ELECTRON DELOCALIZATION INTERACTIONS AND NMR SPIN-SPIN COUPLING CONSTANTS IN SATURATED CAGE COMPOUNDS

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Dedicated to Prof. Imre G. Csizmadia on the occasion of his 75th birthday

Abstract

Since the cage substrate of 1-X;3-Y-bicyclo[1.1.1]pentanes is notably strained, it is expected that in compounds of this type important trans-cage spin-spin coupling constants, SSCCs, could be observed. Such SSCCs should be dominated to a great extent by the Fermi Contact, FC, contribution since this term, for long-range couplings, is transmitted by electron-transfer interactions, which in strained compounds are particularly enhanced. In this paper, both theoretically and experimentally, ${}^4J({}^{13}C_\alpha,{}^1H_3)$ SSCCs in 1-X-bicyclo[1.1.1]pentanes, where the α–atom of group X is ${}^{13}C$, are studied. Results are compared with similar trans-cage SSCCs in analogous compounds. Insights into electron delocalization interactions defining the experimental trends are obtained through the study of σ-hyperconjugative interactions of cage bonds. These interactions are studied using the Natural Bond Orbital, NBO, method. Results suggest that multipath additivity should hold in compounds where trans-cage SSCCs are determined by charge transfer interactions.

Resumen

Dado que la estructura cerrada del sustrato de los pentanos1-X;3-Y-biciclo[1.1.1]se encuentra tensionada, es de esperar que en compuestos de este tipo existan acoplamientos spin-spin "trans-cage", SSCCs. Tales SSCCs deberían ser dominadas por la contribución del Contacto Fermi, FC, ya que este término, para acoplamientos de largo alcance, se transmite por interacciones de transferencia electrónica, las cuales se potencian en compuestos tensionados. En este trabajo se estudian, teórica y prácticamente, $^{4}J(^{13}C_{\alpha},^{1}H_{3})$ *SSCCs en 1-X-biciclo[1.1.1]pentanos donde el átomo* σ *del grupo X es* ^{13}C*. Los resultados son comparados con SSCCs "trans-cage"en compuestos análogos. Se obtiene información sobre las interacciones de delocalización electrónica que definen las tendencias experimentales a partir del estudio de interacciones* σ*-hiperconjugadas de los enlaces en la estructura. Estas interacciones son estudiadas usando el método NBO. Los resultados sugieren que la aditividad multimecanística debería ser válida en compuestos donde los "trans-cage" SSCCs son determinados por interacciones de transferencia de carga.*

Introduction

Indirect spin-spin coupling constants, SSCCs, originate in magnetic electron-nucleus interactions [1]. The non-relativistic theory of these spectral parameters was presented by Ramsey more than a half century ago [2,3]. According to such a theory, isotropic SSCCs, commonly known as "scalar couplings", are made up of four different contributions, namely, Fermi contact, FC, spin-dipolar, SD, paramagnetic spin-orbit, PSO, and diamagnetic spin-orbit, DSO, eq. (1).

$$J_{NM} = {}^{FC}J_{NM} + {}^{SD}J_{NM} + {}^{PSO}J_{NM} + {}^{DSO}J_{NM} \qquad (1)$$

There is no experimental form to determine separately the influence of each contribution. The accurate theoretical calculation of these spectroscopic parameters is a real challenge for Quantum Chemistry since their calculation is computationally very demanding. For this reason the most evolved post-Hartree-Fock approaches can, at present, only be applied to small compounds containing only light atoms[4,5]. In the mid 1990's the first calculations of SSCCs within the DFT framework were reported, [6,7,8] and a few years later, using the coupled-perturbed (CP-DFT) approach, a large breakthrough in such calculations was achieved [9,10,11]. Within this approach reasonable good results of SSCCs for medium sized compounds can be calculated [12].

