^{13}C detected Scalar Nitrogen - Nitrogen Couplings across the Intramolecular Symmetric NHN-Hydrogen Bond of Proton Sponge

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Standard supporting information

In this section, we describe the line shape analysis of the ^{13}C-^{15}N----^{15}N-^{12}C three spin systems of DMANH$^+$. ^{13}C was observed at natural abundance and the nitrogen atoms sites where enriched to about 98%. These spin systems observed are of the ABX type; we note that the two ^{15}N nuclei A and B - although they are normally chemically equivalent -exhibit a slightly different isotropic chemical shift because of the different carbon isotope neighbors. Without the isotope shift $d = |\Delta^{15}\mathrm{N}\{^{13}\mathrm{C}\}|\ \nu^\circ \times 10^{-6}$ in Hz - where $\nu^\circ = \gamma B_o/2\pi$ is the Larmor frequency, γ the gyromagnetic ratio and B_o the magnetic field - it is principally impossible to obtain the coupling constant $J_{AB} = {}^{2h}J_{NN}$ from the X= ^{13}C signal as the system would be of the AA'X type.

The theory of the ABX spectrum has been described in Ref. 28. In the AB part of the multiplet 8 lines should be observed, from which one could obtain J_{AB} directly by line shape simulation. However, we have not been able to determine J_{AB} in this way because of the central ^{15}N line arising from the dominant ^{12}C-^{15}N----^{15}N-^{12}C units. No attempts were made in this study to suppress this line in suitable two-dimensional pulse experiments.

On the other hand, a simple direct analysis of the part X of multiplet is not sufficient to determine J_{AB} as depicted in Figure S1.

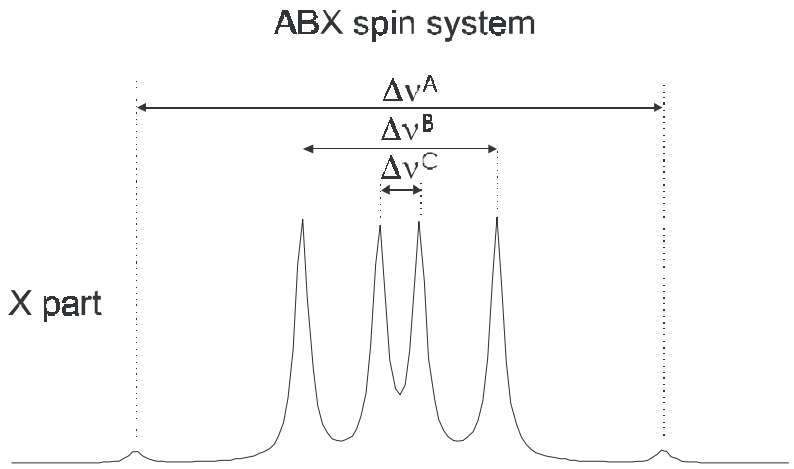

Fig. S1 View of the part X of the ABX high order spin system

According to Ref. 28, the line splittings in Fig. S1 are given by

$$\Delta\nu^{A} = 2\left\{\sqrt{0.25J_{AB}^{2} + \left(0.5d + 0.25\left(J_{AX} - J_{BX}\right)\right)^{2}} + \sqrt{0.25J_{AB}^{2} + \left(0.5d - 0.25\left(J_{AX} - J_{BX}\right)\right)^{2}}\right\} \quad (1)$$

$$\Delta\nu^{B} = \left|J_{AX} + J_{BX}\right| \quad (2)$$

$$\Delta\nu^{C} = \left|2\left\{\sqrt{0.25J_{AB}^{2} + \left(0.5d + 0.25\left(J_{AX} - J_{BX}\right)\right)^{2}} - \sqrt{0.25J_{AB}^{2} + \left(0.5d - 0.25\left(J_{AX} - J_{BX}\right)\right)^{2}}\right\}\right| \quad (3)$$

Only the parameters $\Delta\nu^{A}$, $\Delta\nu^{B}$ and $\Delta\nu^{C}$ can be obtained experimentally besides the ^{13}C chemical shift. They are not sufficient in order to determine the four unkown parameters J_{AB}, J_{AX}, J_{BX} and d in eqs 1-3. However, by measuring $\Delta\nu^{A}$, $\Delta\nu^{B}$ and $\Delta\nu^{C}$ at two different fields, we were able to obtain the field independent parameter set J_{AB}, J_{AX}, J_{BX}, $|\Delta^{15}N\{^{13}C\}|$ from eqs 1 to 3.

