NMR Spin–Spin Coupling Constants and Hyperconjugative Interactions

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ABSTRACT: The potential of NMR spin–spin coupling constants as probes to study fine details of electronic molecular structures is briefly discussed in this work through two different examples. A qualitative analysis of the polarization propagator expression for the Fermi contact term is applied for predicting factors affecting $^1J_{CH}$, and comments are made about how to generalize those results to different types of one-bond spin-spin couplings. Moreover, the Natural J Coupling method is applied to get insight into electronic factors defining a Karplus relationship of type $^3J_{HH}$ (180°) < $^3J_{HH}$(0°) known in the literature for some amino acids.   © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 110: 532–539, 2010

Key words: NMR; NJC; coupling constants; hyperconjugative interactions; natural bond orbitals

Introduction

At present, the potential of spin–spin coupling constants (SSCCs) for studying fine details of electronic molecular structures is very well recognized [1]. It is also accepted that the accurate calculation of this type of parameters is a hard task for Quantum Chemistry [2]. However, in several scientific fields, an approach for the prediction of SSCC trends along a series of compounds is more appreciated than a method for calculating accurate values. In this work, such approach is discussed and some results reported in recently published articles are briefly reviewed to provide a few pictorial and illustrative examples. The present study will be restricted to the Fermi contact (FC) term (*vide infra*) because many coupling trends in either organic or biological compounds are known to be dominated by this term. On the other hand, it is now well known [3] that its transmission through the electronic molecular system is closely related to the behavior of the "Fermi hole." For this reason, two clearly different cases should, in general, be considered, namely, short-range SSCCs, i.e., $^nJ_{NM}$ with $n \leq 3$ and long-range SSCCs with $n > 3$. It must be emphasized that this partition is made because molecules having a classical Lewis structure would not show measurable long-range SSCCs ($n > 3$) unless a through-space transmission is present [4], where the overlap of the electronic clouds belonging to two proximate moieties transmits the "Fermi hole" by exchange interactions. Therefore, it is now well recognized that departures of classical Lewis structures play a key role in the transmission of the FC term in long-range SSCCs [5].

For short-range SSCCs, the polarization propagator (PP) approach, as described by Oddershede [6a] and by Contreras and coworkers [6b–g], can be used to get insight into the influence of hyperconjugative interactions on SSCCs. For longer range SSCCs, the role played by charge transfer interactions for transmitting the "Fermi-hole" was recently discussed [5]. It is important to stress that currently the most used approach to quantify charge transfer interactions is the Natural Bond Orbitals (NBO) approach of Weinhold and coworkers [7]. This approach was also extended by Wilkens et al. [8] to decompose the FC term into localized natural molecular orbital contributions, dubbed the "Natural J-coupling method" (NJC).

In this article, some trends already studied for $^1J_{CH}$ and $^3J_{HH}$ SSCCs are briefly discussed, the former using a qualitative analysis of the expression of the FC contribution in terms of the polarization propagator formalism and the latter employing the NJC method as implemented in the NBO 5.0 program [9].

Theoretical Considerations

THE NJC METHOD

The natural J-coupling (NJC) method developed by Wilkens et al. [8] allows the analysis of the scalar FC contribution to J_{NM} on the basis of the NBO method [7] and in the framework of finite perturbation theory (FPT). Within this approach, the calculated FC contribution J^{FC} can be partitioned into three main parts:

$$J_{NM}^{FC} = J_{NM}^{Lewis} + J_{NM}^{deloc} + J_{NM}^{repol} \tag{1}$$

The Lewis part, J_{NM}^{Lewis}, includes the individual orbital contributions from the natural Lewis structure of the molecule. The delocalization part, J_{NM}^{deloc}, involves the terms or contributions from donor–acceptor interactions, i.e., effects of conjugative or hyperconjugative type:

$$J_{NM}^{deloc.} = \sum_i^{Lewis} \sum_j^{non\text{-}Lewis} J_{NM}^{\sigma_i \to \sigma_j^*} \tag{2}$$

where $J_{NM}^{\sigma_i \to \sigma_j^*}$ is the contribution to the FC SSCC from the donor–acceptor interaction $\sigma_i \to \sigma_j^*$. σ_i is a Lewis NBO and σ_j^* corresponds to an antibond or Rydberg type orbital. The repolarization part, J_{NM}^{repol}, is a residual and generally small part corresponding to correlation-like interactions. In this work, the repolarization part will be included together with the Lewis part. See Ref. [8b] for a more detailed explanation of these three parts.