In many instances different approaches [3,14,15,16] were developed in order to study how the nucleus-electron magnetic interaction is transmitted between regions inside a molecule, or from one molecule to another in a complex. With those approaches it is sought to increase the ability of high resolution NMR spectroscopy to provide invaluable information about fine details of molecular electronic structures. Although in this paper a better understanding of the transmission in long-range SSCCs saturated compounds is sought, a different approach is followed, based in the following considerations. Many SSCCs are now known to be by far dominated by the FC interaction, although there are also known conspicuous exceptions to this statement [17, 18]. Owing to the importance of the FC term special emphasis was made to understand how this interaction is transmitted through the electronic molecular system. It is known that the FC interaction induces a slight electron spin polarization, which is transmitted through the electronic system by exchange interactions (spin correlation), i.e. its transmission is closely related to that of the so called "Fermi hole" [19]. This suggests that the overlap between two occupied localized molecular orbitals, LMOs, is an efficient pathway for transmitting the FC spin information [20]. There are many examples where this condition can be observed, e.g. when two moieties are spacially close. In this particular case it constitutes what is known in the literature as the "through-space" transmission of the FC term [12]. It can also be observed for two LMOs representing two bonds which share one atom; this mechanism should be important for transmission of, for instance, *geminal* SSCCs. This phenomenon attenuates rapidly when increasing the number of bonds separating the coupling nuclei, it would be very difficult to observe any measurable effect beyond three bonds (*vicinal* couplings). If this is the only mechanism for transmitting the FC term. Why then long-range couplings, ${}^{n}J_{NM}$, with n > 3, are frequently observed?. Although electron delocalization is known to play an important role in transmitting the FC interaction [21], it is better answering this question by considering separately, a) unsaturated compounds, b) saturated compounds.

For unsaturated compounds this question was answered many years ago [22,23]; for saturated compounds we have recently addressed this topic [24] which, until few years ago, it was a kind of a puzzle [25]. In saturated compounds delocalization interactions are not so well known as in unsaturated systems; for this reason in general long range couplings in saturated compounds are not so well known as, for instance, in conjugated systems. However, σ-hyperconjugative interactions can be quantitatively described by the NBO approach of Weinhold *et al.* [26] and, therefore, the ability of different saturated compounds to transmit long-range couplings can be assessed, at least qualitatively, comparing adequately long-range SSCCs with such interactions. In this work we study long-range SSCCs ${}^{4}J(C_{\alpha},H_{3})$ transmitted through σ-delocalization like those described recently when rationalizing "*trans*-cage" SSCCs in 1-F,4-X-cubanes [24], **I**. It was observed that this system is very efficient for transmitting the FC term since there are six equivalent coupling pathways, and each of them is equally efficient owing mainly to these two factors: the arrangement of bonds is such that they favor electron delocalization interactions; each of these interactions is important since the substrate of these compounds is strained and therefore, electron delocalization interactions are enhanced [27]. In a strained cage hydrocarbon the C—C bonds are very good electron donors, while the corresponding (C—C)* antibonds are rather poor electron acceptors. In Figure 3 the six equivalent coupling pathways for transmitting the FC term of ${}^{5}J(F_{1},C_{\alpha})$ SSCC in **I** are sketched, highlighting the six donor bonds that undergo important interactions of types $(C—C)\rightarrow(C_{1}—F)^{*}$ and $(C—C)\rightarrow(C_{1}—X)^{*}$. With this idea in mind it is possible to rationalize, for instance, ${}^{7}J(F,F) = 2.8$ Hz in difluorodiadamantane [28], where the suggested three-coupling pathways for transmitting such a long-range SSCC are highlighted, Figure 4.

In this paper the "trans-cage" long-range ${}^{4}J({}^{13}C_{\alpha},{}^{1}H_{3})$ SSCCs are studied in several members of series 1-X-bicyclo[1.1.1]pentanes, **II**, where the α atom of substituent X is ${}^{13}C$. Since these experimental SSCCs were not reported , they were also measured for X = CH_3, CH_2OH, t-Bu, Ph, $COCH_3$, CO_2H, CO_2CH_3, CN as part of this work. For five members of this series, X = CH_3, CH_2OH, $COCH_3$, CO_2H, CN, i.e. for compounds containing the simplest side-chains, the respective four contributions to ${}^{4}J({}^{13}C_{\alpha},{}^{1}H_{3})$ SSCCs were calculated at the B3LYP/EPR-III level. The relevant σ-hyperconjugative interactions were studied using the Weinhold's Natural Bond Orbitals, NBO, approach [26].

