Supplementary data:

Exploring Partial Structural Disorder in Anhydrous Paraxanthine through Combined Experiment, Solid-State Computational Modelling, and Molecular Docking

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Table S1. The ^{14}N NQR parameters for PX calculated theoretically at the GGA/RPBE level with TS DFT-D correction.

| Structure	Site	ν_+ [MHz]	ν_- [MHz]	ν_0 [MHz]	e^2qQ/h [MHz]	η	s, r^2, intercept, slope
150K X-ray	>N(1)CH$_3$	2.692	2.535	0.157	-3.485	0.09	0.329
	>N(3)H	2.913	1.735	1.178	-3.099	0.76	0.967
	>N(7)CH$_3$	2.020	1.721	0.299	-2.494	0.24	0.069
	-N(9)=	2.833	2.365	0.468	-3.465	0.27	0.980

**Table S2.** The ^{14}N NQR parameters for PX calculated theoretically at the m-GGA/RSCAN level.

Structure	Site	ν_+ [MHz]	ν_- [MHz]	ν_0 [MHz]	e^2qQ/h [MHz]	η	s, r^2, intercept, slope
150K X-ray	>N(1)CH$_3$	2.733	2.523	0.210	-3.504	0.12	0.430
	>N(3)H	2.934	1.686	1.247	-3.080	0.81	0.958
	>N(7)CH$_3$	1.970	1.667	0.303	-2.425	0.25	0.071
	-N(9)=	2.916	2.484	0.432	-3.600	0.24	0.989
150K protons optimised	>N(1)CH$_3$	2.526	2.347	0.179	-3.249	0.11	0.036
	>N(3)H	2.564	1.870	0.695	-2.956	0.47	0.996
	>N(7)CH$_3$	1.924	1.606	0.318	-2.353	0.27	0.012
	-N(9)=	2.745	2.276	0.469	-3.347	0.28	0.945
150K full optimisation	>N(1)CH$_3$	2.445	2.256	0.188	-3.134	0.12	0.265
	>N(3)H	2.472	1.569	0.902	-2.694	0.67	0.969
	>N(7)CH$_3$	1.866	1.579	0.287	-2.296	0.25	0.032
	-N(9)=	2.819	2.401	0.418	-3.480	0.24	0.918
RT ABC protons optimised	>N(1)CH$_3$	2.42	2.234	0.186	-3.103	0.12	0.067
	>N(3)H	2.464	1.499	0.964	-2.642	0.73	0.994
	>N(7)CH$_3$	1.84	1.578	0.262	-2.279	0.23	-0.044
	-N(9)=	2.824	2.405	0.418	-3.486	0.24	1.036
RT DEF protons optimised	>N(1)CH$_3$	2.462	2.272	0.189	-3.156	0.12	0.294
	>N(3)H	2.464	1.543	0.921	-2.671	0.69	0.967
	>N(7)CH$_3$	1.875	1.597	0.278	-2.315	0.24	0.031
	-N(9)=	2.802	2.403	0.399	-3.47	0.23	0.919
RT ABCDEF averaged protons optimised	>N(1)CH$_3$	2.441	2.253	0.188	-3.129	0.12	0.321
	>N(3)H	2.464	1.521	0.943	-2.656	0.71	0.964
	>N(7)CH$_3$	1.858	1.588	0.270	-2.297	0.24	0.035
	-N(9)=	2.813	2.404	0.409	-3.478	0.24	0.914
direct disorder protons optimised	>N(1)CH$_3$	2.903	2.716	0.187	-3.746	0.10	0.813
	>N(3)H	2.982	1.752	1.231	-3.156	0.78	0.821
	>N(7)CH$_3$	4.829	2.897	1.932	-5.151	0.75	1.039
	-N(9)=	2.578	2.226	0.352	-3.203	0.22	0.372

