Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary information

Microcrystal Electron Diffraction (MicroED) Structure Determination of a Mechanochemically Synthesized Co-crystal not Affordable from Solution Crystallization

Toshiyuki Sasaki,*# Takanori Nakane,# Akihiro Kawamoto, Tomohiro Nishizawa, Genji Kurisu*
# Contributed equally as co-first author

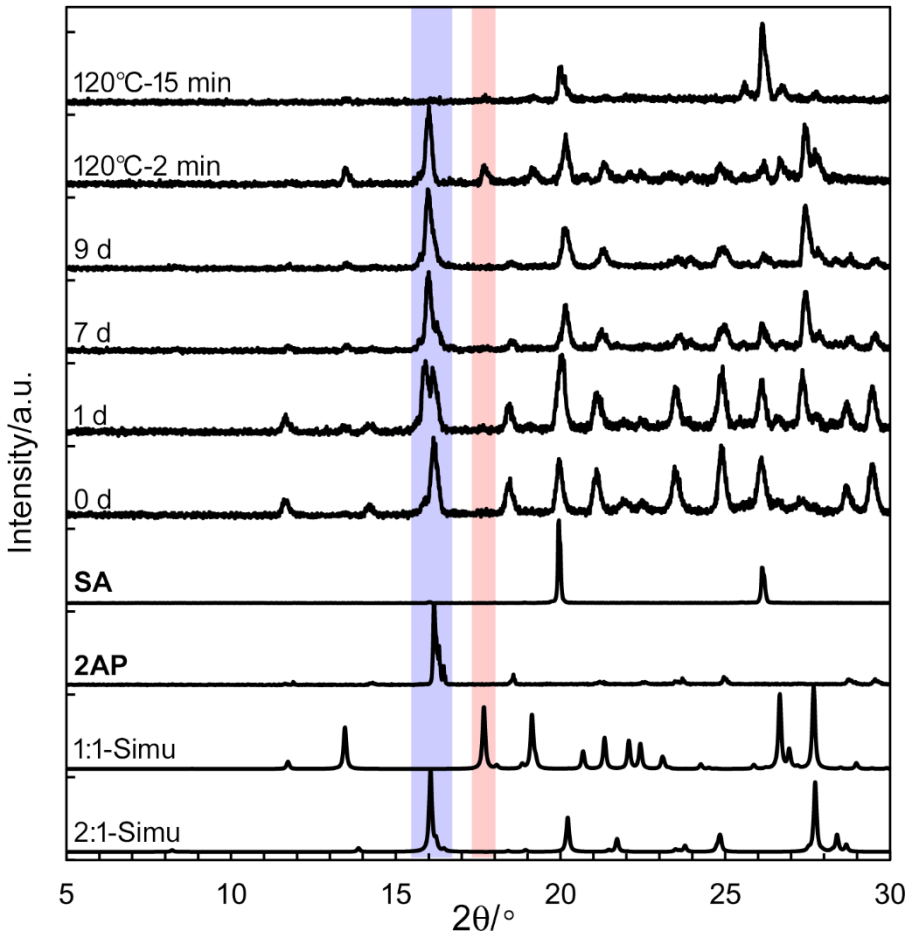

Figure S1. Powder XRD patterns: simulated from the crystal structures of the 2:1 co-crystal (2:1-Simu) and 1:1 co-crystal (1:1-Simu), and experimental patterns of as-purchased **2AP** (**2AP**), as-purchased **SA** (**SA**), the 2:1 co-crystal prepared by SSG after room temperature aging for 0 day (0 d), 1 day (1 d), 7 days (7 d), and 9 days (9 d). Powder XRD patterns of the 2:1 co-crystal heated by a hot stage (120°C) are shown for 120°C-2min and 120°C-15 min. Representative diffraction peaks of the 2:1 and 1:1 co-crystals are highlighted by blue and red, respectively.

The powder XRD measurements at 0 d in Figure S1 indicate that the ground sample was initially a mixture of **2AP** and **SA**. The mixture partially became a 2:1 co-crystal upon aging at room temperature for 1 d, as indicated by a bifurcated peak at 2θ=16°. After 9 d, the 2:1 co-crystal became the primary component of the ground sample.

