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${}^{13}C$–${}^{13}C$ Spin–Spin Coupling Constants in Structural Studies: XXXI. Bicyclo[2.1.0]pentane Heteroanalogs*

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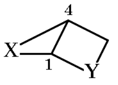
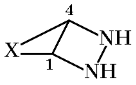
Abstract—${}^{13}C$–${}^{13}C$ spin–spin coupling constants and orbital hybridization of the bridging bond in bicyclo-[2.1.0]pentane heteroanalogs and their unsaturated derivatives were calculated in terms of the self-consistent finite perturbation theory (SCPT INDO). The results showed that the bridging C–C bond in all the examined compounds has an anomaloulsy low *s* character.

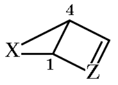
Bicyclo[2.1.0]pentane heteroanalogs **I**–**XLII** and their unsaturated derivatives **XLIII**–**LX** have been studied very poorly. The reasons are their low accessibility and difficulties in preparation. However, these compounds attract strong theoretical interest from the viewpoint of steric and electronic structure. Nevertheless, some representatives of bicyclo[2.1.0]-pentane heteroanalogs have been synthesized under specific conditions (as derivatives) or detected as reactive intermediates [1]. According to a few data available, bicyclo[2.1.0]pentane heteroanalogs are extremely unstable compounds, and the bridging carbon–carbon bond therein is very reactive.



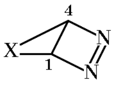
I–XXXVI



XXXVII–XLII



XLIII–LIV



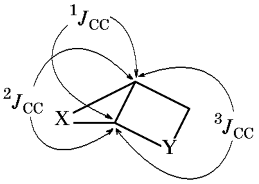
LV–LX

I, **VII**, **XIII**, **XIX**, **XXV**, **XXXI**, **XXXVII**, **XLIII**, **XLIX**, **LV**, X = CH_2; **II**, **VIII**, **XIV**, **XX**, **XXVI**, **XXXII**, **XXXVIII**, **XLIV**, **L**, **LVI**, X = SiH_2; **III**, **IX**, **XV**, **XXI**, **XXVII**, **XXXIII**, **XXXIX**, **XLV**, **XLV**, **LI**, **LVII**, X = NH; **IV**, **X**, **XVI**, **XXII**, **XXVIII**, **XXXIV**, **XL**, **XLVI**, **LII**, **LVIII**, X = PH; **V**, **XI**, **XVII**, **XXIII**, **XXIX**, **XXXV**, **XLI**, **XLVII**, **LIII**, **LIX**, X = O; **VI**, **XII**, **XVIII**, **XXIV**, **XXX**, **XXXVI**, **XLII**, **XLVIII**, **LIV**, **LX**, X = S; **I–VI**, Y = CH_2; **VII–XII**, Y = SiH_2; **XIII–XVIII**, Y = NH; **XIX–XXIV**, Y = PH; **XXV–XXX**, Y = O; **XXXI–XXXVI**, Y = S; **XLIII–XLVIII**), Z = CH; **XLIX–LIV**, Z = N.

In continuation of our studies on sterically strained carbo- and heterocycles [2–4], the present communication reports on the results of calculations of ${}^{13}C$–${}^{13}C$ coupling constants and orbital hybridization of the bridging bond in compounds **I**–**LX**, which were performed with full geometry optimization.

The *s*-character and orbital hybridization of the bridging bond were calculated by the previously developed procedure [2] which is based on correlation equation (2) in keeping with the additive scheme of spin–spin coupling transmission between the bridgehead carbon nuclei (Scheme 1).

Scheme 1.



$$ {}^{1}J_{CC} = J_{CC}(TO) - ({}^{2}J_{CC} + {}^{3}J_{CC}); \quad (1) $$

$$ {}^{1}J_{CC} = 0.06838(\%S_i)(\%S_j) - 10; \quad (2) $$

$$ sp^n:\ n = \frac{100-(\%S)}{(\%S)}. \quad (3) $$

Here, $\%S_i$ and $\%S_j$ are the *s*-characters of the bridge hybrids; sp^n is the orbital hybridization of the

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bridging bond; J_{CC}(TO) is the calculated total ^{13}C–^{13}C coupling constant; $^1J_{CC}$ is its direct constituent (transmitted through the bonding electron pair); and $^2J_{CC}$ and $^3J_{CC}$ are its geminal and vicinal increments (Hz), which were determined by us previously using a model series of monoheterocycles [3].

