–XII** we can determine the contributions of the geminal and vicinal coupling paths.

$$J_{\text{CC}}(\text{N}, \text{N}') = {}^1J_{\text{CC}} + {}^nJ_{\text{CC}}; \quad (1)$$

$$n = 2, 3.$$

$${}^1J_{\text{CC}} = 653.7P_{\text{SS}}^2 - 9.5. \quad (2)$$

The second approach is based on the formalism of the polarization propagator theory [14] with the use of localized molecular orbitals (LMO) or the so-called CLOPPA approach [13] in the INDO approximation [12]. According to this method, coupling constant between N and N' nuclei is divided into a large number of elementary contributions $J_{ia,jb}(\text{N}, \text{N}')$ which appear as a result of two-particle excitation involving two occupied (i, j) and two vacant (a, b) localized molecular orbitals (LMO); the latter may be related to lone electron pairs (LEP) of heteroatoms, chemical bonds, and particular molecular fragments in keeping with the MO localization performed and Eqs. (3) and (4). Thus, the CLOPPA approach makes it possible to directly calculate on a semiempirical level the contributions of direct, geminal, and vicinal coupling paths (represented as a combination of chemical bonds and LEPs on heteroatoms) to the calculated total ^{13}C - ^{13}C coupling constant.

$$J_{\text{CC}}(\text{N}, \text{N}') = \sum_{ia,jb} J_{ia,jb}(\text{N}, \text{N}'); \quad (3)$$

$$J_{ia,jb}(\text{N}, \text{N}') = \Omega \hat{V}_{ia,\text{N}} {}^sP_{ia,jb} \hat{V}_{jb,\text{N}'}. \quad (4)$$

Here, Ω is a numerical constant, and ${}^sP_{ia,jb}$ is the singlet ($s = 1$) or triplet ($s = 3$) propagator matrix, depending on the contribution being calculated ($s = 1$ for Fermi-contact and diamagnetic spin-orbital contributions, and $s = 3$ for paramagnetic spin-orbital and spin-dipole contributions); this matrix is affected by perturbation operators corresponding to the above contributions.

The results obtained in terms of the two approaches can be compared on a quantitative level, for both these [restricted Hartree-Fock (RHF, CHF or RPA)

[17] in the SCPT method and polarization propagator [14] in the CLOPPA method] utilize the same INDO approximation. The total ^{13}C - ^{13}C coupling constants (without division into components) calculated by the two methods are identical.

We calculated the total ^{13}C - ^{13}C coupling constants in terms of the fundamental Ramsey theory [18] on a semiempirical level using the SCPT INDO and CLOPPA INDO methods with account taken of Fermi-contact and spin-dipole contributions (nuclear spin interaction through bond electron spins) and also diamagnetic and paramagnetic spin-orbital contributions (interaction of nuclear spins with angular rotational moments of bond electrons). Thus the total spin-spin coupling constant $J(\text{TO})$ may be represented as the sum of three constituents (provided that the diamagnetic and paramagnetic constituents of spin-orbital interaction are not separated): Fermi-contact $J(\text{FC})$, spin-orbital $J(\text{SO})$, and spin-dipole $J(\text{SD})$:

$$J(\text{TO}) = J(\text{FC}) + J(\text{SO}) + J(\text{SD}). \quad (5)$$

An important problem encountered while calculating coupling constants is proper choice of the procedure for optimization of geometric parameters. We compared three semiempirical (MNDO, AM1, PM3) and some RHF-based nonempirical methods with different basis sets (with account taken of electron correlation in terms of the second-order Moeller-Plesset theory) as applied to optimization of geometric parameters of several monocyclic compounds. The parameters were the C-C bond lengths and CCX bond angles ($\text{X} = \text{CH}_2, \text{NH}, \text{O}, \text{SiH}_2, \text{PH}, \text{S}$); they were compared with the X-ray diffraction data [19]. The given parameters exert the strongest effect on the ^{13}C - ^{13}C coupling constants in this series of compounds. We also compared the efficiency of the semiempirical and nonempirical methods used for optimization of geometric parameters of some carbonyl and heterocycles in the calculation of ^{13}C - ^{13}C coupling constants against the available experimental data. In all cases, the efficiency of one or another method was estimated by the mean-square deviation (MSD) of a calculated parameter (C-C bond length, CCX bond angle, or ^{13}C - ^{13}C coupling constant) from the corresponding experimental value.

