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A tetrathiafulvalene salt of the nitrite (NO_2^-) anion: investigations of the spin-Peierls phase

Loïc Soriano, Maylis Orio, Olivier Pilone, Olivier Jeannin, Eric Reinheimer, Nicolas Quéméré, Pascale Auban-Senzier, Marc Fourmigué* and Sylvain Bertaina*

SUPPLEMENTARY INFORMATION

Table S1. Temperature evolutions of the unit cell parameters of (*o*-DMTTF)$_2$NO$_2$. Percentages are given relative to the RT structure.

Param.	RT	150 K	85 K	25 K
a (Å)	7.0717(6)	6.9491(6), −1.73%	6.9158(1), −2.20%	6.9246(1), −2.08%
b (Å)	12.3350(9)	12.325(1), −0.08%	12.3179(2), −0.14%	12.3233(2), −0.09%
c (Å)	12.1501(9)	12.066(1), −0.6%	12.0454(3), −0.8%	12.0619(3), −0.7%
α (°)	90.00	90.00	90.00	90.00
β (°)	103.161(4)	103.318(3)	103.279(2)	103.332(2)
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	1032.01(14)	1005.67(14), −2.55%	998.69(3), −3.23%	1001.56(3), −2.95%

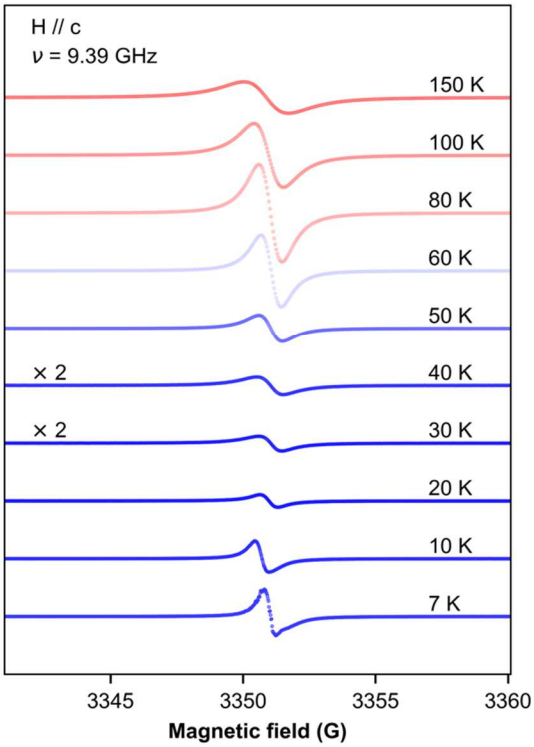

Figure S1. Series of EPR spectra of (o-DMTTF)$_2$NO$_2$ recorded from 150K down to 7K.

