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Revisiting 2-chloro-4-nitroaniline: analysis of intricate supramolecular ordering of a triclinic polymorph featuring high Z value and strong second harmonic generation

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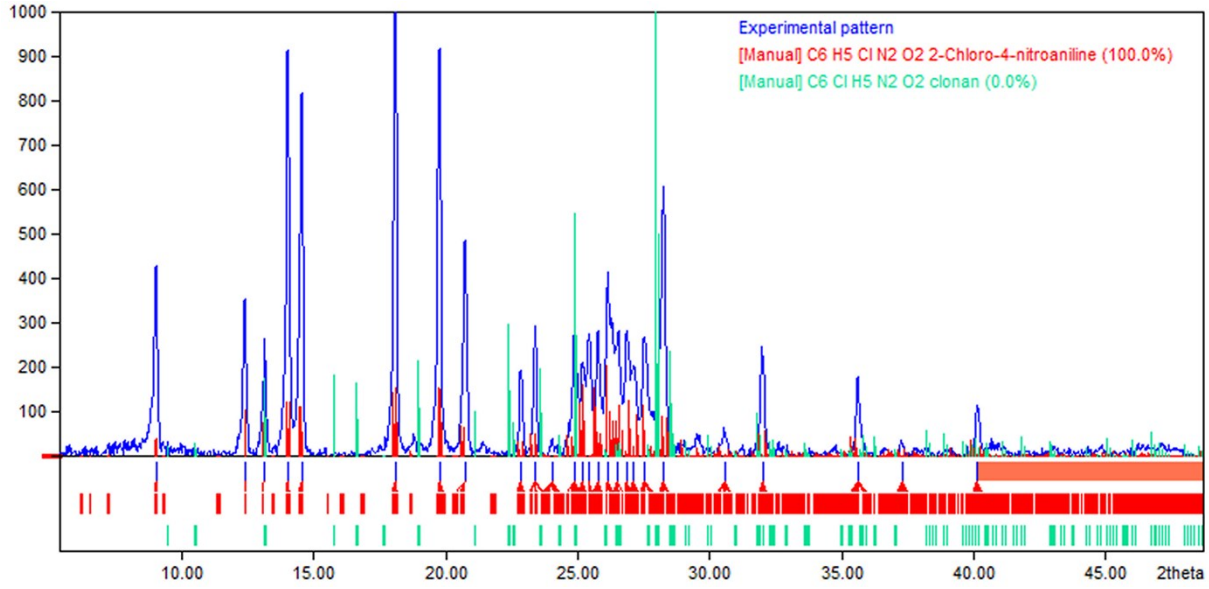

Figure S1. X-ray powder diffraction pattern for the triclinic phase of 2Cl4na re-crystallized from aqueous ethanol (blue), theoretical pattern generated on the basis of X-ray data for single-crystal of triclinic form (red) and pattern generated on the basis of data for orthorhombic phase deposited in the *Cambridge Structural Database* (green).

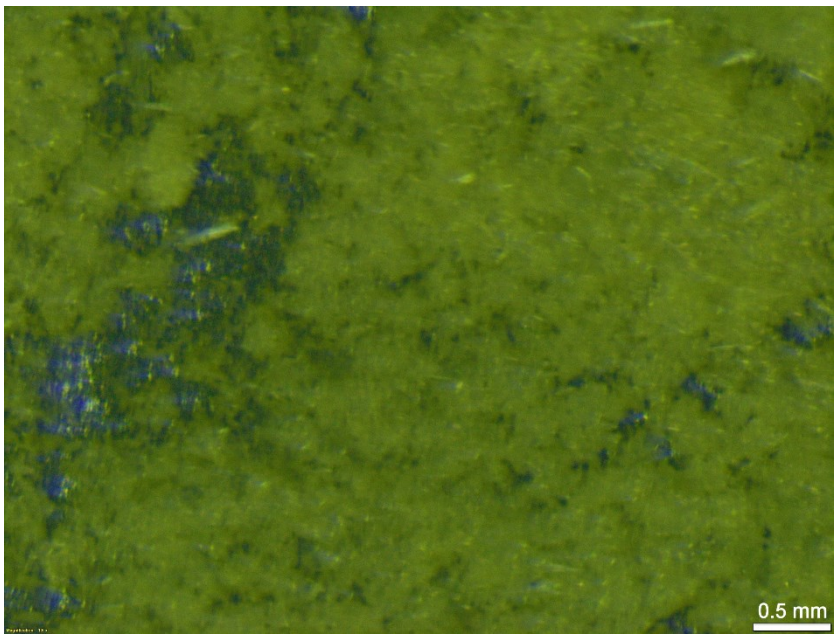

Figure S2. A photo of the microcrystalline sample of triclinic polymorph measured by XRD powder diffractometer.

