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Supporting information for article:

Thermal, spectroscopic and structural analysis of a thermostable phase transformation in Tapentadol hydrochloride

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Table S1

Bond distances (Å) for Ia and Ib (at 250K) and II (at 325K)

		Ia	Ib	II
C1	C2	1.400(3)	1.404(3)	1.387 (4)
C1	C6	1.402(3)	1.393(4)	1.400 (5)
C1	C7	1.521(3)	1.522(3)	1.528 (5)
C2	C3	1.393(4)	1.389(4)	1.370 (5)
C3	C4	1.387(4)	1.389(4)	1.378 (5)
C4	C5	1.393(4)	1.389(4)	1.382 (5)
C5	O1	1.376(3)	1.368(3)	1.363 (4)
C5	C6	1.393(4)	1.402(4)	1.387 (5)
C7	C8	1.548(4)	1.531(4)	1.536 (5)
C7	C10	1.559(4)	1.558(3)	1.541 (4)
C8	C9	1.517(4)	1.514(4)	1.497 (5)
C10	C12	1.517(4)	1.526(3)	1.517 (4)
C10	C11	1.530(4)	1.528(4)	1.524 (5)
C12	N1	1.505(3)	1.509(3)	1.494 (4)
C13	N1	1.493(4)	1.496(3)	1.489 (5)
C14	N1	1.489(4)	1.483(4)	1.487 (5)