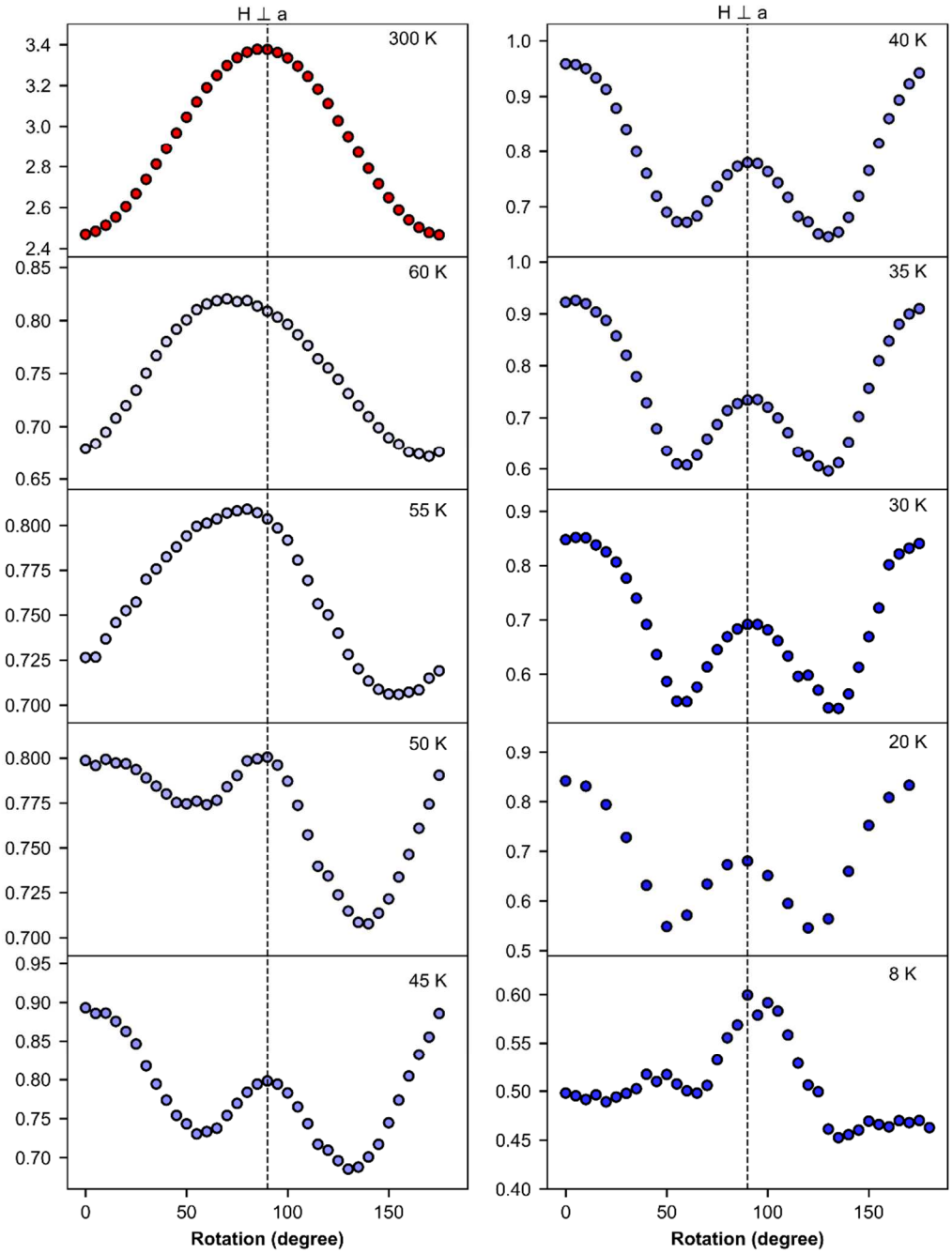

Fig S2. Angular variation of the linewidth in the (ac) plane for different temperatures from room temperature down to 8K. Note that below T_{SP}, the contribution of a triplet gives the $(3\cos^2\theta - 1)$ dependence of the linewidth.

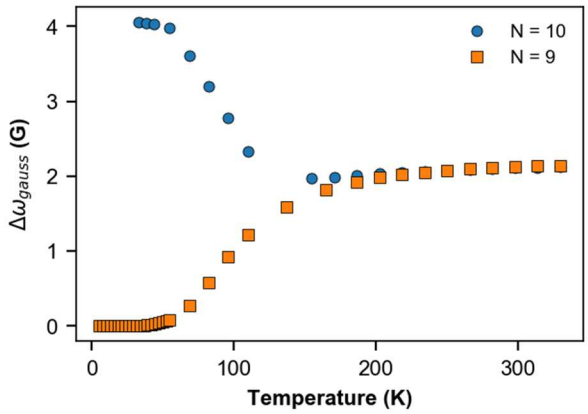

Figure S3. Temperature evolutions of theoretical linewidth calculated by method of moments for a cluster of N=9 spins and N=10 spins. The method consists in: i) exact diagonalization for N coupled spins, ii) calculation of the resonance field and amplitude of probability of each transition and for a given temperature, iii) calculation of the second moment of the transition distributions.

