# Supporting Information

# Uniaxial negative thermal expansion due to aromatic interactions in polymorphic 2-bromobenzophenone

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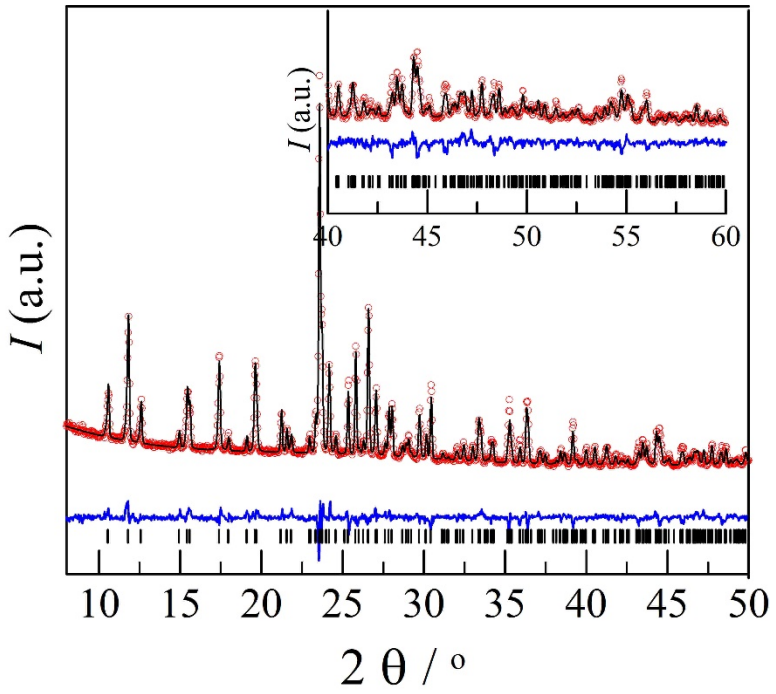


**Figure S1**. Stable form I: Experimental (red circles) and Rietveld refined (black line) diffraction patterns along with the difference profile (blue line) and Bragg reflections (vertical bars) of the monoclinic $P2_1/a$ space group of the stable phase I of 2-Br-benzophenone at 200 K. The inset corresponds to a 4.5-times-magnified intensity scale in the 40-60 º $2\theta$ range for clarity. Results of the Rietveld refinement within the $2\theta$ range 8-70º: $a$ = 7.8160(3) Å, $b$ = 16.7374(7) Å, $c$ = 8.4654(4) Å, $\beta$ = 97.610(4)º, $2\theta$-shift correction= 0.0472(10); overall isotropic temperature factor 0.0212(9) Å$^2$; $R_{wp}$=8.27%, $R_p$ =6.24%.

**Table S1. Results from the Rietveld refinement of metastable phase II of 2-bromo-benzophenone**

| | |
|---|---|
| Chemical Formula | $C_{13}H_{19}BrO$ |
| M / g·mol$^{-1}$ | 261.10 |
| Phase | II |
| 2θ-Angular Range | 8 – 70$^{o}$ |
| Space group | *P2$_1$/c* |
| a /Å | 8.4896 ± 0.0019 |
| b / Å | 6.5438 ± 0.0008 |
| c / Å | 20.253 ± 0.001 |
| α / $^{o}$ | 90 |
| β / $^{o}$ | 104.452 ± 0.006 |
| γ / $^{o}$ | 90 |
| $V_{cell}$ / Å$^3$ | 1089.5± 0.4 |
| Z (Z') | 4(1) |
| Temperature | 200 K |
| $D_x$ / g·cm$^{-3}$ | 1.5918± 0.0006 |
| Radiation type: X-Ray, λ | λ=1.5406 Å |
| 2θ-shift (zero correction) | 0.0321 ± 0.0013 |
| | |
| Profile Parameters | |
| Na | 0.553± 0.025 |
| | |
| Reliability Parameters | |
| $R_{wp}$ | 6.24% |
| $R_p$ | 4.15% |
| | |
| Peak width parameters | |
| U | 0.276 ± 0.036 |
| V | -0.062 ± 0.014 |
| W | 0.021 ± 0.001 |
| Overall isotropic temperature factor, U / Å$^2$ | 0.012 ± 0.001 |
| Preferred Orientation (Rietveld-Toraya function)[1,2] | |
| a* | 0.007 ± 0.015 |
| b* | 0.664 ± 0.009 |
| c* | 0.747 ± 0.008 |
| R0 | 1.556 ± 0.017 |