Table S2**Bond angles ($^{\circ}$) for Ia and Ib (at 250K) and II (at 325K)**

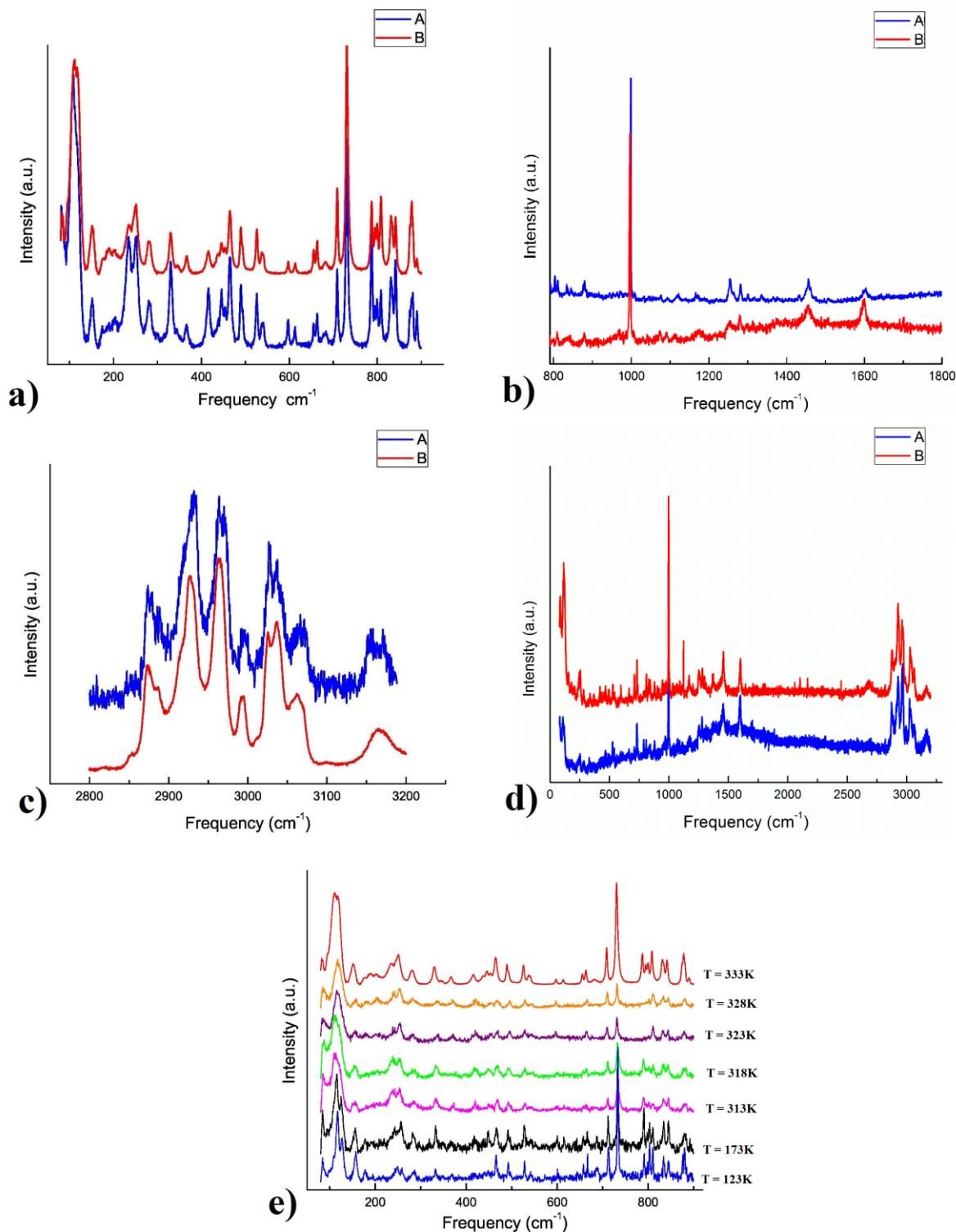
			IA	IB	II
C2	C1	C6	118.4(2)	118.5(2)	117.9 (3)
C2	C1	C7	122.2(2)	121.9(2)	122.0 (3)
C6	C1	C7	119.4(2)	119.5(2)	120.2 (3)
C3	C2	C1	120.1(2)	120.1(3)	120.3 (3)
C4	C3	C2	121.4(2)	121.1(2)	121.6 (3)
C3	C4	C5	118.8(2)	119.4(2)	118.9 (3)
O1	C5	C6	122.4(2)	121.9(2)	122.7 (3)
O1	C5	C4	117.3(2)	118.4(2)	117.4 (3)
C6	C5	C4	120.3(2)	119.7(3)	119.9 (3)
C5	C6	C1	121.0(2)	121.1(2)	121.4 (3)
C1	C7	C8	112.9(2)	111.5(2)	113.6 (3)
C1	C7	C10	113.9(2)	114.0(2)	114.1 (3)
C8	C7	C10	111.3(2)	113.8(2)	111.7 (3)
C9	C8	C7	112.4(2)	114.5(2)	113.5 (3)
C12	C10	C11	111.8(2)	112.0(2)	111.8 (3)
C12	C10	C7	110.95(19)	110.24(18)	111.0 (3)
C11	C10	C7	111.8(2)	112.2(2)	112.4 (3)
N1	C12	C10	114.4(2)	114.79(18)	114.4 (3)
C14	N1	C13	111.1(3)	111.0(2)	111.3 (3)
C14	N1	C12	113.4(2)	113.4(2)	113.8 (3)
C13	N1	C12	109.7(2)	109.7(2)	110.0(3)