As an example, the NJC method [8] is applied in this article to a set of ethyl derivatives (see Fig. 1). The vicinal SSCC, $^3J_{HH}$, of three of these molecules, i.e., thiopropanal (X = S), propanal (X = O), and 1-butene (X = CH_2) have been studied recently [5d]. The variation of the difference $^3J_{HH}(180°)$ $^3J_{HH}(0°)$ vs. the θ angle is qualitatively significant and was initially attributed to two main hyperconjugative interactions $^3J_{HH}^{\sigma_{C_\alpha - H_\alpha} \to \pi_{C=X}^*}$ and $^3J_{HH}^{\sigma_{C_\alpha - C_\beta} \to \pi_{C=X}^*}$ when they take place simultaneously. This rationalization was based on previous experience [5d] and, more qualitatively, on the analysis of the energetic impor-
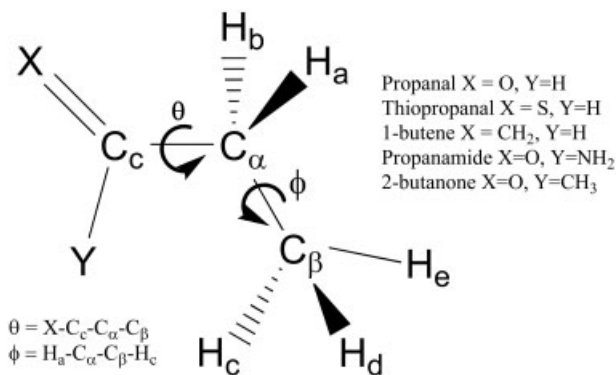
FIGURE 1. Structures of ethyl derivatives.

tance of donor–acceptor interactions which were estimated by using the NBO program (version 3.1) [7] through second-order perturbation theory:

$$\Delta E^{(2)}_{\sigma_i \to \sigma_j^*} = -2 \frac{< \sigma_i | \hat{F} | \sigma_j^* >}{\varepsilon_{\sigma_j^*} - \varepsilon_{\sigma_i}} \quad (3)$$

where $< \sigma_i | \hat{F} | \sigma_j^* >$ is the off-diagonal matrix element of the Fock or Kohn–Sham operator evaluated for σ_i (donor) and σ_j^* (acceptor) NBOs and ε_{σ_i} and $\varepsilon_{\sigma_j^*}$ are their respective energies. As the 5.0 version of the NBO program [8] allows to perform an NJC deconvolution of the FC term of SSCCs this program is now employed to verify whether the previous rationalization is supported by the NJC method. To this end, the FC SSCC contributions originating in each donor–acceptor interaction, Eq. (2) are studied.

Additionally, the dependence of $^3J_{HH}(\phi, \theta)$, see Figure 1, can be analyzed by a double Fourier series [10] on ϕ and θ which can be written as the sum of two parts,

$$^3J_{HH}(\phi, \theta) = {}^3J^\phi_{HH}(\phi) + {}^3J^{\phi,\theta}_{HH}(\phi, \theta) \quad (4)$$

$$^3J^\phi_{HH}(\phi) = C^C_{00} + \sum_{n=1}^{m}(C^C_{n0} \cos n\phi + S^C_{n0} \sin n\phi) \quad (5)$$

$$^3J^{\phi,\theta}_{HH}(\phi, \theta)$$
$$= \sum_{n=0}^{m}\sum_{p=1}^{m'}\left[\begin{array}{l} (C^C_{np} \cos p\theta + C^S_{np} \sin p\theta) \cos n\phi \\ + (S^C_{np} \cos p\theta + S^S_{np} \sin p\theta) \sin n\phi \end{array} \right] \quad (6)$$

In these equations, the maximum value for m and m' depends on the number of calculated cou-

plings. In this work, we got SSCCs for 12 values of ϕ and for 12 values of θ (0, 30, 60, …, 330°) and, therefore, the maximum value of m or m' is five. However, the coefficients K^L_{np} with values of n and p larger than three are small or negligible. For the set of couplings calculated in this work, each term in these equations is the product of a coefficient K^L_{np} by $\cos n\phi(K = C)$ or $\sin n\phi(K = S)$ and by $\cos p\theta(L = C)$ or $\sin p\theta(L = S)$. Equation (5) corresponds to an extended Karplus equation, which is the main contribution to $^3J_{HH}$, and independent on θ. Equation (6) represents the conformational substituent effect on $^3J_{HH}$, which depends on both ϕ and θ.

