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The influence of chain elongation on Karplus-type relationships: a DFT study of scalar coupling constants in polyacetylene derivatives

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The coupling constants of a series of acetylenic derivatives have been calculated using the finite perturbation method. In the case of dimethylated derivatives a Karplus-type relationship has been obtained for coupling constants of hydrogen atoms separated up to 15 bonds. Additional relationships have been obtained between the interatomic distances and the coupling constants.

Introduction

In 1960 Karplus discussed the experimental finding that scalar coupling constants are observed in polyacetylene derivatives up to nine bonds,[1] based on the results reported in Table 1.[2]

Using a valence bond approach, Karplus deduced that the sign of the coupling constant will be positive when the interacting nuclei are separated by an even number of carbon atoms and negative otherwise.[1] Moreover, to explain the long range H–H coupling constants he postulated that in molecules of type **a** (Fig. 1), the resonance structure form **b** is important, that is, that the π-electron coupling mechanism is dominant.

a **b**

Fig. 1 Karplus' π-electron mechanism.

At about the same time, Karplus reported his famous relationship relating vicinal $^3J_{HH}$ coupling constants with dihedral angles.[3,4] A number of studies have extended this equation to other compounds as the pseudorotation of cyclopentane,[5] model peptides,[6] and carbohydrates (Freedberg showed that residual dipolar couplings, RDCs, yielded the same results as Karplus curves).[7] In addition, several reviews have gathered all the information on this issue on recent years.[8–10]

At that time, it was not possible to establish whether the Karplus relationship still holds for acetylene derivatives like some of those reported in Table 1 (compounds **2**, **4** and **5**). In the present article, we have carried out a systematic study of the coupling constants of the H–(C≡C)$_n$–H, CH$_3$–(C≡C)$_n$–H and CH$_3$–(C≡C)$_n$–CH$_3$ families of compounds, where n ranges from 0 to 6. In addition, in the last series of compounds the relationship of the coupling constant with the HC ··· CH dihedral angle has been considered. Compounds with multiple acetylene units have shown significant interest as structural linkers in nanoscale systems.[11–14]

The total coupling constant arises from the contribution of four electron–nuclear components: Fermi contact (FC), paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO) and spin–dipole (SD) terms. In the case of H–H couplings, it is well known that of the four components of the coupling constant, the PSO and DSO term cancel and the SD one is very small, thus the sum of the four terms can be approximated by the FC one.[15–17] This hypothesis has been confirmed specifically for the coupling constants in the rotation of ethane.[18]

The geometry of the systems has been optimised at the B3LYP/6-311++G** level[19,20] within the Gaussian-98 package.[21] No frequency calculations have been performed to verify the minimum nature of the structures. The FC term of the coupling constant has been evaluated with the finite perturbation theory (FPT) approximation, using the Field keyword within the Gaussian-98 package, and the convergence criterion for the wave-function has been set to 10^{-10} au at the UB3LYP/6-311++G** computational level. For those compounds with two methyl groups a scan of the HC ··· CH dihedral angle has been carried out, by optimising each geometrical disposition.

The results for the CH$_3$–(C≡C)$_n$–H and H–(C≡C)$_n$–H families show negative coupling constants in the first case and positive coupling constants in the second case (Table 2). The comparison of the experimental values (Table 1, **1** and **3**) with the calculated ones are very similar, although that of compound **3** is overestimated (−2.0 instead of −1.3 Hz). A smooth decrease of the coupling constant is observed as the distance between the hydrogen atoms increases. A double logarithmic relationship [log(distance) *vs.* log(J)] is obtained for the two families (eqns. (1) and (2)). It is noteworthy that at distances as great as 14 Å the values of the coupling constants are 0.7 Hz. Taking into account that the present instruments allows the detection of coupling constants as small as 0.1 Hz; that value corresponds to a distance of 102.8 and 39.9 Å or 37 and 15 C≡C groups, respectively, according to eqns. (1) and (2).[22]

Table 1 $^nJ_{HH}$ coupling constants/Hz in acetylene derivatives

Compound	Molecule	Number of bonds	|J|
1	H$_3$C–C≡C–H	4	2.9–3.6 Hz ($^4J_{HH}$)
2	H$_3$C–C≡C–CH$_3$	5	2.7 Hz ($^5J_{HH}$)
3	H$_3$C–C≡C–C≡CH	6	1.27 ± 0.05 Hz ($^6J_{HH}$)
4	H$_3$C–C≡C–C≡C–CH$_3$	7	1.3 ± 0.1 Hz ($^7J_{HH}$)
5	H$_3$C–C≡C–C≡C–C≡C–CH$_2$OH	9	0.4 Hz ($^9J_{HH}$)

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Table 2 Calculated ${}^{2n+1}J_{HH}$, ${}^{2n+2}J_{HH}$ and coupling constants/Hz and interatomic distances/Å between the hydrogen atoms involved