Table S1. Merging statistics of the 2:1 co-crystal solved by MicroED

d_max	d_min	#obs	#uniq	mult.	%comp	<I>	<I/sI>	r_mrg	r_means	r_pim	cc1/2
5.2	1.87	1561	137	11.39	100	4.2	34.2	0.117	0.123	0.036	0.994*
1.87	1.50	1993	130	15.33	100	2.4	20.5	0.175	0.182	0.046	0.992*
1.50	1.31	1800	121	14.88	100	1.2	10.4	0.261	0.271	0.069	0.955*
1.31	1.19	2173	124	17.52	100	1.3	10.4	0.229	0.236	0.056	0.989*
1.19	1.11	1936	120	16.13	100	1.2	8.1	0.250	0.258	0.063	0.990*
1.11	1.04	1777	116	15.32	100	1.2	7.3	0.265	0.274	0.068	0.990*
1.04	0.99	2085	115	18.13	100	0.8	5.8	0.336	0.347	0.081	0.968*
0.99	0.95	2259	134	16.86	100	0.6	3.9	0.350	0.361	0.085	0.989*
0.95	0.91	1909	107	17.84	100	0.4	2.7	0.508	0.525	0.125	0.768*
0.91	0.88	1730	112	15.45	100	0.4	2.2	0.552	0.572	0.143	0.925*
0.88	0.85	2156	121	17.82	100	0.3	2.0	0.595	0.612	0.141	0.911*
0.85	0.83	2136	119	17.95	100	0.2	1.7	0.680	0.700	0.160	0.885*
0.83	0.81	2285	129	17.71	100	0.2	1.2	0.792	0.816	0.189	0.890*
0.81	0.79	1835	106	17.31	100	0.2	1.2	0.871	0.900	0.216	0.607*
0.79	0.77	2193	125	17.54	100	0.2	0.9	1.071	1.103	0.258	0.568*
0.77	0.75	1644	100	16.44	100	0.1	0.5	1.564	1.615	0.388	0.532*
0.75	0.74	1992	120	16.60	100	0.1	0.7	1.283	1.324	0.318	0.740*
0.74	0.73	2272	119	19.09	100	0.1	0.5	1.684	1.731	0.387	0.607*
0.73	0.71	2184	120	18.20	100	0.1	0.6	1.492	1.536	0.352	0.575*
0.71	0.70	2101	119	17.66	100	0.1	0.5	1.844	1.898	0.436	0.583*
5.20	0.70	40021	2394	16.72	100	0.8	6.1	0.336	0.347	0.084	0.991*

Table S2. Crystallographic parameters of the 2:1 co-crystal solved by MicroED (λ = 0.02508 Å).

Co-crystal	**2:1**
Formula	C6 H8 N3 O2
M	154.15
Crystal system	Monoclinic
Space group	$P2_1/c$
T /K	77
***a* /Å**	10.759
***b* /Å**	5.200
***c* /Å**	12.760
***α* /deg**	90
***β* /deg**	90.67
***γ* /deg**	90
***V* /Å^3**	713.8
Z	4
***D* / g cm^{-3}**	1.434
No. of measured, independent, and observed reflections [*Fo* > 4σ(*Fo*)]	21698, 1253, 864
R_{int}	0.2442
Resolution for refinement /Å	0.84
Completeness /%	100
Goodness of fit	1.161
***R1* (for all reflections)**	0.1079
***wR*2**	0.3038
S	1.107
No. of parameters	133
No. of restrains	129
Largest diff. peak (hole) /eÅ^3	0.135 (-0.183)
CCDC	2211429

