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Pressure-controlled aggregation in carboxylic-acids. A case study of the polymorphism of bromochlorofluoroaceticacid.

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Abstract: Pressure induces different hydrogen-bonding patterns in the polymorphs of bromochlorofluoroacetic acid, CBrClFCOOH, by affecting the balance between secondary intermolecular interactions involving halogen and oxygen atoms. In polymorph α a pattern of the molecules syn-syn H-bonded into catemers is strongly corrugated, up to the limit imposed by steric hindrances between the neighboring chain members, whereas in polymorph β the molecules are H-bonded into dimers. No phase transition between the catemeric and dimeric CBrClFCOOH polymorphs, despite over-pressurizing phase α by over 1.3 GPa into the stability region of phase β, demonstrates that the preference for dimeric and catemeric forms of carboxylic acids may be impossible for detection as classical solid-state phase transitions, without completely dissolving or melting these compounds and avoiding their nucleation. The smaller volume of the β phase, and hence its high-pressure stability, has been rationalized by more freedom of the zero-dimensional dimers to adjust their positions in the crystal structure, compared to the 1-dimensional catemers. The conformational limitations of the carboxylic-acid aggregates are consistent with the survey of all carboxylic-acid structures determined so far.

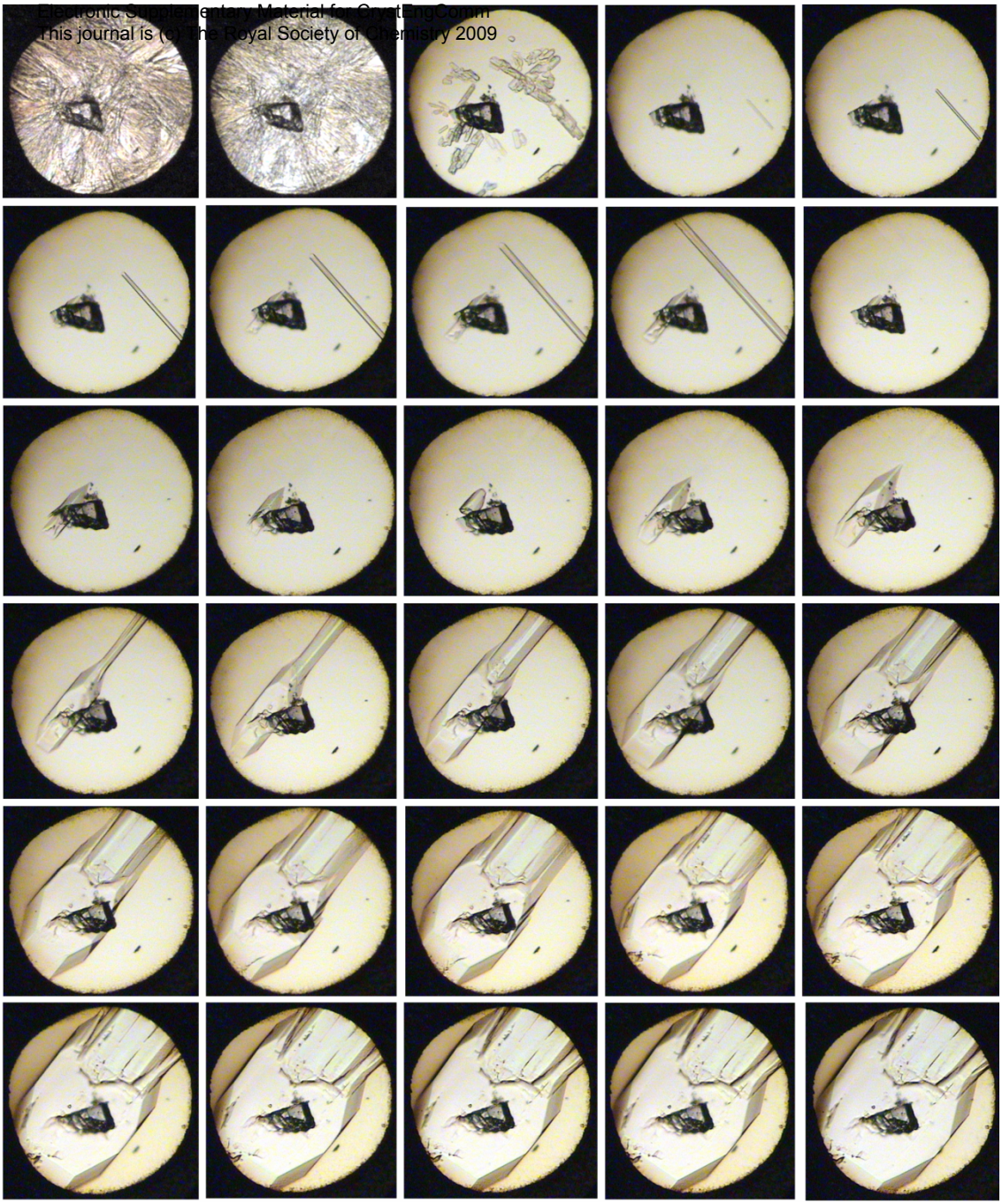

Figure S1. Stages of crystal growth of the CBrClFCOOH polymorph α sample in the DAC from polycrystalline mass to the single crystal at 296 K/ 0.59 GPa. The ruby for pressure calibration is placed below the center of the DAC chamber. Presented sequence of photographs was recorded during 3 hours.

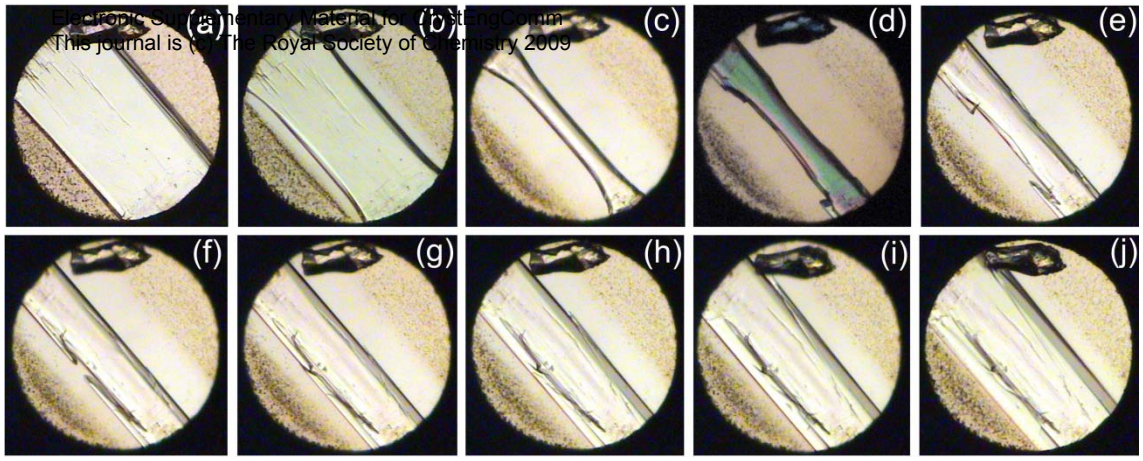

Figure S2. The process of CBrClFCOOH crystal growth of seeded polymorph α in the pressure region of stable polymorph β: (a) polymorph α seed at 0.28 GPa/ 300 K; (c) 370 K; (d) at 370 K immediately after increasing pressure; (e-i) gradual decrease of temperature from 360 to 300 K; and (j) 1.93 GPa/ 296 K. Presented sequence of photographs was recorded during 3 hours.

Table S1. Donohue angles (i.e. angles η'_d = C–O···O' and η'_a = C=O···O') for the hydrogen bonds in CBrClFCOOH molecules in phases α and β.