QUALITATIVE APPROACH BASED ON THE PP FORMALISM

The isotropic part of the SSCC tensor between nuclei N and M, also usually called the "scalar coupling," is made up from four different contributions [11],

$$J_{NM} = \frac{1}{3}Tr(J_{NM}) = J^{TO}_{NM} = J^{FC}_{NM} + J^{SD}_{NM} + J^{PSO}_{NM} + J^{DSO}_{NM} \quad (7)$$

i.e., Fermi contact (FC), spin dipolar (SD), paramagnetic spin-orbit (PSO), and diamagnetic spin-orbit (DSO) terms, respectively.

Although a similar analysis to that shown below can be carried out for the three second-order terms of Eq. (7), the present study is restricted to the FC term. It should be noted that the deconvolution of the DSO term into orbital contributions is straightforward because this can be considered as a "first order quantity." The following two points should be stressed: (i) the FC term is scalar, i.e., it is a zero-rank tensor; (ii) many couplings reported in the literature are dominated by the FC term. The first point makes the present analysis to be more easily understood and, therefore, a clearer description of this analysis can be achieved.

Within the polarization propagator (PP) approach and using the random phase approximation (RPA) the FC term of Eq. (7) can be expressed as,

$$J^{FC}_{NM} = \Omega^{FC} \sum_{ia,jb} U^{FC}_{ia,N}({}^3A - {}^3B)^{-1}_{ia,jb}U^{FC}_{jb,M} = \sum_{ia,jb}J^{FC}_{ia,jb}(N, M) \quad (8)$$

where Ω^{FC} contains, besides universal constants, the coupling nuclei magnetogyric ratios γ_N and γ_M, i

and j are occupied, whereas a and b are vacant molecular orbitals, MOs. As Eq. (8) is invariant under unitary transformations, MOs can be assumed to be Localized MOs (LMOs), where the localization procedure is carried out separately for occupied and vacant LMOs. $(^3A - {}^3B)_{ia,jb}$ are the triplet PP matrix elements and, consequently, $(^3A - {}^3B)_{ia,jb}^{-1} = W_{ia,jb}$ are the inverse triplet PP matrix, W; elements $U_{ia,N}^{FC}$ and $U_{jb,M}^{FC}$ are the "perturbators," i.e., the elements of the FC operator evaluated at the site of each coupling nucleus, e.g., $U_{ia,N}^{FC} = \langle i|\delta(\vec{r} - \vec{R}_N)|a \rangle$, that is, among other factors, they are sensitive to the s % character of the occupied i and the vacant a MOs [12] at the site of nucleus N.

In turn, the triplet matrices are given by

$$^3A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij} - \langle aj|bi \rangle \qquad (9)$$

and

$$^3B_{ia,jb} = \langle ab|ji \rangle \qquad (10)$$

where $\langle aj|ib \rangle = \int d^3r_1 d^3r_2 a^*(1)j^*(2)\,1/r_{12}\,i(1)b(2)$ are bielectronic molecular integrals.

It is emphasized that this analysis is only qualitative or at most semiquantitative, and it is sought to be adequate to predict trends of couplings along a series of compounds. However, in no case the RPA approximation is employed to obtain actual calculations of FC terms. It is known that the "diagonal" elements, i.e., $i = j$ and $a = b$, are the largest elements of the triplet PP matrix. According to Eq. (9) "energy gaps" between a vacant and an occupied LMO are only present in diagonal matrix elements. The next terms in importance are the "quasi" diagonal matrix elements, e.g., $i \neq j$ but $a = b$, and so on. It is observed that changes in each term of J_{NM}^{FC} along a series of compounds can originate in either the PP term or in the "perturbators" that can be sensitive to different types of intramolecular interactions.