Table S3. Topological parameters describing the interactions in PX (electron density at bond critical point, BCP, ($\rho_{BCP}(r)$), its Laplacian ($\Delta\rho_{BCP}(r)$), the potential electron energy density ($V_{BCP}(r)$), the kinetic electron energy density ($G_{BCP}(r)$) and the total electron energy density ($H_{BCP}(r)$) calculated at the M062X/6-311+G** level.

| Type	Proton donor group	Nature	Contact	$\rho_{BCP}(r)$	$\Delta\rho_{BCP}(r)$	V_{BCP} [a.u.]	G_{BCP} [a.u.]	λ_2 [a.u.]
intra	N(1)CH₃	HB, electrostatic	CH···O(6)	0.019415	0.082248	-0.015919	0.018240	-0.008415
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.032732	0.111786	-0.025676	0.026811	-0.045682
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.033009	0.109698	-0.025494	0.026459	-0.046151
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.011137	0.034085	-0.006972	0.007747	-0.010319
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.01114	0.034082	-0.006975	0.007748	-0.010321
contact	-	van der Waals	N(7)···O(6)	0.006256	0.026387	-0.00435	0.005473	-0.002838
inter	N(7)CH₃	HB, electrostatic	CH···O(6)	0.006207	0.026292	-0.004292	0.005433	-0.002806
inter	N(7)CH₃	dispersive	CH···HC	0.005926	0.022961	-0.002851	0.004296	-0.003728
inter	N(7)CH₃	dispersive	CH···HC	0.005917	0.022936	-0.002843	0.004288	-0.003714
inter	N(1)CH₃	HB, electrostatic	CH···O(2)	0.005584	0.021925	-0.003471	0.004476	-0.004292
inter	N(7)CH₃	HB, electrostatic	CH···N(9)	0.005831	0.020395	-0.003269	0.004184	-0.002005
inter	N(1)CH₃	HB, electrostatic	CH···O(6)	0.003243	0.013167	-0.001731	0.002511	-0.002214
inter	N(1)CH₃	dispersive	CH···HC	0.00219	0.008072	-0.000829	0.001424	-0.000435
inter	C(8)H	HB, electrostatic	C(8)H···O(6)	0.010951	0.033945	-0.008072	0.008279	-0.010990
intra	N(1)CH₃	HB, electrostatic	CH···O(6)	0.020088	0.08409	-0.016395	0.018709	-0.009727
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.03101	0.105998	-0.024489	0.025494	-0.042313
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.031257	0.104175	-0.024316	0.02518	-0.042684
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.008666	0.027768	-0.005076	0.006009	-0.007122
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.008664	0.02776	-0.005075	0.006007	-0.007122