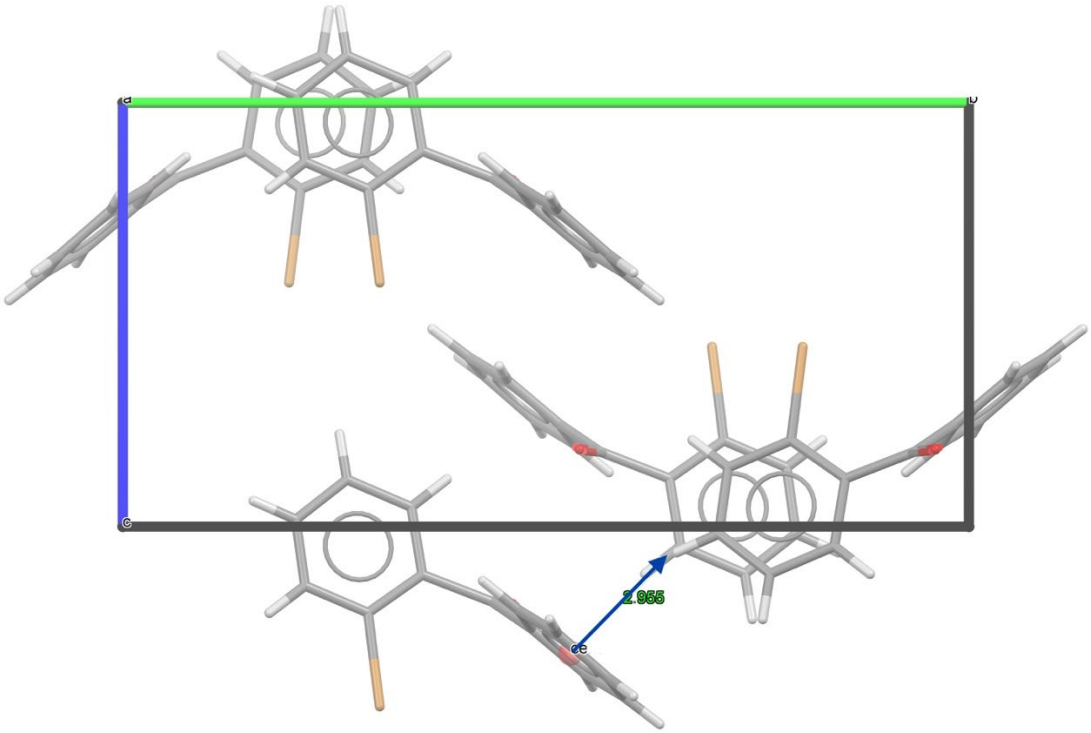


**Figure S2a.** Strong aromatic interaction "C-H···π" along c and b, perpendicular to a (dark blue arrow)

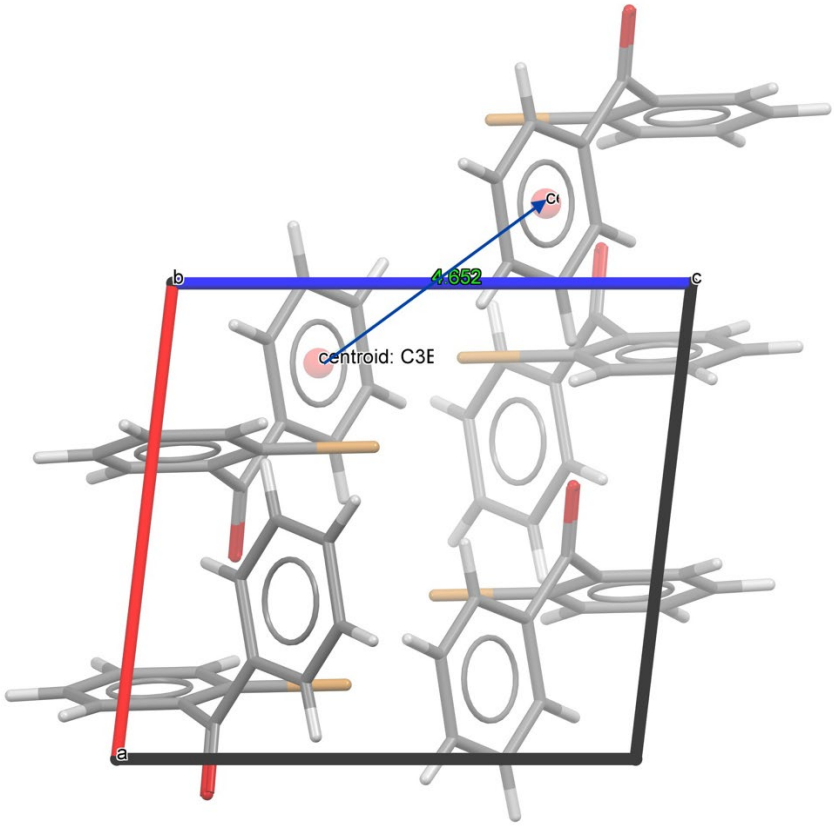


**Figure S2b.** Strong parallel-displaced aromatic interaction along the ac plane (dark blue arrow)

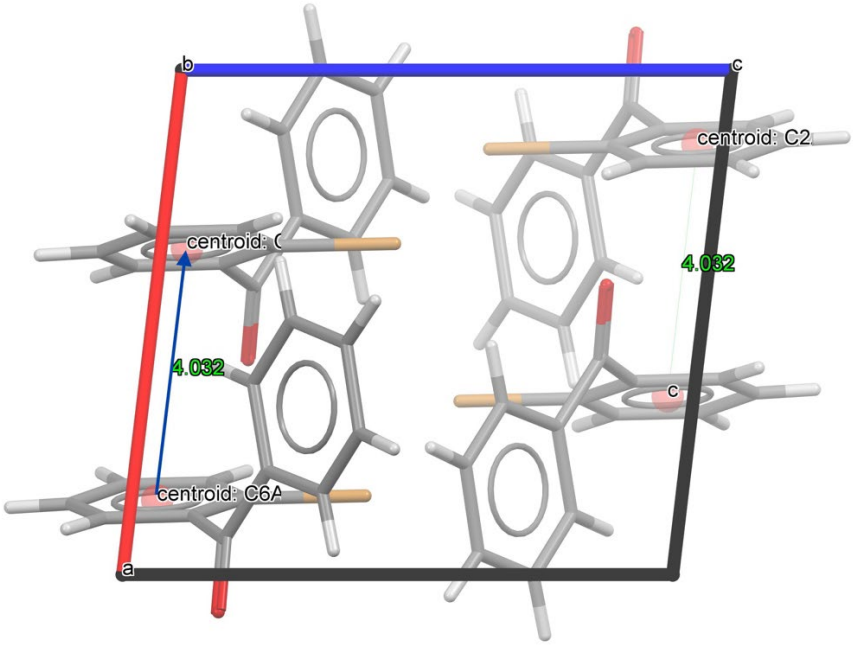


**Figure S2c.** Strong parallel-displaced aromatic interaction along the *a* axis (dark blue arrow)

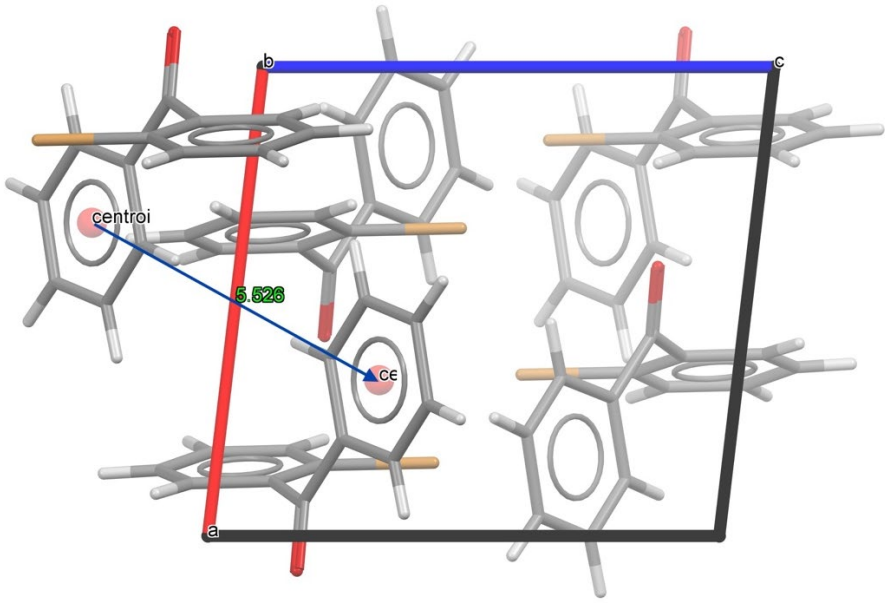


**Figure S2d.** Medium-strong parallel-displaced aromatic interaction along the ac plane (dark blue arrow)

**Table S2. Unique aromatic interactions in the stable form I[3,a]**

| Distance /Å | Relative Orientation (/°) | Score[b] |
|---|---|---|
| 5.11 | 84.89 | 8.4 |
| 4.65 | 0 | 7.7 |
| 4.03 | 23.84 | 7.2 |
| 5.53 | 0 | 6.4 |
| 5.96 | 0 | 5.8 |
| 6.02 | 84.89 | 4.9 |
| 5.98 | 80.32 | 3.3 |
| 5.74 | 80.32 | 2.9 |
| 6.97 | 84.89 | 2.8 |
| 7.11 | 80.32 | 2.3 |
| 7.75 | 0 | 1.3 |
| 7.84 | 0 | 1.2 |
| 7.74 | 80.32 | 1.1 |
| 7.88 | 0 | 1 |
| 7.93 | 84.89 | 1 |
| 7.63 | 80.32 | 0.9 |
| 7.96 | 80.32 | 0.9 |
| 8.49 | 0 | 0.8 |
| 8.59 | 23.84 | 0.6 |
| 7.84 | 0 | 0.3 |
| 8.49 | 0 | 0.3 |
| 9.12 | 77.02 | 0.3 |

[a] The first four interactions are shown in Figures S2[4]a-d, respectively.

[b] Interactions with a Score > 7 are strong.