Important qualitative insight into intramolecular interactions affecting the FC term of SSCCs, either through the PP or the "perturbator" terms can be obtained introducing the following approximations into Eq. (8): (i) it is assumed that LMOs in Eq. (8) show a behavior similar to NBO approach [7]; (ii) the orbital energy differences in the diagonal terms of the W matrix are notably larger than the corresponding bielectronic integrals. Bearing this in mind, it is clear that hyperconjugative interactions
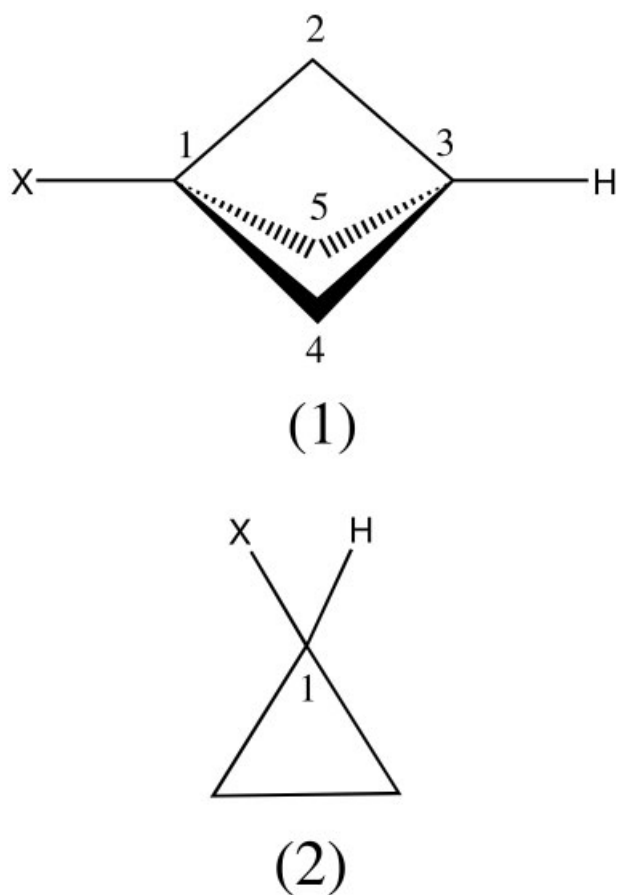

FIGURE 2. Structures of 1-X-bicyclo[1.1.1]pentane (1) and 1-X-cyclopropane (2) derivatives.

involving either the i or the a orbitals should affect the corresponding term in Eq. (8). It is recalled that, according to the perturbed molecular orbital (PMO) theory [13], if an occupied MO is involved in a hyperconjugative interaction its energy is "pushed down." On the other hand, if a vacant MO is involved in a hyperconjugative interaction its energy is "pushed up." Therefore, any of these two types of interactions would widen the $\Delta_{a,i} = (\varepsilon_a - \varepsilon_i)$ energy gap. Obviously, this effect should only influence the "diagonal" elements of $J_{ia,jb}^{FC}$ terms, i.e., those with $i = j; a = b$. When studying $^1J_{CH}$ SSCCs for 1-X-bicyclo[1.1.1]pentane and 1-X-cyclopropane derivatives (see Fig. 2), such term was dubbed the "bond contribution," J^b, and it was found to be positive for usual couplings of that type. Obviously, for such couplings other diagonal elements become irrelevant for this qualitative analysis since their respective perturbators render them too small.

Results and Discussion

HYPERCONJUGATIVE EFFECTS ON $^3J_{HH}$ IN ETHYL DERIVATIVES

A group of ethyl derivatives has been used as model to study the effect on the vicinal SSCCs $^3J_{HH}$ of hyperconjugative or delocalization interactions. Standard geometries [14] were used. The geometries have been generated driving the dihedral angle θ (see Fig. 1) on 30° steps from 0° to 330° for the staggered ($\phi = 180°$) and for the eclipsed ($\phi = 0°$) conformations of the ethyl moiety (24 geometries for each molecule). Additionally, for propanal the angle ϕ was also driven in 30° steps from 0° to 330° to obtain the complete conformational analysis. Both SSCCs and hyperconjugative interactions have been calculated at the B3LYP/TZVP level using the Gaussian 03 [15] and the NBO [8] programs. The combination of B3LYP functional [16] and TZVP basis set [17] has proved to give similar results [5d] to those of the SOPPA and CCSD(SOPPA) methods with larger basis sets for this type of molecules.