Our results show that, among semiempirical methods, the PM3 procedure reproduces the experimental geometry most accurately (MSD 0.014 Å for bond length and 0.4° for bond angle). The best results were obtained for the 3rd Period elements. The MNDO method gives the least reliable data (MSD 0.025 Å and 1.2°, respectively), and it is not recom-

mended for calculation of molecules containing heteroatoms, especially those belonging to the 3rd Period. Good results were also obtained by the AM1 semiempirical method (MSD 0.018 Å and 0.7°, respectively).

Among the RHF-based nonempirical methods, the most efficient basis sets were 6-31G**, 6-311G**, and D95**, while the basis sets including no polarization functions (especially the standard 3-21G basis set) turned out to be the least acceptable. It should be noted that the use of the doubly and triply valence-split basis sets 6-31G** and 6-311G** gives almost the same results. The addition of polarization *d*-functions to valence-split and biexponential basis sets appreciably reduces MSD which becomes equal to 0.03 Å for bond lengths and 1° for bond angles. The addition of polarization *p*-functions for hydrogen atoms leads to further, though less significant reduction of MSD. On the other hand, the addition of diffuse functions for heavy atoms (for proper description of diffuse LEPs of heteroatoms, especially of those belonging to the 3rd Period) had almost no effect on the results of calculations.

The results of *ab initio* calculations are considerably improved by taking into account electron correlation in terms of the MP2 procedure. MP2/6-31G** geometry optimization reduces MSD to 0.013 Å for bond lengths and 0.2° for bond angles (cf. MSD 0.019 Å and 0.4° in RHF/6-31G**). On the whole, semiempirical methods for geometry optimization, especially PM3, are only slightly inferior to the nonempirical calculations. Extension of the basis set to reasonable limits has a weak effect on the accuracy of nonempirical calculations (which is comparable with the accuracy of semiempirical procedures); however, consideration of electron correlation and addition of *d*-polarization functions for 2nd and 3rd Period elements is very important.

In the framework of our study, the most interesting was to compare the ^{13}C - ^{13}C coupling constants for model carbocycles (cyclopropane, cyclobutane, and bicyclobutane) and heterocycles (aziridine, oxirane, and siletane), calculated with the use of different semiempirical and nonempirical methods for geometry optimization. As previously, the efficiency of the calculation methods was estimated by mean-square deviations from the experimental ^{13}C - ^{13}C coupling constants. Here, the most critical was bicyclobutane which is characterized by a unique negative coupling constant between the bridgehead carbon atoms.

We found that the semiempirical and nonempirical methods for geometry optimization give comparable results in the semiempirical SCPT INDO calculation

of ^{13}C - ^{13}C coupling constants. Inclusion of polarization *d*-functions leads to an appreciable (about 0.5 Hz) reduction of MSD which is equal on the average to ~3 Hz for both semiempirical and nonempirical methods of geometry optimization. The AM1 method turned out to be the most accurate (MSD 2.7 Hz) among the examined semiempirical and nonempirical methods, and the best basis sets for nonempirical geometry optimization in the semiempirical calculation of ^{13}C - ^{13}C coupling constants were 6-31G**, 6-311G**, and D95** (MSD 2.8–2.9 Hz). It should be noted that no appreciable improvement was achieved by taking into account electron correlation according to the MP2 procedure.