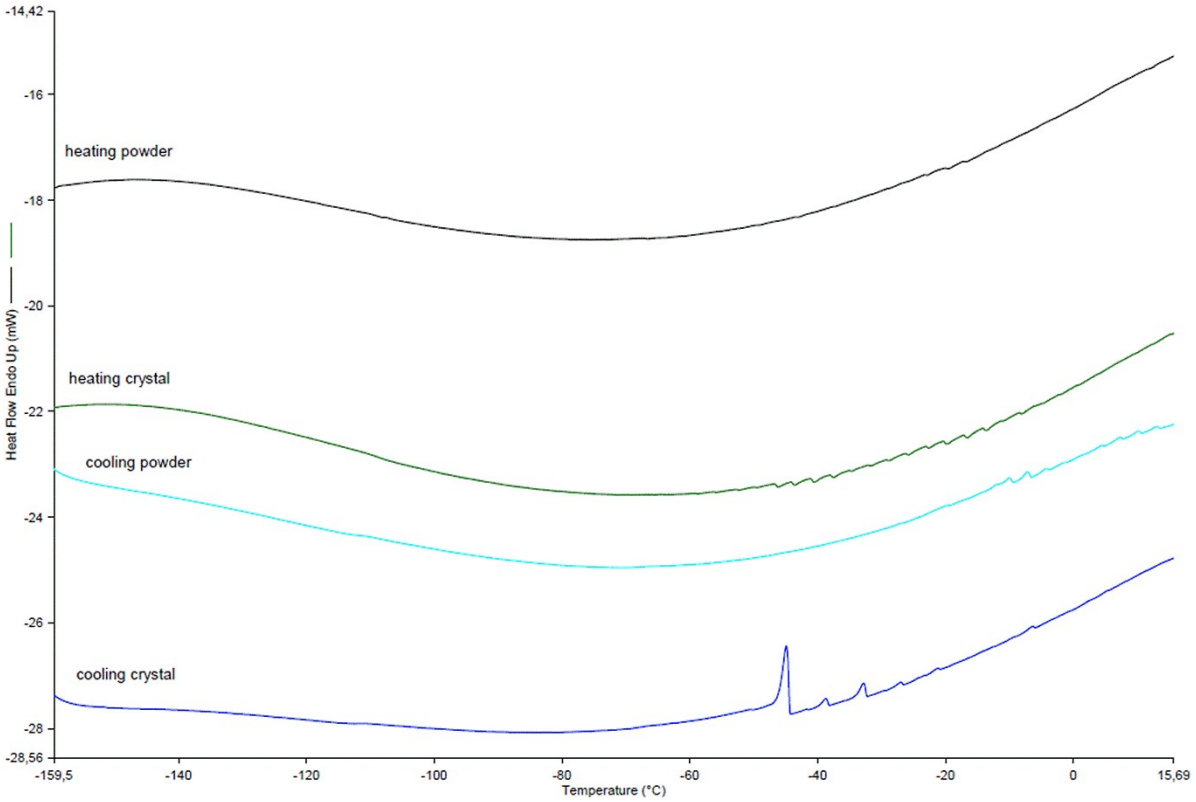

Figure S3. DSC curves for the bulk re-crystallized sample and for a few selected needles of the triclinic polymorph.

Table S1. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the orthorhombic crystal of 2Cl4na.

Dimer	Symmetry operation	E_{int}	Contribution	Interaction
		Building unit is a molecule		
o1	x,y,1+z	–6.10	12.8	stacking
o2	x,y,–1+z	–6.10	12.8	stacking
o3	1/2–x,–1/2+y,1/2+z	–4.75	10.0	N–H···O
o4	1/2–x,1/2+y,–1/2+z	–4.75	10.0	N–H···O
o5	–1/2+x,1/2–y,–1+z	–3.80	8.0	non-specific
o6	1/2+x,1/2–y,1+z	–3.80	8.0	non-specific
o7	1–x,1–y,1/2+z	–3.52	7.4	C–H···Cl
o8	1–x,1–y,–1/2+z	–3.52	7.4	C–H···Cl
o9	1/2+x,1/2–y,z	–2.50	5.3	non-specific
o10	–1/2+x,1/2–y,z	–2.50	5.3	non-specific
o11	1/2–x,1/2+y,1/2+z	–1.62	3.4	non-specific
o12	1/2–x,–1/2+y,–1/2+z	–1.62	3.4	non-specific
o13	–x,1–y,1/2+z	–1.52	3.2	N–H···N
o14	–x,1–y,–1/2+z	–1.52	3.2	N–H···N

Table S2. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na.