inter	N(1)CH₃	HB, electrostatic	CH···O(6)	0.005983	0.02548	-0.004125	0.005248	-0.002449
inter	N(7)CH₃	HB, electrostatic	CH···O(6)	0.005934	0.025417	-0.004073	0.005214	-0.002442
inter	N(7)CH₃	dispersive	CH···HC	0.00563	0.021691	-0.002668	0.004045	-0.003515
inter	N(7)CH₃	dispersive	CH···HC	0.005634	0.021685	-0.002675	0.004048	-0.003523
inter	N(7)CH₃	HB, electrostatic	CH···N(9)	0.005954	0.020752	-0.00335	0.004269	-0.003306
inter	N(1)CH₃	HB, electrostatic	CH···O(2)	0.004742	0.018976	-0.00284	0.003792	-0.003677
inter	N(1)CH₃	HB, electrostatic	CH···O(2)	0.002830	0.011782	-0.001444	0.002195	-0.001819
inter	C\(8)H	HB, electrostatic	C(8)H···O(6)	0.00949	0.030082	-0.006777	0.007157	-0.009274
intra	N(1)CH₃	HB, electrostatic	CH···O(6)	0.02005	0.084041	-0.01635	0.01868	-0.009608
intra	N(7)CH₃	HB, electrostatic	CH···O(6)	0.012975	0.041747	-0.00945	0.009943	-0.011783
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.031117	0.106289	-0.024555	0.025564	-0.042496
inter	N(3)H	HB, electrostatic	N(3)H···O(2)	0.031367	0.104414	-0.024377	0.02524	-0.042879
inter	N(7)CH₃	dispersive	CH···HC	0.020191	0.059867	-0.015644	0.015305	-0.026689
inter	N(7)CH₃	HB, electrostatic	CH···N(9)	0.011148	0.035763	-0.00735	0.008146	-0.009782
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.00866	0.027753	-0.005071	0.006005	-0.007119
inter	N(1)CH₃	HB, electrostatic	CH···N(9)	0.008659	0.027747	-0.00507	0.006003	-0.007119
inter	N(7)CH₃	HB, electrostatic	CH···O(6)	0.006086	0.025919	-0.004206	0.005343	-0.002403
inter	N(7)CH₃	HB, electrostatic	CH···O(6)	0.006019	0.025852	-0.00414	0.005301	-0.002391
inter	N(1)CH₃	HB, electrostatic	CH···O(2)	0.004743	0.018973	-0.00284	0.003791	-0.003675
inter	N(1)CH₃	HB, electrostatic	CH···O(6)	0.002808	0.011705	-0.001431	0.002179	-0.001875
inter	N(1)CH₃	dispersive	CH···HC	0.002367	0.008792	-0.000886	0.001542	-0.000863
inter	C\(8)H	HB, electrostatic	C(8)H···O(6)	0.009484	0.030130	-0.006781	0.007157	-0.009274
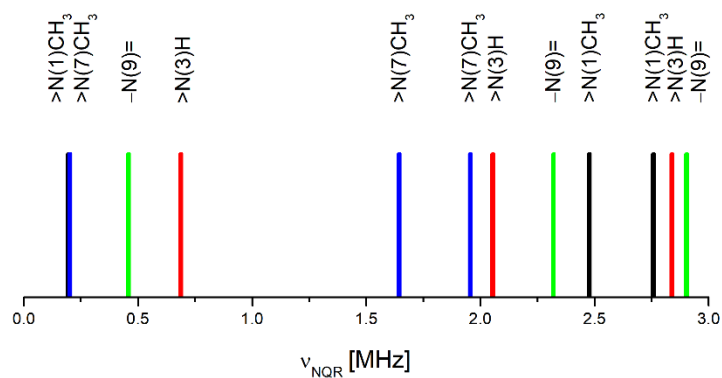
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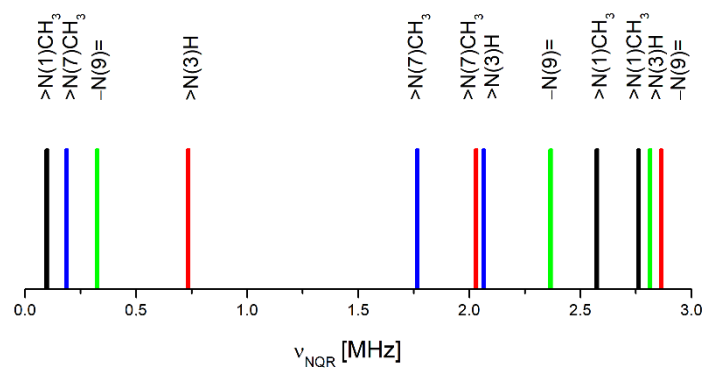
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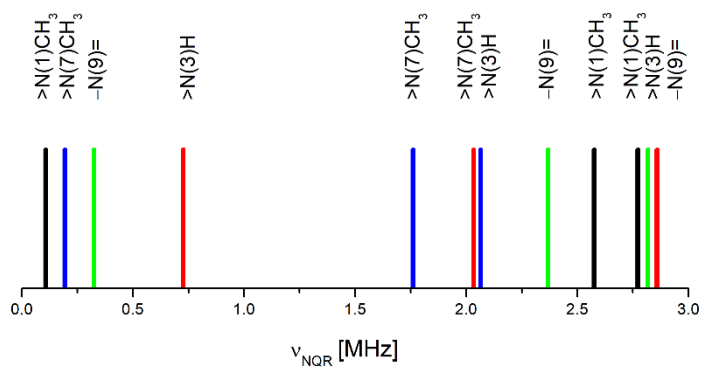
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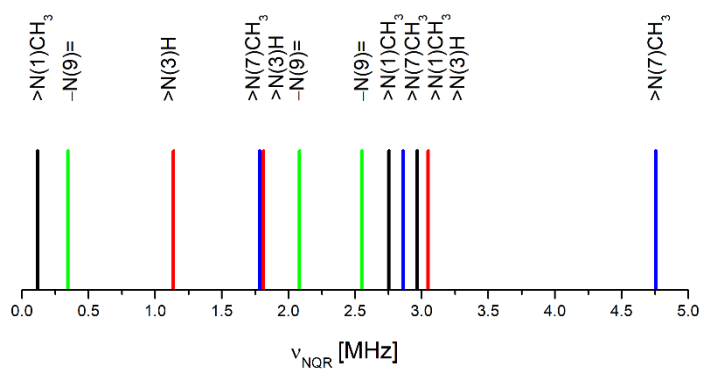
d)