The data characterizing different methods for geometry optimization are given in Tables 1–3. Taking them into account, the geometric parameters of compounds **I–XXX** were optimized by the AM1 method, and the ^{13}C - ^{13}C coupling constants and contributions thereto were calculated by the semiempirical SCPT INDO and CLOPPA INDO methods.

The next step of our study was division of the total ^{13}C - ^{13}C coupling constants into particular constituents in terms of the additivity model using the above approaches. Table 1 gives the results obtained for heterocyclic compounds **I–XII** on the basis of the correlation with *s*-elements of the P_{SS}^2 density matrix. The total ^{13}C - ^{13}C coupling constants calculated by the SCPT INDO method for three-membered rings having 2nd Period atoms are very consistent (within 1 Hz) with the experimental values. There are no experimental data for silirane, phosphirane, and thiirane which contain heteroatoms of the 3rd Period; therefore, the unprecedented J_{CC} value (5.3 Hz) for silirane (**IV**) and unusually low J_{CC} value (16.3 Hz) for phosphirane (**V**) cannot be compared with experimental.

Semiempirical calculation of ^{13}C - ^{13}C coupling constants in four-membered rings overestimates the total values by 5–6 Hz against the experimental constants, except for siletane (**X**). The accuracy of any semiempirical procedure is determined by the corresponding parametrization; therefore, it is difficult to expect a perfect agreement between the calculated and experimental parameters on that level, the more so between second-order parameters (spin–spin coupling constants among them).

The contributions of noncontact interactions in four-membered heterocycles are fairly small relative to the predominant positive Fermi-contact contribution (about 5–6%), and their overall contribution is negligible (on the average, 0.5 Hz) since the spin–orbital and spin–dipole contributions have opposite signs (Table 1). By contrast, the overall contribution

Table 1. ^{13}C - ^{13}C coupling constants (Hz) in heterocycles I–XII, calculated by the SCPT INDO method

Compound no.	P_{SS}^2	$J(\text{FC})$	$J(\text{SO})$	$J(\text{SD})$	$J(\text{TO})^a$	$^1J_{\text{CC}}$	$^nJ_{\text{CC}}$
I	0.04758	17.3	-3.5	-0.5	13.2 (12.4)	21.7	-8.5
II	0.05703	24.8	-3.5	-0.8	20.6 (21.0)	27.8	-7.2
III	0.06518	31.2	-3.5	-0.8	26.9 (28.0)	33.2	-6.3
IV	0.04528	11.1	-5.7	-0.1	5.3	20.2	-14.9
V	0.06327	23.8	-7.0	-0.5	16.3	31.9	-15.6
VI	0.06948	29.0	-7.2	-0.4	21.4	36.0	-14.6
VII	0.04559	33.6	-0.6	1.7	34.6 (28.0)	20.4	14.2
VIII	0.04843	34.1	-1.1	1.4	34.5	22.2	12.3
IX	0.05133	35.6	-0.9	1.4	36.1 (29.5)	24.1	12.0
X	0.04506	27.3	-1.2	1.7	27.7 (24.6)	20.0	7.7
XI	0.05060	33.4	-1.2	1.7	34.0	23.6	10.4
XII	0.05414	35.9	-1.4	1.6	36.1 (31.5)	25.9	10.2

^a In parentheses are given the experimental values from review [1].

Table 2. Contributions of localized molecular orbitals and particular molecular fragments to the total ^{13}C - ^{13}C coupling constants of small heterocycles, calculated by the CLOPPA INDO method

