Supporting information for article:

Thermomechanical effect in molecular crystals: the role of halogen-bonding interactions

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**Table S1:** Hydrogen/halogen bond geometry in crystal structures.

| Interaction | D–H/A | H···A/Å | D···A/Å | ∠D–H···A/Å | Symmetry code |
|-------------|-------|--------|--------|-------------|---------------|
| **A Form I** |       |        |        |             |               |
| O2–H2A···N1 | 0.82  | 1.86   | 2.578(1) | 145         | Intramolecular |
| N2–H2B···N3 | 0.86  | 2.17   | 2.9891(2) | 156        | -x,1/2+y,1/2-z |
| C1–H1···Cl2 | 0.93  | 2.81   | 3.722(2)  | 166        | x,3/2-y,-1/2+z |
| C4–Cl2···Cl1 |        |        | 3.435(6)  | 155        | Intermolecular |
| C2–Cl1···Cl2 |        |        | 3.435(6)  | 96         | Intermolecular |
| **A Form II** |     |        |        |             |               |
| O2–H2A···N1 | 0.84  | 1.88   | 2.617(2)  | 144        | Intramolecular |
| N2–H2B···N3 | 0.86  | 2.24   | 3.083(2)  | 159        | -x,2-y,1/2+z  |
| C10–H10···N3 | 0.95  | 2.59   | 3.511(2)  | 166        | -x,2-y,1/2+z  |
| C11–H11···O1 | 0.95  | 2.40   | 3.341(2)  | 174        | -1/2+x,2-y,z  |
| C13–H13···Cl1 | 0.95  | 2.92   | 3.676(2)  | 136        | x,1+y,-1+z    |
| C4–Cl2···Cl1 |        |        | 3.395(1)  | 151        | Intermolecular |
| C2–Cl1···Cl2 |        |        | 3.395(1)  | 100        | Intermolecular |
| **A Form III** |     |        |        |             |               |
| O2–H2A···N1 | 0.82  | 1.88   | 2.591(11) | 144        | Intramolecular |
| N2–H2B···N3 | 0.86  | 2.23   | 3.048(11) | 159        | 2-x,-1/2+y,1/2-z |
| C10–H10···N3 | 0.93  | 2.56   | 3.466(14) | 166        | 2-x,-1/2+y,1/2-z |
| C11–H11···O1 | 0.93  | 2.47   | 3.391(12) | 174        | x,1/2-y,1/2+z |
| C4–Cl2···Cl1 |        |        | 3.448(4)  | 155.5      | Intermolecular |
| C2–Cl1···Cl2 |        |        | 3.448(4)  | 95         | Intermolecular |
| **B Form I** |       |        |        |             |               |
| O2–H2A···N1 | 0.82  | 1.83   | 2.551(4)  | 146        | Intramolecular |
| N2–H2B···N3 | 0.86  | 2.13   | 2.920(5)  | 152        | -x,-1/2+y,1/2-z |
| C12–H12···O1 | 0.93  | 2.45   | 3.354(5)  | 165        | x,1/2-y,1/2+z |
| C4–Br2···Br1 |        |        | 3.587(1)  | 166        | Intermolecular |
| C2–Br1···Br2 |        |        | 3.587(1)  | 94         | Intermolecular |
| **B Form II** |       |        |        |             |               |
| O2–H2A···N1 | 0.82  | 1.89   | 2.605(5)  | 143        | Intramolecular |
| N2–H2B···O3 | 0.80  | 2.15   | 2.933(6)  | 164        | X,y,z         |
| O4–H4A···N4 | 0.82  | 1.88   | 2.598(6)  | 145        | X,y,z         |
| N5–H5B···O1 | 0.73  | 2.11   | 2.836(6)  | 169        | 1-x,1-y,1-z   |
### Table S2: Crystallographic information.

