Electronic Supplementary Material (ESI) for CrystEngComm


SUPPORTING INFORMATION FOR MANUSCRIPT

# Study of the thermal processes in molecular crystals of peptides by means of NMR Crystallography

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**EXPERIMENTAL** – *2D PASS NMR Spectroscopy*

A 5-$\pi$ pulse 2D PASS scheme and 1000 and 2000 Hz sample spinning speeds were used in the 2D experiments on a BRUKER Avance III 400 spectrometer at a frequency of 100.613 MHz for $^{13}C$ equipped with a MAS probe head using 4 mm $ZrO_2$ rotors.. The $\pi$-pulse length was 8 $\mu$s. Sixteen $t_1$ increments using the timings described by Levitt and co-workers were used in the 2D PASS experiments.[1] For each increment, 360 scans were accumulated. Because the pulse positions in the $t_1$ set return to their original positions after a full cycle and the $t_1$-FID forms a full echo, the 16-point experimental $t_1$ data were replicated to 256 points. After the Fourier transformation in the direct dimension, the 2D spectrum was sheared to align all side bands with the center bands in the indirect dimension of the 2D spectrum. One-dimensional CSA spinning sideband patterns were obtained from $t_1$ slices taken at the isotropic chemical shifts in the $t_2$ dimension of the 2D spectrum. The magnitudes of the principal elements of the CSA tensor were obtained from the best-fit simulated spinning sideband pattern. Simulations of the spinning CSA sideband spectra were performed on a PC using the Topspin program.

**RESULTS AND DISCUSSION**

In this work, we employed the 2D PASS sequence for analysis of $^{13}C$ spectra.[1] This technique offers good sensitivity compared to other methods. This paper, we reported $^{13}C$ $\delta_{ii}$ parameters for samples **1** and **2** analyzing 2D PASS spectra recorded at 2000 and 1000 Hz spinning rate. The Figure S1 and S2 displays the example 2D PASS spectrum of **1** and **2** measured with a sample rotation 2000 Hz. The spectrum exhibits a complex pattern under slow sample spinning. Using proper data shearing (Figure S1B and S2B), it is possible to separate the spinning sidebands for each carbon and to use a calculational procedure to establish the $^{13}C$ $\delta_{ii}$ parameters. It is clear from such a presentation that the F2 projection corresponds to the infinite spinning speed spectrum, whereas F1 represents CSA. A similar procedure was employed to study **1**. The values of all $^{13}C$ $\delta_{ii}$ parameters for **1** and **2** are presented in Table S1 and S2.

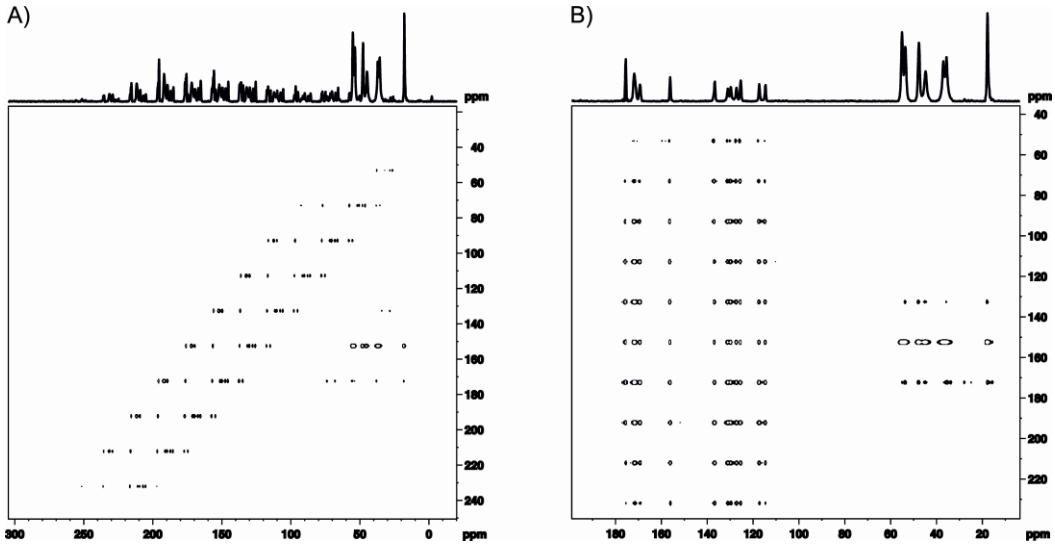


**Figure S1.** 2D PASS spectra for **1** recorded with a spinning rate of 2000 Hz (A) and the aliphatic part of spectrum after data shearing (B).