Compound	Fragment	$\Delta J,^a$ Hz	Compound	Fragment	$\Delta J,^a$ Hz
Cyclopropane	C–H (two fragments)	-0.1	Cyclobutane	C–H (four fragments)	-0.6
	C–C–C	-7.3		C–C–C–C	+5.4
	C–CH ₂ –C (overall)	-7.4 (-8.5)		C–CH ₂ –CH ₂ –C (overall)	+4.8 (+14.2)
	C–C	+20.7 (+21.7)		C–C	+30.4 (+20.4)
Aziridine	LEP	+0.1	Azetidine	LEP	-0.1
	N–H	0.0		N–H	-0.3
	C–N–C	-8.8		C–H (two fragments)	-0.3
	C–NH–C (overall)	-8.7 (-7.2)		C–C–N–C	+4.4
	C–C	+29.2 (+27.8)		C–CH ₂ –NH–C (overall)	+3.7 (+12.3)
Oxirane	LEP (two fragments)	+0.1	Oxetane	C–C	+31.5 (+22.2)
	C–O–C	-8.5		LEP (two fragments)	-0.5
	C–O–C (overall)	-8.4 (-6.3)		C–H (two fragments)	-0.4
	C–C	+35.2 (+33.2)		C–C–O–C	+4.8
				C–CH ₂ –O–C (overall)	+3.9 (+12.0)
			C–C	+33.1 (+24.1)	

^a In parentheses are given the corresponding direct, geminal, and vicinal increments calculated by correlation of the ^{13}C - ^{13}C coupling constant with *s*-elements of the density matrix.

of noncontact interactions in three-membered heterocycles attains up to 30% of the positive Fermi-contact contribution. In the series of three-membered heterocycles, both noncontact contributions are negative, and the spin-orbital contribution in compounds containing 3rd Period elements exceeds 7 Hz in absolute value. The unprecedentedly low calculated J_{CC} value in silirane (**IV**), 5.3 Hz, is explained by the unusually small Fermi-contact contribution (11.1 Hz) due to low *s*-order of the carbon-carbon bond as a result of steric

strain and electron-donor properties of the silicon atom, as well as by a large (in absolute value) spin-orbital contribution (-5.7 Hz).

By substituting squared *s*-elements of the density matrix P_{SS}^2 , calculated in the INDO approximation, into correlation (2) we can calculate the direct (i.e., through one bond) coupling constants $^1J_{\text{CC}}$ in three- and four-membered heterocycles. Subtraction of $^1J_{\text{CC}}$ from the total constants $J(\text{TO})$ gives the corresponding increments $^nJ_{\text{CC}}$, geminal ($n = 2$) for three-membered

Table 3. ^{13}C - ^{13}C coupling constants (Hz) between the bridgehead carbon atoms in polycyclic compounds **XIII–XXX**, calculated by the SCPT INDO method

Compound no.	P_{SS}^2	$J(\text{FC})$	$J(\text{SO})$	$J(\text{SD})$	$J(\text{TO})$	J_{add}	ΔJ
XIII	0.03044	-2.0	-3.6	-1.6	-7.3	-6.6	0.7
XIV	0.05853	17.3	-3.1	-1.6	12.6	14.4	1.8
XV	0.07929	33.7	-2.5	-0.9	30.4	29.8	-0.6
XVI	0.01478	-16.7	-3.3	-0.1	-20.1	-29.6	-9.5
XVII	0.05036	6.6	-7.7	-1.6	-2.7	-7.7	-5.0
XVIII	0.06491	21.0	-7.3	-1.9	11.9	3.8	-8.1
XIX	0.02584	28.2	1.3	1.7	31.3	35.8	4.5
XX	0.03068	31.4	0.7	1.4	33.4	35.2	1.8
XXI	0.03542	32.9	0.5	1.0	34.4	41.1	6.7
XXII	0.02555	16.6	0.5	2.1	19.1	22.7	3.6
XXIII	0.03470	28.6	0.5	2.1	31.1	34.0	2.9
XXIV	0.03983	31.7	-0.2	1.8	33.4	46.4	13.0
XXV	0.02570	7.4	-2.8	-1.0	3.7	13.0	9.3
XXVI	0.03848	16.1	-3.2	-1.2	11.7	20.8	9.1
XXVII	0.04871	24.5	-3.2	-1.2	20.1	28.1	8.0
XXVIII	0.02191	-1.2	-3.1	0.3	-4.0	-2.3	2.6
XXIX	0.03987	11.4	-6.7	-0.7	4.0	11.4	7.4
XXX	0.04979	18.8	-7.0	-0.8	11.0	18.7	7.7