|                  | Compound-A Form I | Compound-A Form II | Compound-A Form III | Compound-B Form I | Compound-B Form II |
|------------------|--------------------|--------------------|---------------------|-------------------|--------------------|
| Empirical Formula| C_{13}H_{9}Cl_{2}N_{3}O_{2} | C_{13}H_{9}Cl_{2}N_{3}O_{2} | C_{13}H_{9}Cl_{2}N_{3}O_{2} | C_{13}H_{9}Br_{2}N_{3}O_{2} | C_{13}H_{9}Br_{2}N_{3}O_{2} |
| Formula weight   | 310.13             | 310.13             | 310.13              | 399.05            | 399.05             |
| Crystal system   | Monoclinic         | Orthorhombic       | Monoclinic          | Monoclinic        | Triclinic          |
| Space group      | P2_1/c             | Pca2_1             | P2_1/c              | P2_1/c            | P-1                |
| T (K)            | 298                | 298                | 338                 | 298               | 298                |
|        | 8.0683(4)  | 15.441(3)  | 8.6916(6)  | 8.266(2)  | 9.8084(7)  |
|--------|------------|------------|------------|-----------|------------|
| a (Å)  | 10.7464(6) | 8.3179(16) | 10.2641(7) | 10.917(2) | 10.7751(8) |
| b (Å)  | 15.6155(8) | 10.6014(18)| 15.4965(10)| 15.734(3) | 13.9516(9) |
| c (Å)  | 90         | 90         | 90         | 90        | 103.219(3) |
| α (deg)| 90.890(2)  | 90.186(2)  | 95.82(3)   | 94.907(3) |
| β (deg)| 90         | 90         | 90         | 90        | 91.018(3)  |
| γ (deg)|            |            |            |           |            |
| V (Å³) | 1353.78(12)| 1361.6(5)  | 1382.46(16)| 1412.7(5) | 1429.11(17) |
| D<sub>calc</sub> (g cm<sup>-3</sup>) | 1.522      | 1.513      | 1.490      | 1.876      | 1.855      |
| μ (mm<sup>-1</sup>) | 0.483      | 0.480      | 0.473      | 5.742      | 5.676      |
| θ range | 2.30 to 27.57 | 2.44 to 25.03 | 2.34 to 25.07 | 3.10 to 28.05 | 2.45 to 24.79 |
| Z/Z    | 4/1        | 4/1        | 4/1        | 4/1       | 4/2        |
| Range h | –10 to 10  | –18 to 18  | –10 to 9   | –10 to 10 | –11 to 11  |
| Range k | –13 to 13  | –9 to 9    | –12 to 12  | –14 to 14 | –12 to 12  |
| Range l | –20 to 20  | –12 to 12  | –18 to 18  | –20 to 20 | –16 to 16  |
| Reflections collected | 35148      | 8992       | 12375      | 18639     | 28553      |
| Total reflections | 3124       | 2379       | 2046       | 3402      | 4894       |
| Observed reflections | 2690       | 2279       | 1677       | 2697      | 4061       |
| R<sub>1</sub> [I > 2 σ (I)] | 0.032      | 0.024      | 0.0811     | 0.0470    | 0.0478     |
| wR<sup>2</sup> (all) | 0.0916     | 0.0626     | 0.2943     | 0.1028    | 0.1180     |
| Goodness-of-fit | 1.034       | 1.096      | 1.535      | 1.053     | 1.042      |
| X-ray diffractometer | Bruker D8 Quest | Bruker D8 Quest | Bruker D8 Venture | Bruker D8 Quest | Bruker D8 Quest |
| CCDC Numbers | 824932     | 1548278    | 1548279    | 1548280   | 1548281    |
|                      | Compound-C Form I | Compound-C Form II | Compound-D | Compound-E |
|----------------------|-------------------|--------------------|------------|------------|
| Empirical Formula    | C₁₃H₉BrClN₃O₂     | C₁₃H₉BrClN₃O₂     | C₁₃H₉I₂N₃O₂| C₁₃H₉F₂N₃O₂|
| Formula weight       | 354.59            | 354.59             | 493.03     | 277.23     |
| Crystal system       | Monoclinic        | Monoclinic         | Monoclinic | Monoclinic |
| Space group          | P₂₁/c             | P₂₁/c              | P₂₁/c      | P₂₁/c      |
| T (K)                | 298               | 368                | 298        | 298        |
| a (Å)                | 8.2475(9)         | 8.651(2)           | 8.2946(5)  | 7.897(2)   |
| b (Å)                | 10.8035(11)       | 10.446(3)          | 11.2673(6) | 10.396(2)  |
| c (Å)                | 15.7971(15)       | 15.680(4)          | 16.2177(10)| 14.989(3)  |
| α (deg)              | 90                | 90                 | 90         | 90.00(3)   |
| β (deg)              | 96.098(3)         | 94.116(11)         | 97.993(2)  | 92.27(3)   |
| γ (deg)              | 90                | 90                 | 90         | 90.00(3)   |
| V (Å³)               | 1399.6(2)         | 1413.3(7)          | 1500.95(15)| 1229.6(5)  |
| D<sub>calc</sub> (g cm⁻³) | 1.683            | 1.667              | 2.182      | 1.498      |
| μ (mm⁻¹)             | 3.131             | 3.101              | 4.194      | 0.124      |
| θ range              | 2.28 to 25.00     | 2.34 to 28.88      | 2.208 to 25.021 | 2.581 to 26.005 |
| Z/Z                  | 4/1               | 4/1                | 4/1        | 4/1        |
| Range h              | −9 to 9           | −11 to 11          | −9 to 9    | −9 to 9    |
| Range k              | −12 to 12         | −13 to 14          | −13 to 13  | −12 to 12  |
| Range l              | −18 to 18         | −21 to 21          | −19 to 19  | −18 to 18  |
| Reflections collected| 10084             | 23004              | 9640       | 30614      |
| Total reflections    | 2457              | 3582               | 2587       | 2336       |
| Observed reflections | 2198 | 2117 | 2357 | 1807 |
|----------------------|------|------|------|------|
| $R_1 \left[ I > 2 \sigma(I) \right]$ | 0.0354 | 0.0878 | 0.0272 | 0.0457 |
| $wR^2$ (all) | 0.0990 | 0.2015 | 0.0698 | 0.1229 |
| Goodness-of-fit | 1.077 | 1.143 | 1.111 | 1.096 |
| X-ray diffractometer | Bruker D8 Quest | Bruker D8 Venture | Bruker D8 Quest | Bruker D8 Quest |
| CCDC Numbers | 1548282 | 1548283 | 1548284 | 1548285 |