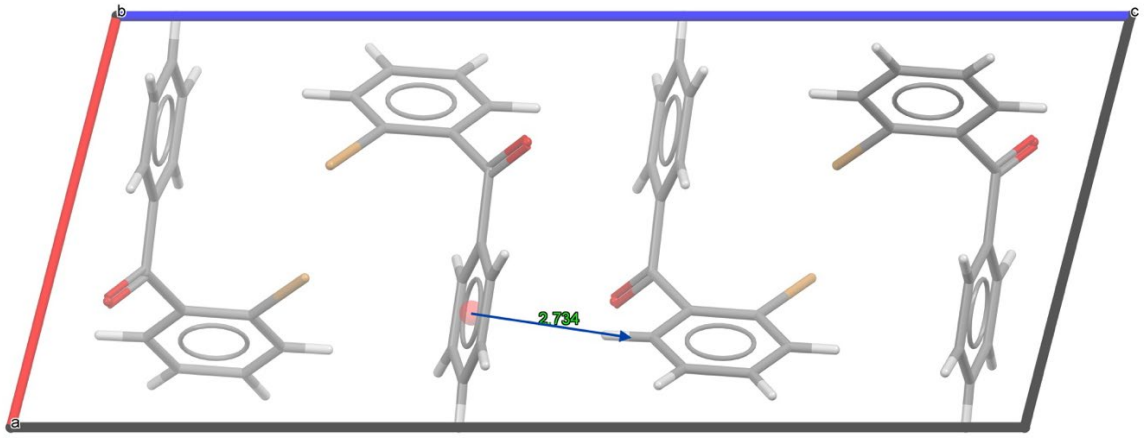


**Figure S3a.** Strong aromatic interaction "C-H···π" along the *ac* plane (dark blue arrow) forming an aromatic 'dimer'

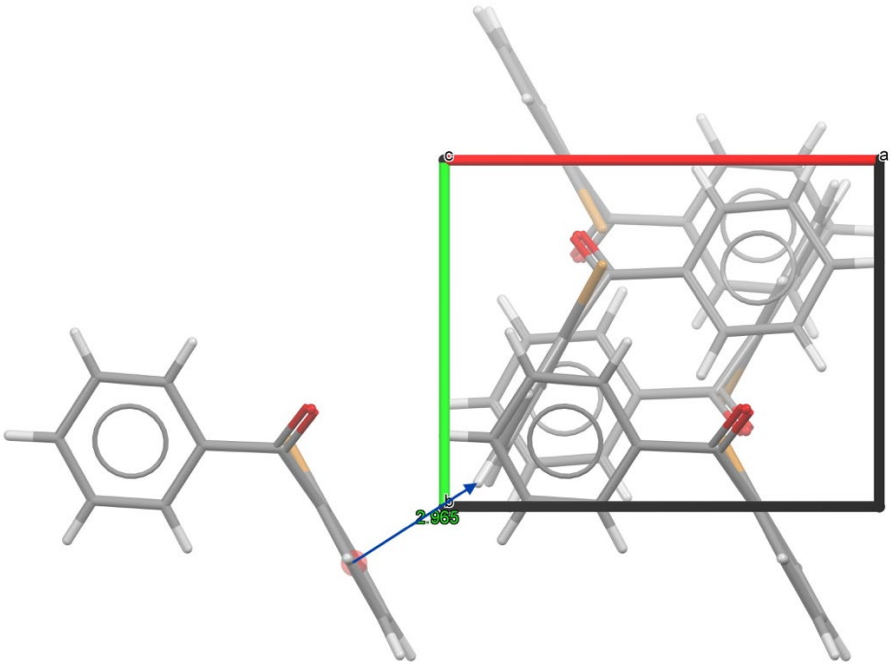


**Figure S3b.** Strong aromatic interaction "C-H···π" along *a*, *b*, and *c* (dark blue arrow)

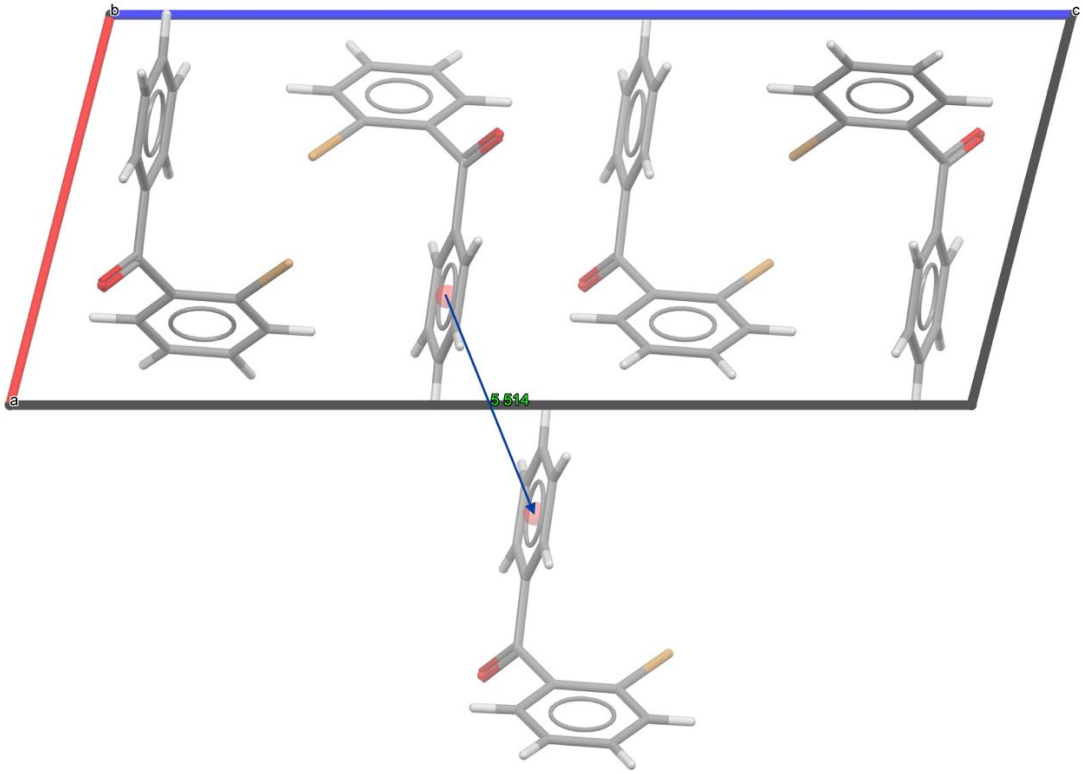


**Figure S3c.** Medium-strong parallel-displaced aromatic interaction along the ac plane (dark blue arrow)

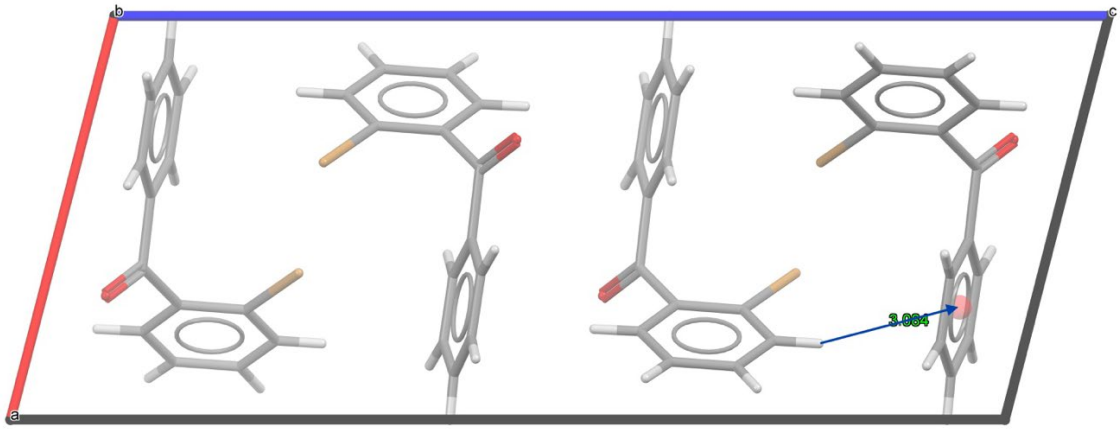


**Figure S3d.** Medium-strong aromatic interaction "C-H···π" along the *ac* plane (dark blue arrow)

**Table S3. Unique aromatic interactions in the metastable form II.[3,a]**

| Distance (Ang.) | Relative Orientation (Degrees) | Score[b] |
|---|---|---|
| 5.01 | 78.49 | 8.1 |
| 5.14 | 58.41 | 7.4 |
| 5.51 | 0 | 6.7 |
| 5.27 | 88.62 | 6.6 |
| 5.57 | 78.49 | 5 |
| 6.39 | 0 | 4.8 |
| 6.54 | 0 | 4.4 |
| 5.93 | 0 | 3.8 |
| 6.76 | 0 | 3.6 |
| 6.54 | 0 | 3.3 |
| 6.07 | 78.49 | 3 |
| 7.14 | 58.41 | 1.5 |
| 7.62 | 88.62 | 1.4 |
| 7.97 | 0 | 1 |
| 8.11 | 78.49 | 0.9 |
| 8.49 | 0 | 0.7 |
| 8.28 | 88.62 | 0.5 |
| 7.87 | 26.47 | 0.5 |
| 8.49 | 0 | 0.2 |
| 9.86 | 78.49 | 0.2 |
| 9.25 | 78.49 | 0.2 |
| 9.93 | 88.62 | 0.1 |

[a] The first four interactions are shown in Figures S3[6]a-d, respectively.

[b] Interactions with a Score > 7 are strong.

