

Substituent effect on $^1J_{CH}$ in benzaldehyde derivatives

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Abstract: NMR spin–spin coupling constants (SSCCs) can lead to insights about the electronic structure of molecules when experimental NMR data are combined with quantum mechanical calculations [1]. This is possible because theoretically, the SSCCs can be decoded in different components of the SSCCs mechanism, which allows the identification of “steric” or “hyperconjugative” origin [2]. In this work, the $^1J_{CH}$ of the formyl group for the substituted benzaldehydes with distinct electronic character in *ortho*, *meta*, and *para* positions were evaluated (Table 1). J -coupling constants and their decompositions were calculated using the method described by Autschbach [3] with the CPL module of ADF package using PBE0 functional and jcpl basis set. Experimental and theoretical results indicated that there is a significant increase on the SSCC when substituents are in *ortho* position, except for hydroxy and methyl groups, compared to benzaldehyde. To understand the origin of this increase, the theoretical SSCCs of these compounds were decomposed into NLMOs contributions that are calculated in Lewis and non-Lewis terms. For halogenates and methoxy substituents, *anti*-conformers are more populated (> 86%) than *syn*-conformers. So, in these cases, the observed SSCCs can be described by the *anti*-conformers and the $^1J_{CH}$ couplings increased for these conformers. The decomposition analysis showed that this increase on $^1J_{CH}$ occurs in the Lewis (L) term of the formyl σ_{C-H} NLMO contribution, suggesting that steric effects are more pronounced than conjugative one. This proposal is supported by two observations: the first one is an increase of s characters on the carbon of formyl C-H bond (about 1%) and on LP_2 for the *ortho* substituent (< 0.2%), indicating an electronic rearrangement to “accommodate/stabilize” electronic density into internal orbitals, and the second one is an increase on $H_f-C_f-C_b$ bond angle, in response of the steric interaction between the formyl C-H bond orbital and the substituent’s lone pairs. The *syn*-conformers showed no significant change on $^1J_{CH}$ compared to benzaldehyde, but the L and NL components of the C-H formyl NLMO contribution showed important variations that are compensated because these terms have opposed signals. These results can be explained by changes in electronic interaction of σ_{C-H} and $\sigma^*_{C_b-CX}$ (C_b is the benzyl carbon bonded to the formyl group and X is the *ortho* substituent) that contribute positively for NL term and, in response, negatively for L term. When benzaldehydes have two *ortho*-substituents, the increase on $^1J_{CH}$ can be interpreted by steric effects on *anti*-conformers contributions for the total SSCC and a balance of steric and delocalization effects on *syn*-conformers. For example, in *o,o*-difluorobenzaldehyde there are no significant delocalization contributions in response of fluorine substituents so, steric effects explain the total $^1J_{CH}$. However, for *o,o*-dichlorobenzaldehyde delocalization contributions (NL term) are as important as steric (L term).



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Table 1: Experimental, theoretical $^1J_{CH}$ and its decomposition contributions changes compared to benzaldehyde for benzaldehyde derivatives and conformers population.

Compound	pop. <i>syn</i>	$^1J_{CH}$ <i>syn</i>	$\Delta\sigma C-H^L$ <i>syn</i>	$\Delta\sigma C-H^{NL}$ <i>syn</i>	pop. <i>anti</i>	$^1J_{CH}$ <i>anti</i>	$\Delta\sigma C-H^L$ <i>anti</i>	$\Delta\sigma C-H^{NL}$ <i>anti</i>	Δ^1J_{CH} teor.	Δ^1J_{CH} exp.
benzaldehyde	-	-	0	0	-	-	0	0	0	0
<i>o</i> -fluorob.	13.5	178.9	-2.5	5.4	86.5	186.2	10.3	-1.8	9.2	8.2
<i>o</i> -chlorob.	5.8	179.6	-10.6	13.7	94.2	188.7	13.8	-3.6	12.4	8.8
<i>o</i> -bromob.	5.3	180.1	-15.7	19.0	94.7	188.5	12.7	-2.5	12.3	7.1
<i>o</i> -iodob.	7.6	180.7	-14.5	17.9	92.4	186.8	7.9	1.3	10.5	7.1
<i>o</i> -methoxyb.	4.2	175.0	-18.6	17.7	95.8	185.7	5.3	2.7	9.5	6.6
<i>o</i> -hydroxyb.	93.9	176.9	-7.4	7.4	6.1	185.8	6.1	1.9	1.6	2.4
<i>o</i> -methylb.	70.2	174.4	-0.6	1.2	29.8	175.8	-15.8	16.5	-1.0	-1.1
<i>o</i> -nitrob.	2.8	187.2	-5.5	15.3	97.2	203.1	23.4	-1.8	26.8	18.3
<i>o,o</i> -difluorob.	-	-	10.6	1.1	-	-	10.6	1.1	14.1	12.8
<i>o,o</i> -dichlorob.	-	-	-4.4	12.8	-	-	-4.4	12.8	10.5	13.7
<i>o</i> -chloro, <i>o</i> -fluorob.	39.1	190.9	-1.9	14.1	60.9	191.4	12.6	0.3	15.4	13.4
<i>o</i> -bromo, <i>o</i> -fluorob.	44.6	190.9	-7.2	19.3	55.4	191.3	13.1	-0.3	15.3	13.3
<i>o</i> -fluoro, <i>o</i> -iodob.	48.1	191.3	-10.5	22.7	51.9	188.8	10.2	0.7	14.2	12.1
<i>m</i> -fluorob.	55.7	178.3	-	-	44.3	178.6	-	-	2.6	2.5
<i>m</i> -chlorob.	51.8	178.6	-	-	48.2	179.4	-	-	3.2	2.6
<i>m</i> -bromob.	51.9	178.7	-	-	48.1	179.2	-	-	3.1	1.4
<i>m</i> -iodob.	49.2	178.4	-	-	50.8	179.2	-	-	3.0	-
<i>m</i> -methoxyb.	44.4	177.1	-	-	55.6	177.0	-	-	1.2	0.6
<i>m</i> -hydroxyb.	69.1	177.3	-	-	30.9	176.4	-	-	1.2	1.0
<i>m</i> -methylb.	52.6	175.7	-	-	47.4	175.7	-	-	-0.1	-0.5
<i>m</i> -nitrob.	41.3	180.4	-	-	58.7	182.6	-	-	5.9	5.1
<i>m,m</i> -difluorob.	-	-	-	-	-	-	-	-	5.3	5.1
<i>p</i> -fluorob.	-	-	-	-	-	-	-	-	0.7	0.6
<i>p</i> -chlorob.	-	-	-	-	-	-	-	-	1.7	1.3
<i>p</i> -bromob.	-	-	-	-	-	-	-	-	1.6	1.4
<i>p</i> -iodob.	-	-	-	-	-	-	-	-	1.7	1.4
<i>p</i> -methoxyb.	-	-	-	-	-	-	-	-	-2.1	-1.9
<i>p</i> -hydroxyb.	-	-	-	-	-	-	-	-	-1.1	-1.6
<i>p</i> -methylb.	-	-	-	-	-	-	-	-	-0.9	-1.1
<i>p</i> -nitrob.	-	-	-	-	-	-	-	-	5.7	4.8

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