

NMR spin-spin couplings involving nuclei in the neighborhood of a carbonyl group. $^3J_{\text{CH}}$ couplings in α -substituted acetamides

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In this work $^3J_{\text{CH}}$ spin-spin coupling constants (SSCCs) for the *cis*- and *trans*-conformers for α -X-acetamides (X = F, Cl, Br and CN) (1–4) were studied in detail since they were found to be notably different for both conformers. These differences are rationalized as originating in the changes of the strong negative hyperconjugative interactions that take place within the carbonyl group. Such changes are found to depend not only on conformation, but also on solvent. For the *cis*-conformers there is a close proximity between the X-substituent and the in-plane oxygen lone pair of pure p character, which affects notably their respective negative hyperconjugative interactions. Both the efficiency for transmitting the Fermi contact (FC) term through the coupling pathway of $^3J_{\text{CH}}$ SSCCs and its potential as a probe to study the stereochemical properties of the XH_2C group are discussed. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: FC transmission; $^3J_{\text{CH}}$ couplings; negative hyperconjugative interactions

Introduction

During the last decade there was a very important breakthrough both in experimental techniques to detect nuclear spin-spin coupling constants,^[1–4] SSCCs, as in theoretical approaches to calculate these spectroscopic parameters.^[5–9] These advances led to an increase in the understanding of how the non-relativistic four isotropic contributions to SSCCs,^[10,11] i.e. Fermi contact, FC, spin-dipolar (SD), paramagnetic spin-orbit (PSO), and diamagnetic spin-orbit (DSO), are transmitted through the molecular electronic structure. This is particularly true for the FC term whose transmission is known to be associated with the Fermi hole^[12–14] and delocalized interactions play an important role in its transmission, especially for long-range couplings.^[15]

$^2J_{\text{XY}}$ through a carbonylcarbon atom are unusually large and they correspond to a positively reduced SSCC, $^2K_{\text{XY}} > 0$;^[16] a few examples are displayed in Table 1, which were taken from the current literature.^[17–21] Recently,^[22] they were rationalized as originating in the FC contribution, which is dramatically increased due to the strong negative hyperconjugative interactions^[23] $n_{\text{O}} \rightarrow \sigma^*_{\text{C-X}}$ and $n_{\text{O}} \rightarrow \sigma^*_{\text{C-Y}}$ that take place within a carbonyl moiety, where n_{O} stands for the in-plane oxygen lone pair of pure p character. Recently, it was reported that such interactions are affected not only by interactions with proximate groups, but also they are slightly inhibited by a polar solvent.^[24]

From the above comments the following question arises, how SSCCs involving nuclei in the neighborhood of a carbonyl group are affected by the $n_{\text{O}} \rightarrow \sigma^*_{\text{C-X}}$ and $n_{\text{O}} \rightarrow \sigma^*_{\text{C-Y}}$ interactions that both involve the same lone pair orbital? In this series of papers, an answer to that question for different types of SSCCs as well as for different positions of the coupling nuclei relative to the carbonyl group will be sought. It is known that close to the region of a carbonyl group the α and β substituent effects on $^3J_{\text{CH}}$ SSCCs can be dramatic, as observed e.g. that

positive and negative contributions to such SSCCs for carbonyl and hydroxyl substituent groups can be as high as 5 Hz.^[25] This is a much larger effect than for similar $^3J_{\text{HH}}$ SSCCs, in spite of the smaller magnetogyric ratio for ^{13}C than for ^1H .^[26,27] In a previous paper^[28] the solvent effects in the conformational stability of four α -substituted acetamides were studied both from theoretical and experimental points of view. For the present purpose it must be mentioned that $^3J_{\text{CH}}$ SSCCs transmitted through the C–C–N–H_{syn} coupling pathway were found to strongly depend on the conformation of the substituted methyl group (substituents X = F, Cl, Br, CN) (Scheme 1) although the conformation of the C–C–N–H_{syn} coupling pathway remains *antiperiplanar*. For this reason such compounds are considered in this work as excellent examples for finding an adequate rationalization for such an unusual behavior, specially seeking to understand the role played by the $n_{\text{O}} \rightarrow \sigma^*_{\text{C-X}}$ and $n_{\text{O}} \rightarrow \sigma^*_{\text{C-Y}}$ interactions that take place within the carbonyl group. In this work it is studied how hyperconjugative interactions depend on the conformation of the substituted methyl group. Such interactions are studied with the natural bond orbital (NBO) method of Weinhold *et al.*^[29,30]