Total (TO) vicinal $^3J_{HH}^{TO}$ SSCCs in propanal (see Fig. 1) have recently been studied [5d]. The variation of the $^3J_{HH}^{TO}(\phi = 180°) - ^3J_{HH}^{TO}(\phi = 0°)$ difference, closely related with the C_1 Karplus or Fourier coefficient, was analyzed as a function of the θ angle (O-C_C-C_α-C_β), see Figure 1. That difference, which changes importantly with θ and gets negative values for some θ angles, was interpreted on the basis of hyperconjugative interactions. It should be noted that the sum of noncontact (NC) contributions (SD, PSO, and DSO) for the difference $^3J_{HH}^{NC}(\phi = 180°) - ^3J_{HH}^{NC}(\phi = 0°)$ is negative and, partially, the responsible of the negative value for the total difference $^3J_{HH}^{TO}(\phi = 180°) - ^3J_{HH}^{TO}(\phi = 0°)$. However, the NC difference is constant with the variation of the θ angle and the change of the difference for total couplings with θ only depends on the FC contribution. Now, we evaluate the effect of hyperconjugative interactions on the difference $^3J_{HH}^{FC}(\phi = 180°) - ^3J_{HH}^{FC}(\phi = 0°)$ using the NBO 5.0 program [8]. In Figure 3a, the FC contributions to $^3J_{HH}^{FC}(\phi = 0°)$ and $^3J_{HH}^{FC}(\phi = 180°)$, as well as their difference [Fig. 3(b)], are plotted vs. the θ angle. A variation larger than 2 Hz is obtained for $^3J_{HH}^{FC}(\phi = 180°) - ^3J_{HH}^{FC}(\phi = 0°)$ as θ changes. To analyze this variation, the sum of the effects of the hyperconjugative interaction, $^3J_{HH}^{deloc}(\phi = 180°) - ^3J_{HH}^{deloc}(\phi = 0°)$, are plotted in Figure 3(b), showing that, partially, the trend of the total FC contribu-