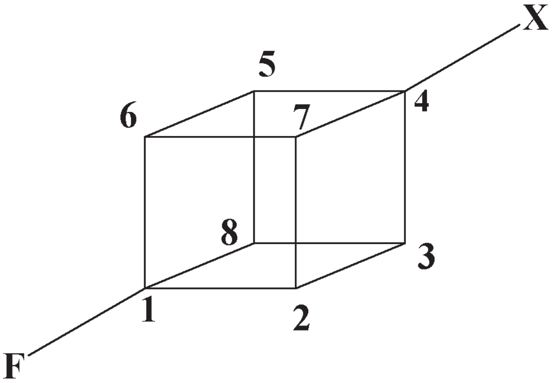

*Figure 1. 1-F,4-X-cubane, **I**.*

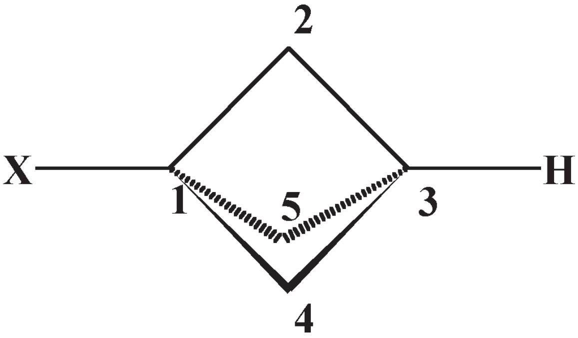

*Figure 2. 1-X-bicyclo[1.1.1]pentane, **II***

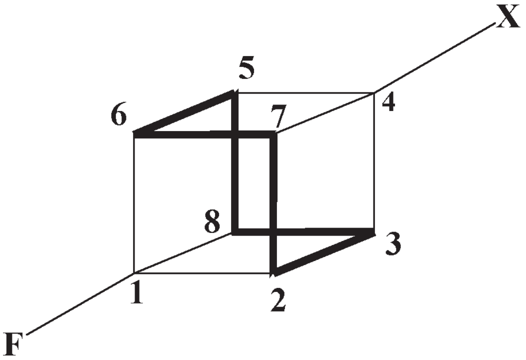

*Figure 3. Coupling pathways for $^5J(F_1,X)$ in **I**.*

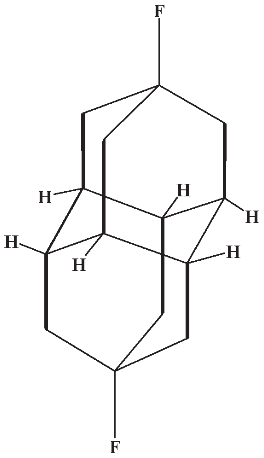

Figure 4. $^7J(F,F)$ = 2.8 Hz in difluorodiadamantane

Experimental and Computational Details

3a. Experimental details

Syntheses of compounds of series **II**(X= CH_3, CH_2OH, t-Bu, Ph, $COCH_3$, CO_2H, CO_2CH_3, CN) were described elsewhere [29]. Samples were prepared in $CDCl_3$ at concentrations of *ca* 0.6 mol l^{-1}. ^{13}C NMR spectra were recorded on a Varian Gemini 300BB instrument, operating at 75.462 MHz. $^4J(^{13}C_\alpha,^1H)$ SSCCs were determined from proton-coupled spectra, measured at 100-500 Hz spectral width with 30-40K digital resolution. Experimental couplings thus obtained are considered to be accurate to ± 0.1 Hz. These measurements were carried out in the Department of Chemistry, Faculty of Science and Engineering, Flinders University of South Australia.