Using the parameter set obtained, we simulated the field-dependent high-order ^{13}C signals and refined the parameters slightly by a simultaneous optical fit of all signals of a given series, leading to the results assembled in Table 2. For this purpose, a home-made computer program based on DNMR2 of Binsch has been used.

An example of this method is illustrated in the following figures which depict the original computer program output (modified program DNMR2, Ref. 29) of the experimental and calculated original spectra of Figure 1d to 1e. In the figures are depicted three lines: experimental, simulated and difference. Parameters listed on the figures:

- name
- chemical shifts (in Hz): δ1, δ2, δ3, δ4
- half-width of the lines (in Hz)
- coupling constants between nuclei (in Hz): J12, J13, J14, J23, J24, J34
- 11 parameters not used in this application
- two last lines contain parameters regulating the range of simulated and experimental spectra on the picture.

In our case the most important parameters are: δ2-δ1=*d*, J12=J_{AB}, J13=J_{AX} and J23=J_{BX}.

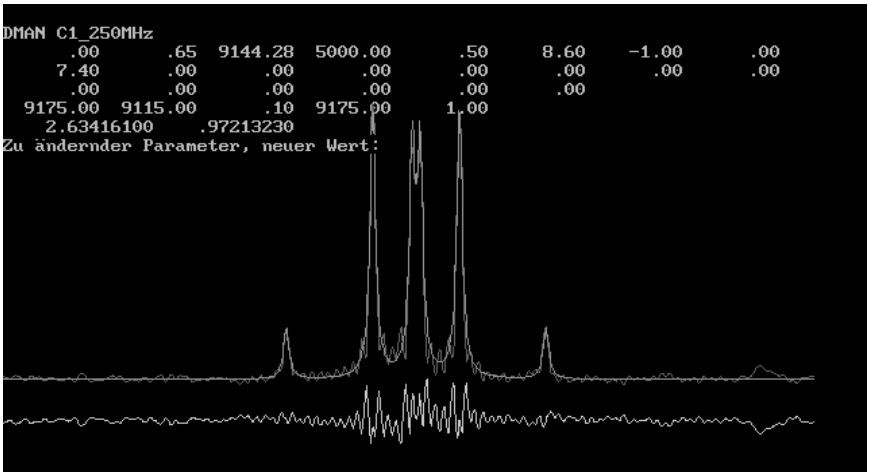

Fig. S2 Simulation of the C1 signal at magnetic field of 5.9 T (see Fig. 1d)

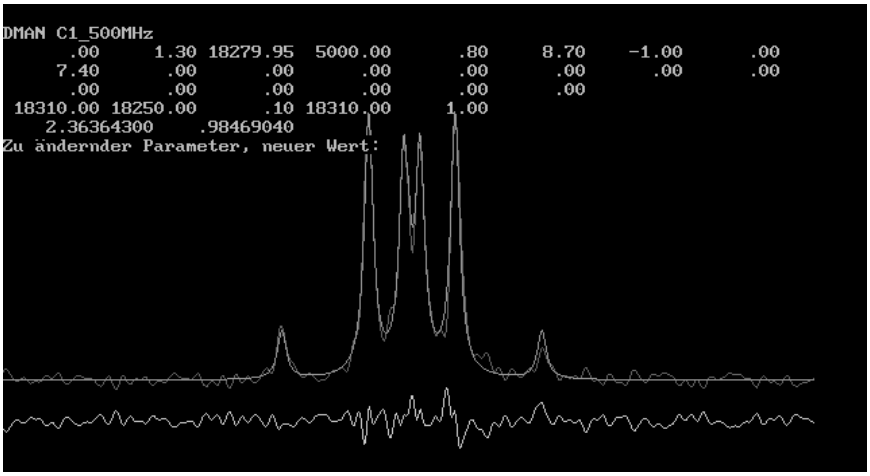

Fig. S3 Simulation of the C1 signal at magnetic field of 11.8 T (see Fig. 1d)