heterocycles and vicinal ($n = 3$) for four-membered heterocycles (Table 1). These data show that all direct paths are positive (in keeping with their physical sense) and are on the average 20–25 Hz, indicating an appreciably reduced s -order of the C–C bonds in both three- and four-membered heterocycles. For example, the ^{13}C - ^{13}C coupling constants in related open-chain compounds are about 35 Hz: 33.0 Hz for propane [20], 35.8 Hz for ethylamine [20], and 37.4 Hz for ethanol [21]. Exception are oxirane (**III**) and thiirane (**VI**) where the direct coupling constants, 33.2 and 36.0 Hz, respectively, approach those typical of open-chain compounds.

The reduced steric strain in oxirane and thiirane is also confirmed by analysis of the highest occupied molecular orbital (HOMO) of cyclopropane heteroanalogs. Unlike other compounds of this series in which the HOMO involves banana-like bonds, the HOMO of oxirane and thiirane is contributed mainly by lone electron pairs of the heteroatoms (the electron density distribution map for the HOMO is available from the authors). As seen from Table 1, all geminal coupling paths are negative while vicinal couplings are positive.

The geminal constituents clearly demonstrate the heavy atom effect. In fact, replacement of a 2nd Period element in the geminal path by its isoelectron analog of the 3rd Period leads to doubling of the

corresponding increment in absolute value. Thus the small total ^{13}C - ^{13}C coupling constants in cyclopropane heteroanalogs containing 3rd Period elements (silirane, phosphirane, and thiirane) result from the large negative contribution of the geminal coupling path. On the other hand, all vicinal constituents are positive, as in the corresponding open-chain compounds, and are ~10–12 Hz. No heavy atom effect is observed for the vicinal couplings. An exception is replacement of carbon by silicon, which leads to a sharp reduction of the corresponding increment. By contrast, replacement of nitrogen by phosphorus almost does not affect the vicinal increment.

Table 2 shows the results of division of the total ^{13}C - ^{13}C coupling constants in terms of the polarization propagator theory (CLOPPA INDO) for three- and four-membered heterocycles containing only 2nd Period elements (the procedure lacks parametrization for 3rd Period elements). The geminal and vicinal contributions were calculated as a combination of LMOs of the constituent chemical bonds and LEPs of heteroatoms according to the Engelmann procedure for multistep localization of initial molecular orbitals [14]. The contributions of LMOs corresponding to the nitrogen and oxygen atoms and N–H and C–H bonds constituting the geminal and vicinal fragments are negligible, as compared to the contributions of LMOs of σ bonds which are directly involved in the above

coupling paths (Table 2). The overall contributions of the geminal paths for three-membered heterocycles, calculated by the CLOPPA INDO method, are -7.4 (I), -8.7 (II), and -8.4 Hz (III); these values coincide within 1–2 Hz with the geminal increments calculated by the SCPT INDO procedure (-8.5 , -7.2 , and -6.3 Hz, respectively). Likewise, a good agreement (within 1–2 Hz) is observed for the direct couplings (through one bond) calculated by these two methods.

The results of SCPT INDO and CLOPPA INDO calculations of the geminal and vicinal coupling constants in four-membered heterocycles in terms of the additivity model are much less consistent. However, in both cases, the positive contribution of the vicinal paths is reproduced. Comparison with the known vicinal ^{13}C - ^{13}C coupling constants in structurally related open-chain compounds [2] shows that SCPT INDO somewhat overestimates while CLOPPA INDO underestimates the positive contribution of vicinal paths in four-membered heterocycles. On the other hand, the contribution of the direct path determined by CLOPPA INDO for cyclobutane (VII), azetane (VIII), and oxetane (IX) is by 9–10 Hz greater than that calculated by SCPT INDO. Nevertheless, the two methods equally predict a reduced s order of the carbon–carbon bond in four-membered heterocycles.