3b. Computational details

The geometries for five members of series **II,** were optimized using the hybrid B3LYP functional, which corresponds to Lee *et al.* correlated functional [30] and the exchange part is treated according to the Becke's three parameter approach [31,32]. For such optimizations the 6-311G(d,p) basis set was chosen. Calculations of all four terms of SSCCs, i.e. FC, SD, PSO and DSO, were carried out using the B3LYP functional and the EPR-III basis set [33]. This basis set was chosen since SSCCs calculated at the B3LYP/EPR-III level are known to be close to the basis-set converged limit [34]. The EPR-III basis set is of a triple-zeta quality and includes diffuse and polarization functions. The s part of the EPR-III basis set is enhanced to better reproduce the electronic density in the nuclear regions; this point is particularly important when calculating the FC term. The CP-DFT perturbative approach [9,10] as implemented in the Gaussian 03 package of programs [35] was used for calculating all the three second-order terms of spin-spin couplings, i.e. FC, SD, and PSO; the DSO term is treated as a first-order quantity and therefore it is evaluated as an expectation value over the electronic ground state. All DFT calculations were carried out with the Gaussian 03 package of programs [35]. σ-Hyperconjugative interactions were studied using the NBO approach [36].

Results and Discussion

In Table 1 the experimental values measured in this work for the "trans-cage" $^4J(^{13}C_\alpha,^1H)$ SSCCs measured in 8 members of series **II** are displayed. These values are compared with the corresponding $^4J(^{13}C_\alpha,^{19}F)$ SSCCs (taken from Ref. [37]) in a series similar to **II**, but where the H atom placed at position 3, has been replaced by an F atom, i.e. 1-X;3-F-bicyclo[1.1.1]pentanes, **II-F**. This extra series of experimental values was added to Table 1 since it was considered convenient to observe that the sensitivity to a given substituent is notably enhanced in the substrate with F at position 3 as compared with the substrate with H at the same position. It is worth noting that there is no exact parallelism in these two series of values, although they follow the same trend. SSCCs in the series **II-F** were not calculated in this work due to the difficulty to obtain these parameters when at least a fluorine atom is involved[38]. However, some considerations will be made to rationalize the larger efficiency for transmitting the *trans*-cage couplings. To obtain a better idea about the sensitivity for transmitting the FC term in "*trans*-cage" SSCCs, it is interesting to consider also the parent hydrocarbon, i.e. bicyclo[1.1.1]pentane where it is known that $^4J(H_1,H_3) = 18$ Hz [39], and compound 1-F-bicyclo[1.1.1]pentane, where $^4J(F_1,H_3) = 71$ Hz [40] (= 69.71 Hz according to Ref. [37]). At this point it is important to recall that, when comparing SSCCs involving different isotopic species, it must be taken into account that J_{AB} SSCC is proportional to the gyromagnetic ratios γ_A and γ_B of nuclei A and B, respectively. In this way $^4J(H,H)$, $^4J(C,H)$, $^4J(C,F)$ SSCCs can be converted into "equivalent" $^4J(H,H)eq$ SSCCs, multiplying, respectively, by ; $\gamma_H/\gamma_H = 1$; $\gamma_H/\gamma_C = 3.9761$; and $(\gamma_H/\gamma_F)^2 = 1.0624$.

Table 1. *Comparison of experimental trans-cage* $^4J(C_\alpha,X_3)$ *couplings in series* ***II*** *and* ***II-F****. All SSCCs are given in Hz.*

X	$^4J(C_\alpha,H_3)^a$	$^4J(C_\alpha,F)^b$
CH_3	11.7	25.1
CH_2OH	11.5	27.40
t-Bu	9.6	21.90
Ph	9.6	26.60
$COCH_3$	11.3	29.20
CO_2H	14.0	36.70
CO_2CH_3	14.4	37.10
CN	16.5	37.81

(a) This work
b)Taken from Ref. [36].