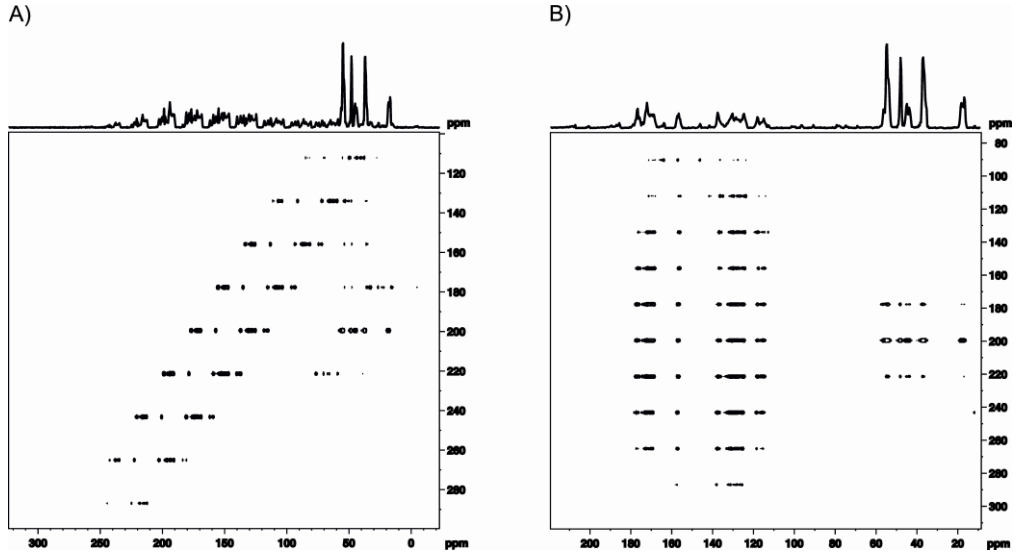


**Figure S2.** 2D PASS spectra for **2** recorded with a spinning rate of 2000 Hz (A) and the aliphatic part of spectrum after data shearing (B).

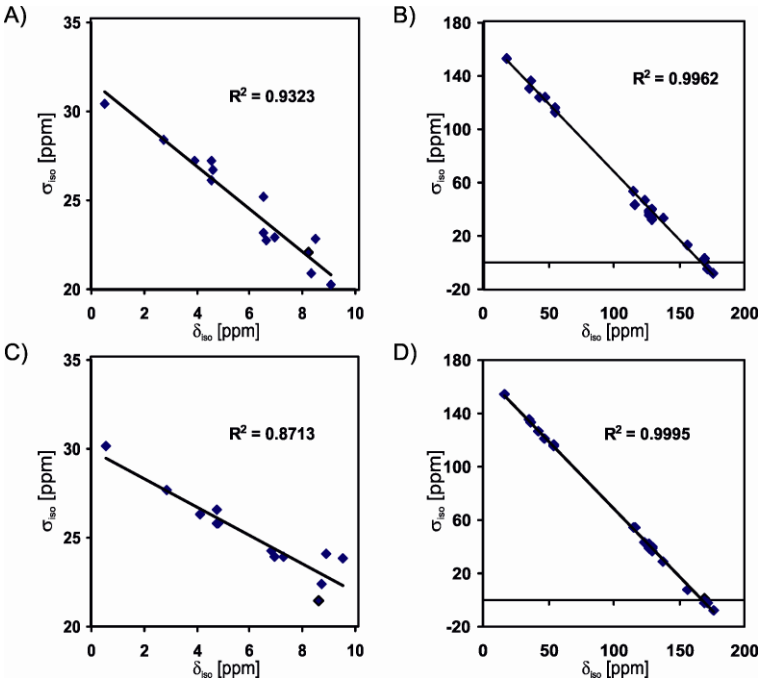


**Figure S3.** Correlation of the experimental isotropic chemical shift (δiso) versus the computed isotropic nuclear shielding ($\sigma_{iso}$) parameters ($^{1}$H –A, C and $^{13}$C –B, D) for structure **2**. Calculations were done with increase (A and B) and decrease (C and D) unit cell dimensions of 10%.