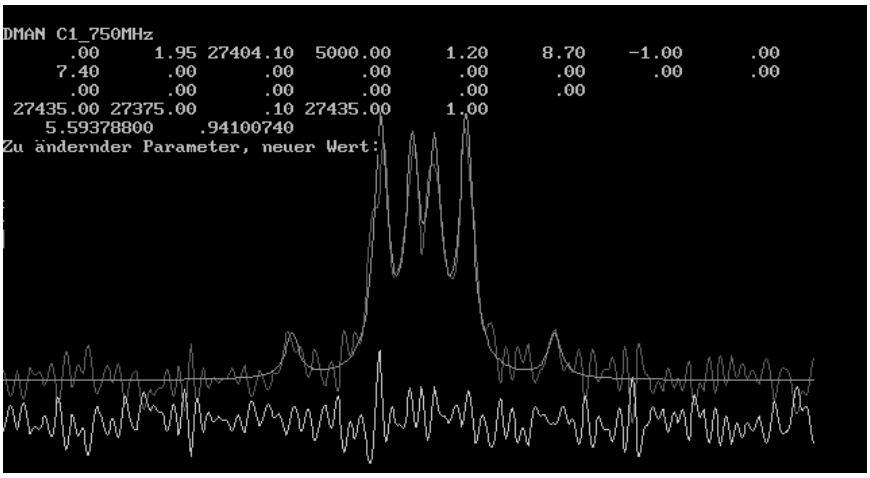

Fig. S4 Simulation of the C1 signal at magnetic field of 17.7 T (see Fig. 1d)

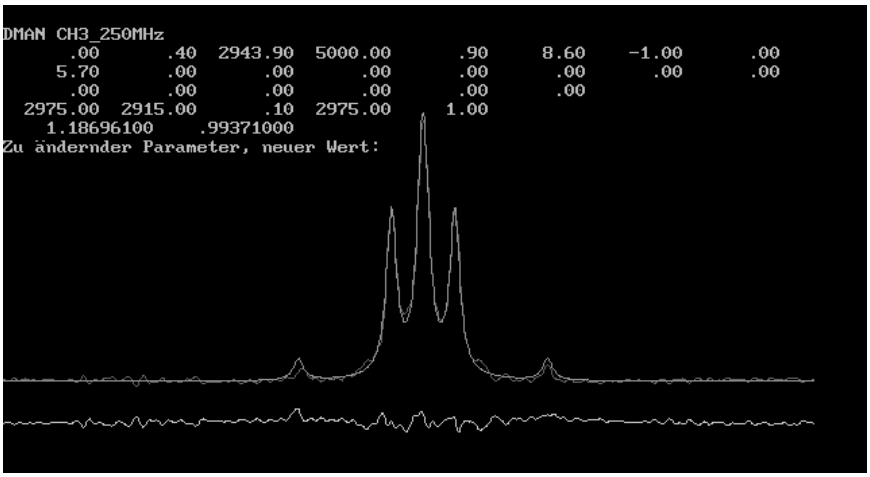

Fig. S5 Simulation of the CH_3 signal at magnetic field of 5.9 T (see Fig. 1e)

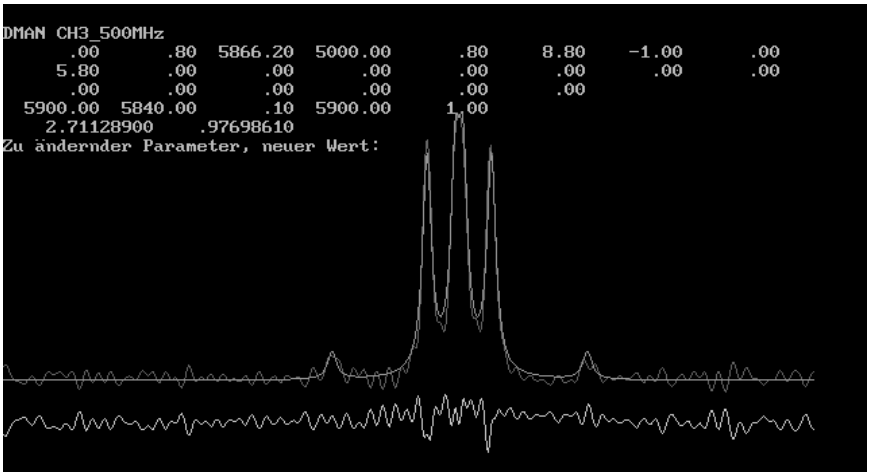

Fig. S6 Simulation of the CH_3 signal at magnetic field of 11.8 T (see Fig. 1e)