

## The Perlin Effect in terms of molecular orbitals

Kahlil Schwanka Salome, Cláudio Francisco Tormena

*Institute of Chemistry – University of Campinas*

**Abstract:** Many studies have shown the importance of scalar spin-spin coupling constants (SSCCs) obtained by NMR spectroscopy in conformational analysis of molecules, in cyclohexane derivatives SSCCs are used to determine conformation and relative stereochemistry [1]. For instance, in 1,3-dioxane (**1**, figure 1) the  $^1J_{C_1-H_{ax}}$  is smaller than  $^1J_{C_1-H_{eq}}$  and in 1,3-dithiane (**2**, figure 1) the  $^1J_{C_1-H_{ax}}$  is larger than  $^1J_{C_1-H_{eq}}$ . These differences are known as Perlin and reverse-Perlin effect respectively and are usually interpreted in terms of hyperconjugation effects such as  $LP_O \rightarrow \sigma^*_{C_1-H_{ax}}$  and  $\sigma_{C-S} \rightarrow \sigma^*_{C_1-H_{eq}}$ , which are reflected in the bond length of the  $C_1-H_{ax}$  and  $C_1-H_{eq}$  [2]. Although these interpretations seem reasonable, it is not compatible with computational results. In both compounds, not only for **1**, the calculated bond length and hyperconjugation effects are larger for  $C_1-H_{ax}$  than  $C_1-H_{eq}$ , so, considering only the classical explanation of Perlin effect, both  $^1J_{C_1-H_{ax}}$  should be larger than  $^1J_{C_1-H_{eq}}$ , but this is not what experimental results show (table 1). Also, when comparing both molecules, one can clearly see the small difference in  $^1J_{C_1-H_{ax}}$  and the large difference in  $^1J_{C_1-H_{eq}}$  between both molecules. Therefore, the aim of this work is to study the origins of Perlin effect for **1** and **2**. In order to do that, the structures were optimized and the SSCCs were calculated and decomposed using the ADF 2017 program with several levels of theory. To understand the effects responsible for these SSCCs, the  $J$ -couplings were analyzed in terms of molecular orbitals (MO) and its natural bond orbitals (NBO) contributions. Both  $^1J_{C_1-H_{ax}}$  are similar, and this decomposition revealed that the MOs relevant for  $J$ -coupling are constituted of analogous NBOs, resulting in close values of SSCC, and surprisingly, the LP (**2**) has a very small contribution for **1** and **2** in these MOs. In fact, LP (**1**) showed a greater contribution than LP (**2**) for both cases. For the  $^1J_{C_1-H_{eq}}$ , the decomposition showed more delocalized MOs in **2**, meaning that more NBOs contribute to the total SSCC in **2** than in **1**. Moreover, the MOs which contributes the most to the SSCC presented a decrease in the contribution of  $\sigma_{C_1-H_{eq}}$  and an increase of adjacent NBOs. Decreasing the  $\sigma_{C_1-H_{eq}}$  contribution, lowers the total value of  $^1J_{C_1-H_{eq}}$  and at the same time, increasing adjacent NBOs contributions to MOs, also lowers the  $^1J_{C_1-H_{eq}}$  since the contribution of these orbitals to  $^1J_{C_1-H_{eq}}$  is negative (table 2), as stated in the literature [3,4]. With this work, we were able to identify the origin of Perlin effect in **1** and **2** and attribute it to contributions of MOs, mainly to the  $\sigma_{C_1-H_{eq}}$ .

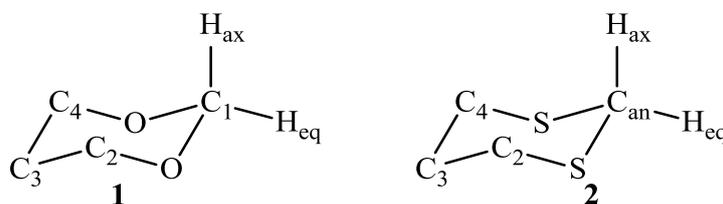


Figure 1: compounds studied in this work



# XIX SBOQT

Simpósio Brasileiro de Química Teórica 2017

12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Table 1:  $^1J_{C_1-H}$  and bond length values of **1** and **2**.

Molecule/bond	Bond length (theor) <sup>a</sup>	$^1J_{C_{an}-H}$ (expt) <sup>b</sup>	$^1J_{C_{an}-H}$ (theor) <sup>c</sup>
<b>1</b> /C <sub>1</sub> -H <sub>ax</sub>	1.102	158.6	154.3
<b>1</b> /C <sub>1</sub> -H <sub>eq</sub>	1.085	167.5	168.6
<b>2</b> /C <sub>1</sub> -H <sub>ax</sub>	1.902	154.2	157.0
<b>2</b> /C <sub>1</sub> -H <sub>eq</sub>	1.089	146.2	145.8

<sup>a</sup>optimized with MP2/aug-cc-pvdz. <sup>b</sup>obtained at -80°C in CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup>calculated with pbe0/jcpl

Table 2: contributions of selected MOs to SSCC and its NBOs.

1, C-Heq			2, C-Heq		
MO	Contribution to SSCC (Hz)	Main NBO contribution to MO	MO	Contribution to SSCC (Hz)	Main NBO contribution to MO
3	-10.4	CR (1) O (99%)	3	-10.6	CR (1) S (99%)
7	10.9	C <sub>1</sub> -O (44%)	15	16.8	C <sub>2/4</sub> -C <sub>3</sub> (26%)
9	16.9	C <sub>2/4</sub> -C <sub>3</sub> (46%)	16	47.4	C <sub>2/4</sub> -C <sub>3</sub> (28%)
11	80.3	C <sub>1</sub> -Heq (17%)	18	56.9	C <sub>1</sub> -Heq (15%)
12	12.8	C <sub>1</sub> -Hax (21%)	20	22.9	C <sub>2/4</sub> -Hax (34%)
13	16.1	C <sub>1</sub> -Heq (26%)	21	10.4	C <sub>2/4</sub> -Heq (53%)
15	-1.1	C <sub>1</sub> -Hax (37%)	22	-5.2	C <sub>1</sub> -Hax (31%)
16	23.1	C <sub>3</sub> -Heq (47%)	23	16.2	C <sub>3</sub> -Heq (39%)
18	-8.7	C <sub>1</sub> -Heq (24%)	26	-20.2	C <sub>1</sub> -S (36%)
21	28.8	C <sub>1</sub> -Heq (17%)	30	11.2	C <sub>2/4</sub> -S (38%)
Total	168.6		Total	145.8	

**Key-words:** Perlin effect, *J*-coupling decomposition, molecular orbitals.

**Support:** This work has been supported by CAPES, CNPq, FAPESP

**References:**

- [1] Tormena, C. F., Prog. Nuc. Mag. Reson. Spec. 96, 73 (2016).
- [2] Juaristi, E. and Cuevas, G., Acc. Chem. Res. 40, 961 (2007).
- [3] Neto, A. et. al. The J. Phys. Chem. A. 112, 11956 (2008).
- [4] Contreras, R. et. al. Int. J. of Quant. Chem. 110, 532 (2010).