**Table S3:** Stabilization energies of halogen bonds.

| Name of the Compound | Moiety | Stabilization Energy (kCal/mol) |
|----------------------|--------|-------------------------------|
| Compound-A Form I | ![Image](image1.png) | -4.18 |
| Compound-A Form II | ![Image](image2.png) | -5.31 |
| Compound-B Form I | ![Image](image3.png) | -4.39 |
**Figure S1a:** Compound-A $^1$H-NMR.
Figure S1b: Compound-A $^{13}$C-NMR.

Figure S1c: Compound-B $^1$H-NMR.
**Figure S1d**: Compound-B $^{13}$C-NMR.

**Figure S1e**: Compound-C $^1$H-NMR.
**Figure S1f:** Compound-C $^{13}$C-NMR.

**Figure S1g:** Compound-D $^1$H-NMR.
Figure S1h: Compound-E $^1$H-NMR.

Figure S2a: FT-IR comparison for Form I and Form II (Compound-A)
**Figure S2b:** FT-IR comparison for Form I and Form II (Compound-B)

A= (E)-N’-(3,5-dichloro-2-hydroxybenzylidene)isonicotinohydrazide  
B= (E)-N’-(3,5-dibromo-2-hydroxybenzylidene)isonicotinohydrazide  
C= (E)-N’-(3-bromo-5-chloro-2-hydroxybenzylidene)isonicotinohydrazide  
D= (E)-N’-(3,5-diiodo-2-hydroxybenzylidene)isonicotinohydrazide  
E= (E)-N’-(3,5-difluoro-2-hydroxybenzylidene)isonicotinohydrazide

**Figure S3:** ORTEP diagram of salinazids structures.
**Figure S4:** Hot stage microscope images during heating of Compound-B thermosalient crystals.