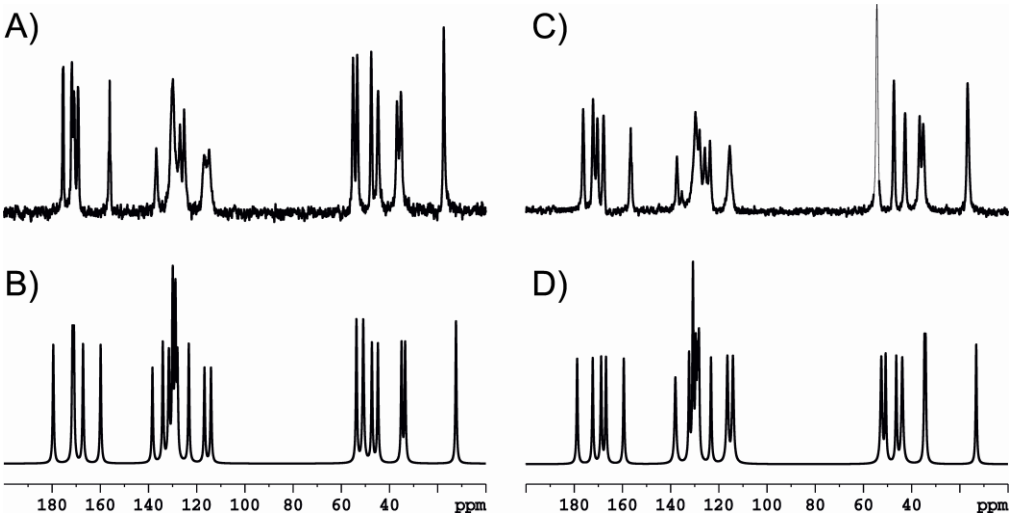


**Figure S4.** The $^{13}$C NMR experimental spectrum of sample **1** and **2** recorded with spinning rate 55 kHz (Figure A and C respectively). The $^{13}$C NMR simulated spectrum of sample **1** and **2** processed with line broadening equal to 70 Hz (GIPAW results).

**Table S1.** Experimental NMR chemical shift tensors [in ppm] for structure **1**.

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 168.9 | 243 | 173 | 91 | 152 | 0.08 |
| **C-11** | 54.8 | 69 | 58 | 37 | 32 | 0.30 |
| **C-12** | 35.8 | 46 | 44 | 17 | 29 | 0.85 |
| **C-13** | 125.3 | 221 | 150 | 5 | 216 | 0.34 |
| **C-14** | 129.7 | 239 | 142 | 8 | 231 | 0.16 |
| **C-15** | 114.4 | 194 | 124 | 25 | 169 | 0.17 |
| **C-16** | 155.8 | 247 | 157 | 63 | 184 | 0.02 |
| **C-17** | 117.2 | 198 | 134 | 20 | 178 | 0.28 |
| **C-18** | 130.9 | 223 | 149 | 21 | 202 | 0.27 |
| **C-20** | 171.5 | 246 | 185 | 84 | 162 | 0.25 |
| **C-21** | 47.4 | 66 | 52 | 24 | 42 | 0.33 |
| **C-22** | 17.8 | 32 | 29 | –7 | 39 | 0.86 |
| **C-30** | 171.5 | 246 | 185 | 84 | 162 | 0.25 |
| **C-31** | 53.5 | 73 | 55 | 33 | 40 | 0.11 |
| **C-32** | 37.0 | 52 | 30 | 30 | 22 | –0.95 |
| **C-33** | 136.6 | 229 | 166 | 15 | 214 | 0.41 |
| **C-34** | 130.9 | 223 | 149 | 21 | 202 | 0.27 |
| **C-35** | 127.2 | 224 | 153 | 5 | 219 | 0.35 |
| **C-36** | 127.2 | 224 | 153 | 5 | 219 | 0.35 |
| **C-37** | 127.2 | 224 | 153 | 5 | 219 | 0.35 |
| **C-38** | 130.9 | 223 | 149 | 21 | 202 | 0.27 |
| **C-40** | 175.2 | 236 | 176 | 114 | 122 | 0.02 |
| **C-41** | 44.4 | 66 | 50 | 17 | 49 | 0.34 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S2.** Experimental NMR chemical shift tensors [in ppm] for structure **2**.

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 169.2 | 249 | 169 | 90 | 159 | 0.00 |
| **C-11** | 54.3 | 72 | 47 | 44 | 28 | –0.79 |
| **C-12** | 35.0 | 48 | 29 | 28 | 20 | –0.90 |
| **C-13** | 123.7 | 218 | 143 | 10 | 208 | 0.28 |
| **C-14** | 129.5 | 222 | 143 | 25 | 197 | 0.21 |
| **C-15** | 115.1 | 197 | 126 | 23 | 174 | 0.19 |
| **C-16** | 156.7 | 245 | 164 | 61 | 185 | 0.12 |
| **C-17** | 116.3 | 191 | 133 | 25 | 166 | 0.30 |
| **C-18** | 129.5 | 222 | 143 | 25 | 197 | 0.21 |
| **C-20** | 169.8 | 251 | 171 | 87 | 163 | 0.02 |
| **C-21** | 47.2 | 68 | 46 | 29 | 39 | –0.09 |
| **C-22** | 17.0 | -[c] | -[c] | -[c] | -[c] | -[c] |
| **C-30** | 171.7 | 243 | 184 | 88 | 155 | 0.24 |
| **C-31** | 54.3 | 72 | 47 | 44 | 28 | –0.79 |
| **C-32** | 36.5 | 55 | 28 | 27 | 28 | –0.91 |
| **C-33** | 137.5 | 230 | 168 | 14 | 216 | 0.42 |
| **C-34** | 129.5 | 222 | 141 | 26 | 196 | 0.17 |
| **C-35** | 127.1 | 226 | 145 | 10 | 216 | 0.25 |
| **C-36** | 127.1 | 226 | 145 | 10 | 216 | 0.25 |
| **C-37** | 127.1 | 226 | 145 | 10 | 216 | 0.25 |
| **C-38** | 129.5 | 222 | 143 | 25 | 197 | 0.21 |
| **C-40** | 176.1 | 238 | 172 | 118 | 120 | –0.10 |
| **C-41** | 42.8 | 70 | 41 | 18 | 52 | –0.10 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

[c] Experimental data can not be obtained

**Table S3.** CASTEP calculations. NMR chemical shift tensors [in ppm] for structure **1** calculated using PBE0 functional with ultrasoft pseudopotential and GIPAW approach. Geometry (only hydrogen positions) was optimized with PBE0 functional and ultrasoft pseudopotential. Cut-off energy was: 550 eV. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 171.0 - \sigma_i$.(C).