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tA1	B	–1+x,y,z	–7.51	14.2	N–H···O[b], C–H···O
tA2	A	1+x,y,z	–6.25	11.9	stacking
tA3	A	–1+x,y,z	–6.25	11.9	stacking
tA4	D	x,y,–1+z	–6.07	11.5	N–H···O[b]
tA5	G	x,y,z	–5.36	10.2	N–H···O
tA6	G	–1+x,–1+y,z	–5.18	9.8	N–H···O, C–H···Cl
tA7	G	–1+x,y,z	–3.78	7.2	C–H···O
tA8	D	–1+x,y,–1+z	–2.99	5.7	non-specific
tA9	H	–1+x,–1+y,z	–2.88	5.5	non-specific
tA10	H	x,–1+y,z	–2.81	5.3	C–H···Cl
tA11	G	x,–1+y,z	–2.57	4.9	non-specific
tA12	B	x,y,z	–2.30	4.4	non-specific
tA13	H	–1+x,y,z	1.23	–2.3	non-specific
		Total	–45.23		

Table S3. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na (molecule B).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tB1	A	1+x,y,z	–7.51	13.9	N–H···O[b], C–H···O
tB2	C	–1+x,y,z	–6.94	12.9	N–H···O
tB3	F	–1+x,y,z	–5.68	10.5	N–H···O, C–H···Cl
tB4	B	–1+x,y,z	–5.58	10.4	stacking
tB5	B	1+x,y,z	–5.58	10.4	stacking
tB6	F	1+x,–1+y,z	–5.21	9.7	N–H···O
tB7	F	x,y,z	–3.97	7.4	non-specific
tB8	G	x,y,z	–3.29	6.1	C–H···Cl
tB9	F	x,–1+y,z	–3.22	6.0	non-specific
tB10	G	–1+x,y,z	–3.07	5.7	C–H···Cl
tB11	C	x,y,z	–2.71	5.0	C–H···O
tB12	A	x,y,z	–2.30	4.3	non-specific
tB13	G	x,–1+y,z	1.16	–2.1	non-specific
		Total	–46.39		

Table S4. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na (molecule C).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tC1	B	1+x,y,z	–6.94	13.3	N–H···O
tC2	D	–1+x,y,z	–6.12	11.7	N–H···O, C–H···O
tC3	C	–1+x,y,z	–5.77	11.1	stacking
tC4	C	1+x,y,z	–5.77	11.1	stacking
tC5	E	x,–1+y,z	–5.71	11.0	N–H···O
tC6	E	1+x,y,z	–5.67	10.9	N–H···O, C–H···Cl
tC7	E	1+x,–1+y,z	–3.78	7.2	non-specific
tC8	F	1+x,–1+y,z	–2.92	5.6	C–H···Cl
tC9	F	x,–1+y,z	–2.72	5.2	C–H···Cl
tC10	B	x,y,z	–2.71	5.2	C–H···O
tC11	E	x,y,z	–2.67	5.1	non-specific
tC12	D	x,y,z	–2.53	4.9	non-specific
tC13	F	x,y,z	1.20	–2.3	non-specific
		Total	–45.18		

Table S5. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of o–2Cl4na (molecule D).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tD1	C	1+x,y,z	–6.12	12.1	N–H···O, C–H···O
tD2	A	x,y,1+z	–6.07	12.0	N–H···O[b], C–H···O
tD3	D	1+x,y,z	–6.03	11.9	stacking
tD4	D	–1+x,y,z	–6.03	11.9	stacking
tD5	H	–1+x,y,1+z	–5.34	10.6	N–H···O
tD6	H	1+x,–1+y,1+z	–5.13	10.1	N–H···O
tD7	H	x,y,1+z	–3.02	6.0	non-specific
tD8	H	x,–1+y,1+z	–3.00	5.9	non-specific
tD9	A	1+x,y,1+z	–2.99	5.9	non-specific
tD10	E	1+x,y,z	–2.83	5.6	non-specific
tD11	E	x,y,z	–2.79	5.5	C–H···Cl
tD12	C	x,y,z	–2.53	5.0	non-specific
tD13	E	1+x,–1+y,z	1.29	–2.5	non-specific
		Total	–44.47		

