

# **C-HETSERF: Distinction of Cis/Trans-isomers and Measurement of Long Range Couplings between Chemically Equivalent Nuclei in Polycyclic Aromatic Hydrocarbons**

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## Index

1. Description of C-HETSERF Experiment	S1
2. 2D C-HETSERF spectrum of but-2-yne-1,4-diyl bis(perfluorophenyl) dicarbonate and the measured couplings	S2
3. Experimental and Processing Parameters	S3
4. References	S4

### Description of C-HETSERF Experiment:

Major difficulty associated with the measurement of long range couplings is their very small magnitudes. Measurement of separation between two peaks (i.e. the coupling) is a difficult task when they are in close proximity or overlapped in a single cross-section of a 2D spectrum. However, such smaller couplings can be determined if the peaks are made to appear in different cross-sections. This unique feature, being present in the C-HetSERF experiment [1,2], allows the determination of very small long range heteronuclear couplings. The experiment provides E-COSY type multiplet pattern for the cross peaks that have an analogy to the other methods like HETLOC [3,4] for the extraction of long-range  ${}^nJ_{XH}$ . The pulse scheme for this experiment is given in Figure S2(a). The sequence begins with an INEPT block in which at the end of the second delay  $\tau_1$ , the antiphase proton magnetization ( $2I_xS_z$ ) is converted into longitudinal two-spin order (i.e.  $2I_zS_z$ ) by the  ${}^1\text{H}$   $90^\circ$  pulse applied along the  $y$  axis ( $I$  is proton and  $S$  is carbon). The first gradient which acts as a  $z$ -purge does not affect this term and eliminates coherences that are not oriented along the  $z$  axis or those arising from proton attached to  ${}^{12}\text{C}$ . It is followed by an X-filter, which is a combination of two  $90^\circ$  pulses with phases  $(x, x)$  and  $(x, -x)$ , respectively. The first scan with  $(x, x)$  phases of both  $90^\circ$  pulses collectively acts as a  $180^\circ$  pulse and inverts only the magnetization of  ${}^1\text{H}$  attached to  ${}^{13}\text{C}$  ( $I_y - 2I_zS_z$ , where  $I_y$  is the transverse magnetization of a proton not attached to  ${}^{13}\text{C}$ ), whereas in the subsequent scan,  $(x, -x)$  phases of both  $90^\circ$  pulses collectively executes  $0^\circ$  pulse ( $I_y + 2I_zS_z$ ). Editing of the proton magnetization attached to  ${}^{13}\text{C}$  is subsequently carried out by the subtraction of the signals which gives a term  $2I_yS_z$ . This term is finally converted into antiphase proton magnetization by the semi-selective  $90^\circ$  pulse on proton  ${}^1\text{H}$  just before the  $t_1$  evolution period and is subsequently utilized for the spin selective

correlation. The use of semi-selective  $90^\circ$  is essential only to select a bunch of frequencies in the indirect dimension and can be replaced by a non-selective  $\pi/2$  pulse to cover the entire spectral range enabling the determination of all the couplings in a single experiment. Due to the application of the small angle mixing pulse ( $\beta < 90^\circ$ ), the cross peak in the C-HetSERF spectrum contains components of connected transitions and the unconnected transitions are suppressed resulting in an E-COSY type multiplet pattern. To derive better insight into the C-HetSERF experiment, an AMX spin system as shown in Figure 3(b) is considered where A and A' are protons separated by three bonds and X is a carbon directly bonded to proton A. When the semi-selective  $\pi/2$  pulse is applied on A, the appearance of spectrum and the extraction of couplings from frequency differences in both diagonal and cross peaks are pictorially depicted in Figure S2(b)