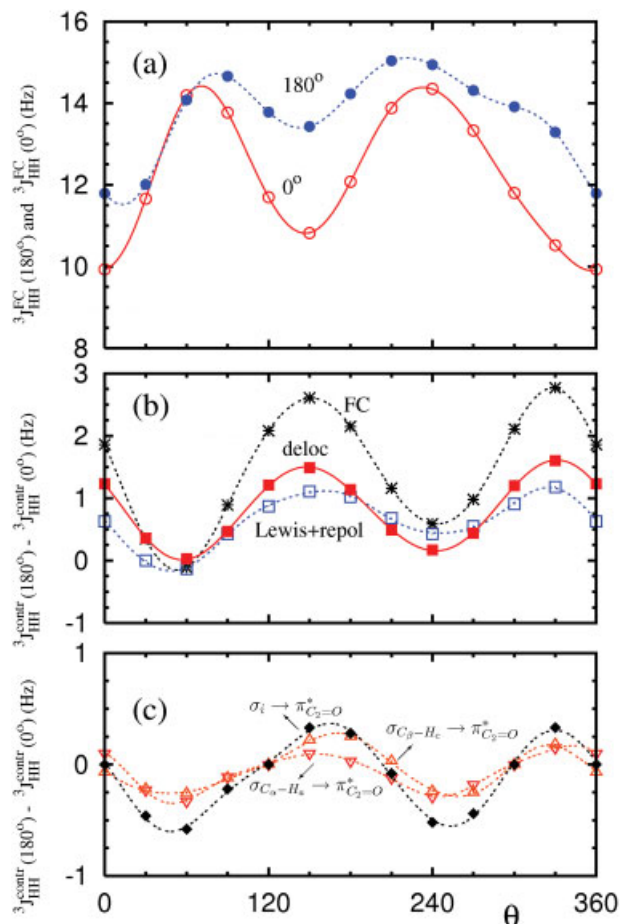**FIGURE 3.** Plots for propanal: (a) $^3J_{HH}^{FC}(0)$ (○) and $^3J_{HH}^{FC}(180)$ (●) (first row), (b) $^3J_{HH}^{FC}(180) - ^3J_{HH}^{FC}(0)$ (∗), $^3J_{HH}^{deloc}(180) - ^3J_{HH}^{deloc}(0)$ (■), and $^3J_{HH}^{Lewis+repol}(180) - ^3J_{HH}^{Lewis+repol}(0)$ (□), and (c) $^3J_{HH}^{\sigma_{C_\alpha-H_a}\to\pi^*_{C=O}}(180) - ^3J_{HH}^{\sigma_{C_\alpha-H_a}\to\pi^*_{C=O}}(0)$ (▽), $^3J_{HH}^{\sigma_{C_\beta-H_c}\to\pi^*_{C=O}}(180) - ^3J_{HH}^{\sigma_{C_\beta-H_c}\to\pi^*_{C=O}}(0)$ (△), and $\sum_i^{Lewis} {}^3J_{HH}^{\sigma_i\to\pi^*_{C=O}}(180) - ^3J_{HH}^{\sigma_i\to\pi^*_{C=O}}(0)$ (◆). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion is correctly represented by those interactions. It should be noted that the sum of Lewis and repolarization contributions, $^3J_{HH}^{Lewis}(\phi = 180°) - ^3J_{HH}^{Lewis}(\phi = 0°)$, also follows the same trend. Moreover, contributions from hyperconjugative interactions $^3J_{HH}^{\sigma_{C_\alpha-H_a}\to\pi^*_{C=O}}(180°) - ^3J_{HH}^{\sigma_{C_\alpha-H_a}\to\pi^*_{C=O}}(0°)$, $^3J_{HH}^{\sigma_{C_\beta-H_c}\to\pi^*_{C=O}}(180°) - ^3J_{HH}^{\sigma_{C_\beta-H_c}\to\pi^*_{C=O}}(0°)$, and $\sum {}^3J_{HH}^{\sigma_i\to\pi^*_{C=O}}(180°) - ^3J_{HH}^{\sigma_i\to\pi^*_{C=O}}(0°)$ are also plotted in Figure 3(c). Although the effect of the hyperconjugative interaction $\sigma_{C_\alpha-H_a}\to\pi^*_{C=O}$ was suggested previously [5d], the effect of the interaction $\sigma_{C_\beta-H_c}\to\pi^*_{C=O}$, that is energetically [Eq. (3)] negligible, seems to be important for the vicinal $^3J_{HH}$ whereas the effect of the hyperconjuga-
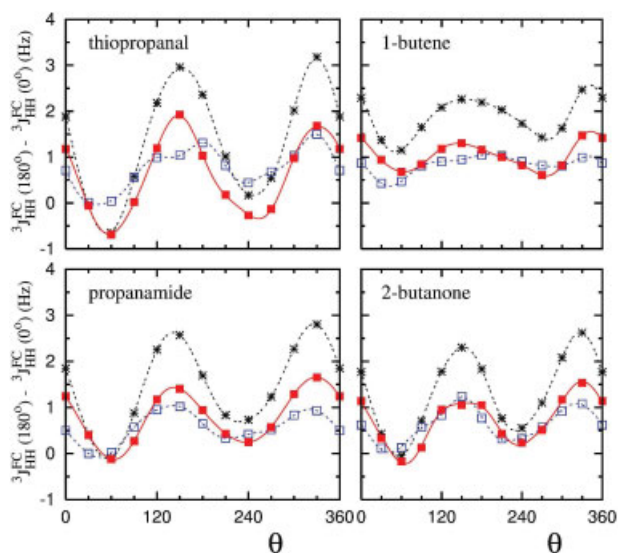
FIGURE 4. Plots of the difference $^3J_{HH}^{FC}(\phi = 180°)$ $- \, ^3J_{HH}^{FC}(\phi = 0°)$ (∗), NBO delocalization difference contribution (■) and NBO Lewis difference contribution (□) for labeled molecules. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion $\sigma_{C_\alpha—C_\beta} \rightarrow \pi^*_{C_c=o}$ is negligible. It is important to highlight that these terms define a new coupling pathway. In Figure 4, calculated $^3J_{HH}^{FC}(\phi = 180°) - \, ^3J_{HH}^{FC}(\phi = 0°)$, $^3J_{HH}^{deloc}(\phi = 180°) - \, ^3J_{HH}^{deloc}(\phi = 0°)$, and $^3J_{HH}^{Lewis}(\phi = 180°) - \, ^3J_{HH}^{Lewis}(\phi = 0°)$ contributions are plotted vs. θ for thiopropanal, 1-butene, propanamide, and 2-butanone. In these four compounds, the delocalization contribution follows the FC trend. In compounds with different X substituents (see Fig. 1), the $^3J_{HH}^{FC}(\phi = 180°) - \, ^3J_{HH}^{FC}(\phi = 0°)$ and $^3J_{HH}^{deloc}(\phi = 180°) - \, ^3J_{HH}^{deloc}(\phi = 0°)$ differences decrease from thiopropanal (X = S) to propanal (X = O) and to 1-butene (X = CH$_2$). This decrease was interpreted [5d] to be related with the electron acceptor behavior of the $\pi^*_{C=X}$ antibonding orbital which follows the order: $\pi^*_{C=S} > \pi^*_{C=O} > \pi^*_{C=CH_2}$. For the propanamide (X = O and Y = NH$_2$), the behavior is similar to that of propanal (X = O and Y = H) whereas for the 2-butanone (X = O and Y = CH$_3$) the variation of the differences are slightly smaller than for propanal.