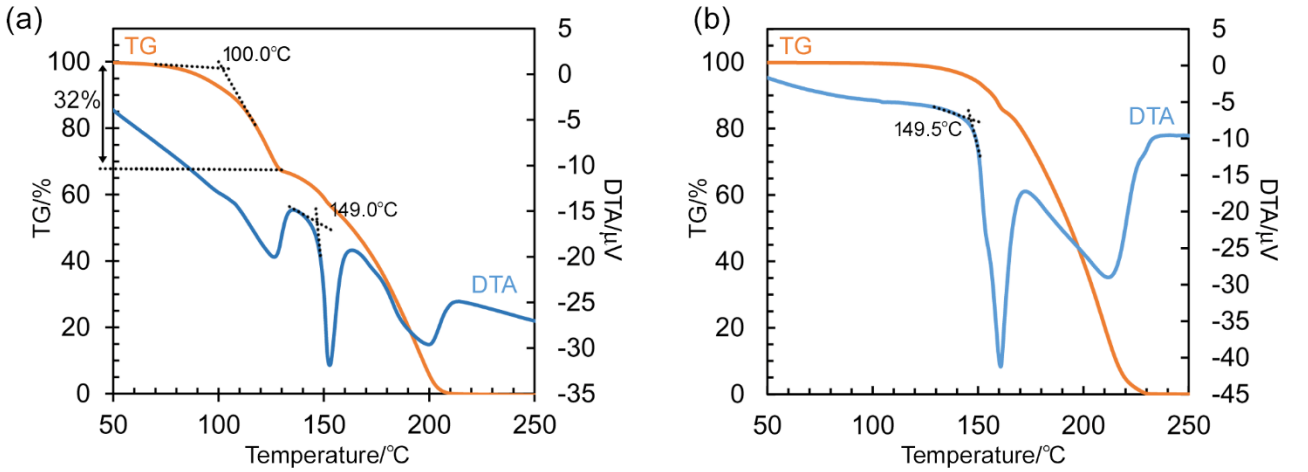

Figure S2. TG/DTA diagrams of (a) the 2:1 and (b) 1:1 co-crystals. The measurements were conducted on a STA7300 instrument (Hitachi High-Technologies Co.) with a ramping rate of 10°C min^{-1} under N_2 flow (200 mL min^{-1}).

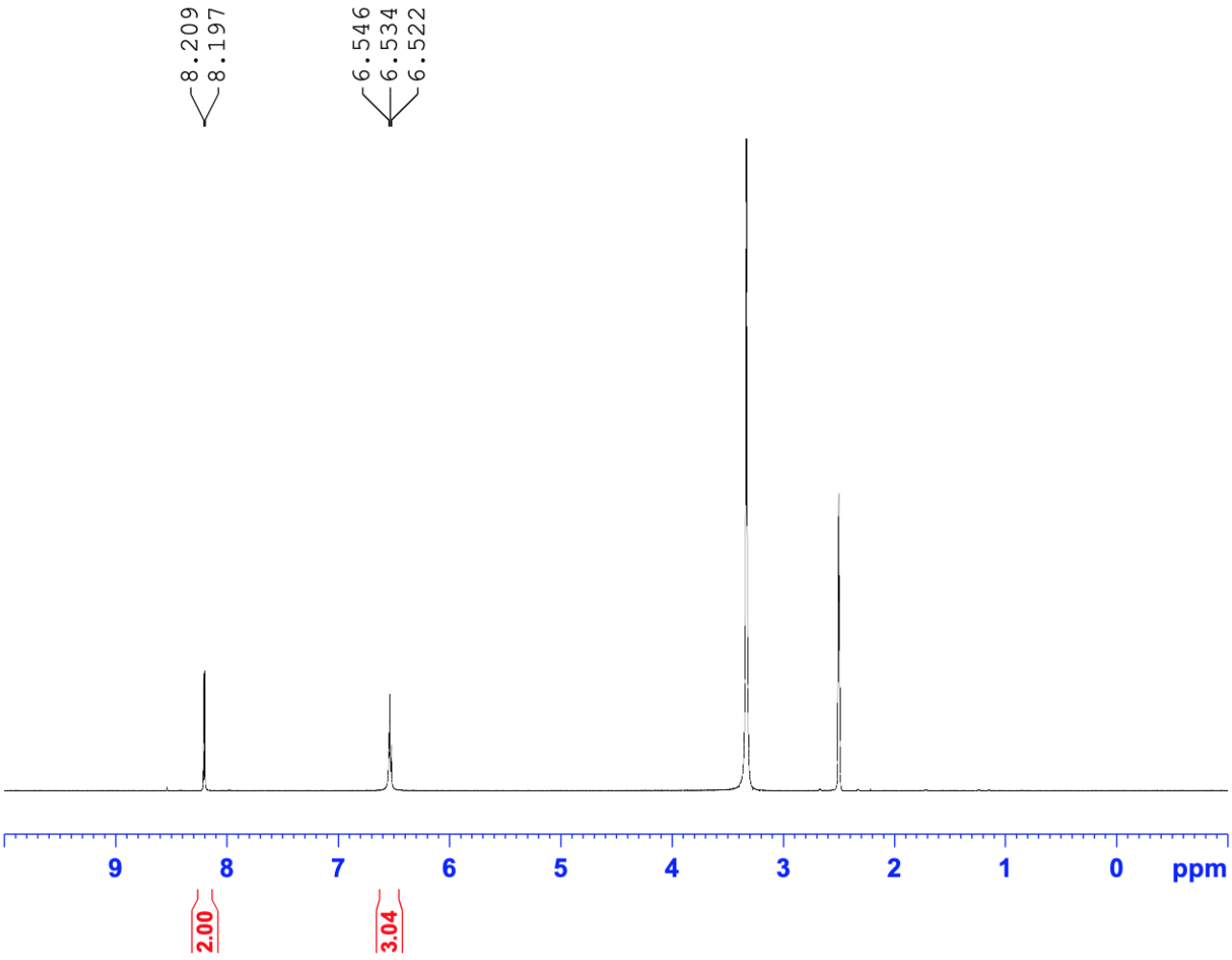

Figure S3. ^{1}H NMR spectrum of the sublimated solid (400 MHz, DMSO-d_6).