Geometric parameters. Principal geometric parameters of compounds **I**–**LX** were optimized by the AM1 procedure. The complete set of data is available from the authors. The length of the bridging bond ranges from 1.50 to 1.57 Å. The shortest bond (1.50–1.53 Å) is typical of saturated compounds having oxirane and thiirane fragments, whereas the bridging bond was the longest (1.55–1.57 Å) in unsaturated compounds possessing a silirane fragment. On the whole, the bridging bond lengths in the molecules under study are similar to those found for the corresponding monoheterocyclopropanes [3], and no anomaly was observed.

The bond angle θ at the heteroatom X in the three-membered ring changes as follows: 61–62° (X = CH_2), 46–51° (X = SiH_2), 63–64° (X = NH), 50–53° (X = PH), 63–64 (X = O), and 50–51° (X = S). As in the corresponding monoheterocyclopropanes [3], the bond angles θ at the S, N, and O atoms (IInd row elements) approach the standard value for cyclopropane (60°). The bond angles at the Si. P, and S atoms (IIIrd row elements) are considerably smaller (on the average, ~50°). First of all, this is the result of considerably longer Si–C, P–C, and S–C bonds, as compared to C–C, N–C, and O–C.

One of the most interesting geometric parameters of bicyclo[2.1.0]pentane heteroanalogs is the folding angle φ, i.e., the dihedral angle XCCY, which changes from 108 to 130°, so that all the compounds of this series have essentially nonpalanar structure.

The molecule of 2,5-dioxabicyclo[2.1.0]pentane (**XXIX**) is bent to the strongest extent (φ = 107.9°), and the oxirane and oxetane fragments are almost orthogonal. This may be due to through-space attractive interactions between unshared electron pairs of the geminal oxygen atoms. The molecule of 2,5-diphosphabicyclo[2.1.0]pentane (**XXII**) is more planar: the angle φ is 130.5°. Presumably, in this case the main factor is repulsion between two large phosphorus atoms which have diffuse unshared electron pairs with a considerable *s*-character.

Coupling constants and contributions thereto. Table contains the total ^{13}C–^{13}C coupling constants J_{CC}(TO), calculated by the SCPT INDO method with account taken of Fermi-contact [J_{CC}(FC)], orbital [J_{CC}(OB)], and spin–dipole interactions [J_{CC}(SD)]. Also, the direct constituent of $^1J_{CC}$(TO) is given. It was calculated by subtracting the sum of the corresponding geminal and vicinal increments from the total constant, in keeping with the additivity scheme (see Scheme 1).

The overall range of variation of the ^{13}C–^{13}C coupling constants for the bridging bond in compounds **I**–**LX** is about 55 Hz: from –3.9 Hz in 2,5-disilabicyclo[2.1.0]pentane (**VIII**) and 2-phospha-5-silabicyclo[2.1.0]pentane (**XX**) to 51.2 Hz in 5-oxa-2,3-diazabicyclo[2.1.0]pent-2-ene (**LIX**). The value of J_{CC}(TO) in 2,3-diaza-5-phosphabicyclo[2.1.0]pent-2-ene (**LVIII**), 219.7 Hz, should be considered as an artefact, for it was obtained when the convergence of the SCPT procedure was poor.

In most cases the positive Fermi-contact contribution predominates over the sum of noncontact interactions. As a rule, both orbital and spin–dipole contrubutions are negative and are on the average –(3–5) and about –1 Hz, respectively. Exceptions are compounds possessing a silirane fragment; they are characterized by anomalously small Fermi-contact contribution, and in some cases it is even smaller (in absolute value) than the sum of noncontact contributions. As a result, the total ^{13}C–^{13}C coupling constant becomes negative. In this respect, the unique compound is 2,5-disilabicyclo[2.1.0]pentane (**VIII**) whose molecule contains two silicon atoms, one in the silirane and the other in the siletane fragment. There are almost no Fermi-contact and spin–dipole interactions between the bridgehead carbon nuclei in molecule **VIII** (the corresponding contributions are close to zero). As a result, the calculated total coupling constant J_{CC}(TO) is determined exclusively by the orbital contribution and is –3.9 Hz. This is one of the rarest cases when the coupling constant between chemically bonded carbon atoms is negative. However, the experimental sign of the coupling constant has not been determined as yet.