DFT Calculations of the *g* tensors

To facilitate comparisons between theory and experiments, the X-ray crystal structure of (*o*-DMTTF)$_2$NO$_2$ was used. We have chosen to work with a minimal model consisting of one *o*-DMTTF unit and surrounded by 1 to 4 nitrite anions. Based on the X-ray structure that identified two equivalent positions for each NO_2^- nitrogen atoms, we have considered several configurations in which the S•••N distances can vary from 3.027 to 5.455 angstroms to randomly sample the different situations encountered by one *o*-DMTTF cation (Figure S4). The DFT molecular models were then optimized while constraining the positions of all heavy atoms to their experimentally derived coordinates. Only the positions of the hydrogen atoms were relaxed because these are not reliably determined from the X-ray structure. Table S2 gives the calculated *g* values for eight configurations with one single NO_2^- anion at proximity of the *o*-DMTTF radical cation, as well as for two extreme configurations (last lines) where four nitrite anions are surrounding the *o*-DMTTF cation, at the shortest or the largest distances

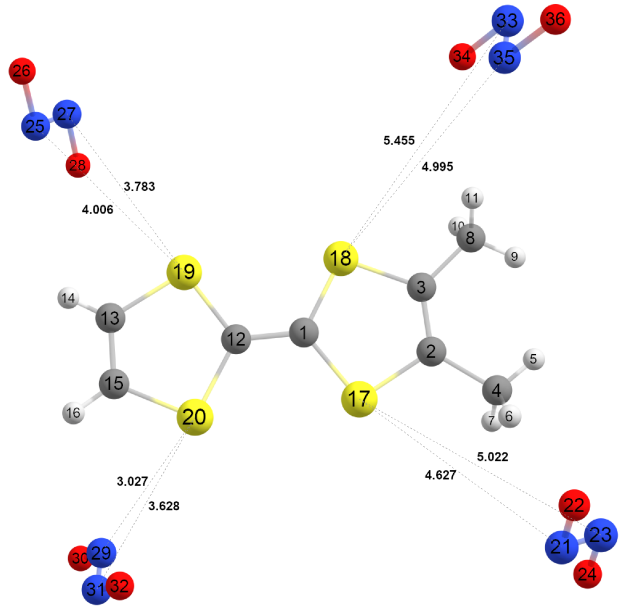

Figure S4. Minimal model used for computing the *g*-tensor parameters in (*o*-DMTTF)$_2$NO$_2$, showing numbering of all atoms, and the equivalent positions of the nitrogen atoms in the disordered nitrite anions. Color code S: yellow, N: blue, O: red, C: grey, H: white.

Table S2. Calculated *g*-tensor parameters for minimal models consisting of one *o*-DMTTF unit and surrounded by 1 or 4 nitrite anions, in one of the disordered nitrogen atom position (Cf Fig. S4). Extreme values are shown in red.

Contact(s)	d(S•••N) (Å)	g_{min}	g_{int}	g_{max}	g_{av}
S17•••N21	4.627	1.990827	2.001867	2.004760	1.999152
S17•••N23	5.022	1.990437	2.001867	2.004355	1.998887
S19•••N25	4.006	1.990908	2.001913	2.004790	1.999203
S19•••N27	3.783	1.990526	2.001871	2.004547	1.998982
S20•••N29	3.027	1.991213	2.001910	2.004885	1.999336
S20•••N31	3.628	1.990533	2.001897	2.004188	1.998873
S18•••N33	5.455	1.990484	2.001793	2.004339	1.998872
S18•••N35	4.995	1.993903	2.001803	2.004924	1.999256
S17•••N21 S19•••N27 S20•••N29 S18•••N35	4.627 3.783 3.027 4.995	1.993903	2.002525	2.008016	2.001481
S17•••N23 S19•••N25 S20•••N31 S18•••N33	5.022 4.066 3.628 5.455	1.990949	2.001689	2.004114	1.998917