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 168.4 | 243.4 | 171.9 | 89.9 | 153.5 | 0.07 |
| **C-11** | 53.6 | 65.2 | 55.3 | 40.4 | 24.8 | 0.20 |
| **C-12** | 36.3 | 51.7 | 46.1 | 11.2 | 40.5 | 0.73 |
| **C-13** | 124.7 | 220.2 | 148.6 | 5.3 | 214.9 | 0.33 |
| **C-14** | 132.4 | 233.3 | 152.3 | 11.5 | 221.9 | 0.27 |
| **C-15** | 115.7 | 201.8 | 130.9 | 14.5 | 187.3 | 0.24 |
| **C-16** | 161.1 | 243.4 | 174.5 | 65.5 | 178.0 | 0.23 |
| **C-17** | 118.8 | 201.4 | 140.8 | 14.2 | 187.2 | 0.35 |
| **C-18** | 129.8 | 231.0 | 130.3 | 28.1 | 203.0 | 0.01 |
| **C-20** | 170.6 | 244.3 | 176.1 | 91.3 | 153.0 | 0.11 |
| **C-21** | 45.7 | 64.0 | 50.0 | 23.2 | 40.8 | 0.31 |
| **C-22** | 14.3 | 30.8 | 18.1 | –5.9 | 36.7 | 0.31 |
| **C-30** | 168.7 | 238.6 | 179.2 | 88.4 | 150.2 | 0.21 |
| **C-31** | 52.6 | 71.9 | 57.6 | 28.4 | 43.6 | 0.34 |
| **C-32** | 38.6 | 51.1 | 44.5 | 20.3 | 30.8 | 0.57 |
| **C-33** | 139.0 | 237.8 | 173.7 | 5.4 | 232.4 | 0.45 |
| **C-34** | 135.0 | 240.2 | 150.7 | 14.0 | 226.2 | 0.21 |
| **C-35** | 131.6 | 241.8 | 144.5 | 8.4 | 233.5 | 0.17 |
| **C-36** | 125.6 | 231.2 | 146.5 | –0.9 | 232.2 | 0.27 |
| **C-37** | 130.7 | 236.5 | 150.9 | 4.7 | 231.8 | 0.26 |
| **C-38** | 132.0 | 238.8 | 137.7 | 19.6 | 219.2 | 0.08 |
| **C-40** | 162.6 | 226.2 | 168.9 | 92.8 | 133.4 | 0.14 |
| **C-41** | 43.1 | 64.3 | 47.8 | 17.3 | 47.0 | 0.30 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S4.** CASTEP calculations. NMR chemical shift tensors [in ppm] for structure **1** calculated using PBE0 functional with ultrasoft pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and ultrasoft pseudopotential. Cut-off energy was: 550 eV. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 168.8 - \sigma_i$.(C).

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 171.0 | 244.1 | 181.9 | 86.9 | 157.2 | 0.21 |
| **C-11** | 53.7 | 63.7 | 52.0 | 45.3 | 18.4 | –0.28 |
| **C-12** | 33.5 | 47.7 | 41.0 | 11.9 | 35.8 | 0.63 |
| **C-13** | 123.3 | 219.1 | 147.2 | 3.6 | 215.5 | 0.33 |
| **C-14** | 130.1 | 234.3 | 145.7 | 10.4 | 224.0 | 0.21 |
| **C-15** | 114.4 | 199.0 | 131.7 | 12.4 | 186.6 | 0.28 |
| **C-16** | 159.9 | 243.3 | 174.0 | 62.3 | 181.1 | 0.23 |
| **C-17** | 116.8 | 200.7 | 137.8 | 12.0 | 188.7 | 0.33 |
| **C-18** | 129.9 | 232.3 | 137.0 | 20.3 | 212.0 | 0.10 |
| **C-20** | 167.2 | 244.3 | 167.6 | 89.8 | 154.5 | 0.01 |
| **C-21** | 47.3 | 69.2 | 45.6 | 27.0 | 42.2 | –0.12 |
| **C-22** | 12.4 | 26.8 | 16.8 | –6.5 | 33.3 | 0.40 |
| **C-30** | 171.6 | 240.3 | 186.2 | 88.4 | 151.9 | 0.29 |
| **C-31** | 50.9 | 72.9 | 54.1 | 25.7 | 47.2 | 0.20 |
| **C-32** | 35.0 | 47.4 | 41.1 | 16.7 | 30.7 | 0.59 |
| **C-33** | 138.4 | 238.0 | 173.4 | 3.7 | 234.3 | 0.45 |
| **C-34** | 134.1 | 240.0 | 151.3 | 10.9 | 229.2 | 0.23 |
| **C-35** | 128.8 | 237.3 | 144.3 | 4.8 | 232.5 | 0.20 |
| **C-36** | 128.0 | 235.1 | 151.5 | –2.7 | 237.8 | 0.30 |
| **C-37** | 131.6 | 240.3 | 151.5 | 2.9 | 237.4 | 0.25 |
| **C-38** | 129.0 | 235.0 | 135.2 | 16.9 | 218.1 | 0.08 |
| **C-40** | 179.5 | 245.8 | 187.3 | 105.4 | 140.4 | 0.17 |
| **C-41** | 44.8 | 64.8 | 47.5 | 22.1 | 42.7 | 0.19 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S5.** CASTEP calculations. NMR chemical shift tensors [in ppm] for structure **2** calculated using PBE0 functional with ultrasoft pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and ultrasoft pseudopotential. Cut-off energy was: 550 eV. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 168.5 - \sigma_i$.(C).