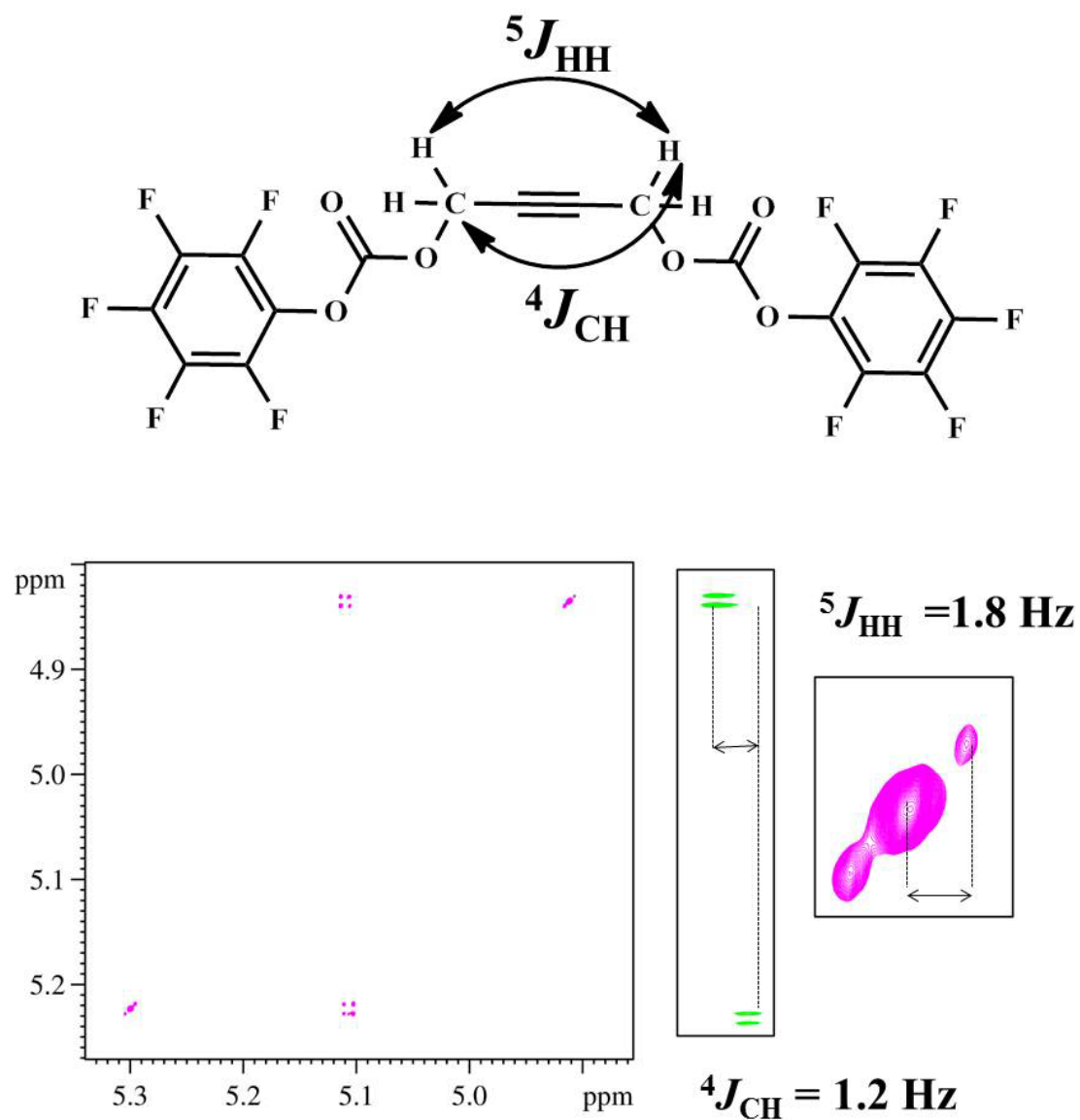


Figure S3: Measured couplings are marked as double headed arrows in but-2-yne-1,4-diyol bis(perfluorophenyl) dicarbonate and the 2D C-HETSERF spectrum.

Table: Experimental and processing parameters. The unshifted sine bell was used as a window function for all the 2D experiments before Fourier transformation.

Systems	Spectral width (ppm)		Data points		Zero filling		Delay “Δ” (ms)	Number of scans
	F2	F1	F2	F1	F2	F1		
Cis-Stilbene(1) and Trans-stilbene(2)	2.45	2.45	2314	300	4k	1k	2	8
Cis-dichloroethene(5) and Trans-dichloroethene(6)	0.86	0.86	2054	256	4k	512	1.31	8
Maleic acid (cis-isomer)(4) and Fumaric acid (trans-isomer)(3)	1.6	1.6	1534	256	4k	512	1.5	8
Phenanthrene(8)	2.82	2.82	2048	256	4K	512	1.5	8
But-2-yne-1,4-diyl bis(perfluorophenyl) dicarbonate (7)	0.86	0.86	600	300	2K	1K	1.61	8
Pyrene(9)	1	1	2054	256	4k	512	3.5	8
Porphyrin(10)	2.8	2.8	2054	256	4k	512	3.4	8

## References

1. a) N. Nath, N. Suryaprakash, *J. Phys. Chem. B*, **2011**, *115*, 6868-6875; b) N. Nath, N. Suryaprakash, *Chem. Phys. Lett.* **2010**, *496*, 175–182.
2. N. Nath, Ph. D. Thesis, *Indian Institute of Science*, Bangalore, **2011**.
3. M. Kurz, P. Schmieder, H. Kessler, *Angew. Chem. Int. Ed.* **1991**, *30*, 1329-1331.
4. P. Schmieder, M. Kurz, H. Kessler, *J. Biomol. NMR*, 1991, *1*, 403-420.