Orbital hybridization of the bridging bond. The *s*-characters of the bridge hybrids and the corresponding orbital hybridizations of the bridging bond in compounds **I**–**LX** are given in table. The bridge hybrids in the parent carbocycles, bicyclo[2.1.0]pentane (**I**) and bicyclo[2.1.0]pent-2-ene (**XLIII**), are almost pure *p* orbitals (%*S* < 10%). Their heteroanalogs also have anomalously low *s*-characters of the bridging orbitals, though the contribution of of *p* orbitals is considerably greater: on the average, the *s*-character is 15–20%.

The lowest *s*-character (11–15%) is typical of nitrogen-containing bicyclo[2.1.0]pentane heteroanalogs. For example, in 2,3-diazabicyclo[2.1.0]pentane it is

^{13}C–^{13}C coupling constants (Hz) and orbital hybridizations of the bridging bond in bicyclo[2.1.0]pentane heteroanalogs and their unsaturated derivatives

Compound no.	$J_{1,4}$(FC)	$J_{1,4}$(OB)	$J_{1,4}$(SD)	$J_{1,4}$(TO)	$^1J_{1,4}$(TO)	*s*-Character		Orbital hybridization
						S(C^1)	S(C^4)	
I	7.2	–2.6	–1.1	3.4	–5.0	8.52	8.52	$sp^{10.74}$–$sp^{10.74}$
II	3.3	–3.6	0.0	–0.3	1.8	13.11	13.11	$sp^{6.63}$–$sp^{6.63}$
III	13.4	–2.7	–1.6	9.1	–2.8	10.23	10.23	$sp^{8.78}$–$sp^{8.78}$
IV	11.9	–5.4	–0.9	5.7	5.2	14.89	14.89	$sp^{5.72}$–$sp^{5.72}$
V	23.2	–3.4	–1.6	18.1	2.8	13.66	13.66	$sp^{6.32}$–$sp^{6.32}$
VI	14.7	–6.2	–1.1	7.3	4.2	14.39	14.39	$sp^{5.95}$–$sp^{5.95}$
VII	4.0	–2.7	–0.7	0.7	1.2	19.16	8.52	$sp^{4.22}$–$sp^{10.74}$
VIII	0.0	–3.9	0.0	–3.9	7.1	19.03	13.11	$sp^{4.25}$–$sp^{6.63}$
IX	11.5	–2.8	–1.3	7.4	4.4	20.53	10.23	$sp^{3.87}$–$sp^{8.78}$
X	5.7	–5.7	–0.6	–0.7	7.7	17.34	14.89	$sp^{4.77}$–$sp^{5.72}$
XI	14.7	–3.6	–1.2	10.0	3.6	14.52	13.66	$sp^{5.89}$–$sp^{6.32}$
XII	9.4	–6.5	–0.8	2.1	7.9	18.15	14.39	$sp^{4.51}$–$sp^{5.95}$
XIII	8.1	–2.7	–1.3	4.1	–4.3	9.72	8.52	$sp^{9.29}$–$sp^{10.74}$
XIV	3.1	–3.7	–0.1	–0.8	1.3	12.56	13.11	$sp^{6.96}$–$sp^{6.63}$