**Table S4. Lattice parameters of the stable phase I and metastable phase II as a function of temperature**

| T/K | a(σ) / Å | b(σ) / Å | c(σ) / Å | β (σ) / ° |
|---|---|---|---|---|
| Form I | | | | |
| 110 | 7.7807(3) | 16.6503(7) | 8.4255(4) | 98.321(3) |
| 160 | 7.7985(4) | 16.6871(7) | 8.4464(4) | 97.960(3) |
| 200 | 7.8127(4) | 16.7308(8) | 8.4618(5) | 97.601(4) |
| 225 | 7.8192(3) | 16.7569(7) | 8.4720(4) | 97.377(3) |
| 250 | 7.8302(5) | 16.7919(9) | 8.4860(5) | 97.1170(5) |
| 270 | 7.8349(4) | 16.8145(8) | 8.4920(5) | 96.937(4) |
| 280 | 7.8386(3) | 16.8272(7) | 8.4966(4) | 96.849(3) |
| 290 | 7.8392(4) | 16.8379(8) | 8.4974(5) | 96.771(4) |
| 305 | 7.8444(5) | 16.8581(10) | 8.5022(5) | 96.665(5) |
| 310 | 7.8458(4) | 16.8669(9) | 8.5075(4) | 96.565(5) |
| | | | | |
| Form II | | | | |
| 110 | 8.4616 (24) | 6.4832(21) | 20.1552(69) | 104.998(22) |
| 150 | 8.4874(15) | 6.4995(18) | 20.2008(45) | 104.776(17) |
| 200 | 8.4872(18) | 6.5300(24) | 20.2473(51) | 104.487(18) |
| 225 | 8.4930(12) | 6.5436(9) | 20.2970(30) | 104.540 (10) |
| 250 | 8.4939(36) | 6.5772(33) | 20.3231(60) | 104.299 (25) |
| 260 | 8.4920(18) | 6.5874(21) | 20.3238(45) | 104.154 (17) |
| 270 | 8.4941(18) | 6.5956(21) | 20.3396(45) | 104.084 (17) |
| 280 | 8.4930(15) | 6.6063(18) | 20.3591(36) | 104.009 (15) |
| 285 | 8.4952(24) | 6.6092(27) | 20.3631(54) | 104.072 (23) |
| 290 | 8.5047(33) | 6.6110(30) | 20.3930(72) | 104.214 (27) |
| | | | | |