The decomposition of $^3J_{HH}^{FC}$ into delocalized $^3J_{HH}^{deloc}$ and Lewis $^3J_{HH}^{Lewis}$ contributions (that of repolarization is negligible for propanal) has been studied by a double Fourier series, Eq. (4). Each of these three contributions (contr = FC, delocalized, and

Lewis) can be split into two components: one that only depends on ϕ, $^3J_{HH}^{\phi,contr}$ and another that depends on both ϕ and θ, $^3J_{HH}^{\phi,\theta contr}$ [see Eqs. (5) and (6)]. Values calculated at the B3LYP/TZVP level for propanal are represented in Figure 5. In the left column of Figure 5, the three components (FC, deloc., and Lewis) independent on θ, $^3J_{HH}^{\phi,contr}$, are plotted [Fig. 5(a–c)]. All of them follow the same typical Karplus shape with two maxima in 0° and 180° and two minima, one between 90° and 120° and, the other, symmetrically, between −90° and −120°. The delocalized part, $^3J_{HH}^{\phi,deloc}$, is approximately 20% of the total FC contribution, $^3J_{HH}^{\phi,FC}$, whereas the Lewis part is the remaining 80%. In the right column of Figure 5, the $^3J_{HH}^{\phi,\theta,FC}$ contribution and its two components (deloc. and Lewis) are also plotted; although their dependence on ϕ and θ are rather complicated, all three plots follow similar trends. The delocalization component, $^3J_{HH}^{\phi,\theta,deloc}$, is relatively more significant
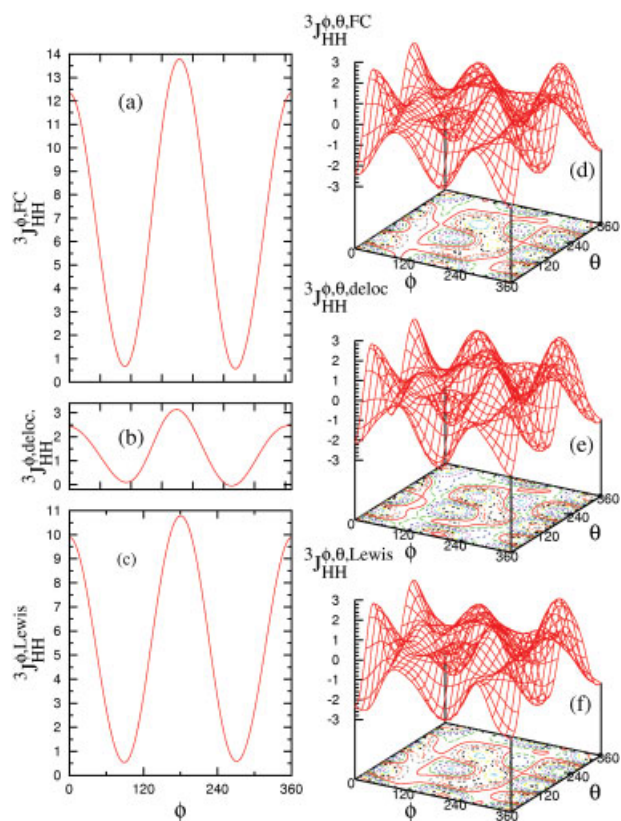

FIGURE 5. Contributions (in Hz) calculated at the B3LYP/TZVP level for propanal: (a) $^3J_{HH}^{\phi,FC}$, (b) $^3J_{HH}^{\phi,deloc}$, and (c) $^3J_{HH}^{\phi,Lewis}$ vs. ϕ angle, and (d) $^3J_{HH}^{\phi,\theta,FC}$, (e) $^3J_{HH}^{\phi,\theta,deloc} \times 3$, and (f) $^3J_{HH}^{\phi,\theta,Lewis} \times 3/2$ vs. ϕ and θ angles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

being close to $(1/3)\ ^3J_{HH}^{\phi,\theta,FC}$ whereas the Lewis contribution $^3J_{HH}^{\phi,\theta,Lewis}$ is the remaining part, i.e., $(2/3)$ $^3J_{HH}^{\phi,\theta,FC}$. To obtain similar plots, in Figure 5 the $^3J_{HH}^{\phi,\theta,deloc}$ contribution is multiplied by 3 and that of $^3J_{HH}^{\phi,\theta,Lewis}$ by 2/3.

