Coupling Constants

The Origin of One-Bond C–H Coupling Constants in OCH Fragments: Not Primarily $n_O \rightarrow \sigma^*_{CH}$ Delocalization**

Gabriel Cuevas, Karina Martínez-Mayorga, María del Carmen Fernández-Alonso, Jesús Jiménez-Barbero, Charles L. Perrin,* Eusebio Juaristi, and Néstor López-Mora*

One-bond coupling constants $^1J_{CH}$ for axial bonds adjacent to oxygen or nitrogen atoms in molecules with chair conformers are smaller than for equatorial bonds. This is known as the Perlin effect[1] and is useful for assigning the stereochemistry of carbohydrates. It is generally interpreted in terms of $n_O \rightarrow \sigma^*_{CH}$ delocalization.[2] In tetrahydropyran (**1**) this corresponds to a resonance form (Figure 1) that weakens the axial C–H

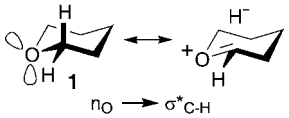

Figure 1. $n_O \rightarrow \sigma^*_{CH}$ delocalization and double bond–no bond resonance in tetrahydropyran.

[*] Dr. G. Cuevas, K. Martínez-Mayorga, N. López-Mora
Instituto de Química
Universidad Nacional Autónoma de México
Cd. Universitaria
Apdo. Postal 70213, 04510, México, D.F. (Mexico)
Fax: (+52) 55-5616-2217

Dr. C. L. Perrin
Department of Chemistry
University of California-San Diego
La Jolla, CA 92093-0358 (USA)
Fax: (+1) 858-534-2164
E-mail: cperrin@ucsd.edu

M. C. Fernández-Alonso, Dr. J. Jiménez-Barbero
Centro de Investigaciones Biológicas
Consejo Superior de Investigaciones Científicas
c/Ramiro Maetzu 9, 28040, Madrid (Spain)

Dr. E. Juaristi
Departamento de Química
Centro de Investigación y de Estudios Avanzados
del Instituto Politécnico Nacional
Apdo. Postal 14-740, 07000 México, D.F. (Mexico)
E-mail: gecgb@servidor.unam.mx

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Supporting information for this article (separation of $^1J_{CH}$ values into Fermi contact, paramagnetic spin-orbit, and diamagnetic spin-orbit contributions; variation of d_{CH} with HCOC dihedral angle; coordinates of tetrahydropyran conformers) is available on the WWW under http://www.angewandte.org or from the author.

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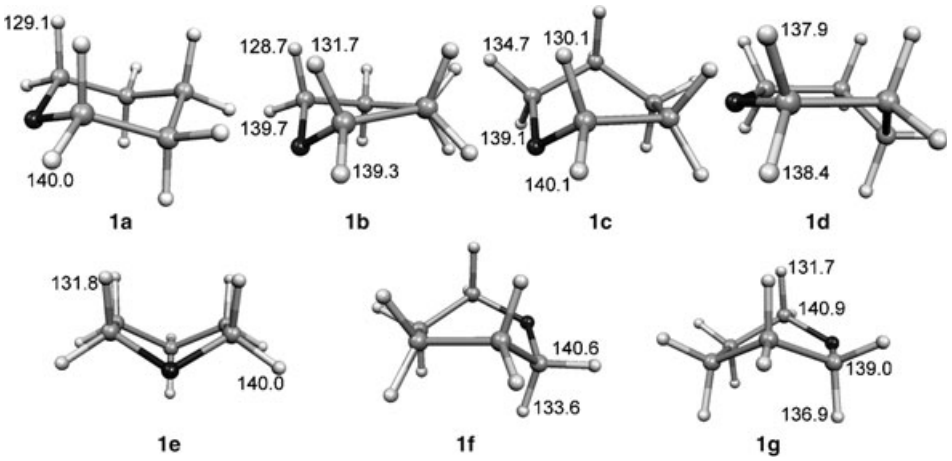

Figure 2. $^1J_{CH}$ in the conformations related by inversion of **1**.

bond and decreases the J value. Through computational analysis we have now probed the conformational dependence of ^1J values. However, we found that delocalization is not the origin of this lower J value, and we propose an alternative explanation.