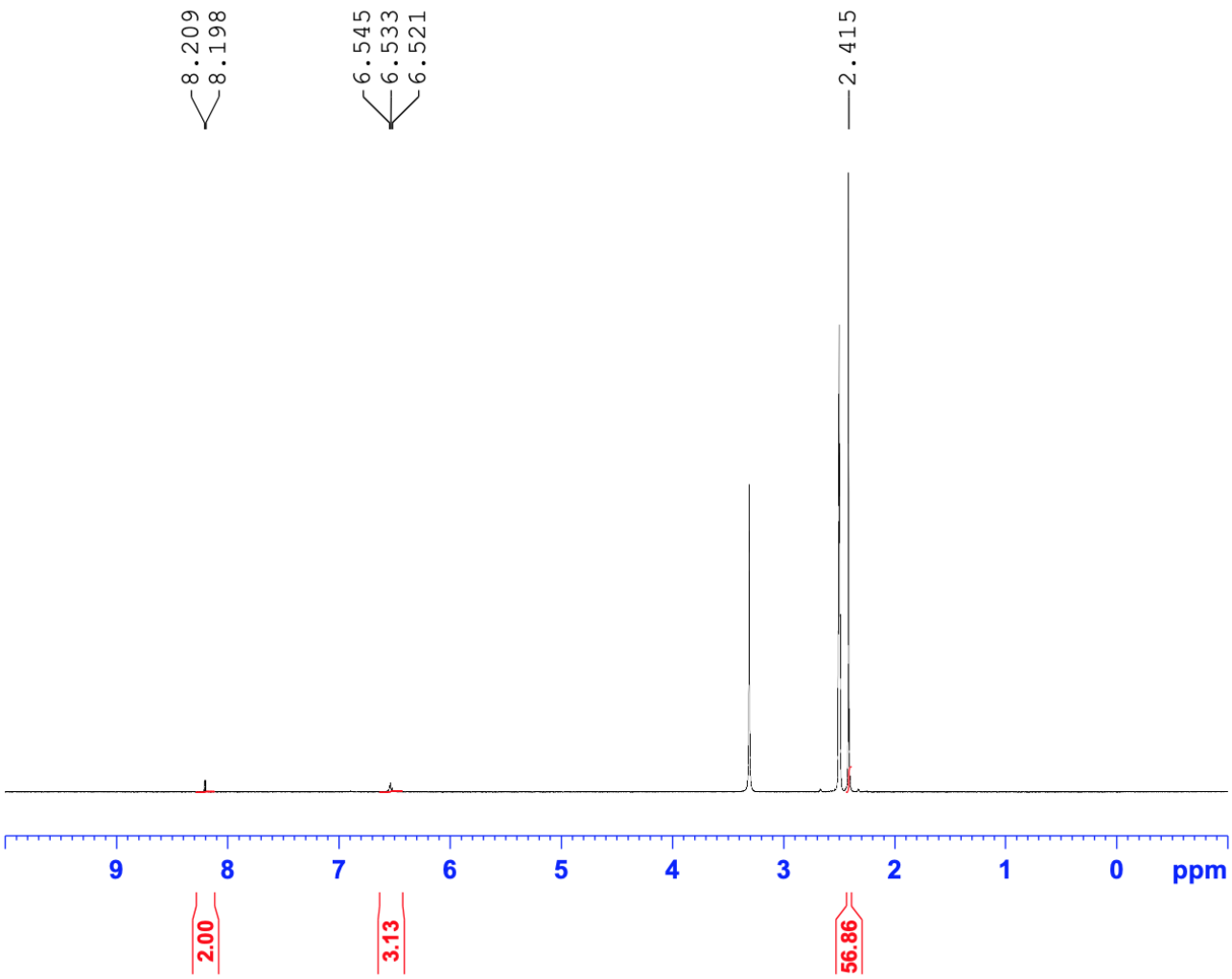

Figure S4. ^{1}H NMR spectrum of the 2:1 co-crystal after heating at 120 °C for 15 minutes (400 MHz, DMSO-d_6).