	Molecule A		Molecule B	
Pressure (GPa)	η'_a (°)	η'_d (°)	η'_a (°)	η'_d (°)
0.28 phase α	145(2)	111(1)	137(3)	111(2)
0.59 phase α	146(1)	111(1)	134(1)	114(1)
0.80 phase β	121.1(9)	111.7(8)	–	–
1.37 phase β	119.3(7)	111.4(7)	–	–
1.93 phase α	136(4)	107(2)	136(3)	110(3)

Table S2. Selected experimental and crystal data for CBrClFCOOH at phase α and β.

Pressure (GPa)	0.28	0.59	0.80	1.37	1.93
Temperature (K)	296	296	296	296	296
Crystal data					
Chemical formula	$C_2HBrClFO_2$	$C_2HBrClFO_2$	$C_2HBrClFO_2$	$C_2HBrClFO_2$	$C_2HBrClFO_2$
M_r	191.39	191.39	191.39	191.39	191.39
Cell setting, space group	Orthorhombic *Pbcn*	Orthorhombic *Pbcn*	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$	Orthorhombic *Pbcn*
a (Å)	16.458 (5)	16.169 (4)	7.898 (2)	7.730 (3)	15.274 (4)
b (Å)	6.0708 (4)	6.0038 (16)	7.840 (3)	7.685 (3)	5.8537 (3)
c (Å)	21.0950 (12)	20.971 (4)	8.043 (2)	7.997 (2)	20.7562 (12)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	95.553 (14)	95.74 (2)	90.00
V (Å)	2107.7 (6)	2035.7 (9)	495.6 (2)	472.7 (3)	1855.9 (5)
Z	16	16	4	4	16
D_x (Mg m^{-3})	2.413	2.498	2.565	2.689	2.740
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	8.21	8.50	8.73	9.15	9.33
Crystal form, colour	colourless	colourless	colourless	colourless	colourless
Crystal size (mm)	0.450 × 0.450 × 0.085	0.460 × 0.470 × 0.085	0.460 × 0.470 × 0.085	0.450 × 0.460 × 0.085	0.430 × 0.430 × 0.085
Data collection					
Diffractometer	Kuma KM4 CCD κ geometry	Kuma KM4 CCD κ geometry	Kuma KM4 CCD κ geometry	Kuma KM4 CCD κ geometry	Kuma KM4 CCD κ geometry
Data collection method	ω scans	ω scans	ω scans	ω scans	ω scans
Absorption correction	analytical	analytical	analytical	analytical	analytical
T_{min}	0.33	0.32	0.33	0.33	0.33

T_{max}	0.49	0.49	0.49	0.49	0.49
No. of measured, independent and observed reflections	6686, 481, 413	7980, 706, 628	2252, 320, 308	1961, 277, 259	7353, 439, 407
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.056	0.069	0.051	0.061	0.109
θ_{max} (°)	25.0	25.0	25.0	25.0	25.0
range of h, k, l	-4<=h<=4	-14<=h<=14	-7<=h<=7	-7<=h<=7	-3<=h<=3
	-7<=k<=7	-5<=k<=5	-7<=k<=7	-7<=k<=7	-6<=k<=6
	-25<=l<=25	-24<=l<=24	-9<=l<=9	-9<=l<=9	-24<=l<=24
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.068, 0.170, 1.20	0.062, 0.153, 1.03	0.058, 0.175, 1.20	0.044, 0.120, 1.17	0.108, 0.282, 1.24
No. of relections	481 reflections	706 reflections	320 reflections	277 reflections	439 reflections
No. of parameters	92	122	55	55	82
H-atom treatment	constrained refinement	constrained refinement	constrained refinement	constrained refinement	constrained refinement
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0861P)^2 + 12.5069P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 20.276P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0959P)^2 + 4.4939P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 3.4947P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1475P)^2 + 59.0716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	0.001	<0.0001	<0.0001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, –0.33	0.36, –0.36	0.56, –0.47	0.40, –0.41	0.69, –0.68