	$H–(C{\equiv}C)_n–H$		$CH_3–(C{\equiv}C)_n–H$	
n	${}^{2n+1}J_{HH}$	Distance	${}^{2n+2}J_{HH}$	Distance
1	8.48	3.33	−3.45	3.22
2	2.16	5.90	−2.00	6.77
3	1.43	8.47	−1.37	9.31
4	1.03	11.04	−1.00	11.87
5	0.66	13.60	−0.67	14.42

$$\ln(|J|) = (2.65 \pm 0.17) - (1.13 \pm 0.08)\ln(d), \quad R^2 = 0.98[CH_3–(C{\equiv}C)_n–H] \quad (1)$$

$$\ln(J) = (4.09 \pm 0.32) - (1.74 \pm 0.15)\ln(d), \quad R^2 = 0.98[H–(C{\equiv}C)_n–H] \quad (2)$$

The coupling constants for all the members of the $CH_3–(C{\equiv}C)_n–CH_3$ family in 10° steps of the HC ··· CH dihedral angle have been graphically represented (Fig. 2, from $n = 0$ to $n = 6$) and the corresponding values at 0°, 90° and 180° gathered in Table 3. Previous results obtained for ethane with the OEM-CCSD method were systematically 10% smaller than the ones reported here.[23]

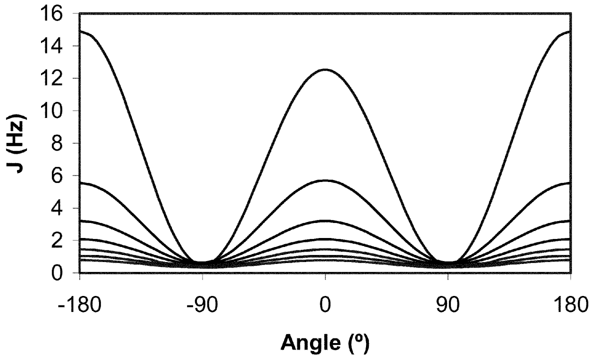

Fig. 2 Coupling constant in the $CH_3–(C{\equiv}C)_n–CH_3$ family *vs.* the HC ··· CH dihedral angle from top ($n = 0$) to bottom ($n = 6$).

When the data of Tables 1, 2 and 3 are compared (assuming that the experimental values of J_{vic} for compounds **1** and **3** are negative) the following linear relationships are found:

$$J_{calc}/\mathrm{Hz} = (1.1 \pm 0.3) + (1.61 \pm 0.16)J_{exp}/\mathrm{Hz},\ n = 5,\ R^2 = 0.97 \quad (3)$$

and removing compound **3**:

$$J_{calc}/\mathrm{Hz} = (1.40 \pm 0.08) + (1.52 \pm 0.04)J_{exp}/\mathrm{Hz},\ n = 4,\ R^2 = 0.999 \quad (4)$$

Table 4 Parameters fitted to the equation: ${}^nJ_{HH} = A\cos(2a) + B\cos(a) + C$ for $CH_3–(C{\equiv}C)_n–CH_3$ family. In all cases 18 independent points have been considered

n	*A*	*B*	*C*	R^2
0	6.63 ± 0.04	−0.99 ± 0.04	7.15 ± 0.03	0.9988
1	2.49 ± 0.01		3.13 ± 0.01	0.9991
2	1.301 ± 0.001		1.900 ± 0.001	0.99998
3	0.779 ± 0.001		1.307 ± 0.001	0.99994
4	0.498 ± 0.001		0.957 ± 0.001	0.9998
5	0.330 ± 0.002		0.725 ± 0.001	0.9993
6	0.227 ± 0.001		0.568 ± 0.001	0.9996

It is clear from Fig. 2 that all the molecules follow the same rules. The fitting of the data to the Karplus-type equation shows that only in the case of ethane, three terms are needed while in the rest of the cases two are enough (Table 4).

The energetic values obtained for the different conformations follow almost perfectly the curve corresponding to a Pitzer potential[24–26] in the case of ethane (eqn. (5)), while in the rest of the cases all the conformations have almost identical energies (maximum difference less than 0.08 kJ mol⁻¹).

$$E_{rel}/\mathrm{kJ\ mol^{-1}} = (5.694 \pm 0.005) + (5.649 \pm 0.007)\cos(3a),\ R^2 = 0.9999 \quad (5)$$

Integration of the weighted coupling constant shows that the expected value is equal to the constant term reported in Table 4. The results corresponding to ethane (7.15 Hz) nicely compare with the experimental (8.00 Hz) and *ab initio* results (7.20 Hz).[27] Similarly, good agrements are obtained between the experimental data of **2**, **4** and **5** (Table 1) and the corresponding energy average values (parameter *A* of Table 4).