**Figure S5:** Chain extending through N-H…N H bond interactions (Compound-E).

**Figure S6a:** DSC thermogram of Compound-A Form I.
**Figure S6b:** VT-PXRD for Compound-A Form I (a) and II (b).

**Figure S7a:** DSC thermogram of Compound-C.
**Figure S7b**: VT-PXRD for Compound-C Form I (label a) which converts to Form II at 120 °C (label c).

**Figure S8**: DSC thermogram of Compound-D.
Figure S9: DSC thermogram of Compound-E.
**Figure S10:** Overlay of experimental PXRD pattern with calculated lines from the X-ray structure.
XPac Analysis:

(a)

(b)

Figure S11a: (a) XPac analysis of compound-A Form I and II. (b) The interplanar angular deviation ($\delta_p$, x-axis) vs. angular deviation ($\delta_a$, y-axis) plot (in $^\circ$) indicates a dissimilarity index of 4.3 due to the 3D isostructurality.
**Figure S11b**: (a) XPac analysis of compound-A and B. (b) The interplanar angular deviation ($\delta_p$, x-axis) vs. angular deviation ($\delta_a$, y-axis) plot (in °) indicates a dissimilarity index of 4.8 due to the 3D isostructurality.
Figure S11c: (a) XPac analysis of compound-A and C. (b) The interplanar angular deviation ($\delta_p$, x-axis) vs. angular deviation ($\delta_a$, y-axis) plot (in °) indicates a dissimilarity index of 3.5 due to the 3D isostructurality.
Figure S11d: (a) XPac analysis of compound-A and D. (b) The interplanar angular deviation ($\delta_p$, x-axis) vs. angular deviation ($\delta_a$, y-axis) plot (in °) indicates a dissimilarity index of 7.5 due to the 3D isostructurality.
**Figure S11**: (a) XPac analysis of compound-A and E. (b) The interplanar angular deviation (δp, x-axis) vs. angular deviation (δa, y-axis) plot (in °) indicates a dissimilarity index of 5.4 due to the 3D isostructurality.
Hirshfeld Surface Analysis:

**Compound-A Form I:**

![Hirshfeld Surface Analysis for Compound-A Form I](image1)

Cl…Cl 3.0%  Cl…H 21.9%  H…H 19.1%  N…H 7.6%  O…H 13.2%

**Compound-A Form II:**

![Hirshfeld Surface Analysis for Compound-A Form II](image2)

Cl…Cl 2.8%  Cl…H 21.7%  H…H 18.5%  N…H 10.2%  O…H 12.6%

**Compound-A Form III:**

![Hirshfeld Surface Analysis for Compound-A Form III](image3)

Cl…Cl 3.9%  Cl…H 21.5%  H…H 19.9%  N…H 8.4%  O…H 13.6%
Compound-B Form I:

Br…Br 3.2%  
Br…H 23.2%  
H…H 18.6%  
N…H 7.4%  
O…H 9.8%

Compound-B Form II:

Br…Br 5.9%  
Br…H 25.8%  
H…H 15.8%  
N…H 8.1%  
O…H 11.5%

Compound-C Form I:

Br…Cl 2.6%  
Br…H 12.9%  
Cl…Cl 0.7%  
Cl…H 9.7%  
H…H 20.3%
N…H 7.7%  O…H 10.6%

Compound-C Form II:

Br…Cl 2.8%  Br…H 13.2%  Cl…Cl 1.1%  Cl…H 8.4%  H…H 20.5%

N…H 8.4%  O…H 12.2%

Compound-D:

I…H 21.3%  I…I 3.4%  I…O 1.5%  N…H 7.1%  O…H 7.9%
Figure S12: Hirshfeld Surface analysis for Compound A-D.

Figure S13: Morphology and faces of crystals.