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 166.9 | 245.3 | 165.8 | 89.8 | 155.5 | –0.02 |
| **C-11** | 52.6 | 62.0 | 51.4 | 44.3 | 17.6 | –0.20 |
| **C-12** | 34.2 | 49.6 | 40.7 | 12.5 | 37.0 | 0.52 |
| **C-13** | 123.3 | 219.2 | 147.2 | 3.4 | 215.8 | 0.33 |
| **C-14** | 130.8 | 234.6 | 148.4 | 9.3 | 225.3 | 0.23 |
| **C-15** | 114.2 | 199.2 | 131.0 | 12.5 | 186.8 | 0.27 |
| **C-16** | 159.5 | 243.2 | 173.1 | 62.2 | 181.0 | 0.23 |
| **C-17** | 116.5 | 200.0 | 137.4 | 12.1 | 187.9 | 0.33 |
| **C-18** | 129.6 | 231.5 | 134.9 | 22.3 | 209.2 | 0.08 |
| **C-20** | 168.9 | 243.9 | 172.4 | 90.4 | 153.5 | 0.07 |
| **C-21** | 46.4 | 68.3 | 45.4 | 25.5 | 42.9 | –0.07 |
| **C-22** | 13.2 | 29.1 | 17.1 | –6.4 | 35.5 | 0.32 |
| **C-30** | 172.4 | 239.7 | 188.7 | 88.9 | 150.8 | 0.32 |
| **C-31** | 50.8 | 72.2 | 55.3 | 24.8 | 47.4 | 0.29 |
| **C-32** | 34.7 | 46.6 | 40.3 | 17.2 | 29.4 | 0.57 |
| **C-33** | 138.1 | 236.9 | 173.7 | 3.8 | 233.1 | 0.46 |
| **C-34** | 132.4 | 238.7 | 147.6 | 11.0 | 227.7 | 0.20 |
| **C-35** | 128.3 | 237.8 | 142.5 | 4.6 | 233.1 | 0.18 |
| **C-36** | 128.2 | 236.1 | 151.1 | –2.5 | 238.7 | 0.29 |
| **C-37** | 130.8 | 240.1 | 150.1 | 2.4 | 237.7 | 0.24 |
| **C-38** | 128.9 | 234.5 | 135.1 | 17.2 | 217.4 | 0.08 |
| **C-40** | 178.8 | 245.0 | 187.4 | 104.0 | 141.0 | 0.18 |
| **C-41** | 43.9 | 63.2 | 48.0 | 20.6 | 42.6 | 0.29 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S6.** Quantum Espresso calculations. NMR chemical shift tensors [in ppm] for structure **1** calculated using PBE0 functional with of the norm-conserving Troullier−Martins pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and norm-conserving Troullier−Martins pseudopotential. Cut-off energy was: 60 Ryd. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 163.1 - \sigma_i$.(C).