Recently, the conformational inversion of **1** was monitored through a series of stationary states with different orientations of 2-H relative to the lone pairs of electrons.[3] Figure 2 shows these structures, including transition states **1b** and **1d**, derived from the chair **1a**, as well as transition states **1e** and **1g** for topomerization of skewed boats **1c** and **1f**. These allow the calculation of CH coupling constants and C–H bond lengths at C2 and the determination of how these depend on the 2-H–C2–O1–C6 dihedral angle τ. Calculations were also performed on ethyl methyl ether (**2**) and dimethyl ether (**3**).

Conformations were optimized and characterized at the B3LYP/6-311++G(*2d,2p*) level with Gaussian 94,[4] which includes NBO analyses.[5] The density-functional calculation of coupling constants was performed by using the approach of Malkin et al.[6] at the BP/IGLO-III//B3LYP/6-311++G(*2d,2p*) level.[7]

We had fully expected that $^1J_{CH}$ would be minimum at $\tau = 60$ or 90°. Instead, we found that $^1J_{CH}$ decreases continually from its maximum near 180° and approaches a minimum near 0°. The variations in the coupling constants and C–H bond lengths of **1** with dihedral angle are reported in Table 1. The

Table 1: Coupling constants and C–H bond lengths in tetrahydropyran conformations.

Conf.	τ_{HCOC} [°]	$^1J_{CH}$ [Hz]	d_{CH} [Å]	Conf.	τ_{HCOC} [°]	$^1J_{CH}$ [Hz]	d_{CH} [Å]
1a	62.5	129.1	1.100	**1d**	112.5	137.8	1.094
1a	178.6	140.0	1.089	**1d**	133.2	138.4	1.092
1b	63.9	131.7	1.098	**1e**	63.7	131.8	1.097
1b	179.1	139.3	1.088	**1e**	170.2	140.0	1.088
1b	49.0	128.7	1.099	**1f**	152.2	140.5	1.090
1b	165.3	139.7	1.089	**1f**	92.3	133.6	1.097
1c	86.1	134.7	1.097	**1g**	172.7	140.8	1.089
1c	158.2	139.1	1.090	**1g**	71.9	131.7	1.097
1c	53.3	130.1	1.097	**1g**	119.0	136.9	1.095
1c	169.1	140.1	1.088	**1g**	125.5	139.0	1.093

dominant contribution to $^1J_{CH}$ is the Fermi contact term, and the spin-orbit contributions are not only negligible but hardly depend on τ (Supporting Information). Figure 3a shows the variation of $^1J_{CH}$ with τ. Three-term Fourier analysis gives Equation (1) (correlation coefficient $r = 0.984$), which is superimposed on the figure.

$$^1J_{CH} = 133.63 - 7.321\cos\tau - 0.880\cos 2\tau \quad (1)$$

The dependence of $^1J_{CH}$ for the pro-*R* and pro-*S* hydrogen atoms of **2** is reported in Table 2

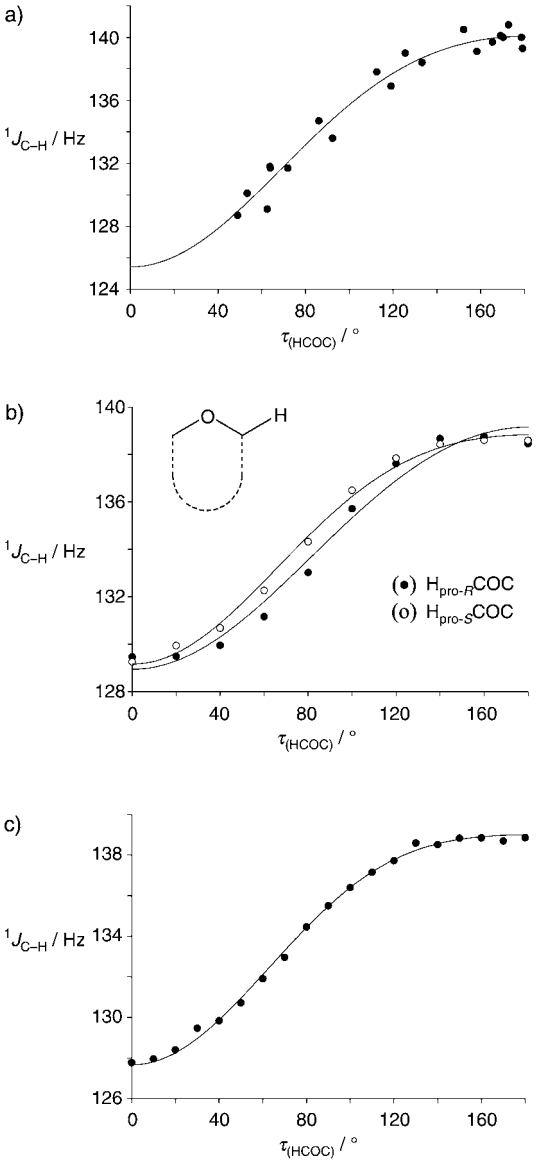

Figure 3. Variation of $^1J_{CH}$ (Hz) with dihedral angle: a) **1**; b) ethyl methyl ether; c) dimethyl ether.