Table S3**Torsion angles ($^{\circ}$) for Ia and Ib (at 250K) and II (at 325K)**

				IA	IB	II
C6	C1	C2	C3	-0.3(4)	0.4(4)	0.2 (5)
C7	C1	C2	C3	180.0(2)	-178.3(2)	-179.4 (3)
C1	C2	C3	C4	0.6(4)	0.6(4)	-0.8 (5)
C2	C3	C4	C5	-0.8(4)	-0.8(4)	0.5 (5)
C3	C4	C5	O1	179.6(3)	178.5(3)	179.5 (3)
C3	C4	C5	C6	0.7(4)	0.0(4)	0.4 (5)
O1	C5	C6	C1	-179.4(2)	-177.4(3)	180.0 (3)
C4	C5	C6	C1	-0.4(4)	1.1(4)	-1.0 (5)
C2	C1	C6	C5	0.3(4)	-1.2(4)	0.7 (5)
C7	C1	C6	C5	179.9(2)	177.5(2)	-179.7 (3)
C2	C1	C7	C8	44.8(3)	41.8(3)	42.4 (4)
C6	C1	C7	C8	-134.9(2)	-136.9(2)	-137.2 (3)
C2	C1	C7	C10	-83.4(3)	-88.8(3)	-87.2 (4)
C6	C1	C7	C10	96.9(3)	92.5(3)	93.3 (3)
C1	C7	C8	C9	63.9(3)	172.1(2)	62.0 (4)
C10	C7	C8	C9	-166.6(2)	-57.2(3)	-167.3 (3)
C1	C7	C10	C12	62.4(3)	65.5(3)	62.8 (3)
C8	C7	C10	C12	-66.6(3)	-64.0(3)	-67.7 (4)
C1	C7	C10	C11	-63.2(3)	-60.1(3)	-63.2 (4)
C8	C7	C10	C11	167.8(2)	170.4(2)	166.3 (3)
C11	C10	C12	N1	-62.3(3)	-57.1(3)	-62.2 (4)
C7	C10	C12	N1	172.1(2)	177.2(2)	171.4 (3)
C10	C12	N1	C14	-53.6(3)	-52.3(3)	-54.0 (4)
C10	C12	N1	C13	-178.5(2)	-177.1(2)	-179.7 (3)

Table S4**Misfit distances (\AA) in the L.S. fit of Ia-II and Ib-II**

FITTED ATOMS	$\Delta(\text{Ia-II}) (\text{\AA})$	$\Delta(\text{Ib-II}) (\text{\AA})$
C1	0.025	0.032
C2	0.043	0.053
C3	0.081	0.070
C4	0.01	0.045
C5	0.026	0.039
C6	0.061	0.065
C10	0.033	0.044
C11	0.054	0.029
C12	0.011	0.079
C13	0.075	0.119
C14	0.038	0.138
N1	0.032	0.031
O1	0.106	0.061
R.M.S._dev	0.052	0.070
NON_FITTED ATOMS	$\Delta(\text{Ia-II}) (\text{\AA})$	$\Delta(\text{Ib-II}) (\text{\AA})$
C7	0.03	0.077
C8	0.056	0.155
C9	0.179	1.407

**Figure S1.** Raman spectra.

Colour code for SF1a to SF1d: Blue (A) T = 293K; Red (B) T = 333K

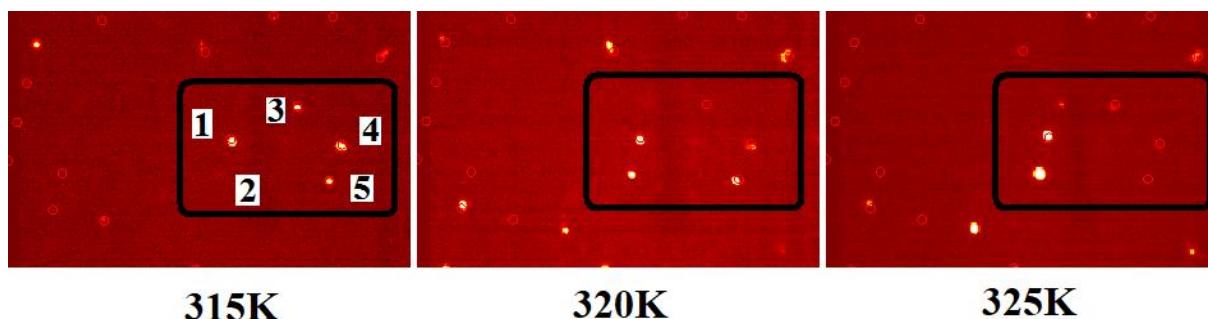


Figure S2. A series of frames taken at rising temperatures around T_c , with small circles denoting the position of spots for form **I**, as calculated with the 315K cell. Extreme-most frames show form **I** ($T < T_c$) and form **II** ($T > T_c$), respectively. The intermediate frame taken in the transition region (320K) shows instead coexistence of phases, with vanishing of the (lower temperature) monoclinic phase **I** and the concomitant appearance of the (higher temperature) orthorhombic **II**. Indices in the highlighted region: 1: (1,2,-1); 2: (1,1,0); 3: (0,3,-3); 4: (-1,2,-3); 5: (-1,1,-2)