XV	15.6	–2.6	–1.8	11.2	–0.7	15.42	10.23	$sp^{5.49}$–$sp^{8.78}$
XVI	13.2	–5.3	–0.9	7.0	6.5	16.17	14.89	$sp^{5.18}$–$sp^{5.72}$
XVII	27.2	–3.4	–1.6	22.2	6.9	18.05	13.66	$sp^{4.54}$–$sp^{6.32}$
XVIII	17.1	–6.0	–1.2	9.9	6.8	17.03	14.39	$sp^{4.87}$–$sp^{5.95}$
XIX	6.9	–2.6	–0.9	3.5	0.1	17.27	8.52	$sp^{4.79}$–$sp^{10.74}$
XX	0.4	–4.1	–0.1	–3.9	3.2	14.68	13.11	$sp^{5.81}$–$sp^{6.63}$
XXI	12.4	–2.7	–1.3	8.4	1.5	16.38	10.23	$sp^{5.11}$–$sp^{8.73}$
XXII	7.8	–5.8	–0.8	1.0	5.5	15.18	14.89	$sp^{5.59}$–$sp^{5.72}$
XXIII	20.8	–3.4	–1.3	16.0	5.7	16.77	13.66	$sp^{4.96}$–$sp^{6.32}$
XXIV	12.1	–6.5	–1.0	4.7	6.6	16.83	14.39	$sp^{4.94}$–$sp^{5.95}$
XXV	11.0	–2.7	–1.3	7.0	–1.6	14.35	8.52	$sp^{5.97}$–$sp^{10.74}$
XXVI	3.2	–3.7	–0.2	–0.7	1.2	12.45	13.11	$sp^{7.03}$–$sp^{6.63}$
XXVII	20.5	–2.6	–1.8	16.1	4.0	19.96	10.23	$sp^{4.01}$–$sp^{8.78}$
XXVIII	15.4	–5.1	–0.9	9.3	8.6	18.23	14.89	$sp^{4.49}$–$sp^{5.72}$
XXIX	35.0	–3.1	–1.5	30.4	14.9	26.61	13.66	$sp^{2.76}$–$sp^{6.32}$
XXX	19.8	–5.8	–1.2	12.8	9.5	9.78	14.39	$sp^{4.22}$–$sp^{5.95}$
XXXI	9.6	–2.9	0.9	5.8	1.2	19.16	8.52	$sp^{4.22}$–$sp^{10.74}$
XXXII	3.7	–4.1	0.0	–0.4	5.5	17.25	13.11	$sp^{4.80}$–$sp^{6.63}$
XXXIII	16.7	–2.7	–1.4	12.6	4.5	20.67	10.23	$sp^{3.84}$–$sp^{10.23}$
XXXIV	13.7	–5.6	–0.7	7.4	10.7	20.29	14.89	$sp^{3.93}$–$sp^{5.72}$
XXXV	26.5	–3.5	–1.4	21.7	10.2	21.58	13.66	$sp^{3.63}$–$sp^{6.32}$
XXXVI	16.4	–6.2	–0.9	9.2	9.9	20.18	14.39	$sp^{3.96}$–$sp^{5.95}$
XXXVII	10.3	–2.6	–1.4	6.3	–3.4	9.79	9.79	$sp^{9.21}$–$sp^{9.21}$
XXXVIII	4.7	–3.6	–0.3	0.8	1.6	13.00	13.00	$sp^{6.69}$–$sp^{6.69}$
XXXIX	19.2	–2.6	–1.9	14.7	1.5	12.95	12.95	$sp^{6.72}$–$sp^{6.72}$
XL	14.8	–5.0	–1.0	8.8	7.0	15.75	15.75	$sp^{5.35}$–$sp^{5.35}$
XLI	32.4	–3.4	–1.6	27.4	10.8	17.42	17.42	$sp^{4.74}$–$sp^{4.74}$
XLII	19.1	–5.8	–1.2	12.1	7.7	16.07	16.07	$sp^{5.22}$–$sp^{5.22}$
XLIII	8.1	–2.0	–1.3	4.7	–6.8	6.80	6.80	$sp^{13.7}$–$sp^{13.7}$
XLIV	3.2	–2.1	0.4	1.5	0.5	12.37	12.37	$sp^{7.08}$–$sp^{7.08}$