Table 2: Coupling constants and C–H bond lengths for the pro-*R* and pro-*S* hydrogen atoms in ethyl methyl ether. The dihedral angle restricted was $H_{pro\text{-}S}COC$ or $H_{pro\text{-}R}COC$, respectively.

τ_{HCOC} [°]	$^1J_{CH}$ [Hz][a]	$^1J_{CH}$ [Hz][b]	d_{CH} [Å][a]	d_{CH} [Å][b]
0	129.46	129.25	1.0992	1.0992
20	129.49	129.94	1.1000	1.1007
40	129.95	130.68	1.1023	1.1029
60	131.16	132.26	1.1039	1.1040
80	133.02	134.32	1.1039	1.1020
100	135.71	136.49	1.1026	1.1015
120	137.61	137.84	1.0998	1.0991
140	138.67	138.43	1.0967	1.0969
160	138.75	138.60	1.0951	1.0947
180	138.46	138.59	1.0947	1.0954

[a] Pro-*R* hydrogen atom. [b] Pro-*S* hydrogen atom.

and shown in Figure 3b. Fitting gave Equation (2) ($r = 0.991$), which is superimposed on the figure. Table 3, Figure 3c, and Equation (3) ($r = 0.998$) show $^1J_{CH}$ for **3**. All of these are very

$$^1J_{CH} = 134.48 - 4.969\cos\tau - 0.459\cos 2\tau \quad (2)$$

$$^1J_{CH} = 134.41 - 5.657\cos\tau - 1.070\cos 2\tau \quad (3)$$

similar, but the last two give rise to *J* values at dihedral angles τ near 0°.

Deletion energies obtained by NBO (natural bond orbital) analysis can identify stereoelectronic interactions.[8] The lone pairs of electrons on the oxygen atom do not occupy sp^3 hybrid orbitals, but n_p and n_s orbitals. Figure 4 shows the separate and total dependence of $n_p \rightarrow \sigma^*_{CH}$ and $n_s \rightarrow \sigma^*_{CH}$ delocalizations on τ in **1** and **2**. Since electrons in the n_s orbital are held more tightly, $n_p \rightarrow \sigma^*_{CH}$ delocalization is stronger. Fourier analysis is given for **1** in Equations (4)–(6)

$$E_p = 4.28 + 0.22\cos\tau - 4.18\cos 2\tau \quad (4)$$

$$E_s = 1.50 - 0.26\cos\tau + 0.86\cos 2\tau \quad (5)$$

$$E_{total} = 6.12 + 0.70\cos\tau - 2.54\cos 2\tau \quad (6)$$

($r = 0.997$, 0.70, 0.996, respectively). For **2** the coefficients are similar. The fittings are superimposed on the figures.

The largest angle-dependent coefficient is 4.18 for n_p, consistent with the above assertion that n_p is more delocalized. Moreover, this is for the $\cos 2\tau$ term. This is exactly the behavior expected from n_p since either lobe can overlap with σ*.