As shown previously for the $CH_3–(C{\equiv}C)_n–H$ and $H–(C{\equiv}C)_n–H$ families, a double logarithmic relationship can be found in this case for the values obtained in the *anti* configuration (eqn. (6)). An extrapolation of these equations indicated that a value of the coupling constant equal to 0.1 Hz will correspond to the $CH_3–(C{\equiv}C)_{25}–CH_3$ molecule. Should this compound be prepared and the coupling constant measured (through ^{13}C satellites), the distance between coupled hydrogen atoms should be 64.6 Å.

$$\ln(J) = (4.52 \pm 0.06) - (1.63 \pm 0.03)\ln(d),\ R^2 = 0.999 \quad (6)$$

In conclusion, we have established that the Karplus relationship can be extended to polyacetylenes bearing terminal alkyl groups (this could seem obvious but some examples of its breakdown are known),[28] observation that is probably true for other conjugated systems. We have also demonstrated the efficiency of the polyacetylenes for transmitting magnetic information and this can be relevant for the properties of these compounds as molecular wires.[29]

Table 3 Calculated ${}^{2n+3}J_{HH}$ coupling constants/Hz and interatomic distances/Å between the hydrogen atoms involved in the $CH_3–(C{\equiv}C)_n–CH_3$ family

Number of C≡C bonds	0°		90°		180°	
	${}^{2n+3}J_{HH}$	Distance	${}^{2n+3}J_{HH}$	Distance	${}^{2n+3}J_{HH}$	Distance
0	12.53	2.36	0.48	2.75	14.92	3.09
1	5.71	4.91	0.64	5.12	5.55	5.32
2	3.20	7.48	0.60	7.62	3.20	7.75
3	2.09	10.04	0.53	10.15	2.09	10.25
4	1.44	12.61	0.46	12.69	1.46	12.77
5	1.04	15.17	0.40	15.24	1.06	15.31
6	0.79	17.73	0.34	17.79	0.80	17.85

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References

1 M. Karplus, *J. Chem. Phys.*, 1960, **33**, 1842; M. Barfield and M. Karplus, *J. Am. Chem. Soc.*, 1969, **91**, 1.

2 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1965, vol. 1, p. 177.

3 M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; M. Karplus, *J. Phys. Chem.*, 1960, **64**, 1793; M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870.

4 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1965, vol. 2, p. 678.

5 A. Wu, D. Cremer, A. A. Auer and J. Gauss, *J. Phys. Chem. A*, 2002, **106**, 657.

6 S. A. Perera and R. J. Bartlett, *Magn. Reson. Chem.*, 2001, **39**, S183.

7 D. I. Freedberg, *J. Am. Chem. Soc.*, 2002, **124**, 2358.

8 A. P. Marchand, *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*, VCH, Deerfield Beach, FL, 1982.

9 P. E. Hansen, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1980, **14**, 175.

10 W. A. Thomas, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **30**, 183.

11 M. Scheffler, A. Dorenbeck, S. Jordan, M. Wüstefeld and G. von Kiedrowski, *Angew. Chem., Int. Engl. Ed.*, 1999, **22**, 3312.

12 T. Aida and K. Tajima, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 3803.

13 M. B. Nielsen and F. Diederich, *Synlett*, 2002, 544.

14 F. Diederich, *Chem. Comm.*, 2001, 219.

15 A. Bagno, *Chem. Eur. J.*, 2000, **6**, 2925.

16 T. Onak, J. Jaballas and M. Barfield, *J. Am. Chem. Soc.*, 1999, **121**, 2850.

17 I. Alkorta and J. Elguero, *Int. J. Mol. Sci.*, in press.

18 M. Grayson and S. P. A. Sauer, *Mol. Phys.*, 2000, **98**, 1981.

19 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

20 M. J. Frisch, J. A. Pople, R. Krishnam and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

21 M. J. Frisch, *et al.*, *Gaussian 98*, Gaussian, Inc., Pittsburgh, PA, 1998.

22 The distance between the H atoms in any member of these families can be obtained through a linear relationship between this property and the number of C≡C groups.

23 H. Sekino and R. J. Bartlett, *Chem. Phys. Lett.*, 1994, **225**, 486.

24 K. S. Pitzer, *Discuss. Faraday Soc.*, 1951, **107**, 4519.

25 E. M. Engler, J. D. Andose and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1973, **95**, 8005.

26 K. B. Wiberg and E. Martin, *J. Am. Chem. Soc.*, 1985, **107**, 5035.

27 J. Kaski, P. Lantto, J. Vaara and J. Jokisaari, *J. Am. Chem. Soc.*, 1998, **120**, 3993.

28 T. Parella, F. Sánchez-Ferrando and A. Virgili, *Magn. Reson. Chem.*, 1997, **35**, 30.

29 R. Ziessel, M. Hissler, A. El-Ghayoury and A. Harriman, *Coord. Chem. Rev.*, 1998, **178–180**, 1251; F. Diederich, *Pure Appl. Chem.*, 1999, **71**, 265.