Table. (Contd.)

Compound no.	$J_{1,4}$(FC)	$J_{1,4}$(OB)	$J_{1,4}$(SD)	$J_{1,4}$(TO)	$^1J_{1,4}$(TO)	*s*-Character		Orbital hybridization
						$S(C^1)$	$S(C^4)$	
XLV	16.6	–2.0	–2.0	12.6	–2.4	10.51	10.51	$sp^{8.51}$–$sp^{8.51}$
XLVI	11.8	–4.2	–0.8	6.8	3.2	13.87	13.87	$sp^{6.21}$–$sp^{6.21}$
XLVII	30.2	–2.7	–2.1	25.5	7.1	15.80	15.80	$sp^{5.33}$–$sp^{5.33}$
XLVIII	16.9	–4.8	–0.9	11.2	5.0	14.79	14.79	$sp^{5.76}$–$sp^{5.76}$
XLIX	12.0	–2.0	–1.6	8.4	–4.9	10.88	6.80	$sp^{8.19}$–$sp^{13.7}$
L	5.2	–2.1	0.1	3.2	0.4	12.25	12.37	$sp^{7.16}$–$sp^{7.08}$
LI	21.9	–2.1	–2.2	17.7	0.9	15.11	10.51	$sp^{5.62}$–$sp^{8.51}$
LII	14.9	–4.1	–1.1	9.7	4.3	15.03	13.87	$sp^{5.65}$–$sp^{6.21}$
LIII	38.8	–2.8	–2.1	33.9	13.7	21.9	15.08	$sp^{3.57}$–$sp^{5.33}$
LIV	23.1	–4.9	–0.5	17.8	9.8	19.54	14.79	$sp^{4.12}$–$sp^{5.76}$
LV	29.7	–1.8	–1.4	26.5	4.6	14.59	14.59	$sp^{5.85}$–$sp^{5.85}$
LVI	16.4	–1.6	0.2	15.0	3.6	14.08	14.08	$sp^{6.10}$–$sp^{6.10}$
LVII	39.5	–2.1	–1.3	36.1	10.7	17.38	17.38	$sp^{4.75}$–$sp^{4.75}$
LVIII[a]	224.5	–3.8	–1.0	219.7	205.7	56.16	56.16	$sp^{0.78}$–$sp^{0.78}$
LIX	56.7	–3.4	–2.1	51.2	22.4	21.75	21.75	$sp^{3.60}$–$sp^{3.60}$
LX	36.17	–4.8	–1.4	30.0	13.4	18.48	18.48	$sp^{4.41}$–$sp^{4.41}$

[a] Poor convergence of the self-consistency procedure (SCPT); the results are invalid.

as low as 9.79%, which corresponds to the formal hybridization $sp^{9.21}$. On the whole, the bridging C–C bond in bicyclo[2.1.0]pentane is characterized by considerably lower *s*-order, as compared to the corresponding monoheterocyclopropanes [3] (Scheme 2). The observed pattern may be explained by stronger steric strain in bicyclo[2.1.0]pentane heteroanalogs.

Analysis of the electron density distribution charts for molecular orbitals participating in the formation of the bridging bond also indicates its increased *p*-character. The charts are available from the authors.

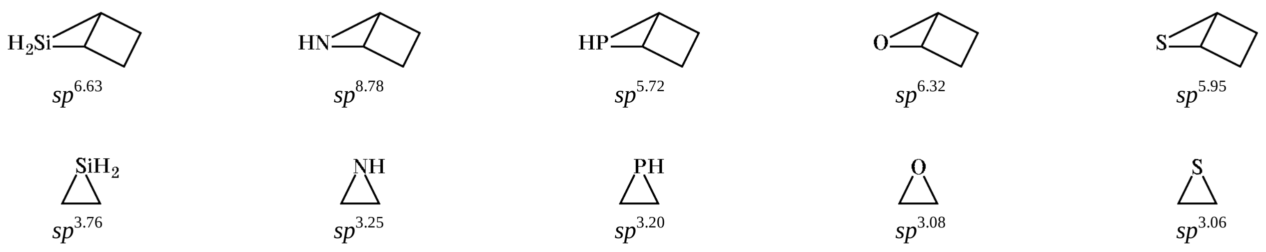
A characteristic sign of the reduced *s*-order of the bridging bond is deviation of electron density of the corresponding MO from the main bond axis. As a result, the MO acquires some π-character, remaining essentially a σ-like orbital.

EXPERIMENTAL

Quantum-chemical calculations were performed on a Pentium-133 PC. The initial data were prepared using PCMODEL program (graphical representation of molecules in the form of *Z*-matrices and preliminary molecular-mechanics optimization of geometric parameters). The geometric parameters of the compounds under study were optimized by the AM1 method with standard parametrization [5] in terms of the Broyden–Fletcher–Goldfarb–Shanno gradient algorithm [6] using MOPAC software. The eigenvector-following routine was applied with a gradient convergence criterion GNORM of 0.01 and a self-consistency convergence criterion SCFCRT of 0.0001.

The ^{13}C–^{13}C coupling constants were calculated in terms of the self-consistent finite perturbation theory,

Scheme 2.



taking into account Fermi-contact, orbital, and spin–dipole mechanisms [7], using the Blizzard–Santri algorithm [8] in the INDO approximation [9]; the calculations were performed by SCPTINDO program provided by G.E. Sal’nikov (Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences). The following parameters for carbon atom were used: $s^2_{C(O)}$ = 3.6762 and $<r^{-3}>$ = 2.8256. The MO electron density distribution charts were calculated and plotted in terms of the INDO approximation [9] using HYPERCHEM program.

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