**Table S5. Polynomials for the fits of lattice parameters and lattice volume as a function of the temperature and the reliability R factor for stable and metastable phases.**

***Stable phase I***

| *parameter* | $p_o$ | $p_1 \cdot 10^3$ | $p_2 \cdot 10^5$ | $R \cdot 10^5$ |
|---|---|---|---|---|
| *a /Å* | 7.735(4) | 0.44(4) | -0.027(9) | 12 |
| *b/Å* | 16.583(10) | 0.41(9) | 0.16(2) | 13 |
| *c/Å* | 8.375(7) | 0.47(7) | -0.016(16) | 18 |
| *β/°* | 99.1(1) | -6.9(9) | -0.47(22) | 21 |
| $V/Å^3$ | 1060.6(2.2) | 168(22) | 5.8(5) | 43 |

***Metastable phase II***

| *parameter* | $p_o$ | $p_1 \cdot 10^3$ | $p_2 \cdot 10^5$ | $R \cdot 10^5$ |
|---|---|---|---|---|
| *a/Å* | 8.468(8) | 0.14(8) | -0.02(2) | 16 |
| *b/Å* | 6.469(2) | -0.10(2) | 0.21(6) | 60 |
| *c/Å* | 20.046(3) | 0.91(3) | 6.9(9) | 28 |
| *β/°* | 105.3(3) | -0.15(4) | -1.0(9) | 67 |
| $V/Å^3$ | 1059.6(3.3) | 55(4) | 42(9) | 52 |