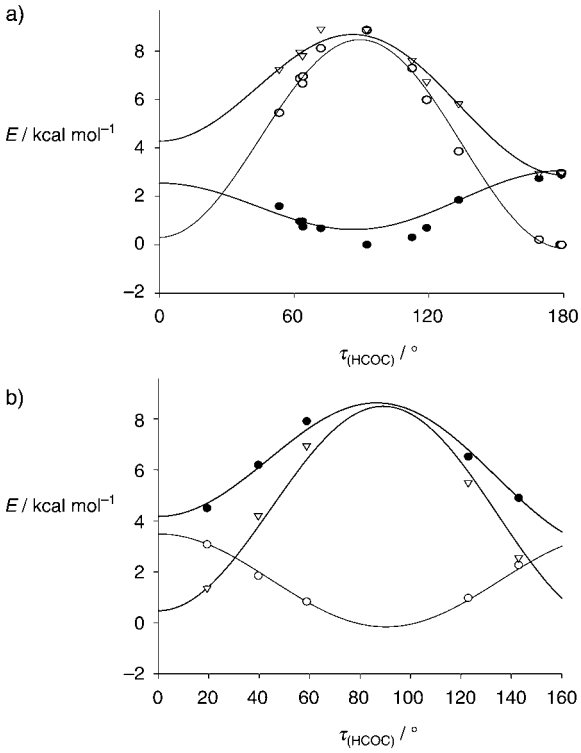

Figure 4. Dependence on dihedral angle of strength of $n_p \rightarrow \sigma^*_{CH}$ (○), $n_s \rightarrow \sigma^*_{CH}$ (●), and $n_s + n_p \rightarrow \sigma^*_{CH}$ ⁎ (△) delocalizations in a) **1**, b) ethyl methyl ether.

The variations in C–H bond lengths in **1**, **2** (pro-*R* and pro-*S*), and **3** with τ can be fit to Equations (7)–(9) ($r = 0.982$, 0.971, 0.986, respectively; see Supporting Information). As reported previously[7] there is no correlation between *d* and *J*.

$$d_{CH} = 1.095 + 0.0044\cos\tau - 0.0020\cos 2\tau \quad (7)$$

$$d_{CH} = 1.100 + 0.0029\cos\tau - 0.0029\cos 2\tau \quad (8)$$

$$d_{CH} = 1.098 + 0.0032\cos\tau - 0.0030\cos 2\tau \quad (9)$$

All the data are scattered because energy minimization is imperfect (as demonstrated by different results in Table 3 from identical structures) and because *J* and *d* do not depend only on the dihedral angle (as demonstrated by different results in Table 2 from pro-*R* and pro-*S* hydrogen atoms and by differences among **1**–**3** arising from steric or torsional effects on the COC angle).

In chair conformer **1a** the dihedral angles are 62.5° and 178.6°. The $C–H_{ax}$ bond is antiperiplanar to a lone pair, permitting $n_O \rightarrow \sigma^*_{CH}$ delocalization and a decrease in *J*. Indeed, the calculated $^1J_{CH_{ax}}$ (129.1 Hz) is lower than the $^1J_{CH_{eq}} =$ 140.0 Hz. Thus the Perlin effect can be

Table 3: Coupling constants and C–H bond lengths in dimethyl ether.

$\lvert\tau_{HCOC}\rvert$ [°]	$^1J_{CH}$ [Hz][a]	$^1J_{CH}$ [Hz][b]	d_{CH} [Å]	$\lvert\tau_{HCOC}\rvert$ [°]	$^1J_{CH}$ [Hz][a]	$^1J_{CH}$ [Hz][b]	d_{CH} [Å]
0	127.78	127.78	1.0975	100	136.40	136.56	1.1000
10	127.96	127.89	1.0978	110	137.15	137.30	1.0988
20	128.40	128.19	1.0986	120	137.72	137.87	1.0975
30	129.47	128.91	1.0997	130	138.59	139.25	1.0962
40	129.84	129.73	1.1008	140	138.51	138.60	1.0950
50	130.72	130.77	1.1017	150	138.83	138.90	1.0940
60	131.91	132.13	1.1021	160	138.85	138.75	1.0932
70	132.96	133.00	1.1020	170	138.69	138.61	1.0927
80	134.46	134.28	1.1016	180	138.86	138.86	1.0926
90	135.50	135.34	1.1009				

[a] $\tau > 0$. [b] $\tau < 0$.

reproduced computationally. Moreover, in transition state **1d** τ increases to 112.5° or 133.3°, neither of which is favorable to delocalization, and J increases. In conformer **1c** the hydrogen atom that is antiperiplanar to a lone pair of electrons shows $J = 130.1$ Hz, whereas the hydrogen atoms on the other methylene group show higher a J value. Similar analyses would appear to explain the other coupling constants.

