Comparison of Some Theoretical Models for the Determination of Dialkylphosphorylhydrazones NMR Spectral Data

Catarina De Nigris Del Cistia[1,2] (PQ), Vinícius Tomaz Gonçalves[1,3] (FM), João Batista Neves da Costa[1] (PQ), Carlos Maurício R. Sant'Anna[1]* (PQ) santanna@ufrrj.br.

[1]*Departamento de Química, ICE, UFRRJ;* [2]*Departamento de Matemática, ICE, UFRRJ;* [3]*CEFET/RJ - Centro Federal de Educação Tecnológica Celso Suckow da Fonseca, Itaguaí, RJ.*

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Abstract

Theoretical methods were tested to evaluate which one is the best for the determination of the dialkylphosphorylhydrazones NMR spectral data.

Introduction

Natural products and organic synthesis research groups use NMR spectroscopy for structural determination of their extracted or synthesized compounds. To help this determination, theoretical models would be excellent to compare the theoretical spectra with those obtained experimentally. Dialkylphosphorylhydrazones (DAPH) are compounds synthetized by our group which presented some biological activities[1] (**Scheme 1**). Here, we use some of these compounds to compare theoretically generated spectra with those experimentally obtained, in order to define the best theoretical model for prediction of NMR data from these compounds.

Scheme 1. Structures of DAPHs.
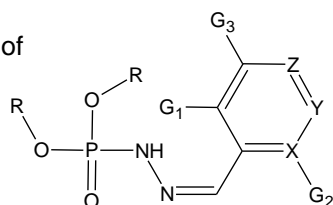
|	R	G1	G2	G3	X	Y	Z
v1	-CH$_2$CH$_3$	H	H	H	C	C	N
v2	-CH(CH$_3$)$_2$	H	--	H	N	C	C
v3	-CH$_2$CH$_2$CH$_2$CH$_3$	H	Cl	H	C	N	C
v4	-CH$_2$CH(CH$_3$)$_2$	H	Cl	H	C	N	C
v5	-CH(CH$_3$)$_2$	H	H	Br	C	N	C
v6	-CH(CH$_3$)CH$_2$CH$_3$	H	H	Br	C	N	C
v7	-CH(CH$_3$)CH$_2$CH$_3$	H	Br	H	C	N	C
v8	-CH$_2$CH(CH$_3$)$_2$	H	Cl	H	C	C	N
v9	-CH$_2$CH$_2$CH$_2$CH$_3$	Cl	Cl	H	C	C	N

Results and Discussion

The Spartan'14 program (Wavefunction Inc.) was used for the determination of the NMR chemical shift data, which can be calculated using the Density Functional Theory (DFT; B3LYP/6-31G*) and Hartree-Fock (HF/6-31G*) methods. The program also allows the use of continuum models for some solvents to be selected when the compounds are minimized. So, solvents employed in the experimental methods can be used during compounds minimization, allowing results even closer to the values obtained experimentally. In **Table 1** is shown a comparison between the experimental values[1] and those calculated with the program, using the DFT and HF methods, without solvent (vacuum) and with the solvent used (DMSO); the compound **v1** is used for example.

Table 1. ^{13}C experimental NMR values (EXP), calculated values with DFT in vacuum (DFV), DFT in DMSO (DFD), HF in vacuum (HFV) and HF in DMSO (HFD) for **v1** compound.

v1	EXP	DF V	DF D	HF V	HF D
C2	150,13	157,31	153,45	158,56	**149,08**
C3	120,23	122,14	**120,30**	121,31	117,25
C4	141,76	144,71	**141,73**	148,67	142,79
C5	120,23	122,14	**120,30**	121,31	117,25
C6	150,13	157,31	153,45	158,56	**149,08**
C7	141,46	**144,51**	145,68	146,59	145,74
C9	62,57	65,54	**64,03**	60,60	55,75
C10	16,06	18,11	**16,39**	19,18	16,54
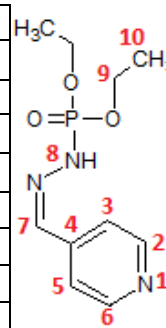
The bold values at Table 1 are closer to the experimental data.

Conclusions

As can be seen in Table 1, the DFT method is better than the HF method for the determination of NMR values. The selection of the solvent used in the experimental method (DMSO) for the minimization of the compound made the values even closer to the experimental ones, making the results even better. This methodology will be of great help elucidating the structure of extracted and synthesized compounds.

Acknowledgements

[1] Gonçalves, Vinícius Tomaz. Doctoral Thesis. *UFRRJ*, **2014**.