In Table 2 calculated $^4J(C_\alpha,H_3)$ SSCCs in five members of series **II** are compared with the respective experimental values. All four contributions to such SSCCs are explicitly shown to convey the idea of the relative importance of each contribution, i.e. they are by far dominated by the FC term. It is also noteworthy that the PSO and DSO terms almost cancel each other, a situation observed for several types of SSCCs, although there are also many cases where such cancellation does not take place. Their values are shown with two decimal figures to stress the low sensitivity of non-contact contributions to the X-substituent. For comparing with experimental values, total calculated SSCCs are rounded off to only 1 decimal figure. For each of the compounds with X = CH_2OH; $COCH_3$; and CO_2H two conformations were considered, as shown in Table 2. In general the agreement between calculated and experimental couplings is very good, observing the largest difference for X = CN; however, the experimental trend is correctly reproduced.

Table 2*. Comparison between calculated* $^4J(C_\alpha,H_3)$ *SSCCs (in Hz) with their experimental values, measured as part of this work.*

X	FC	SD	PSO	DSO	Total	Exp.
CH_3	11.66	0.01	0.38	-0.45	11.6	11.7
CH_2OH^a	11.67	0.01	0.35	-0.41	11.6	11.5
CH_2OH^b	11.97	0.02	0.35	-0.41	11.9	11.5
$COCH_3{}^c$	11.86	0.01	0.34	-0.36	11.9	11.3
$COCH_3{}^d$	11.78	0.01	0.34	-0.36	11.8	11.3
CO_2H^e	14.02	0.01	0.34	-0.34	14.0	14.0
CO_2H^f	14.09	0.01	0.34	-0.34	14.1	14.0
CN	15.36	0.01	0.37	-0.40	15.3	16.5

[a] *This corresponds to the preferential conformation with the dihedral angle $OC_{\alpha}C_{1}C_{2}$ = 180°.*

[b)] *The second conformer corresponds to $OC_{\alpha}C_{1}C_{2}$ = 0°; it is 2.9 kcal/mol above the preferential conformation..*

[c)] *This corresponds to the preferential conformation with the dihedral angle $OC_{\alpha}C_{1}C_{2}$ = 0°.*

[d)] *The second conformer corresponds to $OC_{\alpha}C_{1}C_{2}$ = 180°; it is 0.7 kcal/mol above the preferential conformation..*

[e)] *This corresponds to the preferential conformation with the dihedral angle $OC_{\alpha}C_{1}C_{2}$ = 0°.*

[f)] *The second conformer corresponds to $OC_{\alpha}C_{1}C_{2}$ = 180°; it is 0.4 kcal/mol above the preferential conformation.*

It is now well known that in the bicyclo[1.1.1]pentane cage the six C—C bonds, C_1—C_2, C_1—C_4 and C_1—C_5, i.e. C_1—C_i; and C_2—C_3, C_4—C_3 and C_5—C_3, i.e. C_i—C_3, are excellent electron donors, and their corresponding antibonds, (C—C)*, are bad electron acceptors for σ-hyperconjugative interactions. For this reason, we can expect that the main hyperconjugative interactions transmitting the spin information associated to the FC term from C_α to H_3 (or, equivalently, from H_3 to C_α) should be $(C_1—C_i)\rightarrow(C_3—H)^*$, and $(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$, interactions called of type **1** and type **2**, respectively. It is interesting to note that for an X group with a three-fold symmetry axes the three interactions of type **1** are equivalent, the same holds for the three $(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$ interactions. From an experimental point of view an effective equivalence of this type holds since in all cases the barrier for inner rotations around the C_1—C_α bond are low enough and all compounds displayed in Table 1 show an effective three-fold symmetry axes at room temperature. For this reason, in Table 3 the sum of the three interactions of type **1** and the sum of the three interactions of type **2**, are given in the first and second columns, respectively.