Although $^1J_{CH}$ in **1a** is lower at 60° than at 180°, consistent with delocalization of an antiperiplanar lone pair of electrons, that lone pair occupies an sp^3 hybrid, whereas the strongest $n_O \rightarrow \sigma^*_{CH}$ delocalization, according to Equation (4), is with the p orbital. Figure 5 shows the overlap between that orbital and

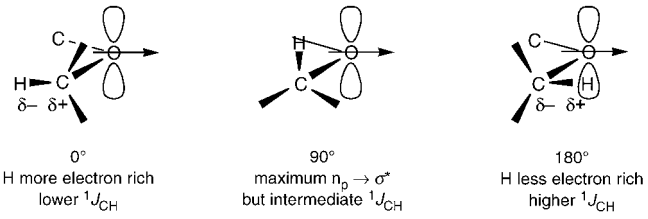

Figure 5. Variation with dihedral angle of the overlap between the n_p orbital and the C–H bond and of the C–H dipole induced by electrostatic interaction with the oxygen dipole.

the C–H at dihedral angles of 0, 90, and 180°. It follows that delocalization should be maximum at 90°, and J should be minimum at this angle. Instead the data in Figure 3a are monotonic, with intermediate J at intermediate τ, including $J = 134.7$ Hz and 133.6 at $\tau = 86°$ or 92°.

Tables 2 and 3 show further contradictions, apparent in acyclic ethers. Although the maximum $n_O \rightarrow \sigma^*_{CH}$ delocalization and minimum $^1J_{CH}$ ought to be at $\tau = 90°$, again the data are monotonic. The minimum $^1J_{CH}$ value occurs at an angle near 0°, when the C–H bond is not antiperiplanar to any lone pair of electrons. (In agreement, $^1J_{CC}$ in ethanol was calculated to be minimum at $\tau_{CCOH} = 0°$.[9]) The minimum $n_O \rightarrow \sigma^*_{CH}$ delocalizations are at $\tau = 0°$ and 180°, where σ* is orthogonal to the n_p lone pair of electrons, as in Figure 5. At these torsion angles τ, $^1J_{CH}$ should be maximum and nearly the same at both. These expectations are very different from what is calculated!

The fittings of Equation (1)–(3) are informative. If $^1J_{CH}$ were determined by $n_O \rightarrow \sigma^*_{CH}$ delocalization, it would have paralleled E_p [Eq. (4)], with the $\cos 2\tau$ term larger. Instead the coefficients of $\cos\tau$ are the larger values. Therefore $^1J_{CH}$ is not determined predominantly by delocalization! *This is an astounding result.*

What then determines the value of $^1J_{CH}$? What parameter follows $\cos\tau$, rather than $\cos 2\tau$? We suggest a dipolar interaction. If the C–H bond interacts with the dipole moment of the lone pairs of electrons and the C–O bonds (Figure 5), the interactions at $\tau = 0°$ and 180° are opposite. This then accounts for why J at 0° and 180° are so different, and why J takes intermediate values between 60° and 120°, where delocalization would be maximum.

It would seem that a dipolar interaction cannot be significant, because the C–H bond is nonpolar. Nevertheless, the electric field of the oxygen dipole might polarize the electron distribution in the C–H bond. Indeed, the calculated electron density at H decreases from $\tau = 0°$ to $\tau = 180°$ (with a corresponding increase at O). For example, the charge at the pro-*R* H atom of **2** can be fit to $q_H = 0.207 – 0.015\cos\tau + 0.006\cos 2\tau$. Furthermore, this means that the charge at H is determined somewhat more by the dipolar interaction than by $n_O \rightarrow \sigma^*_{CH}$ delocalization.

We cannot specify how the electron-density changes affect the ^1J value. It is not through the hybridization, according to our calculations. However, an electric field is known to affect both electron density and coupling constants.[10]

The C–H bond lengths are more complicated. The lengthening of a C–H or C–O bond antiperiplanar to a lone pair of electrons is generally attributed to $n_O \rightarrow \sigma^*_{CH}$ delocalization.[11] Yet Equations (7)–(9) have nearly equal $\cos 2\tau$ and $\cos\tau$ terms. Therefore, dipolar interactions also affect the lengthening of the C–H or C–O bond, as had been suggested.[12] However, it may also be indirect, through the electron population.

In summary, the $^1J_{CH}$ value in HCOC fragments is definitely not a consequence of $n_O \rightarrow \sigma^*_{CH}$ delocalization, despite expectations, although a small contribution cannot be excluded. Instead, $^1J_{CH}$ is found to follow a $\cos\tau$ dependence, which is proposed to arise from dipolar interactions. This conclusion is not necessarily general, and further calculations are in progress on N and S analogues, along with experimental tests of $^1J_{CC}$ in ethers.

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