While studying the additivity of coupling paths between the bridgehead carbon atoms in fused derivatives XIII–XXX of small heterocycles we used geminal and vicinal increments calculated by the SCPT INDO method (Table 1), and direct coupling paths were estimated by correlation (2) on the basis of s -elements of the density matrix, calculated by the INDO method (Table 3). Table 3 contains the calculated ^{13}C - ^{13}C coupling constants $J(\text{TO})$, contributions thereto, additive values J_{add} calculated as the algebraic sum of the direct and two indirect couplings (two geminal, geminal and vicinal, or two vicinal), and also deviations of the additive values from the total ^{13}C - ^{13}C coupling constants (ΔJ).

Bicyclo[1.1.0]butane heteroanalogs XIII–XVIII are the most sterically strained among the examined series. They are characterized by a very large contribution of noncontact interactions. This primarily applies to bicyclobutane XIII itself and its diphosphane analog XVII, for which the Fermi-contact contribution is even appreciably smaller than the overall contribution of noncontact interactions. An anomalous pattern is observed for disilabicyclobutane XVI; in this case (as with unsubstituted bicyclobutane), all three contributions are negative, and the total coupling constant between the bridgehead carbon atoms is unprecedentedly low, 20.1 Hz. The same compound is

characterized by the greatest deviation from the additive value ($\Delta J = -9.5$ Hz). On the other hand, bicyclobutane heteroanalogs XIV and XV containing 2nd Period elements, as well as bicyclobutane XIII, show a very high additivity in the ^{13}C - ^{13}C coupling constants for the bridgehead carbon atoms.

The contribution of noncontact interactions in less sterically strained bicyclo[2.2.0]hexane derivatives XIX–XXIV is negligible, and the total ^{13}C - ^{13}C coupling constants between the bridgehead carbon atoms approach those for single bonds in open-chain unstrained compounds [1]. An exception is disilabicyclohexane for which the Fermi-contact contribution is as small as 16.6 Hz and the total coupling constant is 22.7 Hz. This could be explained by anomalously low s order of the carbon–carbon bond due to strong steric strain; however, we believe that the most probable reason is improper parametrization for the silicon atom rather than electronic effects. The ^{13}C - ^{13}C coupling constants in this series of compounds are almost additive provided that dithia derivative XXIV is excluded.

The Fermi-contact contribution predominates for bicyclo[2.1.0]pentane heteroanalogs XXV–XXX (except for the corresponding disilabicyclopentane XXVIII, where the Fermi-contact contribution is -1.2 Hz, the spin–orbital contribution is -3.1 Hz, and the spin–dipole contribution is close to zero). Thus the total ^{13}C - ^{13}C coupling constant between the bridgehead carbon atoms is -4 Hz which seems to be unreal and is likely to result from improper parametrization of the silicon atom in the original INDO procedure [12]. Nevertheless, the additivity model gives a value of -2.3 Hz, which is close to the calculated one (-4.0 Hz). On the whole, bicyclo[2.1.0]pentane heteroanalogs are characterized by the maximal deviations from the additive values (7–9 Hz).

Quantum-chemical calculations were performed with the use of SCPTINDO [11], CLOPPA [13], MOPAC [22], GAMESS [23], and DALTON [24] software packages under SuSE Linux 6.2 (Kernel 2.2.10), Pentium III 500 PC. Standard INDO parameters [12] for the carbon atom, $s_{\text{C(O)}}^2 = 3.6762$ and $\langle r^{-3} \rangle = 2.8256$, were used in the calculation of ^{13}C - ^{13}C coupling constants.

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