Table 3. *Electron delocalization interactions **1** and **2** (in kcal/mol) expected to be efficient for transmitting the FC term of $^4J(C_\alpha,H_3)$ SSCCs in series **II**. The C_α s % character of the C_1—C_α bond is also shown since the actual value of this coupling also depends on it.*

X	**1**[a]	**2**[b]	C_α s %	$^4J(C_\alpha,H_3)$
CH_3	27.2	35.0	32.7	11.7
CH_2OH	27.5	35.4	32.8	11.5
$COCH_3$	27.0	33.1	35.5	11.3
CO_2H	26.9	33.8	59.6	14.0
CN	25.8	33.5	52.75	16.5

[a] *1: Sum of the three $(C_1—C_i)\rightarrow(C_3—H)^*$ interactions (I = 2, 4 and 5).*

[b] *2: Sum of the three $(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$ interactions (i = 2, 4 and 5).*

The C_α s % character of the C_1—C_α is also shown since the actual value of $^4J(C_\alpha,H_3)$ SSCC depends on it [41]. It is observed that the sum of interactions $(C_1—C_i)\rightarrow(C_3—H)^*$, **1**, is much less sensitive to substituents placed at position 1 than the sum of interactions

$(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$, **2**. For comparison purposes in Table 4 the corresponding interactions in the parent hydrocarbon, bicyclo[1.1.1]pentane, in **II**(X = CH_3) and in 1-F-bicyclo[1.1.1]pentane are also shown, together with the respective experimental values of *trans*-cage SSCCs, together with their "equivalent" J(H,H) values. Due to symmetry reasons, in bicyclo[1.1.1]pentane the $(C_1—C_i)\rightarrow(C_3—H)^*$ interactions are exactly the same as the $(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$ interactions. It is noted that the former are close to $(C_1—C_i)\rightarrow(C_3—H)^*$ in compounds of series **II**; which indicates that the main difference in the ability for transmitting the FC interaction corresponding to $^4J(X,H_3)$ can be ascribed to the different $(C_1—X)^*$ antibond acceptor capability. It is noted that, according to Table 4, the $(C_1—F)^*$ antibond in 1-F-bicyclo[1.1.1]pentane, is notably a better electron acceptor than $(C_1—X_\alpha)^*$ antibond in series **II**.

***Table 4**: Comparison of σ-hyperconjugative interactions of types **1** and **2** in bicyclo[1.1.1]pentane; in **II**(X = CH_3) and in 1-F-bicyclo[1.1.1]pentane. The experimental trans-cage $^4J(X,H_3)$ SSCCs (in Hz) are also compared.*

X	**1**[a]	**2**[b]	$^4J(X,H_3)$	J(H,H)eq[c]
H	27.3	27.3	18[d]	18
CH_3	27.2	35.0	11.7	46.5
F	28.2	50.6	69.71[e]	74.1

[a] ***1***: *Sum of the three $(C_1—C_i)\rightarrow(C_3—H)^*$ interactions (i = 2, 4 and 5).*
[b] ***2***: *Sum of the three $(C_i—C_3)\rightarrow(C_1—C_\alpha)^*$ interactions (i = 2, 4 and 5).*
[c] $J(H,H)_{eq} = (\gamma_H/\gamma_X)^4J(X,H_3)$.
[d] *Taken from Ref. [38].*
[e] *Taken from Ref. [39].*

Concluding Remarks

In the series of compounds 1-X-bicyclo[1.1.1]pentanes *trans*-cage $^4J(^{13}C_\alpha,^1H_3)$ SSCCs studied in this work are new examples of the efficiency for transmitting the FC spin information through a strained cage compound. The capability for these cage compounds for transmitting substituent effects on such couplings is fundamentally determined by the different electron acceptor ability of the $(X_\alpha—C_1)^*$ antibonding orbital for different substituents. On the other hand, the better ability of compounds 1-X;3-F-bicyclo[1.1.1]pentanes (see Table 1) than 1-X-bicyclo[1.1.1]pentanes originate in the much better electron acceptor ability of the $(C_3—F)^*$ antibond in the former than that of the $(C_3—H)^*$ antibond in the latter.

Since electron delocalization interactions take place in all three bridges of these bicyclo-compounds, it is observed that SSCCs transmitted through strained cage compounds, should follow a multipath additivity. It is important to recall that, recently, the multipath additiviy in cyclopropane and bicyclobutane has been questioned [42].

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