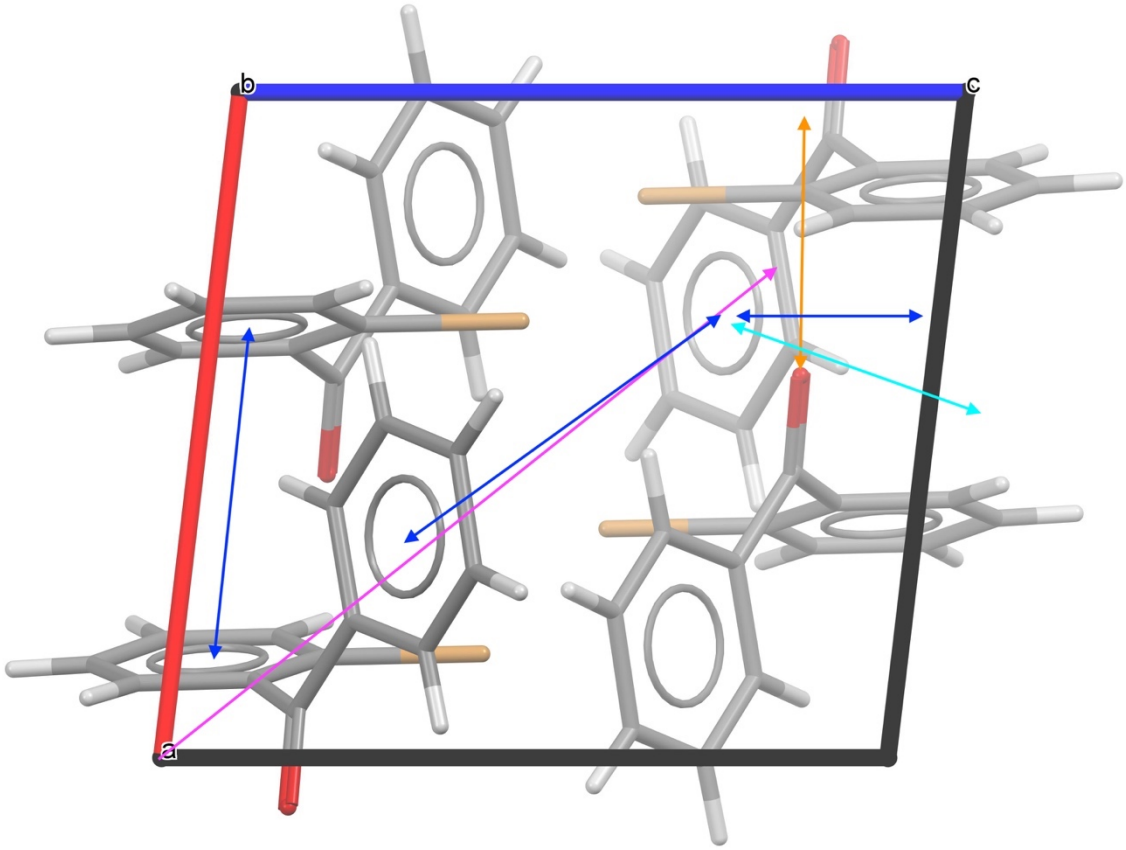


**Figure S4.** Uniaxial negative thermal expansion (pink arrow) in stable form I caused by aromatic interactions (dark blue double arrows: directions of the strong interactions, light blue double arrows: directions of the medium-strong interactions). The direction of the weak hydrogen bond C=O···H-$C_{ring}$ is indicated in orange.

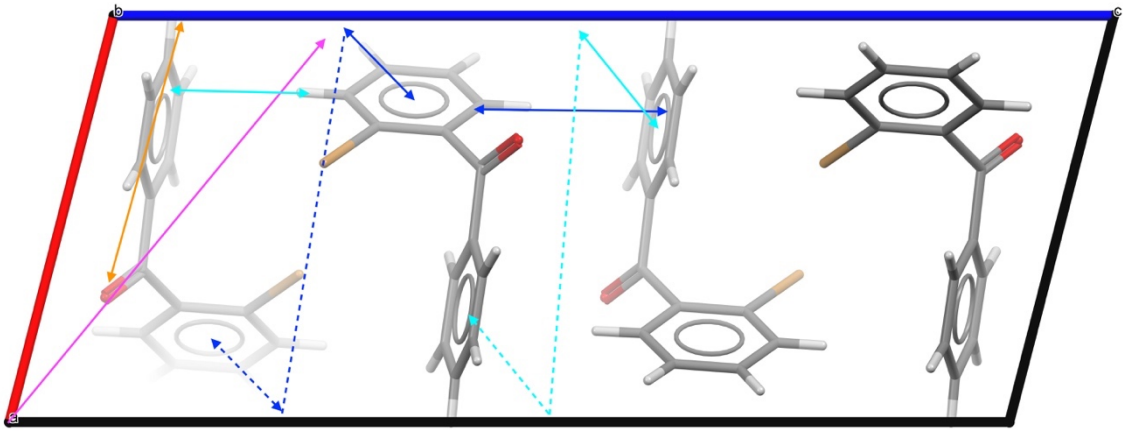


**Figure S5.** Uniaxial negative thermal expansion (pink arrow) in metastable form II caused by aromatic interactions (dark blue double arrows: directions of the strong interactions, light blue double arrows: directions of the medium-strong interactions). The direction of the weak hydrogen bond C=O···H-$C_{ring}$ is indicated in orange.

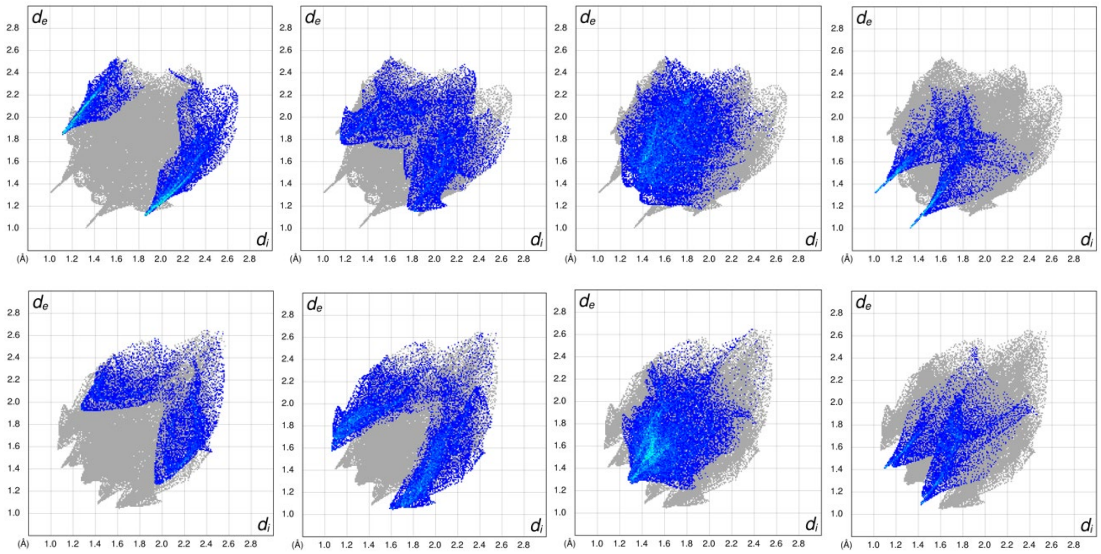


**Figure S6.** Fingerprint plots of form I (top) and form II (bottom);
from left to right: H-Br, H-C, H-H, and O-H distances