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 175.3 | 250.8 | 189.1 | 86.1 | 164.7 | 0.25 |
| **C-11** | 51.7 | 62.2 | 50.5 | 42.5 | 19.7 | –0.18 |
| **C-12** | 30.7 | 45.6 | 38.0 | 8.6 | 36.9 | 0.59 |
| **C-13** | 123.1 | 221.2 | 147.8 | 0.3 | 221.0 | 0.34 |
| **C-14** | 129.7 | 234.6 | 148.7 | 5.9 | 228.7 | 0.25 |
| **C-15** | 112.7 | 199.9 | 131.4 | 6.9 | 193.0 | 0.29 |
| **C-16** | 161.3 | 246.4 | 176.4 | 61.0 | 185.4 | 0.24 |
| **C-17** | 118.4 | 205.0 | 144.1 | 6.2 | 198.8 | 0.39 |
| **C-18** | 129.4 | 232.7 | 138.7 | 16.7 | 216.1 | 0.13 |
| **C-20** | 171.0 | 249.8 | 175.1 | 87.9 | 161.9 | 0.08 |
| **C-21** | 46.4 | 69.0 | 43.1 | 27.2 | 41.8 | –0.24 |
| **C-22** | 10.6 | 25.9 | 15.8 | –10.0 | 35.9 | 0.43 |
| **C-30** | 175.2 | 245.0 | 194.1 | 86.4 | 158.7 | 0.36 |
| **C-31** | 51.0 | 72.0 | 56.4 | 24.7 | 47.3 | 0.34 |
| **C-32** | 32.8 | 44.6 | 38.6 | 15.3 | 29.3 | 0.59 |
| **C-33** | 138.1 | 240.2 | 173.8 | 0.3 | 239.8 | 0.45 |
| **C-34** | 131.7 | 240.4 | 148.0 | 6.6 | 233.8 | 0.21 |
| **C-35** | 127.2 | 239.1 | 142.7 | –0.3 | 239.4 | 0.19 |
| **C-36** | 127.1 | 237.2 | 152.4 | –8.4 | 245.6 | 0.31 |
| **C-37** | 130.9 | 242.1 | 153.2 | –2.8 | 244.9 | 0.27 |
| **C-38** | 127.1 | 235.1 | 135.7 | 10.6 | 224.5 | 0.11 |
| **C-40** | 186.3 | 256.2 | 197.1 | 105.5 | 150.7 | 0.22 |
| **C-41** | 43.5 | 63.8 | 46.3 | 20.4 | 43.4 | 0.19 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S7.** Quantum Espresso calculations. NMR chemical shift tensors [in ppm] for structure **1** calculated using PBE0 functional with of the norm-conserving Troullier−Martins pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and norm-conserving Troullier−Martins pseudopotential. The van der Waals (vdW) interactions were included using vdW-DF exchange-correlation Cut-off energy was: 60 Ryd. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 164.1 - \sigma_i.(C)$.

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 175.6 | 242.8 | 199.1 | 85.0 | 157.8 | 0.45 |
| **C-11** | 52.4 | 62.0 | 51.1 | 44.2 | 17.8 | –0.23 |
| **C-12** | 31.6 | 46.7 | 40.5 | 7.4 | 39.3 | 0.68 |
| **C-13** | 123.5 | 221.8 | 148.1 | 0.6 | 221.2 | 0.33 |
| **C-14** | 130.6 | 234.2 | 149.5 | 8.2 | 226.1 | 0.25 |
| **C-15** | 113.6 | 199.7 | 130.8 | 10.3 | 189.4 | 0.27 |
| **C-16** | 161.4 | 246.6 | 178.0 | 59.6 | 187.0 | 0.27 |
| **C-17** | 119.0 | 204.0 | 145.0 | 8.0 | 196.1 | 0.40 |
| **C-18** | 127.3 | 229.2 | 133.1 | 19.6 | 209.7 | 0.08 |
| **C-20** | 169.3 | 244.5 | 175.9 | 87.6 | 156.8 | 0.13 |
| **C-21** | 46.1 | 67.2 | 44.0 | 27.3 | 39.9 | –0.16 |
| **C-22** | 11.3 | 27.4 | 16.4 | –10.0 | 37.5 | 0.41 |
| **C-30** | 173.0 | 236.8 | 196.7 | 85.5 | 151.3 | 0.47 |
| **C-31** | 50.6 | 70.0 | 58.5 | 23.3 | 46.7 | 0.51 |
| **C-32** | 34.4 | 47.4 | 39.7 | 16.2 | 31.2 | 0.51 |
| **C-33** | 137.6 | 240.4 | 172.4 | 0.0 | 240.3 | 0.43 |
| **C-34** | 132.8 | 240.3 | 148.5 | 9.7 | 230.6 | 0.20 |
| **C-35** | 128.0 | 238.7 | 144.0 | 1.4 | 237.2 | 0.20 |
| **C-36** | 127.2 | 236.4 | 151.5 | –6.3 | 242.7 | 0.30 |
| **C-37** | 132.3 | 242.1 | 155.0 | –0.4 | 242.5 | 0.28 |
| **C-38** | 127.6 | 234.2 | 136.0 | 12.6 | 221.6 | 0.11 |
| **C-40** | 183.9 | 253.5 | 193.8 | 104.4 | 149.0 | 0.20 |
| **C-41** | 41.8 | 64.2 | 42.5 | 18.8 | 45.5 | 0.05 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S8.** Quantum Espresso calculations. NMR chemical shift tensors [in ppm] for structure **2** calculated using PBE0 functional with of the norm-conserving Troullier−Martins pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and norm-conserving Troullier−Martins pseudopotential. Cut-off energy was: 60 Ryd. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 163.1 - \sigma_i$.(C).