Figure S1. The ^{14}N NQR spectrum in PX: experimental a) and simulated at the GGA/RBPE of theory b) LT, c) averaged model at RT (RT ABCDEF) and d) direct disorder model.
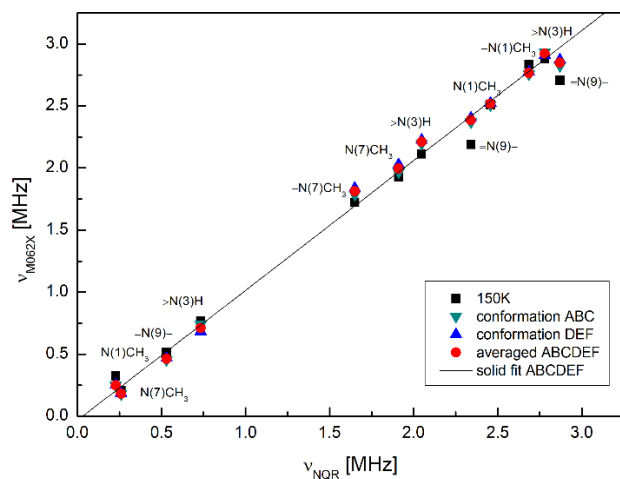
Figure S2. The correlation between the NQR frequencies experimental and calculated at M062X level.
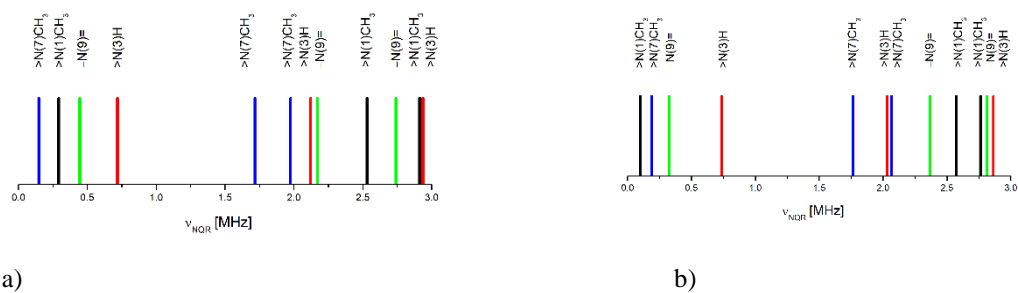

a)

b)