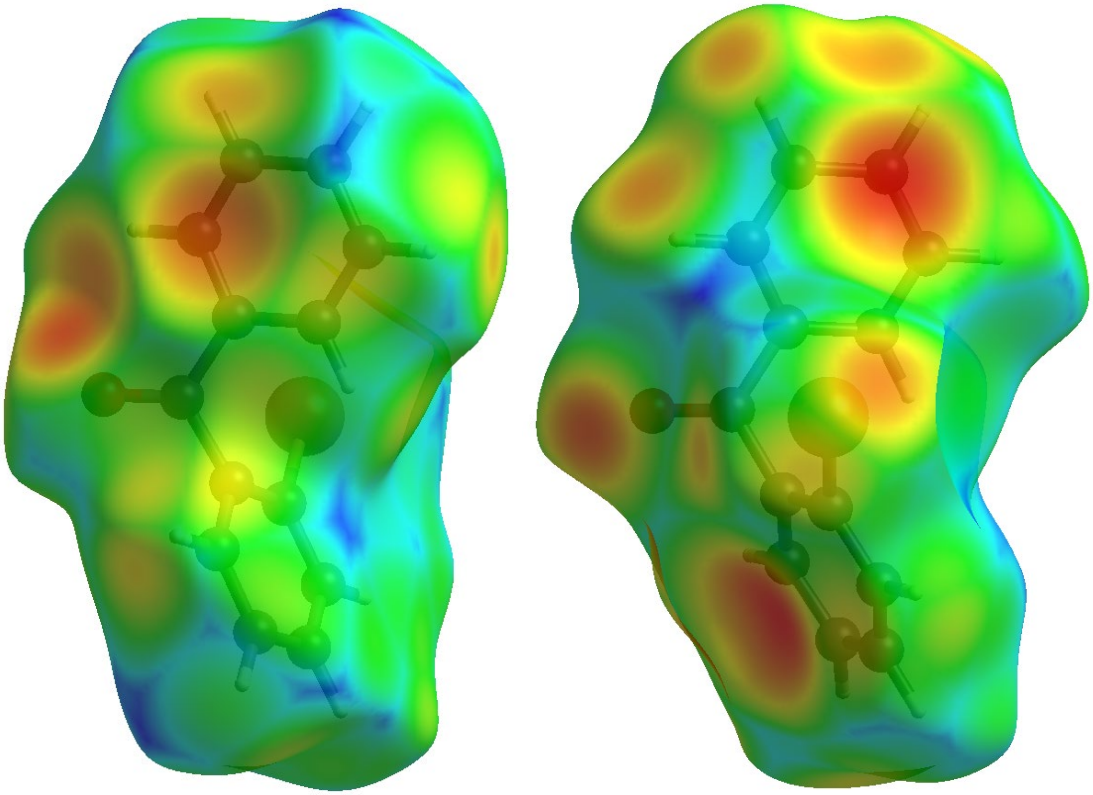

**Figure S7.** Hirschfeld plots of form I (left-hand side) and form II (right-hand side)

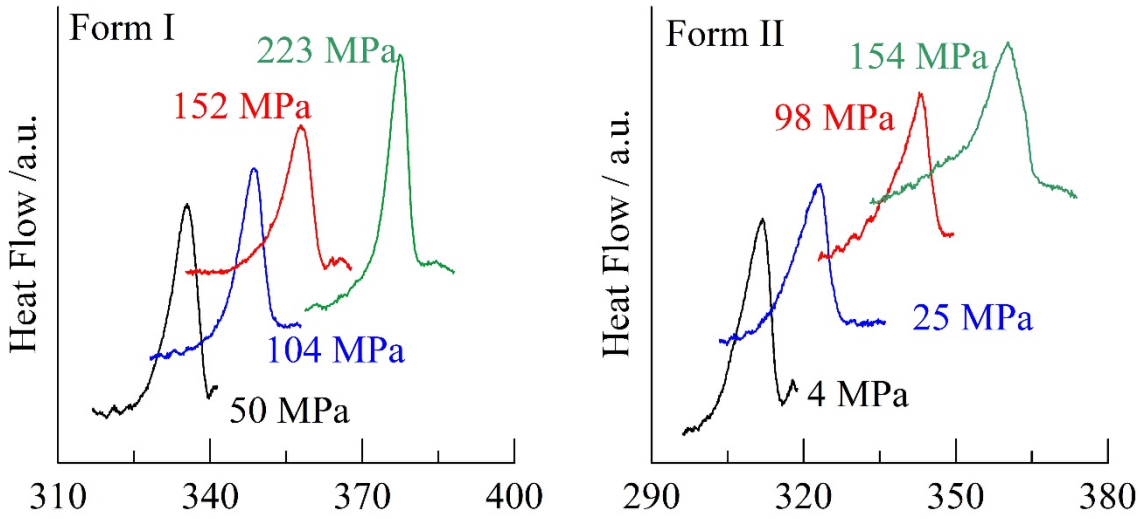


**Figure S8.** High-pressure differential scanning calorimetry curves of the melting transition of form I (left panel) and form II (right panel) of 2-bromo-benzophenone

## References

1. Rietveld, H., A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **1969,** *2* (2), 65-71.
2. Toraya, H.; Marumo, F., Preferred orientation correction in powder pattern-fitting. *Mineral. J.* **1981,** *10* (5), 211-221.
3. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A., Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **2020,** *53* (1), 226-235.