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 172.5 | 252.9 | 176.6 | 87.8 | 165.1 | 0.08 |
| **C-11** | 52.5 | 63.0 | 53.2 | 41.3 | 21.8 | 0.09 |
| **C-12** | 29.2 | 42.9 | 37.8 | 7.0 | 35.8 | 0.71 |
| **C-13** | 124.4 | 222.6 | 149.7 | 1.0 | 221.6 | 0.34 |
| **C-14** | 130.2 | 235.9 | 149.9 | 4.9 | 231.1 | 0.26 |
| **C-15** | 113.9 | 202.6 | 131.1 | 8.1 | 194.6 | 0.26 |
| **C-16** | 161.3 | 246.4 | 176.2 | 61.3 | 185.1 | 0.24 |
| **C-17** | 117.2 | 203.5 | 141.3 | 6.8 | 196.7 | 0.37 |
| **C-18** | 128.1 | 232.4 | 133.3 | 18.7 | 213.7 | 0.07 |
| **C-20** | 172.8 | 249.5 | 180.2 | 88.8 | 160.7 | 0.14 |
| **C-21** | 45.2 | 67.7 | 43.9 | 24.1 | 43.5 | –0.09 |
| **C-22** | 10.1 | 25.6 | 14.7 | –9.9 | 35.5 | 0.39 |
| **C-30** | 174.9 | 244.5 | 192.6 | 87.4 | 157.1 | 0.34 |
| **C-31** | 51.0 | 72.2 | 57.1 | 23.8 | 48.3 | 0.37 |
| **C-32** | 31.7 | 44.0 | 36.9 | 14.1 | 29.9 | 0.53 |
| **C-33** | 137.5 | 239.9 | 172.3 | 0.5 | 239.4 | 0.43 |
| **C-34** | 131.8 | 240.2 | 148.3 | 6.8 | 233.3 | 0.21 |
| **C-35** | 127.4 | 239.2 | 143.0 | 0.0 | 239.2 | 0.20 |
| **C-36** | 127.2 | 237.4 | 152.2 | –8.0 | 245.4 | 0.31 |
| **C-37** | 130.9 | 241.9 | 153.3 | –2.4 | 244.3 | 0.27 |
| **C-38** | 127.1 | 234.7 | 135.1 | 11.3 | 223.4 | 0.11 |
| **C-40** | 184.1 | 262.2 | 183.2 | 106.8 | 155.5 | –0.02 |
| **C-41** | 41.4 | 63.2 | 44.8 | 16.2 | 47.0 | 0.22 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

**Table S9.** Quantum Espresso calculations. NMR chemical shift tensors [in ppm] for structure **2** calculated using PBE0 functional with of the norm-conserving Troullier−Martins pseudopotential and GIPAW approach. Geometry (all positions) was optimized with PBE0 functional and norm-conserving Troullier−Martins pseudopotential. The van der Waals (vdW) interactions were included using vdW-DF exchange-correlation Cut-off energy was: 60 Ryd. The chemical shifts were calculated from shielding parameters ($\sigma_i$) using the equations: $\delta_i = 164.1 - \sigma_i.(C)$.

| Atom | $\delta_{iso}$ | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Omega^a$ | $\kappa^b$ |
|---|---|---|---|---|---|---|
| **C-10** | 171.7 | 247.4 | 180.1 | 87.6 | 159.8 | 0.16 |
| **C-11** | 51.5 | 60.4 | 51.5 | 42.4 | 18.0 | 0.01 |
| **C-12** | 30.9 | 44.8 | 40.8 | 7.1 | 37.8 | 0.78 |
| **C-13** | 123.9 | 222.2 | 149.3 | 0.2 | 222.0 | 0.34 |
| **C-14** | 131.4 | 235.0 | 152.5 | 6.7 | 228.3 | 0.28 |
| **C-15** | 114.2 | 200.7 | 131.4 | 10.5 | 190.3 | 0.27 |
| **C-16** | 161.0 | 246.3 | 176.4 | 60.3 | 186.0 | 0.25 |
| **C-17** | 119.1 | 203.6 | 145.3 | 8.4 | 195.2 | 0.40 |
| **C-18** | 127.3 | 230.0 | 131.3 | 20.6 | 209.4 | 0.06 |
| **C-20** | 171.9 | 243.9 | 183.2 | 88.6 | 155.4 | 0.22 |
| **C-21** | 44.7 | 65.9 | 44.1 | 24.0 | 41.9 | –0.04 |
| **C-22** | 11.0 | 28.5 | 14.8 | –10.3 | 38.8 | 0.29 |
| **C-30** | 173.4 | 235.8 | 197.3 | 87.0 | 148.8 | 0.48 |
| **C-31** | 51.0 | 69.4 | 59.3 | 24.3 | 45.1 | 0.55 |
| **C-32** | 34.1 | 47.7 | 38.7 | 16.0 | 31.8 | 0.43 |
| **C-33** | 137.0 | 239.7 | 171.2 | 0.1 | 239.6 | 0.43 |
| **C-34** | 132.5 | 239.4 | 147.9 | 10.1 | 229.3 | 0.20 |
| **C-35** | 128.0 | 238.3 | 143.9 | 1.8 | 236.5 | 0.20 |
| **C-36** | 127.6 | 236.8 | 152.0 | –6.0 | 242.8 | 0.30 |
| **C-37** | 132.2 | 242.2 | 154.5 | –0.2 | 242.4 | 0.28 |
| **C-38** | 127.5 | 233.6 | 135.8 | 13.0 | 220.6 | 0.11 |
| **C-40** | 182.3 | 254.5 | 186.9 | 105.5 | 149.0 | 0.09 |
| **C-41** | 41.4 | 63.5 | 44.4 | 16.2 | 47.3 | 0.19 |