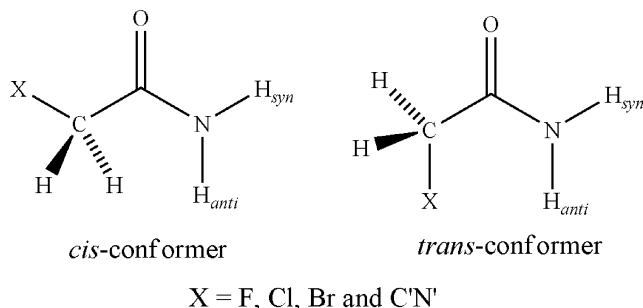
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Table 1. Some experimental values (taken from the literature) of *geminal* couplings through the C atom of a carbonyl group

X	Y	$^2J_{XY}$	(in Hz)	Ref.
H	H	$^2J_{HH}$	46	[17]
H	CH ₃	$^2J_{HC}$	26.7	[18]
CH ₃	CH ₃	$^2J_{CC}$	15	[19]
CH ₃	NH ₂	$^2J_{NC}$	9.5	[20]
CH ₃	F	$^2J_{FC}$	61	[16]
H	OCH ₃	$^2J_{OH}$	38	[21]

**Scheme 1.** α -substituted-acetamides: 1 (F), 2 (Cl), 3 (Br) and 4 (CN).

Results and Discussion

In the previous paper^[28] it was reported that compounds **1–4**, when considering them as isolated molecules, present two stable conformers (*cis*- and *trans*-), where the *trans*-form is the most stable for these four compounds. However, when considering polar solvent effects as given by the PCM model, ($\epsilon = 36.6$),^[31–33] compound **3** presents the *gauche*- and *trans*-conformers as the most stable forms, while for compound **4** the *cis*- form is preferential, followed by the *trans*-one.

For the sake of completeness in Table 2 are reproduced^[28] total calculated and experimental $^3J_{CH}$ SSCCs for compounds **1–4**, which are by far dominated by the FC term. Calculations for *cis*- and *trans*-conformations were obtained at the B3LYP/EPR-III//aug-cc-pVTZ level both for an isolated molecule and for an infinitely diluted acetonitrile solution, SSCC calculations were also performed using the B971 functional, but those obtained using B3LYP are in better agreement with experimental values.

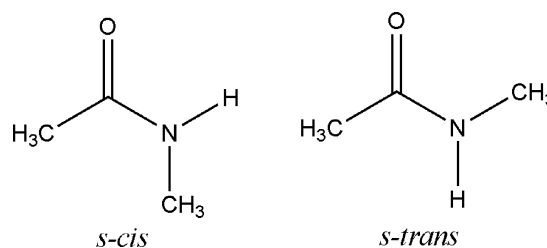
In all four cases calculated $^3J_{CH}$ SSCCs are notably larger for *cis*- than for *trans*-conformers, showing that such differences are practically the same when calculations are carried out with $\epsilon = 1$ and 36.6. It is also noteworthy that for compound **4** such a difference is smaller than for the halogenated compounds, **1–3**. As shown previously,^[28] agreement between calculated and measured SSCCs is very good when calculations are carried out at the preferential conformation.