J^b, J^{ob}, AND J^{oab} CONTRIBUTIONS TO $^1J_{CH}$ SSCCS

A series of very interesting $^1J_{C_3H}$ SSCCs was reported in 1-X-bicyclo[1.1.1]pentanes, (see 1 in Fig. 2). In fact, experimental values ranging from $^1J_{C_3H} = 156.3$ Hz for X = SnBu$_3$ to $^1J_{C_3H} = 181.2$ Hz for X = F were reported [18] and such changes could not be described as originating exclusively in the J^b part of the FC term. Therefore, the second most important term (actually there are three of them) in Eq. (8) was considered. This is the so called "other-bond contribution," J^{ob}, as dubbed previously, and is negative [6f]. From equations given earlier, such term can be written as

$$J^{ob} = W_{11^*,21^*}[U_{11^*,C}U_{21^*,H} + U_{11^*,H}U_{21^*,C}] \quad (11)$$

where 1 and 1* stand for the σ_{C_3-H} bond and antibonding orbital, respectively, and 2 stands for the $\sigma_{C_3-C_2}$ bonding orbital. The first term within the square brackets in Eq. (11) is notably smaller than the second one and, therefore, in a qualitative analysis it can be neglected. On the other hand, the W term in Eq. (11) does not contain any energy gap in its denominator. Therefore, we should have a close look at the $U_{11^*,H}U_{21^*,C}$ term in Eq. (11). It is observed that the largest experimental $^1J_{CH}$ SSCC corresponds to X = F and strong hyperconjugative interactions of $\sigma_{C_3-C_2} \rightarrow \sigma_{C_1-F}^*$ type are expected. These interactions should decrease the C_3 s % character of the $\sigma_{C_3-C_2}$ orbital, decreasing the absolute value of the J^{ob} contribution to $^1J_{C_3H}$ SSCCs, therefore, increasing its value as experimentally observed.

The analogous to Eq. (11) but for the "other antibond term," J^{oab}, is:

$$J^{oab} = W_{11^*,12^*}[U_{11^*,C}U_{12^*,H} + U_{11^*,H}U_{12^*,C}] \quad (12)$$

This corresponds to a positive contribution [6e] and when comparing both terms inside the square brackets it is observed that, again, the first term is much smaller than the second one. Therefore, to have a significant contribution for this term, strong hyperconjugative interactions into the 2* antibonding orbital should take place. Very recently, using this type of rationalization, it was concluded that in

1-X-cyclopropanes, (see 2 in Fig. 2), and because $\sigma_{C_1-X}^*$ is a very good electron acceptor, $^1J_{C_1H}$ SSCCs should have an important J^{oab} contribution. In fact, for cyclopropane the experimental value is $^1J_{CH} = 162.0$ Hz, whereas $^1J_{C_1H} = 192.7$ Hz for 1-F-cyclopropane [19].

Conclusions

SSCCs are now recognized as excellent molecular probes to study conjugative and hyperconjugative interactions and in this work two different approaches are described, which are supported with adequate either experimental or theoretical data. On the one hand, the NJC method of Weinhold et al., as implemented into the NBO 5.0 program, is used successfully to study in detail the electronic origin of the "inversion" of the Karplus relationship observed in some aminoacids, instead of the "normal" relationship, i.e., $^3J_{HH}(180°) > \ ^3J_{HH}(0°)$, the observed relationship indicates that in some cases $^3J_{HH}(180°) > \ ^3J_{HH}(0°)$ can hold [20]. In a previous article, it was inferred from propanal taken as a model compound, Figure 1, (X = O), that the carbonyl group close to the ethyl moiety defines a new coupling pathway for the FC term of such SSCCs through the simultaneous hyperconjugative interactions of types $\sigma_{C_\alpha-C_\beta} \rightarrow \pi_{C=O}^*$ by $\sigma_{C_\alpha-H_a} \rightarrow \pi_{C=O}^*$. Actually, this "activated" coupling pathway was not very surprising because it resembles that of homoallylic SSCCs, being the main discrepancy between the two, the different symmetry of the "intermediate" antibonding orbital. Present results indicate that a new hyperconjugative interaction of type $\sigma_{C_\beta-H_c} \rightarrow \pi_{C=O}^*$ is important for this coupling constant.

The conformational analysis of the $^3J_{HH}(\phi,\theta)$ couplings in propanal molecule shows that the substituent delocalization contribution $^3J_{HH}^{\phi,\theta,deloc}(\phi,\theta)$ is important and represents 1/3 of the total FC contribution, corresponding the remaining to the Lewis part. In the pure torsional dependence, the delocalization part $^3J_{HH}^{\phi,deloc}(\phi)$ is smaller, amounting 1/5 of total FC contribution.

In the second example, although discussions are based on $^1J_{CH}$ SSCCs, it can be appreciated that similar analyses are expected to hold for other types of one-bond SSCCs. Besides, this type of analysis can easily be extended to both two- and three-bond SSCCs.

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