[a] Span is expressed as: $\Omega = \delta_{11} - \delta_{33}$

[b] Skew is expressed as: $\kappa = (\delta_{22} - \delta_{iso})/\Omega$

Coordinates for sample **2.**

| | | | |
|---|---|---|---|
| O | 1.054070 | 7.161871 | 6.179545 |
| O | 4.440367 | 1.435661 | 3.551614 |
| H | 5.066213 | 0.772178 | 3.947614 |
| N | 2.609496 | 7.087253 | 8.704379 |
| H | 3.108864 | 7.985366 | 8.727247 |
| H | 3.023636 | 6.542297 | 9.539829 |
| H | 1.582723 | 7.236086 | 8.925057 |
| C | 2.290924 | 7.039977 | 6.250627 |
| C | 2.926433 | 6.343360 | 7.456541 |
| H | 4.021495 | 6.344707 | 7.365259 |
| C | 2.405152 | 4.901638 | 7.582887 |
| H | 2.711710 | 4.520600 | 8.569076 |
| H | 1.304745 | 4.930058 | 7.562115 |
| C | 2.943034 | 3.993963 | 6.508656 |
| C | 2.422902 | 3.989114 | 5.205743 |
| H | 1.575839 | 4.632393 | 4.959720 |
| C | 2.938376 | 3.149052 | 4.221269 |
| H | 2.515293 | 3.143799 | 3.216786 |
| C | 3.987092 | 2.272624 | 4.528465 |
| C | 4.522806 | 2.272624 | 5.822802 |
| H | 5.328395 | 1.582608 | 6.062727 |
| C | 4.003087 | 3.125481 | 6.791840 |
| H | 4.414770 | 3.095176 | 7.802993 |
| O | 4.552995 | 9.574439 | 3.848519 |
| N | 3.160327 | 7.439467 | 5.304267 |
| H | 4.170355 | 7.339797 | 5.477684 |
| C | 3.322255 | 9.402305 | 3.880344 |
| C | 2.733576 | 7.992639 | 4.023651 |
| H | 1.637792 | 8.052846 | 4.057000 |
| C | 3.190410 | 7.107726 | 2.864426 |

| | | | |
|---|---|---|---|
| H | 2.773226 | 6.098359 | 2.969048 |
| H | 4.286042 | 7.040246 | 2.846894 |
| H | 2.857103 | 7.527420 | 1.905870 |
| O | 0.978451 | 12.957986 | 4.785350 |
| N | 2.407551 | 10.387158 | 3.794207 |
| H | 1.406548 | 10.143504 | 3.827366 |
| C | 2.163836 | 12.549202 | 4.809934 |
| C | 2.757103 | 11.790089 | 3.618313 |
| H | 3.853271 | 11.852720 | 3.645754 |
| C | 2.217331 | 12.347840 | 2.284719 |
| H | 1.124124 | 12.227697 | 2.276905 |
| H | 2.430703 | 13.426573 | 2.268330 |
| C | 2.830284 | 11.678835 | 1.083569 |
| C | 2.394651 | 10.414500 | 0.657840 |
| H | 1.549260 | 9.940122 | 1.158081 |
| C | 3.012635 | 9.769739 | -0.414104 |
| H | 2.660450 | 8.785155 | -0.728541 |
| C | 4.065963 | 10.384195 | -1.094813 |
| H | 4.557055 | 9.869544 | -1.921687 |
| C | 4.482523 | 11.657958 | -0.702433 |
| H | 5.302448 | 12.146075 | -1.226495 |
| C | 3.871124 | 12.297601 | 0.376943 |
| H | 4.208238 | 13.291209 | 0.683376 |
| O | 4.425016 | 12.635942 | 8.223767 |
| O | 3.075647 | 14.134907 | 9.220437 |
| N | 2.939167 | 12.690626 | 5.891788 |
| H | 3.926480 | 12.420169 | 5.873874 |
| C | 3.389248 | 13.368656 | 8.255020 |
| C | 2.439429 | 13.376333 | 7.068926 |
| H | 1.479679 | 12.931991 | 7.376883 |
| H | 2.239861 | 14.431360 | 6.833574 |

[1] O. N. Antzutkin, S. C. Shekar, M. H. Levitt, *J. Magn. Reson. Ser. A*, 1995, **115**, 7.