Since $^1H\gamma/^{13}C\gamma = 3.9761$, *vicinal* SSCCs displayed in Table 2 are notably larger than $^3J_{HH}$ SSCCs transmitted through an H–C–N–H coupling pathway. Comparing the product $(^1H\gamma/^{13}C\gamma)J_{CH}$ for SSCCs displayed in Table 2, with those calculated by Perera and Bartlett^[34] using the EOM–CCSD method^[35–38] for $^3J_{HNHMe}$ in *s-cis*- and *s-trans*-*N*-methylacetamide (Scheme 2). Perera and Bartlett performed such calculations for different angles, ϕ , around the *N*–Me bond and fitted their values with a Karplus-like equation, obtaining Eqn (1) for the *s-cis*-conformer and Eqn (2) for the *s-trans*-conformer. For SSCCs in Table 2, it is obtained

Table 2. Calculated (at the B3LYP/EPR-III//aug-ccpVTZ level) and measured (in acetonitrile, $\epsilon = 36.6$) $^3J_{CH}$ in compounds **1–4** (Taken from Ref. [28])

Compound	<i>Cis</i> -conformers		<i>Trans</i> -conformers		Exp.
	$\epsilon = 1.0$	$\epsilon = 36.6$	$\epsilon = 1.0$	$\epsilon = 36.6$	
1	11.4	11.6	5.7	5.7	6.2
2	11.1	11.6	7.3	7.2	8.0
3	10.8	9.2 ^a	7.7	7.4	8.6
4	9.2	9.7	7.6	7.6	8.8

^a *Gauche* conformer.

**Scheme 2.** *N*-methylacetamide, *s-cis*- and *s-trans*-conformations.

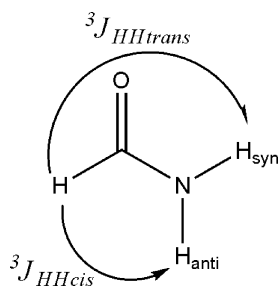
$(^1H\gamma/^{13}C\gamma)J_{CH} = 45.3$ Hz for the *s-cis*-conformer of **1**, while Eqn (1) yields $^3J_{HNHMe}(\phi = 180^\circ) = 9.96$ Hz, and Eqn (2) yields 11.15 Hz.

$$^3J_{HNHMe}(\text{in Hz}) = (8.09 \pm 0.42) \cos^2 \phi - (1.17 \pm 0.16) \cos \phi + (0.70 \pm 0.31) \quad (1)$$

$$^3J_{HNHMe}(\text{in Hz}) = (9.27 \pm 0.20) \cos^2 \phi - (1.19 \pm 0.08) \cos \phi + (0.69 \pm 0.15) \quad (2)$$

The efficiency for transmitting the FC term in compounds **1–4** is dramatically different than those for the *s-cis*- and *s-trans*-conformers of *N*-methylacetamide. Therefore, in this work adequate rationalizations are sought not only for the large difference of the $^3J_{CH}$ SSCCs in *cis*- and *trans*-conformers but also on such different efficiencies.

As mentioned above, very strong $n_O \rightarrow \sigma^*_{C-C}$ and $n_O \rightarrow \sigma^*_{C-N}$ interactions take place in compounds **1–4**. Moreover, recently,^[39] it was reported that in a peptide fragment the calculation of the $^3J_{C'H\beta}$ SSCC, where *C'* stands for the carbonylcarbon atom, for torsion angles $\phi = 0^\circ$ and $\phi = 180^\circ$ led to values of 6.23 and 8.57 Hz, respectively. Their coupling pathways are also very efficient since $(^1H\gamma/^{13}C\gamma)J_{C'H\beta}(\phi = 0^\circ) = 24.77$ Hz and $(^1H\gamma/^{13}C\gamma)J_{C'H\beta}(\phi = 180^\circ) = 34.08$ Hz. This suggests that a strong charge-transfer interaction into the $\sigma^*_{C'-C\alpha}$ antibonding orbital increases notably the efficiency of such coupling pathway. It is also known^[22] that for a *cis*-coupling pathway of type H–C–C–H a charge-transfer interaction into the σ^*_{C-C} antibonding orbital reduces the efficiency for the corresponding $^3J_{HH}$ SSCC. A point in case is the *vicinal* $J_{H_2H_3}$ in pyridine whose experimental value amounts to only 4.84 Hz,^[40] while the analogous coupling in benzene derivatives is *ca* 7–8 Hz. Similarly, in formamide (Scheme 3), *cis*- $^3J_{HH} = 2.25$ Hz, while *trans*- $^3J_{HH} = 13.90$ Hz.^[41] The H–C–N–H Karplus-like relationship of Hu and Bax^[42] yields 7.22 and 10.06 Hz, respectively. This suggests that in formamide, Scheme 3, the *cis*-SSCC is notably reduced, while the *trans*-SSCC is notably increased, probably, as a consequence of the strong