Figure S3 The resonance line positions in NQR spectrum simulated at the M062X level: a) cluster, LT, b) cluster, averaged model RT (RT ABCDEF).
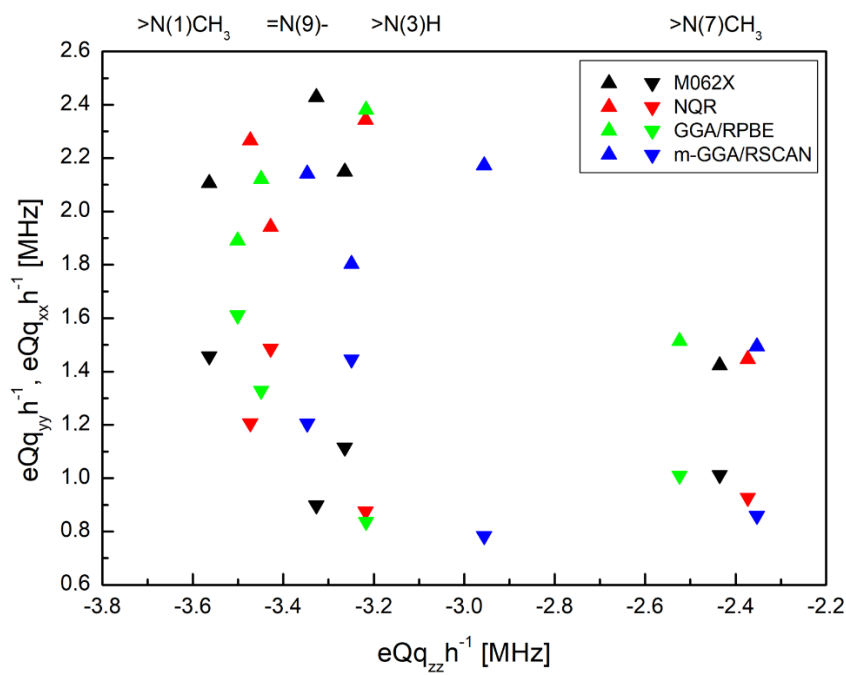
Figure S4. The correlation between the EFG tensor components.
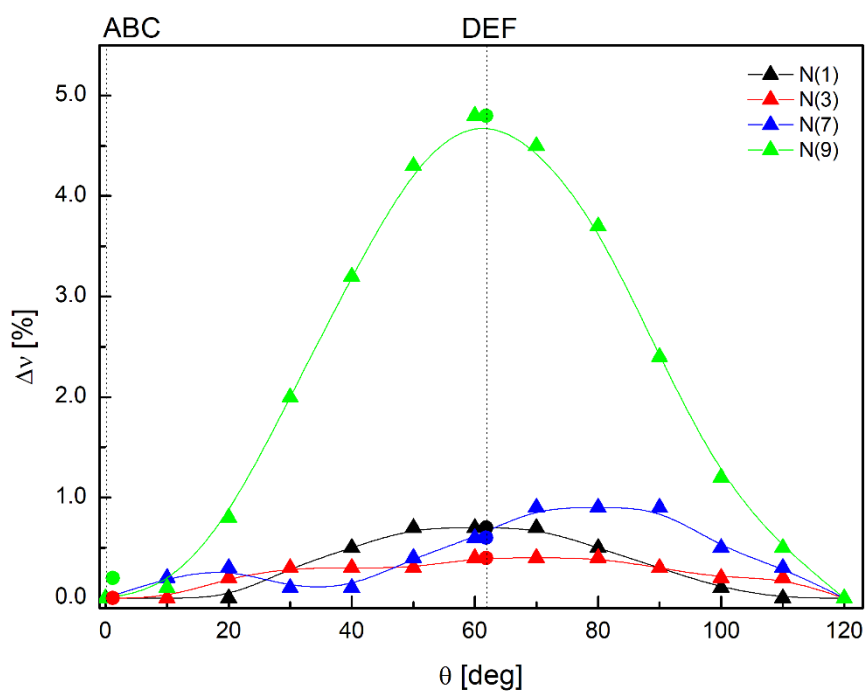