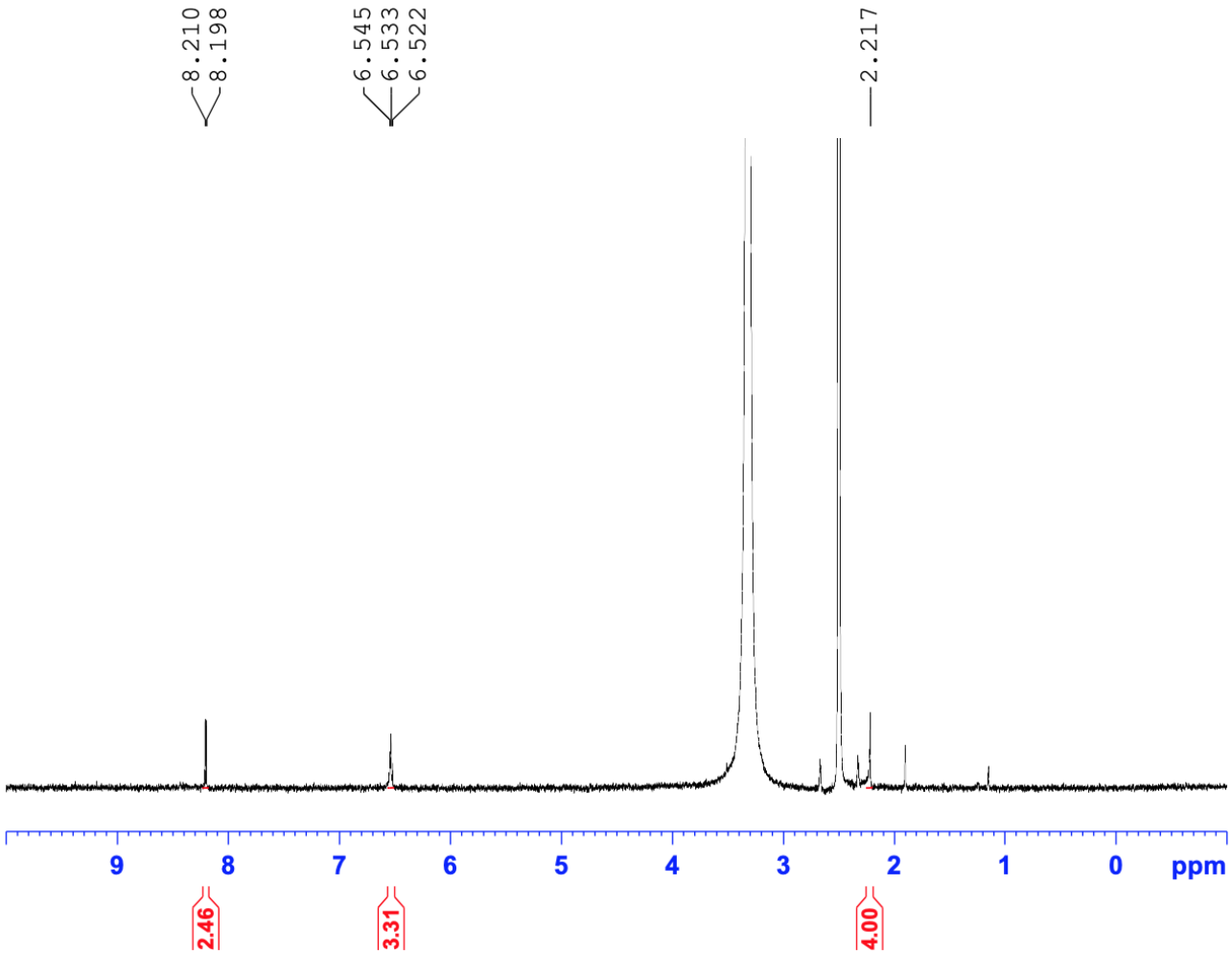

Figure S5. ^{1}H NMR spectrum of the 2:1 co-crystal after room temperature aging for 3 months (400 MHz, DMSO-d_6).

Table S3. Crystallographic parameters of the 2:1 and 1:1 co-crystals optimized as a triclinic *P*1 space group by CONFLEX (MMFF94s).[S1–S12]

Co-crystal	**2:1**	**1:1**
Formula	C24 H32 N12 O8	C32 H44 N12 O16
Crystal system	Triclinic	Triclinic
Space group	*P*1	*P*1
***a* /Å**	10.19030	5.16547
***b* /Å**	5.33927	13.12736
***c* /Å**	14.20800	15.48699
***α* /deg**	90.00025	89.99911
***β* /deg**	87.46076	89.14460
***γ* /deg**	89.99973	89.99940
Z	1	1
***V* /Å^3**	772.28064	1050.03961
D / g cm^{-3}	1.32504	1.34783

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