Scheme 3. Notations of atoms and spin–spin coupling constants in formamide.

Table 3. Comparison of calculated ($\epsilon = 1$) hyperconjugative interactions (kcal mol^{-1}) involving either bonding or antibonding orbitals belonging to the ${}^3J_{\text{CH}}$ coupling pathway for the *cis*- and *trans*-conformers of compounds **1–4**. The three negative hyperconjugative interactions values calculated with $\epsilon = 36.6$ are also shown in the lowest three rows

	1		2		3		4	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>Trans</i>
$\epsilon = 1$								
$n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$	25.9	22.9	26.4	22.8	25.6	22.4	27.0	24.7
$n_{\text{X}} \rightarrow \sigma_{\text{C-C}}^*$	8.1	7.4	6.1	5.7	5.2	4.8	–	–
$n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$	25.6	24.9	26.0	24.0	26.0	22.9	25.6	24.5
$\sigma_{\text{C-C}} \rightarrow \sigma_{\text{NHsyn}}^*$	3.1	3.3	3.0	3.1	3.0	3.0	3.0	3.0
$\sigma_{\text{C-X}} \rightarrow \sigma_{\text{C-N}}^*$	1.4	<0.5	2.7	<0.5	3.1	<0.5	2.4	<0.5
$\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C-N}}^*$	<0.5	1.6	<0.5	1.9	<0.5	2.0	<0.5	1.7
$\epsilon = 36.6$								
$n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$	23.6	21.4	24.6	21.2	24.2 ^a	21.2	25.2	23.1
$n_{\text{X}} \rightarrow \sigma_{\text{C-C}}^*$	7.6	7.4	5.7	5.7	5.0 ^a	4.8	–	–
$n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$	23.0	23.2	23.2	22.2	23.4 ^a	21.9	23.0	22.7

^a *Gauche* conformer.

$n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-H}}^*$ interactions. Considerations presented above, suggest comparing the *cis*- and *trans*-conformers of **1–4**, the main hyperconjugative interactions involving either bonding or antibonding orbitals belonging to the ${}^3J_{\text{CH}}$ SSC coupling pathway. These interactions are displayed in Table 3 for calculations performed taking $\epsilon = 1$ and 36.6, where several features of those data are worth commenting.

The $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions, for $\epsilon = 1$, are remarkably different for *cis*- and *trans*-conformers, such difference being larger for the former than for the latter. Taking into account the comments made above, the differences between calculated ${}^3J_{\text{CH}}$ SSCs for *cis*- and *trans*-conformers can be rationalized as originating from different hyperconjugative interactions into both $\sigma_{\text{C-C}}^*$ and $\sigma_{\text{C-N}}^*$ antibonding orbitals, belonging to the coupling pathway. In compounds **1–3** the $n_{\text{X}} \rightarrow \sigma_{\text{C-C}}^*$ interaction is also somewhat larger for the *cis*- than for the *trans*-conformer.