Figure S5. The changes in the FWHM of the resonance line upon the rotation of the methyl group at N(7).
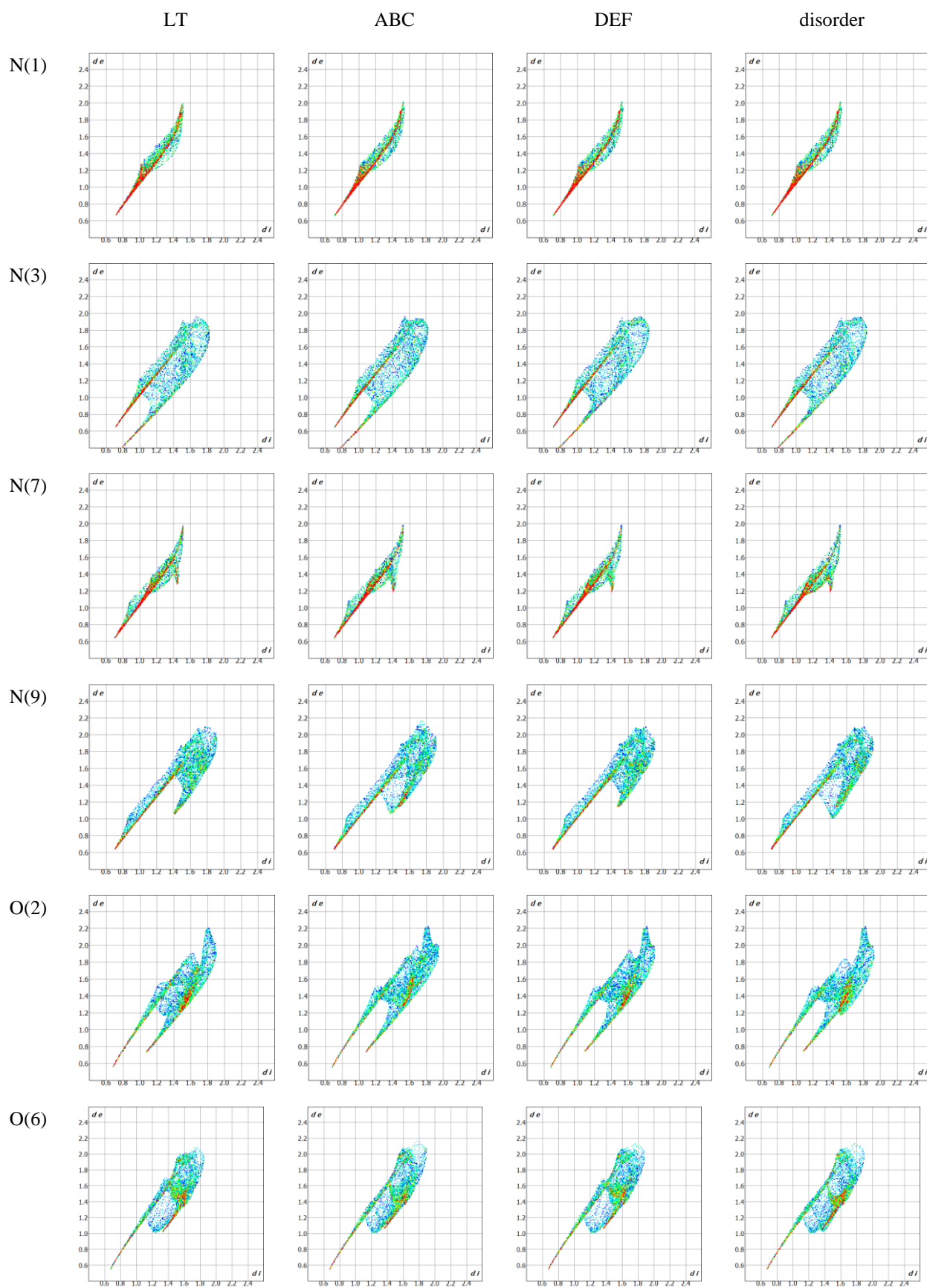
Figure S6. Local 2D molecular fingerprinting of the interactions pattern in PX (protons optimized).
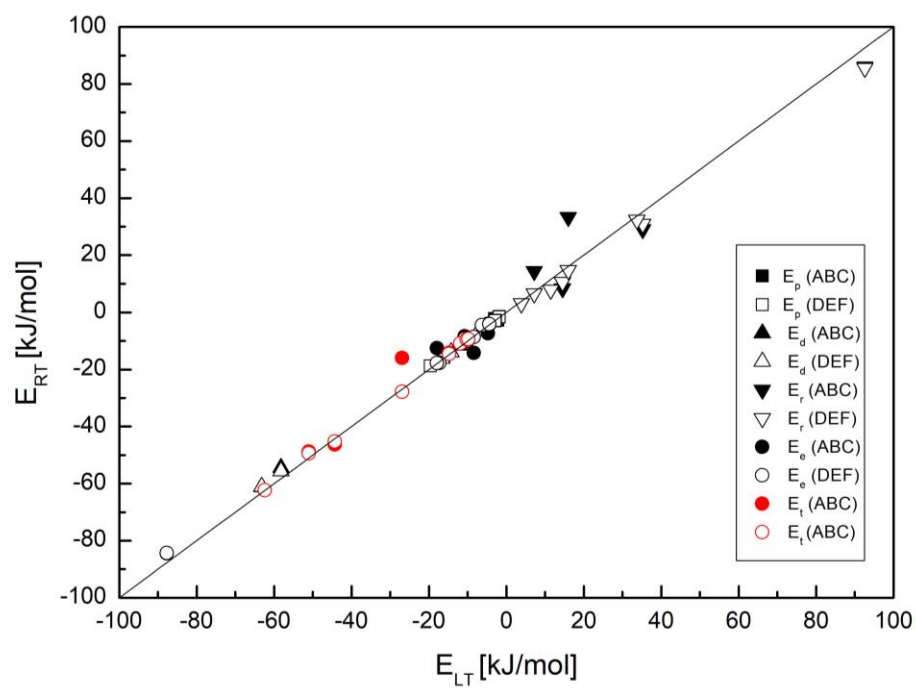