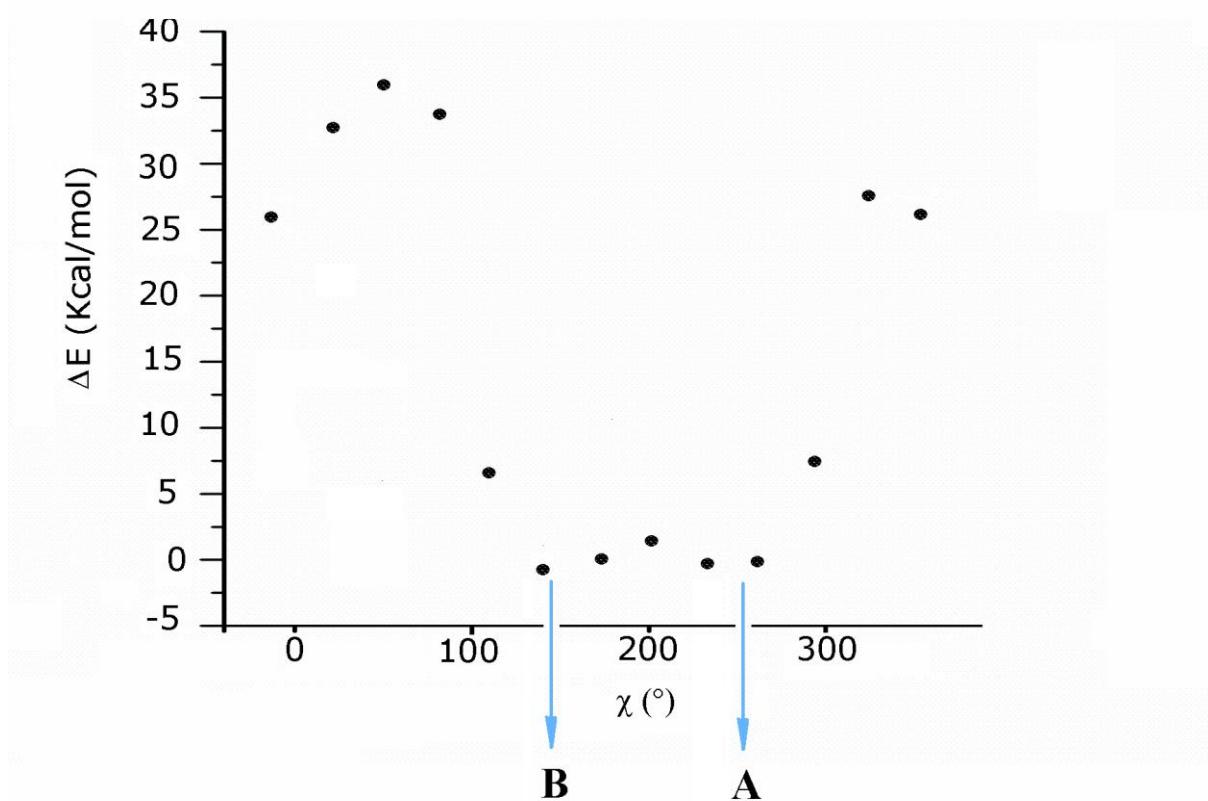


Figure S3. Energy calculation for moiety B (performed at the PBEPBE-D/6-311++G(d,p) level of theory using the crystallographic coordinates (single point calculations) within the GAUSSIAN09 program (Frisch, M. J. et al. (2009). GAUSSIAN09. Gaussian Inc., Wallingford, Connecticut, USA.))

Point A corresponds to the real conformation; point B, to the equal conformation state.

χ : rotation angle for the C8B-C9B ethyl group (arbitrary origin)

Video S1: optical microscope experiments going through the phase transition (SV1a: heating at 10°C/min; starting at 38°C; SV1b: cooling at 10°C/min; starting at 30°C) disclosing the thermosalient behaviour of Tapentadol Hydrochloride.