The rationalization made above about the difference between ${}^3J_{\text{CH}}$ SSCs, in the *cis*- and *trans*-conformers, suggests that large charge-transfer interactions into the $\sigma_{\text{C-C}}^*$ and $\sigma_{\text{C-N}}^*$ antibonding orbitals belonging to the ${}^3J_{\text{CH}}$ coupling pathway increase its ability for transmitting its FC term. Since such interactions are unusually strong, although different for both conformers, a similar rationalization for the relationship of $({}^1\text{H}\gamma/{}^{13}\text{C}\gamma)$ ${}^3J_{\text{CH}}$ in **1–4** being much larger than ${}^3J_{\text{HNHMe}}$ ($\phi = 180^\circ$) in *N*-methylacetamide,

i.e. the notably larger efficiency for the former than that of the latter pathway, originates mainly in the $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions, which are present in the **1–4** compounds.

The large difference, between the $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions for the *cis*- and *trans*-conformers of **1–4**, suggests that for the former rotamer there is a close proximity between the n_{O} and the in-plane halogen lone pair in **1–3**, and to the cyano moiety in **4**. These proximities seem to enhance the $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions increasing the efficiency of the ${}^3J_{\text{CH}}$ coupling pathway. For **1–3** this proximity seems also to overlap the in-plane oxygen and halogen lone-pairs, which may lead to a repulsive interaction, defining the *trans*- conformation for $\epsilon = 1$, as preferential. For a polar solvent, $\epsilon = 36.6$, a shielding of the $n_{\text{O}}-n_{\text{X}}$ interaction is expected, and it seems to be important enough to define as preferential, in **3** and **4**, the *gauche*- and *cis*-conformations, respectively. Apparently, the solvent effect is working in two different ways, on the one hand, it shields the electrostatic interaction between both proximate moieties, and on the other hand, the $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$, $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ and $n_{\text{X}} \rightarrow \sigma_{\text{C-C}}^*$ interactions are slightly inhibited as shown previously.^[43,44]

Concluding Remarks

The study presented above suggests that ${}^3J_{\text{CH}}$ SSC in **1–4** is an adequate probe to study the stereochemistry of the α -substituent, due to the following reasons.

1. The studied SSC includes the C–C–N fragment into its coupling pathway, where the corresponding antibonding orbitals, $\sigma_{\text{C-C}}^*$ and $\sigma_{\text{C-N}}^*$ undergo very strong, $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions. These interactions determine that the C–C–N– H_{syn} coupling pathway of ${}^3J_{\text{CH}_{\text{syn}}}$ is very efficient for transmitting its FC term. This large efficiency is easily altered, since small perturbations can lead to significant changes in this SSC.
2. In compounds **1–4**, perturbations into the ${}^3J_{\text{CH}}$ coupling pathway are introduced in the *cis*- conformers by the close proximity between the X-substituent and the in-plane n_{O} lone pair with pure p character, which enhances the $n_{\text{O}} \rightarrow \sigma_{\text{C-C}}^*$ and $n_{\text{O}} \rightarrow \sigma_{\text{C-N}}^*$ interactions.
3. Solvent effects on those interactions are very important, and seem to be working in two different ways, (i) shielding the electrostatic part of the steric interaction; (ii) inhibiting the negative hyperconjugative interactions.^[45]
4. In this work, it was not possible to detect any ${}^3J_{\text{CH}_{\text{anti}}}$ SSC and theoretical calculations yielded a value close to 0 Hz. This calculated value is in agreement with the trend commented above for analogous ${}^3J_{\text{HH}}$ couplings in formamide, where lower efficiency than ‘normal’ was observed when the coupling pathway corresponds to a *cis*-configuration, while an efficiency larger than ‘normal’ was observed for a *trans*-conformation of the coupling pathway.

Experimental and Computational Details

Experimental and computational details are given in Ref. [28] where the measurement and the calculations of ${}^3J_{\text{CH}}$ and NBO in compounds **1–4** were reported.

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