Figure S7. The correlation between the total energy and its components (data from Table 6) for LT, RT ABC and RT DEF structures (solid line $E_{RT}=E_{LT}$).
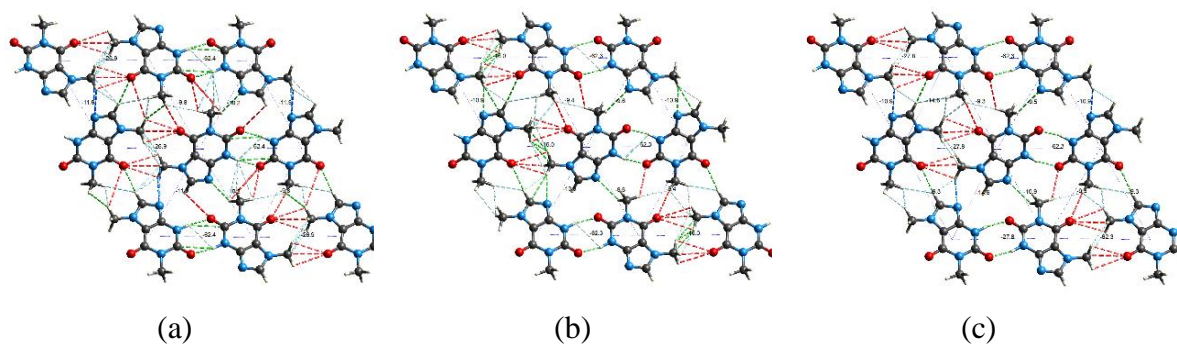

| (a) | (b) | (c) |

Figure S8. Interactions pattern in the PX structure (along the a-axis): (a) LT, (b) RT ABC and (c) RT DEF.