Table S6. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na (molecule E).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tE1	F	–1+x,y,z	–7.06	13.3	N–H···O[b], C–H···O
tE2	H	x,y,1+z	–6.61	12.5	N–H···O, C–H···O
tE3	E	1+x,y,z	–5.87	11.1	stacking
tE4	E	–1+x,y,z	–5.87	11.1	stacking
tE5	C	x,1+y,z	–5.71	10.8	N–H···O
tE6	C	–1+x,y,z	–5.67	10.7	N–H···O, C–H···Cl
tE7	C	–1+x,1+y,z	–3.78	7.1	non-specific
tE8	H	–1+x,y,1+z	–3.09	5.8	non-specific
tE9	D	–1+x,y,z	–2.83	5.3	non-specific
tE10	D	x,y,z	–2.79	5.3	C–H···Cl
tE11	C	x,y,z	–2.67	5.0	non-specific
tE12	F	x,y,z	–2.36	4.5	non-specific
tE13	D	–1+x,1+y,z	1.29	–2.4	non-specific
			–45.96		

Table S7. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na (molecule F).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tF1	G	–1+x,y,z	–7.32	13.7	N–H···O
tF2	E	1+x,y,z	–7.06	13.2	N–H···O[b], C–H···O
tF3	F	–1+x,y,z	–6.00	11.2	stacking
tF4	F	1+x,y,z	–6.00	11.2	stacking
tF5	B	1+x,y,z	–5.68	10.6	N–H···O
tF6	B	–1+x,1+y,z	–5.21	9.8	non-specific
tF7	B	x,y,z	–3.97	7.4	non-specific
tF8	B	x,1+y,z	–3.22	6.0	non-specific
tF9	C	–1+x,1+y,z	–2.92	5.5	C–H···Cl
tF10	C	x,1+y,z	–2.72	5.1	C–H···Cl
tF11	E	x,y,z	–2.36	4.4	non-specific
tF12	G	x,y,z	–2.11	3.9	non-specific
tF13	C	x,y,z	1.20	–2.2	non-specific
		Total	–46.04		

Table S8. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of 2Cl4na (molecule G).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tG1	F	1+x,y,z	–7.32	14.1	N–H···O
tG2	H	–1+x,y,z	–6.13	11.8	N–H···O
tG3	G	–1+x,y,z	–5.81	11.2	stacking
tG4	G	1+x,y,z	–5.81	11.2	stacking
tG5	A	x,y,z	–5.36	10.3	N–H···O
tG6	A	1+x,1+y,z	–5.18	10.0	N–H···O, C–H···Cl
tG7	A	1+x,y,z	–3.78	7.3	non-specific
tG8	B	x,y,z	–3.29	6.3	C–H···Cl
tG9	B	1+x,y,z	–3.07	5.9	C–H···Cl
tG10	A	x,1+y,z	–2.57	5.0	non-specific
tG11	H	x,y,z	–2.57	5.0	non-specific
tG12	F	x,y,z	–2.11	4.1	non-specific
tG13	B	x,1+y,z	1.16	–2.2	non-specific
			–51.84		

Table S9. Symmetry codes, bonding type, interaction energy of the basic building unit with neighbouring ones (E_{int}, kcal/mol) and the contribution of this energy to the total interaction energy (%) in the triclinic crystal of o–2Cl4na (molecule H).

Dimer	Mol.	Symmetry operation	E_{int}	Contribution	Interaction
tH1	E	x,y,–1+z	–6.61	12.8	N–H···O[b]
tH2	G	1+x,y,z	–6.13	11.9	N–H···O
tH3	H	–1+x,y,z	–6.05	11.8	stacking
tH4	H	1+x,y,z	–6.05	11.8	stacking
tH5	D	1+x,y,–1+z	–5.34	10.4	N–H···O
tH6	D	–1+x,1+y,–1+z	–5.13	10.0	N–H···O
tH7	E	1+x,y,–1+z	–3.09	6.0	non-specific
tH8	D	x,y,–1+z	–3.02	5.9	non-specific
tH9	D	x,1+y,–1+z	–3.00	5.8	non-specific
tH10	A	1+x,1+y,z	–2.88	5.6	non-specific
tH11	A	x,1+y,z	–2.81	5.5	C–H···Cl
tH12	G	x,y,z	–2.57	5.0	non-specific
tH13	A	1+x,y,z	1.23	–2.4	non-specific
		Total	–44.82		